Manipulation of Multiwalled Carbon Nanotube (MWNT) using AFM and Study of their Frictional Interaction with Surfaces

A Thesis Presented

by

Mithun Chandrasekar

to

Department of Electrical and Computer Engineering

In partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering in the field of MicroElectro Mechanical Systems (MEMS)

Northeastern University

Boston, Massachusetts

April 2012
Acknowledgments

It was a great experience to work with Prof. McGruer, who brought up this topic, guided me through the course of the work and walked me through the compilation of this thesis. I would like to express my appreciation to Prof. Adams for his suggestions and invaluable inputs in making results more accurate.

I would like to thank my fellow students; Anup Singh for helping me understand the AFM, Hui Yu for CNT solution preparation and AFM Tip assembly and Huiyan Pan for providing me with Gold and Thiol Wafers for manipulation. Last but not the least, Peter Ryan for Training me on the AFM and acting as a point of contact during the start of this thesis.

My sincere gratitude goes to my family and all my friends, who were with me during tough times of this work.
Manipulation of Individual Multiwalled Carbon Nanotubes (MWCNT) and Study of Frictional Interaction with Surfaces

Abstract

Most discussions of the structure and associated properties of nanotubes refer to isolated (unsupported) nanotubes. Supported nanotubes, however, should interact strongly with the substrate, and as a result a number of deformations may arise. Experimental studies, however, are mostly performed using nanotubes that are dispersed on a substrate or on nanotubes grown over lithographically defined trenches where they interact with the underlying surfaces. It is important to quantify these interactions for a variety of potential applications of nanotechnology. One such example is a CNT based nanoswitch consisting of a CNT bridging over a trench. Actuation of the CNT causes it to stretch and can lead to slip at the interface. This slip causes the first electromechanical actuation of the CNT bridge to be different from subsequent actuations. Here we investigate such surface interactions using atomic-force microscopy (AFM).

An experimental method to study these deformations of carbon nanotubes for advanced composite structures is presented by analyzing the interaction of Multiwalled Carbon Nanotube (MWCNT) on various surfaces. In this technique an atomic force microscope (AFM) tip is used to drag a CNT along a surface in the contact mode of operation and then the deformed shape of the CNT is observed in the non contact mode of operation. An analysis of the elastically deformed shape allows us to determine the frictional shear stress experienced by the CNTs when dragging them. The shear stress offered by the substrate while dragging is assumed to be constant along the length of the nanotube. However, this may not be true after all, after observing the shape of the deformed CNT.

This work is supported by continuum level modeling, which is used to determine the relationship between the shape of the dragged CNT and the frictional interaction which occurred between the CNT and substrate. The analysis indicate that for high values of the frictional interaction and a very long CNT there is insufficient change in the final shape of the CNT to accurately resolve the shear stress and for low values of frictional interaction CNT slides over the surface, so nanotubes of an intermediate aspect ratio are needed for a successful measurement.
# Table of Contents

Acknowledgements..................................................................................................................2

Abstract........................................................................................................................................3

1. **Introduction**.........................................................................................................................4
   1.1 Carbon Nanotubes (CNTs) and their composites...............................................................7
       1.1.1 Electrical Properties of Carbon Nanotubes...............................................................8
       1.1.2 Mechanical Properties of Carbon Nanotubes ...........................................................11
   1.2 Study of CNTs interaction with surfaces .........................................................................16
       1.2.1 Experimental background .......................................................................................20
   1.3 Instrument for Nanomanipulation of CNT .........................................................................21
       1.3.1 AFM Cantilever selection............................................................................................23
       1.3.2 AFM as a Nanomanipulator.......................................................................................24
       1.3.3 AFM in Non contact Mode and Contact Mode Operation .........................................28

2. **CNT Sample Preparation and Nanomanipulation**.........................................................30
   2.1 CNT Selection....................................................................................................................30
   2.2 CNT Solution Preparation.................................................................................................31
   2.3 Manipulation Surface Preparation.....................................................................................31
   2.4 CNT Nanomanipulation....................................................................................................33

3. **Modeling and Procedure Analysis** .................................................................................39
   3.1 Experimental Modeling .....................................................................................................39
   3.2 Curve fitting procedure and extraction of dimensionless shear stress .........................41
       3.2.1 Curve Drawing............................................................................................................43
1. Introduction

Carbon nanotubes were discovered in 1991\(^1\) by the Japanese electron microscopist Sumio Iijima who was studying the material deposited on the cathode during the arc-evaporation synthesis. Nanotubes show exceptional electronic and mechanical properties that have triggered an ever stronger effort towards applications. From unique electronic properties and a thermal conductivity higher than diamond to mechanical properties where the stiffness, strength and resilience exceeds any current material, carbon nanotubes offer tremendous opportunities for the development of fundamentally new material systems. In particular, the exceptional mechanical properties of carbon nanotubes, combined with their low density, offer scope for the development of nanotube reinforced composite materials. The potential for nanocomposites reinforced with carbon tubes having extraordinary specific stiffness and strength represent tremendous opportunity for application in the 21st century.

Another existing area of research is focused on the mechanical properties of carbon nanotubes. By analogy to carbon fibers, nanotubes are expected to be very strong and have high elastic moduli. They can be twisted, flattened and bent into small circles without breaking and distortion. The mechanical properties of carbon nanotubes would make them ideal for manipulating other nanoscale structures.

Unlike diamond, where a 3-D diamond cubic crystal structure is formed with each carbon atom having four nearest neighbors arranged in a tetrahedron, graphite is formed as a 2-D sheet of carbon atoms arranged in a hexagonal array. In this case, each carbon atom has three nearest neighbors. ‘Rolling’ sheets of graphite into cylinders forms carbon nanotubes. The properties of nanotubes depend on atomic arrangement (how the sheets of graphite are ‘rolled’), the diameter and length of the tubes, and the morphology, or nano structure. Single-walled nanotube is a hollow structure formed by covalently bonded carbon atoms. It can be imagined as a rectangular graphene sheet rolled to form a cylindrical tube. Hemispherical caps seal both ends of the
tube as shown in Fig.1 In the ideal case, a carbon nanotube consists of either one cylindrical graphene sheet (single-wall nanotube - SWNT) or several nested cylinders with an interlayer spacing of 0 - 34 nm (multiwall nanotube - MWNT). Theoretically, Tensile moduli ranging from 270 to 950 GPa, respectively.

These values have been widely used to interpret the mechanical properties of single-walled and multi-walled nanotubes. The size, mechanical strength and electrical properties of nanotubes are highly dependent on their atomic architectures. These nanotubes however, exhibit large variations in their resistivity due to their structural defects or elastic deformations. Presently there is little control over the alignment and shape of these tubes.

In this study we demonstrate that an AFM can be used to control the shape and position of individual MWCNT’s dispersed on a surface. The interaction between nanotubes and the surface is crucial for such manipulations. This makes it important to quantify the frictional interactions between a CNT and various substrates. Such interactions occur in a variety of potential applications of nanotechnology like scanning microscope probes, chemical and biological sensors, manipulation of individual atoms etc. In fabrication of CNT based devices, knowledge of the interactions between CNTs and various contacting substrates is essential in order to understand the assembly processes by which these tubes are deposited.

1.1 Carbon Nanotubes (CNTs) and their composites

In general, the whole family of nanotubes is classified as zigzag, armchair, and chiral tubes of different diameters. The atomic structure of nanotubes is described in terms of the tube chirality, or helicity, which is defined by the chiral vector, $C_h$, and the chiral angle, $\theta$. In Fig. 2, if we visualize cutting the graphite sheet along the dotted lines and rolling the tube so that the tip of the chiral vector touches its tail. The chiral vector, often known as the roll-up vector, can be described by the equation:

$$C_h = n\hat{a}_1 + m\hat{a}_2$$

Fig. 2 Rolling of the sheet to form Nanotube
Where the integers \((n, m)\) are the number of steps along the zigzag carbon bonds of the hexagonal lattice and \(a_1\) and \(a_2\) are unit vectors. The chiral angle determines the amount of the twist in the tube. The two limiting cases exist where the chiral angle is at \(0^0\) and \(30^0\). These limiting cases are referred to as zigzag \((0^0)\) and armchair \((30^0)\) based on the geometry of the carbon bonds around the circumference of the nanotube.

The difference in armchair and zigzag nanotube structures is shown in Fig. 3\(^4\). In terms of the roll-up vector, the zigzag nanotube is \((n, 0)\) and the armchair nanotube is \((n, n)\). The roll-up vector of the nanotube also defines the nanotube diameter since the inter-atomic spacing of the carbon atoms is known.

The electronic structure of carbon nanotubes is determined by the chirality \((n,n)\). An armchair nanotube \((n,n)\) reveals metallic properties, and a zigzag nanotube \((n,0)\) semiconducting properties. Joining a semiconducting to metallic nanotube on the scale of a few Angstroms produces a semiconductor-metal junction on the atomic scale. A metal-semiconducting carbon nanotube junction behaves like a rectifying diode.

Armchair nanotubes exhibit better ductility and electrical conductivity than the zigzag nanotubes [2,3]. In recent years, carbon nanotubes have been utilized as nano-fillers to enhance the mechanical strength of polymeric matrices.

**1.1.1 Electrical Properties of Carbon Nanotubes**

According to International Technology Roadmap for Semiconductors (ITRS) MOSFET scaling will end sometime around 2022 with an 11 nm process\(^5\). Among these are increasing power consumption (particularly through leakage currents), less tolerance for process variation, and increasing cost. As transistors get smaller, they get less ideal. Current flows through paths that should not conduct (No current when off) in an ideal transistor, constitutes almost half of the power consumed by a chip. Another drawback of scaling down the transistors is the decreased ability to handle fabrication process variations. As transistors and
wires become smaller, fewer atoms make up the individual parts and a single misplaced atom can cause large variations. This lack of predictability significantly complicates the design process, and it will only become worse as scaling continues. Also, the cost of a fabrication facility is growing exponentially, along with the exponential growth of the number of transistors per chip. Given the history of the semiconductor industry, most of these issues can probably be solved with current processes. However, the challenge in a shift to nanoelectronics is the paradigm shift in its fabrication procedure. The fundamental element of any nanoelectronic circuit is the devices used to build it. For current very large-scale integration (VLSI) systems, these include silicon transistors and copper wires. For nanoelectronics, it appears that the copper wires will be replaced by either carbon nanotubes (CNTs) or nanowires (NWs). The move to CNT or NW is because they can be chemically assembled at much smaller sizes than copper wires can be patterned with lithography. The current Transistors and Logic devices could be replicated with nanowire or carbon nanotube transistor, these devices offer sizes of a few nanometers and can be self-assembled.\(^6\),\(^7\) Fig. 4(a) shows a CNT transistor with a back gate (gate placed under the channel instead of over it), which uses the silicon substrate to control the conduction through the CNT. This topology is easier to fabricate and is mainly for research work, as we can’t control individual transistors because the substrate is shared between all transistors. Fig. 4(b) CNT transistor possesses the ability to individually control the FETs because the gates are isolated, also the gate on top allows for a thinner gate oxide, which means the controlling voltage (Gate Voltage) can be lower.

\[\text{Fig 4. Carbon Nanotube FET with (a) Back gate (b) Top gate. A back gate uses the substrate to control the conduction through the CNT, while a top gate uses a conventional gate that covers the CNT (channel).}\]\(^3\)

Another advantage of CNTs is their ballistic electron transport, since all of the atoms in the tube are bonded to the same number of neighbors and there is no electron backscattering. This is in contrast to a wire made of a crystal, which has irregular bonds at the surface. Ballistic
electron transport means that transistors with CNTs will exhibit higher on currents that will not be affected by the length of the transistor channel.

Various basic nanotube components have recently been demonstrated, such as molecular wires, diodes, FETs and single-electron transistors\(^6\). The next challenge of development of molecular electronics is to go beyond single-molecule components and integrate such devices onto a chip to produce digital logic operations. Adrian Bachtold, et al. have been able to fabricate and realize logic devices like inverters, NOR gates etc. Later these devices can be combined to make variety of logic gates. Fig. 5 shows the input–output characteristics of an inverter constructed from a nanotube transistor and 100 MΩ off chip bias resistor. An inverter is a basic logic element, when the input is a logical 1 (\(V_{\text{in}} = -1.5\) V), the negative gate voltage induces holes in the tube, thereby lowering CNT resistance than the bias resistor. This pulls the output voltage to 0 V (Logic LOW).

When the input of the inverter is a logical 0 (\(V_{\text{in}} = 0\) V), then nanotube is nonconducting and the output is pulled to –1.5 V (Logic HIGH). Output voltage in this realization makes rapid transition compared to the input by 3 times, which indicates a gain of 3 compared to current logic devices.

Carbon nanotubes however are found to exhibit large variations in their resistivity, a fact which can be attributed to structural defects or elastic deformations\(^8,9,10\). Such studies will greatly benefit from schemes that allow the control of the position and shape of the nanotubes. This is of course also essential if the nanotubes are to be used in any future device technology. However progress toward structurally well-defined nanotube samples has been achieved by the synthesis, presently there is little control over the alignment and shape of absorbed nanotubes. In this study we demonstrate that the tip of an AFM can be used to manipulate multiwalled carbon nanotubes on various surfaces and their interactions are crucial for such manipulations.
1.1.2 Mechanical properties of Carbon Nanotubes

Ever since the discovery of carbon nanotubes, it is realized that the theoretically predicted mechanical properties of these interesting structures—including high strength, high stiffness, low density and structural perfection—could make them ideal for a further generation of technological applications. Some of the exciting applications that take advantage of these properties are nanoprobes, filled nanotubes, nanoelectromechanical systems and nanosensors. Starting from NASA to companies like Samsung and NEC, and many research groups have invested tremendously in CNT technology to take advantage of their low cost, low turn on electric field, high emission density and stability.\textsuperscript{11}

On other fronts, CNTs also show great potential for biomedical applications due to their biocompatibility and high strength. They are seen as prospective alternative replacement for composites used in replacement of bones and teeth’s. It’s could also implanted at the sites where drugs are released slowly over time.\textsuperscript{11}

The mechanical properties of CNTs are closely related to the nature of the bonds between the carbon atoms. The bonding mechanism in a carbon nanotube system is similar to that of graphite, since a CNT can be thought of as a rolled-up graphene sheet. When carbon atoms combine to form graphite, sp\textsuperscript{2} hybridization, and this process forms three hybrid sp\textsuperscript{2} orbital’s at 120° to each other within a plane as shown in Fig.7.\textsuperscript{11} This in-plane bond is referred to as a σ-bond. This is a strong covalent bond that binds the atoms in the plane, and results in the high stiffness and high strength of a CNT. The remaining Π-orbital is perpendicular to the plane and contributes mainly to the interlayer interaction. The Π bonds interact with the Π-bonds in the neighboring layer. This interlayer interaction of atom pairs on neighboring layers is much weaker than σ-bond. Through experimental study of shell sliding\textsuperscript{6} it was found that the shear strength between the outermost shell and the neighboring inner shell was 0.08 MPa and 0.3 MPa for two separate MWNTs.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{graph.png}
\caption{Basic hexagonal bonding structure for one graphite layer (carbon nuclei shown as filled circles), out-of plane Π-bonds represented as delocalized dotted line, and σ-bonds connect the C nuclei in-plane.\textsuperscript{11}}
\end{figure}
The deformation behavior of CNTs has been the subject of numerous experimental, molecular dynamics (MD), and elastic continuum modeling studies.

In the early stages of research only small amounts of CNTs were available and experimental setup to determine the properties were still in infancy stage, however, the ultimate measurements were carried out by Yu et al. in 2000 when they managed to do stress–strain measurements on individual arc-MWNTs inside an electron microscope (Fig. 8 and 9).

For a range of tubes they obtained modulus values of 0.27–0.95 TPa. More interestingly they showed fracture of MWNT at strains of up to 12%, which allowed estimation of nanotube toughness at 1240 J/g.

Measurements on SWNT took longer due to the difficulties in handling them as the properties of larger diameter bundles were dominated by shear slippage of individual
nanotubes within the bundle. Yu et al. were able to measure the tensile properties of bundles by the same method they used for their MWNT study. They saw moduli in the range 0.32–1.47 TPa and strengths between 10 and 52 GPa\textsuperscript{12}. Failure occurred at a maximum strain of 5.3% giving a toughness of approximately 770 J/g. In addition they observed that failure occurred for the nanotubes on the perimeter of the bundle only with the rest of the tubes slipping a part.

For SWNTs intertube slippage within bundles presents a serious limitation to their mechanical properties. The low shear modulus means that effective moduli and strengths for bundles are far below those expected for individual SWNT. It is extremely difficult to debundle SWNT due to their high flexibility and high surface energy.

Also, the band structure of a carbon nanotube (NT) can be dramatically altered by mechanical strain. E. D. Minot et al.\textsuperscript{13} showed that an atomic force microscope (AFM) tip can simultaneously vary the NT strain and electrostatically gate the tube. The strain can open a band gap in a metallic NT and modify the band gap in a semiconducting NT. Theoretical work predicts that band gap changes can range between 100meV per 1% stretch.

Lu et al.\textsuperscript{14} determined the elastic properties of SWCNTs and MWCNTs using an empirical model in his Molecular Dynamics (MD) simulation. A Young’s modulus of ~1 TPa and a shear modulus of ~0.5 TPa were reported based on a simulated tensile test. It was also found that factors such as chirality, radius and the number of walls have little effect on the value of Young’s modulus. Yao et al.\textsuperscript{15} uses similar approach with a different potential model to obtain a Young’s modulus of approximately 1 TPa. The MD Model includes bending; stretching and torsion terms, and their results showed that the strain in the tube is dominated by the torsional terms. Although no agreement has been reached among these publications regarding the value of the Young’s modulus, it should be pointed out that a single value of Young’s modulus is not sufficient to describe both tension/compression and bending behavior. The reason is that tension and compression are mainly governed by the in-plane σ-bond, while pure bending is affected mainly by the out-of-plane Π bond. It may be expected that different values of elastic modulus should be obtained from these two different cases unless different definitions of the thickness are adopted, and that is one reason that accounts for the discrepancies described above.

Although CNTs diameters aren’t much greater than the length of a bond between the carbon atoms, continuum models have been found to describe their mechanical behavior better under
many circumstances. Their miniature feature and small number of defects make CNTs ideal systems for the study of the links between atomic motion and continuum mechanical properties such as Young’s modulus and yield and fracture strengths. Simplified continuum models of CNTs have taken one of two forms: simple beam theory for small deformation and shell theory for larger and more complicated distortions.

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

\[ \frac{\rho A \partial^2 u}{\partial t^2} + \frac{EI \partial^4 u}{\partial x^4} = q(x) \] ……….1

Where ‘u’ is the displacement, ‘P’ is the density, ‘A’ the cross sectional area, ‘E’ Young’s modulus, ‘I’ the moment of inertia, and q(x) a distributed applied load. This equation is derived assuming deflections are small.

Most of the experimental measurements impose the bending of CNT and utilize beam theory to reduce data to an elastic modulus. In many applications, the bending stiffness, EI, of a SWNT or MWNT is given by the classic formula

\[ EI = E \frac{\pi}{4} \left[ (R + \frac{H}{2})^4 - \left( R - \frac{H}{2} \right)^4 \right] \] ……………………………………….2

where ‘R = D/2’ is the mean radius, ‘D’ is the diameter of the tube, ‘H’ is the total wall thickness of the tube, and ‘E’ is the tube modulus. The thickness of a SWNT is then usually taken to be h = 0.340 nm, the equilibrium spacing of two graphite layers. The thickness of the N-layered MWNT is analogously taken as h = N * 0.340 nm. This approach treats the nanotube as a homogenous solid tube of thickness h but does not take into account any specifics regarding structural details of nanotubes such as the nested tube structure of the MWNT and/or the single atomic layer nature of each tube wall.

The above equation is simplified as

\[ EI = E \frac{\pi}{64} D^4 \] ……………………………3

Several important specific features of CNT structure on its deformation behavior has been documented in several microscopy investigations (Iijima et al., 1996; Falvo et al., 1997). Using high-resolution electron microscopy (HREM), Iijima et al. (1996) observed single kinks in SWNTs of diameters 0.8 and 1.2 nm bent to large angles and bending of 5 wall MWNTs were also observed. MWNTs exhibit a complex buckling pattern during bending, first developed a single kink; then, upon further bending, the same tube developed double
kinks. In the HREM images, the distances between respective walls of the nanotube appeared unchanged, even within the kinks produced at high bending angles. Falvo et al. (1997) bent MWNTs using the tip of an AFM and showed that MWNTs could be bent repeatedly through large angles without causing any apparent fracture in the tube. Distributed small regular buckles were observed on the compressive side of the bend. As the tube was bent in the opposite direction, the location of the buckles shifted, with the buckles appearing in regions that had been featureless, and disappearing where they had been observed before. This suggests that the buckling is reversible and not mediated by defects.16

It was experimentally demonstrated that the electrical conductance of nanotubes decreases by almost two orders of magnitude when the middle part of a suspended nanotube is deformed (pushed) by a sharp AFM tip17. The effect was found to be completely reversible, i.e., through repeated cycles of AFM-deformation and tip removal, the electrical conductance displayed a cyclic variation. The drop in conductance in AFM-deformed tubes was much higher than the computationally predicted values for tubes bent under mechanical duress. Calculations, using both tight-binding 18 and semi-empirical extended-Hückel type approaches19 concluded that even under large bending angles the reduction in electrical conductance was less than an order of magnitude

The result is consistent with the fact that the structure remains all-hexagonal, and all atoms remain threefold-coordinated, although the significant $\sigma$-$\Pi$ hybridization affects the electronic
structure due to large local strain-induced deformation. For AFM-deformed nanotubes, on the other hand, O(N) tight-binding calculations show that beyond a critical deformation several C-atoms close to the AFM tip become sp³–coordinated as shown in fig 10 and TEM images shown in fig 11. The estimated reason for drop in conductance is the sp³ coordination ties up delocalized Π- electrons into localized σ states, as verified by explicit transport calculation.¹⁷

1.2 Study of CNTs interaction with substrate

Although CNTs offers exceptional electrical and mechanical properties, fabrication of carbon-nanotube/metal connections to establish electrical contact to the outside world and to perform electrical measurements remains a major challenge. The quality of nanotube substrate junctions depends upon the geometry of the contact region, which in turn depends on the nanotube substrate interaction. Radial deformations of carbon nanotubes have been studied previously only in nanotube bundles or when free tubes with thin shells and large diameters collapse. A closer look at such deformations reveals that nanotubes that cross surface features such as other tubes are not entirely straight but bend and deform elastically. The strain energy that thereby builds up in the tubes is compensated by a gain in binding energy as the tubes maximize their contact area with the substrate. The total energy of such a system can be written as an integral of the strain energy over the local tube curvature and adhesion energy i.e nanotube-substrate interaction potential over the entire tube profile. For a 90Å diameter tube, the binding energy is calculated to be ~1.0eV/Å,¹⁰ these binding energies are mainly attributed to the van der Waals interactions which can be extremely high. The nanotubes when pressed against an obstacle of similar feature exerts nN of force, direct evidences of such forces can be found in fig 12¹⁰, which clearly shows compression of the lower tube in the contact region.

Fig 12. a) Two CNTs (10,10) crossing each other with axial and radial deformations. b) Close up of the crossing point, which shows that both tubes are deformed elastically near the contact region. The force acting on the lower tube is about 5 nN.²¹
This results in a decrease of total height profile than the sum of individual tubes. The observed strong interaction of nanotubes with the surface determines both the normal force that binds them to the substrate and the pinning forces that are responsible for frictional properties when nanotubes are moved laterally across the surface. This interaction is, therefore, also crucial for any attempt to manipulate nanotubes with the AFM tip and for stabilization of nanotubes in strained configurations. Evidence for the strength of the frictional forces can be obtained from images of nanotubes after they have been perturbed by scanning the surface with the AFM tip in non contact mode.

Radial and axial deformations where explored more in detail using molecular-mechanics\textsuperscript{10} on single and multiwall carbon nanotubes. The results of calculations reveal that the extent of the cross-sectional deformation increases dramatically with increasing tube diameter as shown in fig 13a. This trend can be reversed, if inner shells are added to the nanotube, shown in Fig. 13b. The driving force behind these elastic deformations is provided by the gain in binding energy as the contact area with the substrate increases. The addition of more shells inside a tube increases its rigidity and reduces the observed flattening of the tube wall in contact with the substrate.

![Radial deformations of adsorbed carbon nanotubes calculated using molecular mechanics. a) The radial compressions of adsorbed single-walled nanotube with respect to the undistorted free tubes are: 0%, 2%, 13%, and 42%, for 6.7-, 13.5-, 27.1-Å, and 54.2-Å tubes. b) When the number of inner shells is increased the compressions are reduced from 42% to 25%, 5% and to less than 1% for (40,40) tubes with 1, 2, 4, and 8 shells, respectively.\textsuperscript{21}](image)

The increase or decrease of the tube’s contact area with the substrate should have consequences for the properties of adsorbed nanotubes. The computed binding energies for both, optimized single and multiwalled nanotube geometries are summarized in Fig. 14. The open squares give the binding energies obtained for the optimized geometries based on
the MM3 force field. The lower boundary of the gray area gives the Van der Waals binding energy of a perfectly circular tube.

The results in Fig. 14a clearly indicate that the net gain in adhesion energy as a consequence of elastic deformations can be can twice the original value which is given by the upper boundary of the gray area. This reflects the strain energy that develops within the tube due to bond bending and bond stretching.

The radial distortions may also have an effect on the tubes’ bending properties due to the coupling of the cross section to the flexural rigidity, given by EI, where ‘E’ is Young’s modulus and ‘I’ the geometrical moment of inertia. The effect of radial distortions on the nanotubes’ flexural rigidity leading to an elliptical deformation can be calculated from the geometrical moment of inertia, \( I = \iiint y^2 \, dx \, dy \) over the cross section of the tube. This estimate reveals that the flexural rigidity of tubes is reduced almost linearly with compression according to \( B \sim 1.9B_0 \, a/a_0 \) where \( a_0 \) and \( a \) are the outer tube radii for undistorted and elliptically compressed tubes, respectively. Thus, tubes that have undergone significant radial compression can be bent much more easily than perfectly circular tubes.

Nanotubes adsorbed on a substrate, are likely to encounter obstacles or defects, where they will be subject to both radial and axial deformations. This observation is further analyzed by Tobias Hertel et al\(^{21}\), by molecular mechanics simulations, which shows that the local strain associated with these deformations can be as high as 5–10 meV per atom. Such strains will

---

Fig 14. a) Binding energies of adsorbed nanotubes as a function of their diameter. b) Binding energies as a function of number of inner shells.\(^{21}\)
lead to modifications of the electronic structure of adsorbed nanotubes even at small enough temperatures should have implications for electronic transport properties through nanotubes. Perturbing features on the surface such as defects or steps can induce substantial distortions in adsorbed nanotubes due to their strong adhesion to the substrate, which is very likely the cause for degradation of the electronic transport properties. This poses a serious challenge for the control required for processing of nanotube devices if they are not to be affected by surface roughness. On the other hand, there is an opportunity to utilize the surface topography as a tool for tailoring the nanotube’s transport properties.

From the AFM results and the molecular mechanics calculations by Ph. Avouris et al.\textsuperscript{22} conclude that carbon nanotubes in general tend to adjust their structure to follow the surface morphology of the substrate. They define a critical radius of surface curvature $R_c$ above which the nanotube can follow the surface structure or roughness. Given that the strain energy varies more strongly with tube diameter than the adhesion energy, the critical radius is a function of tube diameter shown in Fig. 15 shows the approximate variation of of $R_c$ with $d$ for (5,5) and (10,10) single-wall and multi-wall tubes based on binding and strain energies computed with molecular mechanics.

The van der Waals forces play an important role not only in the interaction of the nanotubes with the substrate but also in their mutual interaction. The different shells of a multi-walled tube interact by van der Waals forces; single-walled tubes form ropes for the same reason.

**Fig 15. Criteria determining whether a nanotube with a particular diameter $d$ conforms to the local topography of the substrate characterized by a radius of curvature $R_c$.**

Based on the above discussions, we estimate the effective contact width of the CNT with the
surfaces for a MWNT could be around 5% the diameter of the tube. Effective contact width of the CNT, parameter ‘B’ is used to determine the CNT shear stress after its manipulation. Its usage is shown in later sections.

1.2.1 Experimental background

Small dimensions of CNTs, with diameters of tens of nanometers for MWNTs and about 1 nm for SWNTs, micron lengths, placement of CNTs in an appropriate testing configuration, the achievement of desired push to obtain the equilibrium shape of the CNT, characterization and measurement of the mechanical deformation at the nanometer length scale impose challenges for experimental determination of mechanical behavior and properties. Another limiting factor is often the lack of information on important structural features such as the tube inner diameter, the number of walls, the possible presence of defects and non-cylindrical shape of the tube. Nevertheless, several experimental studies have attempted to measure the elastic modulus, mechanical deformation of carbon nanotubes.

Treacy et al. (1996) used thermally induced vibration of cantilevered MWNTs within a transmission electron microscope (TEM) and obtained a mean value for the Young’s modulus of 1.8 TPa, but with a large variation from 0.40 to 4.15 TPa and similarly Krishnan et al. (1998) for SWNTs obtained range from 0.90 to 1.70 TPa. Poncharal et al. (1999) used an electric field to induce static and dynamic mechanical deflections in cantilevered MWNTs, giving a modulus in the range of 1 TPa for small-diameter tubes. Wong et al. (1997) conducted bending tests on cantilevered tubes using atomic force microscopy and estimated a Young’s modulus of 1.28 TPa.

Falvo et al.21 bent MWCNTs by using the tip of an AFM and showed that MWNTs could be bent repeatedly through large angles without causing any apparent fracture in the tube. Similar method was used by Hertel et al.21 demonstrated that an AFM tip can be used to control the shape and position of individual multiwalled carbon nanotubes dispersed on a passivated silicon surface. The shear stress offered by the substrate while dragging the CNT is assumed to be constant along the length of the CNT. The analysis shows that the frictional interaction between the CNT and the substrate can be determined simply by observing the deformed shape of the CNT once dragging is completed. Based on modeling and analysis by Palaniappan Nagappan24 and experiments by Kaylee McElroy et al.25, an aspect ratio of 100 - 250 is appropriate for frictional interaction analysis. If the aspect ratio is less than this range then the tube is bound to roll rather than slide and if greater, then the deformation
measurement is not sensitive enough. Thus the results of this experiment provide an estimate of the shear stress and the advantage of such measurements is the simplicity and that the procedure does not require a force measure measurement by AFM. A Park system XE150 AFM was used for the experiment with Asylum AC240Ts Tips to drag the Nanotubes. This research also discusses the various experimental procedures and challenges faced from sample preparation to manipulation of MWCNT’s on different surfaces.

1.3 Instruments for the mechanical study (Nanomanipulators) of carbon nanotubes

Most nanotubes application for nanoelectronics and NEMS involve characterizing, placing, deforming, modifying, and/or connecting nanotubes. Although chemical synthesis provides a way for large scale patterned structures\(^{26}\), and self-assembly may generate better regular structures, we are still facing challenges in building complex nanotube devices.

Nanomanipulation, or positional control at the nanometer scale, is one promising method. At present, nanomanipulation can be applied to the scientific exploration of mesoscopic phenomena and the construction of prototype nanodevices. It is a fundamental technology for property characterization of nano materials, structures and mechanisms, for the preparation of nano building blocks, and for the assembly of nanodevices.

Nanomanipulations were enabled by the inventions of scanning tunneling microscopes (STMs), AFMs, and other types of scanning probe microscopes (NRM, Nano Robotic Manipulator). Characterized by the capability of three-dimensional (3-D) positioning, orientation control, independently actuated deflector, independent real-time observation system, and possibility to combine SPMs inside them, nanorobotic manipulators (NRMs), largely extend the complexity of nanomanipulations.
A simple comparison of an STM, an AFM, and an NRM is shown in Fig. 16\textsuperscript{27}. Though STM has the best atomic resolution, its limited two-dimensional (2-D) positioning and available strategies for manipulations don’t satisfy complex manipulations in 3-D space. Since the invention of the AFM in 1986 it has been quickly accepted as a standard tool for many applications related to surface characterization and Nanomanipulation. High-resolution (nanometer up to atomic resolution) mapping of surface morphology on almost any type of either conductive or non-conductive material can be achieved with an AFM.

AFM consists of three imaging modes i.e., contact mode, tapping mode (periodical contact mode), and noncontact mode. The latter two are also called dynamic modes and can attain higher imaging resolution than contact mode and atomic scale resolution is obtained. Manipulations with an AFM can be done in either contact or dynamic mode. Generally, it involves moving an object by touching it with a tip. In a typical manipulation, the object is first imaged in the noncontact mode, and then sweeps the tip across the object (Contact mode) in contact with the surface and with the feedback disabled. Mechanical pushing can exert larger forces on objects and, hence, can be applied for the manipulation of relatively larger objects, and one-dimensional to 3-D objects can be manipulated in 2-D substrate. However, the manipulation of individual atoms with an AFM is still a challenge. By separating the imaging and manipulation functions, nanorobotic manipulators can have much more degrees of freedom (DOFs) including rotation ones for orientation control and, hence, can be used for the manipulations of zero-dimensional (0-D) (symmetric spheres) to 3-D objects in 3-D free space. However, the availability of the AFM (PSIA XE 150) with desired features, made a favorable choice for Nanomanipulator.
The principle of the microscope is relatively simple. A probe having a force sensitive cantilever with a sharp tip is used as a sensor to physically scan, in close proximity to, the sample surface. The probe is driven by a piezoelectric tube capable of nanometer resolution translations in the x, y and z directions, and the tip normally has a radius of curvature on the order of 10 nm. The force interaction between tip and sample results in deflection of the cantilever. While scanning the sample surface in the x and y directions, the deflection of the cantilever is constantly monitored by a simple optical method, which collects the laser reflected from the back of the tip into the Position Sensitive Photo Detector (PSPD). This is sensed by a feedback electronic circuit that reads the deflection signal and controls the piezoelectric tube that is responsible for keeping a constant force between the tip and the sample surface, and a surface profile of the sample can thus be obtained as shown in the AFM conceptual diagram in Fig 17.

Depending on the type of interaction force involved for sensing, an SPM instrument can include a host of methods, such as AFM, friction force microscopy (FFM), magnetic force microscopy (MFM), electric force microscopy (EFM), and so on. Depending on the mechanism used for measuring the force interaction, scanning probe microscopy also includes many modes of operation.

1.3.1 AFM Cantilever Selection

Selecting the appropriate probe is a critical aspect of using AFM. Choosing a probe means determining the combination of a tip, which interacts with sample surface and a cantilever, which deflects depending on the interatomic forces and quantifies the deflection. Generally, the upper surface of a cantilever is coated with a metal such as gold (Au) or aluminum (Al). This coating, which enhances the surfaces reflectivity, has a thickness of about 1000Å. There are several types of cantilevers that vary in material, shape, softness (represented by the spring constant), intrinsic frequency, and Q-factor. The type of cantilever selected is primarily determined by the measurement mode and the need of the experiment. For the proposed experiment, the AFM tip needed to be used in both “Tapping mode or contact” mode [for manipulation] and “non-contact” mode [for Imaging]. Using a tip with higher stiffness constant which is typically used for non contact mode imaging exerts a larger force on the substrate if used in contact mode. This may lead to cutting of the tubes or damaging the substrate surface. On the other hand, a contact mode tip, which has a very small stiffness constant, if operated in the non contact mode compromises the image quality. After careful inspection, medium soft silicon cantilever OMCL-AC240TS-RS28 tip from asylum research, operating in AC mode, suitable for observing surface topography and viscoelasticity of the sample was chosen. This tip
has an intermediate value of stiffness and operating frequency. Selected AC-240-TS tip did provide excellent image quality and CNT manipulation was achieved. The specifications for the tip are as follows:

Cantilever type = N-type Doped Silicon Substrate, surface resistance of 0.01—0.02 Ω·cm.

Cantilever Stiffness = 2 N/m,

Frequency = 70 kHz; Tip Radius < 10 nm;

Fig. 18 SEM Image of AFM Cantilever Tip

1.3.2 AFM as a Nanomanipulator

A nanomanipulation system generally includes nanomanipulators as the positioning device, as a probe tip and effectors including cantilevers and tweezers and types of sensors (force,
displacement, tactile, strain, etc.) to facilitate the manipulations and/or to determine the properties of the objects. Key technologies for nanomanipulation include observation, actuation, measurement, calibration and control, communication, and human–machine interface.

![PSIA XE150 AFM](image)

**Fig 20.** PSIA XE-150 brings advanced non-contact metrology of the XE-Series to large samples used in data storage, semiconductors, nanoscience, materials science, polymers, and electrochemistry.

PSIA XE150 AFM system available at Center for High Rate Nanomanufacturing (CHN) was used as a Nanomanipulator shown in Fig 20. Apart from being available, PSIA’s AFM possesses impressive AFM imaging resolution and easy procedure to manipulate surface features. The XY motorized sample stage can be optimized for large sample (150 × 150 × 20 mm) placement, which allows full travel of the entire sample resulting in faster image scans. Together with its own acoustic enclosure and advanced active vibration isolation system, the XE-150 ensures an ultimate low noise performance. The sealed acoustic enclosure is required for blocking external optical and acoustical noise and the active vibration isolation system cancels out the floor vibration.

PSIA’s innovative scanner design separates the Z scanner from the XY as shown in Fig 21; Physical separation of the XY scanner from the Z scanner eliminates background
curvature from the images and effectively eliminates the cross-talk and non-linearity problems that are intrinsic to conventional piezoelectric tube based AFM systems. The Z scanner being separate from the XY scanner is designed to have a higher resonant frequency than conventional piezoelectric tube scanners, which enables more than 10 times faster scan rates compared to conventional tube type scanner. This results in increasing the speed of the measurements allowing us to scan large image area quickly and also protecting the tip results in the ability to acquire clear images for an extended period of time.

To align the laser beam, conventional AFMs use additional positioning equipment, the operation of which is often difficult and cumbersome. However, laser beam alignment is very easy and convenient with the XE-Series. Manageable control knobs on the head can be adjusted with the help of the control software and the video monitor display, making location and movement of the laser beam easy and accurate.
The crucial point of the laser alignment is to ensure that the laser beam falls on the same point on the cantilever and the reflected beam hits the same point on the PSPD regardless of the z scanner motion, so that only the deflection of the cantilever will be monitored on the PSPD as shown in the fig 22. Also in the PSIA AFM, innovative optical design allows for direct on-axis optical view of a sample from the top.

Since the CCD camera is aligned directly with the cantilever with nothing blocking its view, it is very convenient to focus on or to observe the sample while moving the camera up and down.

XE’s patented dovetail lock head mount, makes AFM head removal an easy operation\textsuperscript{30}. The AFM head, which includes the Z scanner, is easily inserted or removed by sliding it along a dovetail rail and locking it into place with turn of two thumb locks as shown in fig 23.

Since the tip wears out eventually, it is necessary to replace it after some amount of usage. Probe tip exchange is made easy by just snapping the probe tip to pre-aligned kinematic chip mount that ensures the same position of a probe tip every time you need to exchange the cantilever. Along with easy of handling the AFM instrument, the design of PSIA XE 150 is modular which felicitates removal of components if they don’t work.

The XE Control Electronics incorporates advanced digital circuitry with precision software and hardware components that encompasses high speed and high capacity data processing. It contains fast and powerful DSP (Digital Signal Processor), 14 DACs (Digital to Analog Converters), and 5 ADCs (Analog to Digital Converters). The XE Control Electronics are designed to enable the scanner, the core unit of the AFM, to provide efficient, accurate and fast control, and to facilitate the acquisition of a stable image even beyond a scan speed of 10Hz\textsuperscript{29}. In addition, the controller contains input/output terminals that provide a simple means
for users to design advanced experiments that extend far beyond and are much more complicated than obtaining basic images.

1.3.3 AFM in Non Contact (NC) and Contact Mode Operation

In NC-AFM, a cantilever is vibrated by a piezo-electric modulator with very small amplitude at a fixed frequency near the intrinsic resonance of the cantilever. As the tip approaches a sample, the van der Waals attractive force between the tip and the sample acts upon the cantilever and causes changes in both the amplitude and the phase of the cantilever vibration. These changes are monitored by a Z-servo system feedback loop to control the tip-sample distance. If the Z-servo is not sensitive, the tip may stick to a sample due to meniscus forces and stops the non-contact oscillation. In such cases, a Z-scanner must retract the cantilever far enough to detach the tip from the sample surface.

Contact mode uses the “physical contact” between the probe tip and a sample surface as seen in figure 24, whereas non-contact AFM does not require this physical contact with the sample as shown in the below figure. Also, in non-contact AFM, the force between the tip and a sample is very weak so that there is no unexpected change in the sample during the measurement.

XE has software programs for data acquisition, Image processing and Nanolithography. XEP is a data acquisition program that communicates with the XE Control Electronics in order to control the XE-Series system.
XEP interface allows a user to investigate and analyze a sample surface; XEP controls and operates the XE system to collect sample data. XEP supports all the standard and advanced measurement modes. Switch between the Contact and Non Contact mode of operation for Nanomanipulation and Imaging is achieved by the toolbar in the XEP software.

XEI user interface is an impressive software program that provides user-friendly and dynamic tools for image processing, quantitative analysis and exporting and printing of processed images and measurement results. The XEI software maximizes the system’s potential by allowing users to extract more information from the sample surface by utilizing various analysis tools and also by providing the ability to remove certain artifacts from scan data. Structural details of Carbon Nanotubes like Length, Diameter were extracted from the images using the XEI software package.

XEL is an excellent Nanolithography software program that allows the user to draw the desired pattern on the sample surface by atomic manipulation or manipulates the objects on the surface. The desired pattern or manipulation is achieved by selecting the drawing vector from toolbar and executing it in the contact mode operation.
2. CNT Sample Preparation

2.1 CNT Selection

One the challenge for sample preparation was selection of the nanotube for nanomanipulation. Natural nanotube curvature weren’t desired since there would be insufficient change in the final nanotube curvature to accurately resolve shear stress. Hence the idea of selecting straight nanotubes with few defects was the primary criteria. Nanotubes are manufactured on a large scale by CVD process, this manufacturing method generally possess large quantities of defects. Their physical properties suffer due to the presence of defects with thermal, electronic and mechanical properties deviating significantly from those expected for pristine hexagonal lattice nanotubes. However CVD produced MWNT are important at the industrial level because they can be produced in very large quantities relatively cheaply. Other common methods to produce CNTs for research purposes are electric arc discharge and catalytic decomposition of hydrocarbons. For arc generation, production yields are in general poor while purity can be as low as 10% with the rest of the carbon in the form of species such as turbostratic graphite and carbon onions. However, CNTs produced this way are nearly perfectly straight made relatively defect free\textsuperscript{31}. In some ways, these materials are similar to those of perfect SWNT as the interwall coupling is relatively weak. Electronically, they act as either metals or very small bandgap semi-conductors. Ballistic conduction has been observed by a number of groups\textsuperscript{32} and thermal conductivities as high as 3000 W/m K has been measured.\textsuperscript{33} Based on the above information, CNTs produced by Arc Discharge method were chosen for the experiment.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure28.png}
\caption{TEM images of (a) an arc-MWNT, (b) a CVD-MWNT, AFM images of (c) arc-MWNT and (d) CVD-MWNT lying across a pore. Reproduced from Salvetat JP et al” Elastic modulus of ordered and disordered multiwalled carbon nanotubes” Adv Mater 1999;11(2):161–5.}
\end{figure}
2.2 Procedure for CNT solution preparation

Arc Discharge powered CNTs and ones produced by CVD both were obtained from Sigma Aldrich after careful look at their specifications. CNT solution were to be prepared with a concentration of 0.25 mg/Lt. Initially DI water was used prepare the solution, however after ultrasonication for about an hour to ensure consistency in CNT distribution throughout the solution; It was noticed that insolubility CNT powders had resulted in CNT island formation in the solution. IPA (Isopropyl alcohol) and DMF (Dimethylformamide) were used for solution preparation based on Carbon Nanotubes Dielectrophoresis by Martial Duchamp et al.

After achieving the desired concentration both IPA and DMF, the solutions were ultrasonicated and uniform distribution CNT solutions were obtained. Three different types of solutions were prepared; one is Arc discharge CNT in IPA, second is Arc discharge CNT in DMF and third was CVD CNT in IPA.

All these samples initially were dispersed by micropipette on SiO$_2$ substrate and were imaged using Scanning Electron Microscopy. After imaging all these samples, it was observed that substrates with Arc discharge CNT though weren’t clean as expected; their structure (i.e Aspect ratio = Height/ Diameter) and near perfect straight nature was in line with our experimental requirement. Hence, samples with CVD based CNTs weren’t used anymore in nanomanipulation.

2.3 Manipulation Surface Preparation

Different manipulation surfaces prepared are SiO$_2$, Gold and Thiol on Gold.
**SiO₂ Surface Preparation**

Preparation of SiO₂ surface is started by standard prediffusion cleaned wafers. Standard prediffusion clean is a wafer cleaning process before SiO₂ is grown on it. This cleaning process involves cleaning wafers with Pirana (H₂SO₄:H₂O₂) to remove organic contaminants (Air) followed by HF to remove to native oxide and finally clean with HCL (H₂O₂: HCl) to remove any metal contaminants. After the prediffusion clean, wafers are subjected to thermal oxidation where 0.5µm thickness of SiO₂ is formed on Silicon wafer. This wafer is then diced to chips using diamond tipped scriber and before CNT is dropped on the chips, chips are cleaned with N₂ gun to ensure there are no particles on the chip.

**Gold Surface Preparation**

After Thermal oxidation, Chrome is deposited on SiO₂ by e beam evaporation. Thickness of Chrome is expected to be around 1nm. After Chrome, Gold is deposited by using the same deposition method on the Chrome surface, which yields around 15nm thick gold layer. Chrome layer is required as an adhesion layer between SiO₂ and Gold. For wafers which undergo this process more than 1 hour after oxide growth, a second cleaning must take place with pirana to remove any airborne organics and improve adhesion. **HF and HCL** steps should be skipped because they would remove the SiO₂ from the Si. After all the metal deposition, wafer is diced into chips by Diamond tipped scriber and blown with N₂ gun before CNT solution is dropped on them.

**Thiol Surface Preparation**

Thiol is an organosulfur compound that contains a carbon-bonded sulphydryl (–C–SH or R–SH) group (where R represents an alkane, alkene, or other carbon-containing group of atoms). Thiol is also known as the sulfur analogue of alcohols. Thiol Deposition performed by modifying the gold surface with an alkanethiol layer is assembled onto the gold surface through a strong gold sulfur bonding between gold and the –SH headgroups of the alkanethiol. The pure alkanethiol is dissolved in ethanol to get an ethanolic alkanethiol solution with a concentration of 1mM. The samples are pre-clean in piranha for about 10 mins and then immersed into the alkanethiol solution for 24 hours. After the self-assembly process, the samples are taken out of the solution, rinsed with ethanol and dried with N₂ gun.
2.4 CNT Nanomanipulation

CNT solutions were dropped on the desired chip surfaces (SiO$_2$, Gold, Thiol) by a micropipette and left to dry under clean environment overnight. These chips are then transferred to the AFM scan stage by sticking them with carbon sticky tape onto magnetic plate. Assembled AFM tip is mounted on the AFM tip holder in the scan head and the XEP software is opened. After performing the laser alignment, the AFM tip is resonated by the piezo actuator to determine its natural frequency of operation. The desired area on the sample is selected by looking at the scan area monitor, which displays the aligned optical microscopic images. Once this is done, the ascouctic enclosure is closed by enabling the active vibration table and AFM tip is made to approach the sample in the automated incremental mode. To start with, the ‘$\mu$m x $\mu$m’ scan area is chosen in the XEP software and the Non Contact AFM mode is selected for scanning a sample area in search of nanotubes. CNT on the chip needs to be imaged to determine its location and desired aspect ratio (Height/ Dia). Imaging part of the CNT accomplished by scanning the chip area in the non contact AFM mode of operation with preselected scan speed of the AFM tip. The scan speed is set at 1Hz during scanning for CNT search. Though many CNT are imaged the ones with better aspect ratio greater than 80 were used for nanomanipulation and the one with relative clean surrounding were chosen. Since, our CNT solution weren’t the purest for reason explained earlier; we had to put in the extra effort to locate CNT around a relative clean chip area. This scanning process is repeated by changing the scan position until the desired nanotubes are found. When the desired the Nanotubes are found the scan rate could be decreased to 0.5 Hz to obtain better AFM images. Once selected, AFM mode is changed to contact mode and tip probe is shifted back to the CNT location and a certain amount of vertical force is applied. During our experiment the applied vertical force ranges from 289nN to 719nN. We usually start the manipulation with the lower range of vertical force and then increment it by 50 units for each manipulation trial to check whether manipulation was successful or not. Manipulation is termed successful, when the CNT deforms in a shape according the theoretical modeling.

Now, the selected scan image (the error signal image is preferred) is opened in the XEL software and the desired directional vector is drawn on the nanotube. CNT structures and their location can be better viewed in the error signal image than the original AFM image and was also recommended by other PHD student who was also familiar with manipulation. The vector position is critical for manipulation and ideally should be normal to the CNT w.r.t the
surface and at the midpoint of its length. The vector length drawn should be sufficiently long for the CNTs to reach the final equilibrium deformed shape. Once the vector is started the probe tip executes the vector shape, the switch between XEP and XEL is done by the remote icon in the XEL toolbar. After vector execution, AFM is shifted back to non contact mode and the manipulated carbon nanotube is imaged. If initial vector doesn’t provide the desired result try extending vector in moderate increments and check the CNT behavior until the desired manipulation is obtained. If the manipulation vector becomes very long the drawback is, the deformed CNT may end up out of field of view when compared to the original CNT location. Field of view is defined as the original CNT image scan area displayed on the monitor. In such cases, perform image scans in the direction of the manipulated vector to find the deformed CNT. The original nanotube and the manipulated nanotube images are then processed using XEI software to obtain presentable images.
Fig 29. AFM Images of Original CNT before manipulation scanned in the non-contact mode operation

Fig 30. AFM Images of a Deformed Nanotube scanned in the non contact mode after contact mode operation

Fig 31. XEL Mode of operation. Directional vector is drawn on the CNT to drag it along the surface until final deformed shape of the nanotube is obtained
Structural features of the CNT like the length and diameter of the tubes are also determined by the XEI software. Diameters of the tubes are determined by 3 point measurement to get the most accurate diameter information possible. Diameter is a part of the aspect ratio which does play a role in determining the final shear stress value and also considering the some non uniformity in the tubes geometry.

Fig 32. CNT Length determination using XEI Software. Length of the CNT above is 3.8μm

Fig 33. 3 Point CNT Diameter determination using XEI Software. Dia of the CNT above is 16nm
Apart from theoretical predictions, which says CNT manipulation would lead to deformed nanotube shape due to surface interactions; We also observed other results like, cutting of the tubes (CNT’s are cut into halves by AFM tips) and partial movement of the tube (i.e. half the nanotube moves, other half remains stationary on the surface) and something similar to rolling (CNT moving with the AFM tip along the surface without deformation)

Below manipulation results are similar to CNT rolling; Rolling is a phenomenon where the CNT rotates about the pivot (Drag) point along the surface. Sometimes it also depends on the location of the AFM tip during the push, whether the load application will be able to influence the entire tube length or the whether energy to deform the tube. In our experiment, we observed that during some manipulation trials the CNT translation to new position wasn’t intended and the CNT had flipped the side (phenomenon that occurs with rolling). This could be attributed to the manipulation vector not being long enough, lower aspect ratio tubes (<100) and may be the surfaces didn’t offer uniform friction along the length of the tube. An interesting observation with such flipping of the tubes is a small degree of CNT deformation. More analysis of flipping (similar to rolling) tubes is done by M. R. Falvo et al.37.

Another result observed during manipulation was Partial movement of the tubes, in this case a portion of nanotube moves in the manipulated direction whereas the remaining portion remains
at its original position. Possible reasons for such a behavior could be, the load application wasn’t close to the midpoint of the CNT to move it in the desired direction or adhesion energy of the CNT may be different along the length of the tube.

![Original CNT](image1.png) ![After Manipulation](image2.png)

*Fig 36. Partial CNT movement during Nanomanipulation on Gold Surface*

In the above manipulation and some of the other ones, the nanotube was contaminated with amorphous carbon, as seen from the spotty line left behind at its original position. This contamination may have increased its adhesion to the substrate.\(^\text{10}\)

In an attempt to obtain equilibrium deformed nanotube shape, we sometimes extended the length of the manipulation vector long enough, only to find that the nanotubes stretch significantly before it eventually cut. Possible reasons could be nanotube contamination, very long nanotubes or new AFM tips. New AFM Tips are pretty sharp compared to the ones used after many manipulations (tips used for manipulation lose their sharpness due to repeated scans in contact mode operation).

![Original CNT](image3.png) ![After Manipulation](image4.png)

*Fig 37. Cutting of the CNT during manipulation on SiO\(_2\) Surface*
3 Modeling and Procedure Analysis

3.1 Experimental Modeling

Experimental modeling is based on Palaniappan Nagappan et al.,\textsuperscript{24} where method of analysis for the large deflections of piecewise elastic bars subjected to an arbitrary number of discrete loads is used for experimental interaction between carbon nanotubes and rigid substrates. By combining the general solution of the nonlinear differential equation of bending and the equilibrium equations for each of the intervals between the load points and points of discontinuity in the flexural rigidity, along with the given boundary conditions, the problem is formulated as a system of simultaneous nonlinear equations which is solved by an iteration procedure.

The nanotube is modeled using the equation of equilibrium of a bent elastic rod, the general equation for which is

\[ EI \left( \frac{d^2 \psi}{d\tilde{s}^2} \right) - (T_0 - q_x\tilde{S}) \sin - (S_0 - q_y\tilde{S}) \cos = 0 \ldots \ldots \quad (4) \]

As shown in equation 4, \( T_0 \) and \( S_0 \) are the horizontal and vertical components of the internal force respectively at the origin which at that point correspond to the tension and shear force, \( \psi \) is the angle between the x-axis and the tangent at position \( S \) (positive clockwise), \( E \) is the elastic Young’s modulus, \( I = \frac{\pi}{64} D^4 \) is the second moment of the cross-sectional area of diameter \( D \) of the CNT, and \( q \) are the components of the external load per unit length in the x-and y-directions respectively.

Two different cases were analyzed based on the point of application of the load. These configurations are symmetric loading (the force is applied at the midpoint of the CNT) and non-symmetric loading (the force is applied away from the midpoint of the CNT). In both cases, the force is applied so as to push the CNT in a direction perpendicular to its initial orientation. It is this frictional interaction which is modeled by the \( q_x \) and \( q_y \) terms in equation (1). In our analysis, we assume that the tube is sufficiently long so that the frictional shear stress produces enough bending. In the following experiment we show how a specified frictional interaction during sliding will cause the CNT to deform. The results of this experiment will allow us to determine the frictional interaction which occurred during dragging by observing the deformed shape of the CNT.

When loading corresponds to the force applied at the midpoint of the CNT (figure 34), it’s called \textit{symmetric loading}.
The substrate on which the CNT is placed offers a shear resistance to the applied load as the CNT slides along the substrate. Since the deformation occurs in the y-direction, $q_x$ was taken to vanish and $q_y$ was set equal to the frictional shear stress ($\tau$) multiplied by the effective contact width ($b$). In the case of CNT being dragged along the substrate by applying the force away from the midpoint is non-symmetric loading.

In the following analysis we show how a specified frictional interaction during dragging will cause the CNT to deform. The results of this analysis will allow us to determine the frictional interaction which occurred during dragging by observing the deformed shape of the CNT. We have analyzed two points of load application, one is symmetrical and the other is non-symmetric loading. In case of symmetric loading, the force is applied at the midpoint (50% of length) of the CNT and the substrate on which the CNT is placed offers a shear resistance to the applied load as the CNT slides along the substrate. Similarly for the non-symmetrical case, CNT is dragged along the substrate by applying the force away from the midpoint; the points of interest have been (30% and 40% of the length) load. In both cases, the force is applied so as to push the CNT in a direction perpendicular to its initial orientation. It is this frictional interaction which is modeled by the $q_x$ and $q_y$ terms in Equation (4). Implicit in our analysis is the assumption that the tube is sufficiently long so that the frictional shear stress produces enough bending to make rolling motion unfavorable. In the following analysis we show how a specified frictional interaction during sliding will cause the CNT to deform. The results of this analysis will allow us to determine the frictional interaction which occurred during dragging by observing the deformed shape of the CNT. The analysis also provides an operating window of CNT aspect ratios in which this method can be used.

Figure 38. Schematic representation of symmetric loading of a CNT.
By knowing the rotation angle at every coordinate along the CNT and using numerical integration methods, we can determine the final deformed shape of CNT. A plot of such deformed shapes for various points of load application (50%, 40%, and 30%) values of dimensionless load is shown in Figure 2. As stated earlier an increase in frictional shear stress leads to an increase in the bending of the CNT. In order for this measurement method to be practical there needs to be sufficient sensitivity of the shape to the shear stress interaction. It is seen that for $\tau$ greater than about 300 (which corresponds to $L/D = 230$ for the typical dimensioned case considered $\tau = 2$ MPa), reduced sensitivity becomes an issue. Note that this maximum aspect ratio varies weakly (as the one-third power) with the shear stress.

![Graph showing deformed shapes of CNTs](image)

**Fig 39. Final Deformed shape of the CNTs: Case A (load application at 50% length), Case B (At 40% Length), Case C (30% Length)**

### 3.2 Curve fitting procedure and extraction of dimensionless shear stress

After nanomanipulation, one of the challenges was to define an acceptable curve fitting procedure that would argue well with the theoretical estimation of dimensionless shear stress. Basically the curve fitting procedure describes a methodical approach to closely follow the deformed shape of the CNT and find a good match with the theoretical curves drawn using a MATLAB program written by Palaniappan for Continuum Modeling of Frictional Interaction.$^{24}$ Analysis of the deformed CNT AFM images reveal that though the intended CNT drag (push) was at the midpoint of the CNT, there is a slight shift in the drag position i.e 0.5 push might have been a 0.49, 0.48, 0.45 push. One of the possible reasons for a shift in the drag position could have been the position error by Piezo Creep due to the hysteresis of piezoelectric actuators in the Z scanner.$^{38}$ It was also observed that, the final position of the deformed CNT was slightly
offset w.r.t to the end position of the vector, possibly due to the surface imperfections or the CNT adhesion to the AFM tip\textsuperscript{25}. One of the CNT manipulated images is chosen for explanation of curve fitting procedure and extraction of dimensionless shear stress.

Fig 40. Original CNT

Fig 41. After Manipulation

Fig 42. Manipulating Vector
By observing some of the manipulating vector images and the AFM images of the original CNT and Manipulated CNT, we notice the deviation in the manipulated CNT image w.r.t to the direction of vector tip position drawn for reasons explained earlier. This offset can also be examined by placing the manipulated image on the vector image. The offset is compensated by slight rotation of the extracted curve from the manipulated AFM image to the theoretical one.

3.2.1 Curve Drawing

Deformed CNT shape is traced by using simple Microsoft Power point curve drawing tool as shown below in fig 33 and the image contrast is increased for better curve tracing.

Fig 44. Blue vector line is a reference to position the experimental curve and find a match with the theoretical ones.

3.2.2 Curve Fitting

The blue arrow representing the vector is positioned at the Zero point of the x coordinate and moved towards the curves to match one of the Dimensionless shear stress curves to determine its value. Based on the curve value generated in MATLAB Continuum modeling, deformed shape of the CNT is given a value, in the above example the value of Dimensionless shear stress is estimated...
Various ranges of curves are generated to match the deformed shape of the CNT for different ratio of load application.

3.3 Numerical Calculations

CNT Structural Parameters are extracted from the process described earlier like Dia, Length. Diameter of Carbon Nanotube (D)
Effective contact width (B) which is taken at 5% of the Diameter for reasons explained earlier.
Length of Carbon Nanotube (L)
Elastic Young’s Modulus (E) = 1TPa
Cross-sectional moment of Inertia (I), \( I = \pi/64 \ D^4 \) from equation 3
Dimensionless shear stress (\( \tau^- \)), Determined from the Range of curves
\( \tau^- \) is defined as the shear stress, which the force component acting along the direction of the cross section of material (in this case CNT)

*Numerical example illustrating the shear stress calculation is presented below for the above CNT deformation case.*

**Length (L):** 3.9\( \mu \)m;

**Diameter (D):** 21nm;

**Aspect Ratio (A):** 185.71 (Length/Diameter), Force Applied: 570nN

\( B = 5\% \ \text{of} \ D = \text{0.05}\times D \)

\[
\tau^- = \frac{\tau \ E \ I}{B L^3} = \tau \ E \ \frac{\pi}{0.05 \times 64 \times A^3}
\]

\( E = 1 \times 10^{12} \)

**Dimensionless Shear Stress (\( \tau^- \)):** 450

**Calculated Frictional Shear Stress (\( \tau^- \)):** 69 MPa
4 Data Analysis

4.1 MWCNTs Interaction with Silicon Dioxide (SiO$_2$) Surface

Considering Silicon Dioxide is used in many semiconductors manufacturing process like Gate oxide, field oxide it was our first choice material for CNT surface interaction. Dried CNT solution on SiO$_2$ chip was manipulated using AFM and AFM Images were analyzed to determine the shear stress they experience with the surface. Larger degree of CNT deformation is observed on SiO$_2$ surface, hinting that SiO$_2$ is a rough surface compared to other ones investigated. During the course of this work, we have analyzed 10 data points, with 4 each on SiO$_2$, Gold and 2 on Thiol Surface.

Below are 4 data analyses cases of CNT deformation on SiO$_2$ surface

Case 1:

Nanomanipulation

Fig 4. Shows CNT Manipulation on SiO$_2$ Surface
Length Measurement

Length measurement is performed using XEI, Image processing AFM Software. The red line profile represents the length of the tube, which is approximated to be 1.2µm

Length: 1.2µm

Diameter Determination

A 3 point diameter measurement reveals value around 12nm. The offset (4 units) in the above curves is subtracted from the peak value to obtain better diameter values.

Diameter: 12nm
Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction and the approximate manipulation distance of the CNT.

Dimensionless Shear Stress Extraction (τ value determination)

The drawn curve which represents deformed shape of the CNT along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. The vector is a reference line which is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. To achieve better curve fitting, the vector is moved to either left or right of the 0 x coordinate.

0.48 represents the length ratio of the CNT, where the load is applied. It can be noticed that the curve representing the deformed shape of the CNT doesn’t agree well with the theoretical ones generated by MATLAB, however the curvature around the
drag point is sufficient for a curve match. The curvature around the drag point, matches 450 values theoretical as shown the above figure. \( \tau: 450 \)

**Shear Stress Calculation**

Case 1: Length (L): 1.2\( \mu \)m; Diameter (D): 12nm;

Aspect Ratio (A): 100, Force Applied: 350.91nN

\[ I = \frac{\pi}{64} (D^4) \]

\[ B = 5\% \text{ of } D = 0.05*D \]

\[ \tau = \frac{\tau EI}{BL^3} = \frac{\tau E \pi}{0.05*64*A^3} \]

Dimensionless Shear Stress (\( \tau^* \)): 450

Calculated Frictional Shear Stress (\( \tau \)): 441.7 MPa

Case 2:

Nanomanipulation

![Original CNT](image1.png) ![After Manipulation](image2.png)

Fig 50. CNT Manipulation on SiO\(_2\) Surface

The idea behind two point push is to obtained desirable deformed shape of the CNT, in case the CNT manipulated wasn’t successful in the first attempt. The final deformed shape of the CNT accords with our theoretical modeling.
Length Measurement

The red line profile represents the length of the tube, which is approximated to be 2.3µm. **Length: 2.3µm**

Diameter Determination

A 3 point diameter measurement reveals value curves is subtracted from the peak value to obtain better diameter values. **Diameter: 10nm**

Experimental Curve Fitting
Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction and approximate amount of manipulation distance of the CNT.

\[ \tau: 600 \]

**Dimensionless Shear Stress Extraction (\( \tau \) value determination)**

The drawn curve which represents deformed shape of the CNT along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. The vector is a reference line which is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. 0.5 represents the length ratio of the CNT, where the load is applied. 0.5 represents a perfect symmetrical case of load application at the midpoint of the CNT length. The curvature around the drag point is sufficiently symmetrical to match 600 value theoretical curve as shown the above figure. \( \tau: 600 \)
Shear Stress Calculation

Case 2: Length (L): 2.3µm; Diameter (D): 10nm;

Aspect Ratio (A): 230, Force Applied: 369.91nN

\[ I = \frac{\Pi}{64} (D^4) \]

\[ B = 5\% \ of \ D = 0.05*D \]

\[ \tau' = \tau \frac{E I}{B L^3} = \tau \frac{E \Pi}{0.05*64*A^3} \]

Dimensionless Shear Stress (\( \tau' \)): 600

Calculated Frictional Shear Stress (\( \tau \)): 48.4 MPa

Case 3:

Nanomanipulation

In the above CNT manipulation, CNT is dragged bottom right. The deformed shape does reveal that, CNT has experienced uniform shear stress along its length, while being dragged on SiO₂ surface.

Manipulation Vector Drawn
Nanomanipulation vector is drawn using the XEL AFM Software by the procedure described earlier. Vector is drawn as close to normal as possible to CNT and long enough to allow it to reach equilibrium deformation shape.

**Length Measurement**

The red line profile represents the length of the tube, which is approximated to be 3.9µm. **Length: 3.9µm**
Diameter Determination

A 3 point diameter measurement reveals value around 16nm. The offset (4 units) in the above curves is subtracted from the peak value to obtain better diameter values.

Diameter: 16nm

Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction an approximate amount of manipulation distance of the CNT.

Fig 58. CNT Diameter Determination

Fig 59. Experimental Curve Extraction
Dimensionless Shear Stress Extraction (τ value determination)

The drawn curve along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. Vector as reference line is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. 0.48 represents the length ratio of the CNT, where the load is applied. In this case, we observe non uniform deformation, where one side has curved more than the other. However, the curve around the drag point and one of the sides does provide enough information to match the 350 theoretical curve. $\tau$: 350

**Shear Stress Calculation**

Case 3: Length (L): 3.9 µm; Diameter (D): 16 nm;
Aspect Ratio (A): 243.75, Force Applied: 570.8 nN

$I = \Pi/64 \ (D^4)$

$B = 5\% \ of \ D = 0.05^*D$

$\tau = \tau \ E I / B L^3 = \tau \ E \ Pi / 0.05^*64^*A^3$

Dimensionless Shear Stress ($\tau$): 350

Calculated Frictional Shear Stress ($\tau^\prime$): **23.8 MPa**
Case 4:

Nanomanipulation

In the above CNT manipulation, observing the final deformed shape does reveal that, CNT has experienced uniform shear stress along its length, while being dragged on SiO₂ surface. This result is a near perfect equilibrium deformation CNT shape as seen from the manipulation AFM Image.

Manipulation Vector Drawn

Fig 61. CNT Nanomanipulation

Fig 62. CNT manipulation vector
Nanomanipulation vector is drawn using the XEL AFM Software by the procedure described earlier. Vector is drawn as close to normal as possible to CNT and long enough to allow it to reach equilibrium deformation shape.

**Length Measurement**

The red line profile represents the length of the tube, which is approximated to be 1.4µm. *Length: 1.4µm*

![Length Measurement](image)

**Diameter Measurement**

![Diameter Measurement](image)
A 3 point diameter measurement reveals value around 18nm. There is no offset in the above curve is to subtract from the peak value.

**Diameter: 18nm**

Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction.

*Fig 65. CNT deformation Curve extraction*

Dimensionless Shear Stress Extraction (τ value determination)

The drawn curve along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. Vector as reference line is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. 0.45 represents the length ratio of the CNT, where the load is applied. It’s observed that deformation curve agrees with theoretical ones, with an acceptable deviation on the right side of the curve. **τ: 500**

*Fig 66. Experimental and Theoretical Curve fitting*
**Shear Stress Calculation**

Case 4: Length (L): 1.8µm; Diameter (D): 18nm;
Aspect Ratio (A): 100, Force Applied: 380nN

\[ I = \frac{\pi}{64} (D^4) \]

\[ B = 5\% \text{ of } D = 0.05 \times D \]

\[ \tau' = \tau \frac{E I}{B L^3} = \tau \frac{E \pi}{0.05 \times 64 \times A^3} \]

Dimensionless Shear Stress (\(\tau'\)): 500

Calculated Frictional Shear Stress (\(\tau\)): **490.8 MPa**
4.2 MWCNTs Interaction with Gold Surface

Gold is a useful material for microelectromechanical system (MEMS) switches and is a frequently used material in semiconductors because gold-gold contacts are capable of exhibiting very low resistances and gold being relatively inert forms only modest contamination layers. Hence, we considered investigation of CNT behavior on a gold surface. Below are the 4 cases of shear stress analysis on Gold Surface;

Case 5:

Nanomanipulation

![CNT manipulation](image)

*Fig 67. CNT manipulation*

In the above CNT manipulation, observing the final deformed shape does reveal that, CNT has experienced uniform shear stress along its length, while being dragged on Gold Surface. In the above case, manipulation is done multiple times to achieve the desired CNT deformation. During manipulation CNT might have collided with the particles or dragged the particles along with it. These factors might have influenced the deformed shape of the CNT. Also the deformed point doesn’t coincide with vector position on the CNT; this may be attributed to the Piezo creep of the AFM.
Manipulation Vector Drawn

The manipulation vector is drawn to the drag the CNT to the left. Since the CNT is longer compared to the other manipulated ones, the vector drawn has to be long enough to make the CNT achieve equilibrium deformation or multiple manipulation trials need to be taken until desired manipulation is achieved.

Length Measurement

The red line profile represents the length of the tube, which is approximated to be $4.9\mu m$. 

*Length: $4.9\mu m$*
Diameter Measurement

The 3 point diameter measurement reveals significant offset (5nm), which is subtracted from the peak value (12.5nm) to get diameter value of 7.5nm. **Diameter: 7.5nm**
Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction of CNT manipulation.

*Fig 61. Experimental Curve Extraction*

Dimensionless Shear Stress Extraction (τ value determination)

The drawn curve along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. Vector as reference line is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. It is observed that the vector position agrees with 0.49 length ratio; with one side not deformed as the other. Though the deformation shape doesn’t agree with the theoretical ones, based on the curve fitting we estimate the

*Fig 62 Experimental and Theoretical Curve fitting.*
shear stress to be around 40 to 50. Value 45 is taken as a good approximation, \( \tau: 45 \)

**Shear Stress Calculation**

Case 1: Length (L): 4.9\( \mu \)m; Diameter (D): 7.5nm;

Aspect Ratio (A):650, Force Applied: 650nN

\[ I = \Pi / 64 (D^4) \]

\[ B = 5\% \text{ of } D = 0.05 \times D \]

\[ \tau = \Gamma EI / BL^3 = \Gamma E \Pi / 0.05 \times 64 \times A^3 \]

Dimensionless Shear Stress (\( \tau^- \)): 45

Calculated Frictional Shear Stress (\( \tau^- \)): 0.2 MPa

Case 6:

Nanomanipulation

![Original CNT](Image)

![Manipulated CNT](Image)

**Fig 63. CNT Manipulation**

In the above CNT manipulation, CNT has been dragged far enough providing it with ample opportunity to undergo shear stress along its length. However by observing the final deformed
shape, looks like only the length around the dragged point have experienced shear stress with sides on either side of the bent have experienced minimal stress. Also the surface upon which the drag is performed is does contain particles comparable to the CNT diameter, which might have caused the CNT collision and bouncing of it to a different location CNT. The length around the deformed area contains impurities as seen from the AFM images.

Manipulation Vector Drawn

The manipulation vector drawn is long and normal to the CNT on its surface. Since the CNT is dragged a good distance on the surface with impurities, it has collided with some on the way, which can be seen around the dragged position in the manipulated CNT image. Such surface imperfections might influence the shear stress CNTs experience on the surface.

Length Measurement

The red line profile represents the length of the tube, which is approximated to be 2.5µm. 

Length: 2.5µm
Diameter Measurement

The 3 point diameter measurement reveals a diameter of 8.5nm with an offset (2.5 units) correction. **Diameter: 8.5nm**
Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction of the CNT manipulation.

Fig 67. CNT Manipulation vector

Dimensionless Shear Stress Extraction (τ value determination)

The drawn curve along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. Vector as reference line is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. The vector direction in this case had to be rotated to wee bit to get the vector in line with the deformed shape to the CNT. After the vector rotation, curved shape around the drag length finds a match with 550 value theoretical curve. τ: 550

Fig 68. Experimental and Theoretical fitting
Shear Stress Calculation

Case 6: Length (L): 2.5µm; Diameter (D): 8.5nm;

Aspect Ratio (A): 294, Force Applied: 630nN

\[ I = \frac{\pi}{64} (D^4) \]

\[ B = 5\% \text{ of } D = 0.05*D \]

\[ \tau = \frac{\tau EI}{BL^3} = \tau \frac{E \Pi^4}{0.05^\ast 64^\ast A^3} \]

Dimensionless Shear Stress (\( \tau^* \)): 550

Calculated Frictional Shear Stress (\( \tau^* \)): 21.2 MPa

Case 7:

Nanomanipulation

![Original CNT](image1)

![Manipulated CNT](image2)

Fig 69. CNT Manipulation

In the above CNT manipulation, CNT drag can be observed to the right of the original CNT. On observing the deformed shape, we can estimate minimal shear stress experience along the length of the CNT and the significant bent at the drag point justifies this.
Manipulation Vector Drawn

The manipulation vector is drawn normal to the CNT on the surface. Dragging the CNT with the AFM tip has resulted in a sharp bend at the load application point resulting in kink in the nanotube structure. Also the lower aspect ratio (82) might have resulted in the CNT experiencing minimal shear stress.

Fig 70. CNT manipulation vector

Length Measurement
The red line profile represents the length of the tube, which is approximated to be 2.3µm. **Length: 2.3µm**

**Diameter Measurement**

The 3 point measurement reveals a diameter of around 30nm with a little offset (2 units) correction. **Diameter: 28nm**
Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction. Kink is observed at the drag point.

Fig 73. CNT Deformation Curve extraction

Dimensionless Shear Stress Extraction (τ value determination)

The drawn curve along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. Vector as reference line is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. The deformed shape around the drag point forms a sufficient match with 150 value theoretical curve. There is slight deviation in the deformation on the left side, which can be ignored since the curvature around the drag point agrees with the theoretical one. 0.48 Lower curves represent lower values of

Fig 74. Experimental and Theoretical Curve fitting
Dimensionless shear stress curves for 0.48 length ratio. \( \tau: 150 \)

**Shear Stress Calculation**

Case 7: Length (L): 2.3\( \mu \)m; Diameter (D): 28nm;

Aspect Ratio (A): 82, Force Applied: 589nN

\[ I = \frac{\pi}{64} (D^4) \]

\[ B = 5\% \text{ of } D = 0.05*D \]

\[ \tau' = \frac{\tau EI}{BL^3} = \frac{\tau E \pi}{0.05\times64\times A^3} \]

Dimensionless Shear Stress (\( \tau' \)): 150

Calculated Frictional Shear Stress (\( \tau' \)): **267 MPa**

Case 8:

**Nanomanipulation**

![Original CNT](image1)

![CNT Manipulation](image2)

*Fig 75. CNT Nanomanipulation*
In the above CNT manipulation, CNT drag can be observed to the lower left of the original CNT. On observing the deformed shape, we can see the shift in the drag position upon manipulation for reason explained earlier.

**Manipulation Vector Drawn**

A long manipulation vector is drawn normal to the CNT on the surface providing it with ample opportunity to undergo shear stress deformation along the length. We observe a shift in the drag point and the deformation point may be attributed to piezo creep, also since the vector is a long one during the course of dragging the CNT it might have collided with some visible surface particles and rotated about the drag point.

![Fig 76. CNT Nanomanipulation Vector](image)

**Length Measurement**
The red line profile represents the length of the tube, which is approximated to be $3.2\mu m$.

**Length: 3.2\mu m**

Diameter Measurement

The 3 point measurement reveals a diameter of around $12nm$ with an offset (4 units) correction.

**Diameter: 12nm**
Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction.

*Fig 79. Experimental Curve Extraction*

Dimensionless Shear Stress Extraction (τ value determination)

The drawn curve along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. Vector as reference line is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. The deformed shape around the drag point forms a sufficient match with 100 value theoretical curve. 0.49 Lower Curves represent lower values of

*Fig 80. Experimental and Theoretical Curve Fitting*
Dimensionless shear stress.

\( \tau: 100 \)

Shear Stress Calculation

Case 8: Length (L): 3.2\,\mu m; Diameter (D): 12nm;
Aspect Ratio (A): 266.7, Force Applied: 489nN

\[ I = \frac{\Pi}{64} (D^4) \]

\[ B = 5\% \text{ of } D = 0.05*D \]

\[ \tau' = \frac{\tau EI}{BL^3} = \frac{\tau E \Pi}{0.05*64*A^3} \]

Dimensionless Shear Stress (\( \tau' \)): 100

Calculated Frictional Shear Stress (\( \tau' \)): 5.1MPa
4.3 MWCNTs Interaction with Thiol Surface

Motivation to investigate CNT interaction with Thiol surface was a co student, who is also working on “Shear stress estimation of CNT (SWNT) with surfaces” and this surface is supposedly more slippery among the other two surfaces investigated earlier. The type of thiol used here is Octadecanehiol.

There are more data analysis than just the 2 presented below, however only the below 2 cases are comparable with the theoretical ones.

Case 9:

Nanomanipulation

In the above CNT manipulation, unlike the drag being normal to the CNT lying on the surface, here we have randomly dragged the CNT to the left by some distance considering this a long nanotube. In the above case, manipulation has been done several times by incrementing both the manipulation vector and the vertical force until a desired CNT deformation is achieved. We observe a decent deviation in the manipulated CNT image between the vector end position and
deformed CNT location, possible reasons could be CNT collision with surface particles, AFM Tip adhesion or partial CNT slip with Thiol being a slippery surface.

**Manipulation Vector Drawn**

A long manipulation random vector is drawn dragging the CNT to the left of its original position.

**Length Measurement**

The red line profile represents the length of the tube, which is approximated to be 3.9µm. **Length: 3.9µm**
Diameter Measurement

The 3 point measurement reveals a diameter of around 6nm with an (2 units) offset correction. **Diameter: 6nm**
Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction.

*Fig 85. Experimental Curve Extraction*

Dimensionless Shear Stress Extraction ($\tau$ value determination)

The drawn curve along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. Vector as reference line is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. The above discussed deviation is corrected by rotating the drag vector a bit for better curve matching. However, the non-uniform shear stress experience on either side of the drag point allows us to estimate a range of shear stress.

*Fig 86. Experimental and Theoretical Curve Fitting*
isn’t large it wouldn’t cause a major change in the shear stress value. 0.48 Lower Curves does represent the above deformation reasonably well. Since the median of the range is 75, a value of 75 is chosen as an appropriate value to represent the dimensionless shear stress. $\tau$: 75

**Shear Stress Calculation**

Case 9: Length (L): 3.9 $\mu$m; Diameter (D): 6 nm;  
Aspect Ratio (A): 650, Force Applied: 719 nN  
$I = \Pi / 64 (D^4)$  
$B = 5\%$ of D = 0.05*D  
$\tau' = \tau EI / BL^3 = \tau EI / 0.05*64*A^3$  
Dimensionless Shear Stress ($\tau'$): 75

Calculated Frictional Shear Stress ($\tau$): 0.2 MPa

Case 10:

**Nanomanipulation**

In the above CNT manipulation, CNT drag can be observed to the upper right of the original CNT. As seen from the AFM images, the CNT drag is performed on relatively clean surface when
compared to other ones dragged earlier. Manipulated AFM Image reveals a by non uniform shear stress observation along the length of the tube on either side of the drag point and position of the deformed CNT doesn’t match vector direction. In this case, possible reasons could be AFM Tip adhesion or partial CNT slip iterating that Thiol is a slippery surface compared to the Gold and SiO₂.

Length Measurement

The red line profile represents the length of the tube, which is approximated to be 1µm. **Length: 1µm**

![Fig 88. CNT Length Determination](image)

Diameter Measurement

The 3 point measurement reveals a diameter of around 10nm with an offset correction.

![Fig 89. CNT Diameter Determination](image)
Nanomanipulation of Carbon Nanotubes Using AFM

**Diameter: 10nm**

### Experimental Curve Fitting

Curve is drawn matching the deformed shape of the CNT with the procedure described earlier. The Blue line indicates the vector direction.

*Fig 90. Experimental Curve Extraction*

### Dimensionless Shear Stress Extraction (τ value determination)

The drawn curve along with vector (Blue line) is mapped to the theoretically generated MATLAB curves. Vector as reference line is centered on the 0 x coordinate to theoretically determine the value of the experimental deformed shape. The above discussed deviation is corrected by rotating the drag vector a bit for better curve matching. However, the non uniform shear stress experience on either side of the drag point allows us to estimate a range of shear stress. Since, the range isn’t large it wouldn’t cause a major

*Fig 91. Experimental and Theoretical Curve Fitting*
change in the shear stress value. 0.48 Lower Curves does represent the above deformation reasonably well. Since the median of the range is 85, a value of 85 is chosen as an appropriate value to represent the dimensionless shear stress. \( \tau: 85 \)

**Shear Stress Calculation**

Case 10: Length (L): 1.86\( \mu \)m; Diameter (D): 23nm;

Aspect Ratio (A): 80.8, Force Applied: 380nN

\[ I = \pi/64 \ (D^4) \]

\[ B = 5\% \ of \ D = 0.05*D \]

\[ \tau' = \tau \ EI / BL^3 = \tau \ E \pi / 0.05*64*A^3 \]

Dimensionless Shear Stress (\( \tau' \)): 85

Calculated Frictional Shear Stress (\( \tau' \)): 158 MPa
5 Results and Discussion

The shear stress results of frictional interaction between CNTs and their respective surfaces are summarized in the table below.

Table 5.1 Summary of shear stress computed from manipulated nanotube shapes

<table>
<thead>
<tr>
<th>Case No</th>
<th>Surface</th>
<th>Dia (nm)</th>
<th>Length (µm)</th>
<th>Aspect Ratio</th>
<th>Load app Point</th>
<th>Dimensionless Shear stress</th>
<th>Shear stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO₂</td>
<td>12</td>
<td>1.2</td>
<td>100</td>
<td>0.48</td>
<td>450</td>
<td>441.7</td>
</tr>
<tr>
<td>2</td>
<td>SiO₂</td>
<td>10</td>
<td>2.3</td>
<td>230</td>
<td>0.5</td>
<td>600</td>
<td>48.4</td>
</tr>
<tr>
<td>3</td>
<td>SiO₂</td>
<td>16</td>
<td>3.9</td>
<td>243.7</td>
<td>0.5</td>
<td>350</td>
<td>23.8</td>
</tr>
<tr>
<td>4</td>
<td>SiO₂</td>
<td>16</td>
<td>1.6</td>
<td>100</td>
<td>0.45</td>
<td>500</td>
<td>490.8</td>
</tr>
<tr>
<td>5</td>
<td>Gold</td>
<td>7.5</td>
<td>4.9</td>
<td>653</td>
<td>0.49</td>
<td>45</td>
<td>0.21</td>
</tr>
<tr>
<td>6</td>
<td>Gold</td>
<td>8.5</td>
<td>2.5</td>
<td>294</td>
<td>0.49</td>
<td>550</td>
<td>21.2</td>
</tr>
<tr>
<td>7</td>
<td>Gold</td>
<td>28</td>
<td>2.3</td>
<td>82</td>
<td>0.48</td>
<td>150</td>
<td>267</td>
</tr>
<tr>
<td>8</td>
<td>Gold</td>
<td>12</td>
<td>3.2</td>
<td>266.7</td>
<td>0.49</td>
<td>100</td>
<td>5.1</td>
</tr>
<tr>
<td>9</td>
<td>Thiol</td>
<td>6</td>
<td>3.9</td>
<td>650</td>
<td>0.48</td>
<td>75</td>
<td>0.2</td>
</tr>
<tr>
<td>10</td>
<td>Thiol</td>
<td>1.8</td>
<td>23</td>
<td>80.8</td>
<td>0.48</td>
<td>85</td>
<td>158</td>
</tr>
</tbody>
</table>

The summarized manipulation and shear stress results in the table 5.1 provides us with a general understanding of the frictional shear stress CNTs experience with various surfaces based on simple beam modeling. The higher median shear stress values for SiO₂, intermediate for gold and lowest for thiol functionalized gold tells us something about their interaction with the surface they are manipulated on. Our experiments show that the extracted values of shear stress between the MWNT and the surfaces described in table 5.1 vary over a wide range for gold (0.21-267MPa) and thiol functionalized gold surfaces, Octadecanethiol (0.2–158MPa) and within a smaller range for SiO₂ (23.8-490.8MPa) surfaces. It is still early to estimate the average shear stress on these surfaces based on this method of manipulation. A more consistent range and more manipulation results are needed to draw accurate conclusions regarding CNT interactions with these surfaces.

Though the results cover a wide spectrum, certain cases of manipulation are within a reasonable value when compared to the previous work on shear stress estimation using an AFM. M. R.
Falvo et al.\textsuperscript{42}, based lateral AFM force measurements for sliding and rolling cases, estimated that the energy cost for rolling is larger than that of the sliding cases. Though a shear stress of 2 MPa between MWNTs and a graphite surface were calculated, they didn’t have any comparable insight into rolling owing to a lack of experimental data on microscopic length scales. Tobias Hertel et al.\textsuperscript{10} demonstrated that AFM tip is effective in controlling the shape and position of individual MWNT dispersed on a surface and such manipulations are due to the interaction between nanotubes and the substrate. The direct evidence for such interactions is provided by the study of elastic distortions of the tubes interacting with other tubes and the substrate. Based on the observed nanotube deformations and obtaining their binding energy, 10 MPa between MWNTs and a hydrogenated silicon (100) surface were calculated. J.-H. Hsu et al.\textsuperscript{43} utilized the interaction between MWNTs and silica surface using AFM lateral manipulation for shear stress estimation. The MWCT is mechanically manipulated by AFM tip scanning mechanism and a controlled normal force of the AFM probe, it was found that lateral force applied to the MWCNT could overcome the adhesion between MWCNT and silica surface, causing individual MWCNT to rotate on the silica. According to the results, the shear stresses are 59.6 MPa and 64.8 MPa for the 100 nm dia MWNT and 60 nm dia MWNT respectively. We need more cases for our manipulation method to support the shear stress estimation relatively accurately. Another influence on the calculated results of the shear stress might be the contact width, which is assumed to be 5\% of the MWNT diameter in our model\textsuperscript{21}, while there are other literature papers using 11\% or 23\% of the MWNT diameter, either by an assumption\textsuperscript{43} or a JKR model\textsuperscript{42}. Since the contact width varies with the tube diameter, the shear stress is preferred for comparing different diameter tubes over the shear force per unit length, which is relevant for tubes of the same diameter.

From our experiments, apart from CNT deformation results we also experience other results like partial tube movement, nanotube cutting or breaking and similar to rolling behavior. These different CNT behaviors imply there are other parameters to be taken into account during manipulation than just dropping the CNT solution on the chip and dragging them. Manipulation results which were something like rolling weren’t considered as since the deformation shape wasn’t enough to extract shear stress information and our method of estimating shear stress is by dragging the tube around the midpoint of CNT. M. R. Falvo et al.\textsuperscript{42}, investigated CNT rolling behavior on graphite surfaces and observed that rotation of the CNT depends on the location of the AFM tip during the push. They also observed that by using the lateral force of the AFM tip gradually, CNT rotated by a fixed amount. CNT cutting or breaking behavior was also observed.
by Tobias Hertel et al.,\textsuperscript{10} in attempts to drag the nanotube across the surface. A particular successful cutting experiment showed that the nanotube was significantly stretched before it eventually broke, since the nanotube was contaminated with amorphous carbon and this contamination may have increased its adhesion to the substrate. It would be interesting to check whether the time between the time of dropping the CNT solution and manipulation makes a difference to the CNT behavior. Making separate measurements on IPA and DMF solutions would be interesting as well to determine whether different CNT solution with the same manipulation procedure changes its interaction behavior or not.

There were many more manipulations than just the 10 shown in table 5.1, since it’s not possible to extract shear stress information from behaviors like cutting, partial tube movement and rolling they weren’t included in analysis and summary table. Many of thiol functionalized gold manipulation were similar to rolling of the tubes, partial movement of the tubes; Hence it was relatively more challenging to accumulate deformation cases, leaving us with only two comparable ones. We also observe non uniform deformation in those two cases, indicating CNTs may not experience uniform friction along their length while being dragged on thiol functionalized gold surface or the surface offers different friction energy at various surface points. Comparing results of this experiment on thiol functionalized gold surface with that of Huiyan (Shear stress estimation on Thiol Surface) which is still under progress should provide us with better understanding of CNT behavior on Thiol Surface. Though CNTs were easily displaced from their original position on Thiol surface, deformed shape and position according to the vector end point made it a difficult proposition to drawn any conclusion w.r.t to the theoretical modeling.

During the course of the experiment, some of the manipulated CNT weren’t observed in the Field of View (Scan area on the display monitor); possible reasons could be during the manipulation CNTs might have bumped off the particles and landed at a different location than the intended vector direction, AFM tip adhesion could have caused dropping of the manipulated CNT at different location, during mode change from contact to non-contact mode. Since the surface of manipulation wasn’t the cleanest, collision might have occurred between the CNT and surface particles during drag movement and in turn affected the orientation of some the manipulated results when compared with the vector direction. Such errors could be reduced by procuring very clean CNT Solution to eliminate the surfactants and amorphous carbon particles. Manipulation in vacuum environments wouldn’t be a bad idea just to figure out how much atmospheric moisture on the surfaces adds the measurement error. Tracking CNT movement
during drag by imaging the intermittent positions before the final deformed shape is imaged, helps us to understand AFM tip behavior with the manipulation vector and the nature of CNT movement during such drag operations.

Case numbers 5 and 9 are examples of manipulating very high aspect ratio CNTs (653, 650). Manipulating such high aspect ratio tubes required repeated manipulation trials to obtain the desired deformation behavior. The deformation shape in these examples yields a low value shear stress value, may be because vector wasn’t long enough or the surface particles influenced their manipulation or there could be other reasons we aren’t aware of. Such high aspect ratio tubes require large acceptable manipulation (void of particles) area and a relatively old AFM tip, since the new ones are sharp and may just slip over the nanotube or cut them to drawn any shear stress conclusion based on the current manipulation method.

Usage of new and relatively old AFM tips provides different manipulation behavior. New AFM tips lead to cutting of the tubes more often than the older ones, hence lower range of vertical force is recommended to start with or the sharpness of the tip could be decreased by a few contact mode scan on a relative clean surface before starting manipulation. AFM scanning with surface particles result in the tip contamination; this not only affects AFM imaging by degrading image quality but also may lead to undesired CNT manipulation behavior like tip adhesion and shift in the drag point. Hence, we just can’t emphasize how desirable a clean manipulation surface is to such an experiment. It might also be a good idea to record the required force as a function of aspect ratio of the tube for desired manipulation.
6 Conclusion and Future Work

A simple approach to determine the frictional interaction between a CNT and various surfaces using an AFM has been demonstrated with AFM tip dragging the CNT along the surface, simple Microsoft curve tools used to extract the deformed shape and then an effective curve fitting procedure. Dragging of nanotubes on various surfaces turned out to be an interesting investigation, which provides us with an understanding of the forces that nanotubes experience during their movement on surfaces beneath. This simple investigation method also provides us with a basic understanding surface property and the amount of force needed to manipulate objects on these surfaces.

Progress towards estimating shear stress by dragging the CNT on SiO$_2$, Gold and Octadecanethiol surfaces has been made. Although a wide range of shear stress for gold (0.21–267MPa) and thiol functionalized gold surfaces (0.2–158MPa) are obtained, a smaller range is obtained for SiO$_2$ (23.8-490.8MPa). It’s premature to calculate a median of shear stress on these surfaces based on few cases; hence more manipulation results are needed to support the CNT shear stress study. However, this method manipulation does provide us with an insight into CNT surface interaction with SiO$_2$, gold and octadecanethiol surfaces. The gold and octadecanethiol surfaces are different than those used in similar work done by M. R. Falvo et al.\textsuperscript{42} on graphite surface, Tobias Hertel et al.\textsuperscript{10} on hyrodgenate Si surface and J.-H. Hsu et al.\textsuperscript{43} on silica surfaces. The current shear stresses on SiO$_2$ are comparable to the previous SiO$_2$ (silica) results, although with a large scatter.

Manipulation demonstrated using an AFM tip technique is a simple pragmatic approach for a variety of CNT diameters and lengths, provided the aspect ratios are decent (80<Aspect Ratio<300). High values of aspect ratio (~650) required more manipulation trials to achieve a sufficient change in the final shape of the CNT to accurately resolve the shear stress. The shear stress offered by the substrate while dragging isn’t uniform along the length of the nanotube as observed from the thiol functionalized gold surface. The best results are obtained when manipulation is done with the AFM tip placed around the midpoint to drag the nanotube normal with respect to the nanotube on surface,\textsuperscript{27} decent aspect ratio CNT and relatively clean surface.

The current manipulation procedure required lot of manipulation trials to achieve the desired CNT behavior. To make this manipulation procedure more efficient, certain improvements to
existing experimental procedure are necessary which forms a basis of future work. Carrying this work ahead on a clean surface and precise tracking of the CNT movement according to the vector drawn should bring in some improvement in making this manipulation procedure effective.

The experimental procedure still needs more analysis and the reason for wide range of shear stress value is worth an investigation, although a standard manipulation and deformation curve extraction procedure is established. Better understanding of the experimental procedure is required. Some possible approaches are to explore the CNT surface interaction in vacuum conditions to analyze the surface moisture effect, to check variation in the CNT interaction behavior when different CNT solutions are used, to work to start with cleaner surfaces and collection of more manipulation data on each surface for reasonable consistency. This work is supported by continuum level modeling, which is used to determine the relationship between the shape of the dragged CNT and the frictional interaction which occurred between the CNT and substrate.
7. References:


Nanomanipulation of Carbon Nanotubes Using AFM


21. Tobias Hertel et al., ”Deformation of carbon nanotubes by surface van der Waals forces”, VOLUME 58, NUMBER 20, 1998 The American Physical Society


29. XE-150 TM, Atomic Force Microscope Next Generation AFM/SPM for Large Samples

30. XE150 User manual, Version 1.7 Park Systems Corporation


36 http://en.wikipedia.org/wiki/Thiol
37 M. R. Falvo et al, “Nanometre-scale rolling and sliding of carbon nanotubes”, NATURE | VOL 397 | 21 JANUARY 1999
38 http://www.parkafm.com/application/overview.php
40 Noncontact Atomic Force Microscopy, Volume 2, By Seizō Morita, Franz J. Giessibl, Roland Wiesendange