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RICE UNIVERSITY

Strength Characterization of Suspended Single-Wall Carbon Nanotube Ropes

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

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ABSTRACT

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Carbon nanotubes are expected to have incredible mechanical properties. Before they can be used intelligently in engineering applications, the capabilities and limitations of these properties must be well understood. This research measured the strain-to-failure of single-wall carbon nanotubes (SWNTs) by elastically straining suspended SWNT ropes using an atomic force microscope in lateral force mode. The ropes experienced multiple scanning cycles at high strains with no plastic deformation. The nanotube ropes were observed to strain as elastic strings, instead of as stiff beams. A maximum strain of 5.9 ± 0.9% was observed, which led to a lower bound on the yield strength of 45 ± 7 GPa for single-wall carbon nanotubes. These results are the first experimental evidence that supports the theoretical strain-to-failure of 5% for SWNTs. This research helps to establish single-wall nanotubes as a structural material by further quantifying their mechanical properties.
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1. Introduction

The amazing mechanical applications envisioned for carbon nanotubes cannot be fully realized until their mechanical properties are well understood. Two such fundamental properties that are not completely known are the strain-to-failure and yield strength. Theorized mechanical properties of carbon nanotubes make them an incredible structural materials candidate. The exact mechanical properties of SWNTs are not established, but already nanotubes are known to be lighter, stronger, and more resilient than the best steels or plastics available. However, before these excellent characteristics can be exploited for applications it is important that the capabilities and limitations of nanotubes be fully explored and studied. This research uses an atomic force microscope (AFM) in lateral force mode to apply forces to freely suspended single-wall carbon nanotube (SWNT) ropes in order to better characterize the mechanical properties of SWNTs. This research is the first experimental evidence to support the expected strain-to-failure of 5% predicted by Nardelli et al. [1, 2] and succeeds in providing a lower bound on both the strain-to-failure and yield strength that far surpasses any other structural materials’ attributes.

Because of their nanometer size, carbon nanotubes introduce two critical challenges to the physical investigation of their mechanical properties – sample preparation and experimental execution. The sample must be prepared in a reproducible manner. The execution of the experiment requires the ability to apply and measure small forces that can be directed in a controllable manner on the appropriate scale. For this
thesis research, two key factors allowed the above challenges to be met: semiconductor industry silicon etching techniques were used to prepare the sample of suspended SWNT ropes, and an AFM was used to measure lateral forces on the nanotube ropes.

Nanotubes have been dispersed onto silicon for several years as AFM assays. In addition, the fabrication of micron and submicron sized objects from silicon is well understood due to the semi-conductor industry’s research efforts over years. These two items make silicon the ideal substrate for carbon nanotube mechanical tests. By exposing sections of a silicon substrate to an etchant such as potassium hydroxide, trenches can be created. This research took advantage of such controlled manipulation of silicon to create a single-wall nanotube rope freely suspended over a silicon trench and secured at both ends. The motivation for having freely suspended ropes was to obtain true measurements of mechanical properties, isolated from surface-tip friction complications such as noise, damage to the AFM tip, and anomalous force measurements. Suspended ropes also allowed for much more controllable force measurements with the AFM.

The AFM allows nanometer scale experimental work involving the physical manipulation of objects. Prior to its acceptance, research at this scale relied on optical microscopy and micro-machined parts and tools. In lateral force mode, the forces experienced by the AFM tip are very well measured; coupled with the AFM’s innate abilities to locate and image nanometer-scale objects, this apparatus is the ideal tool for determining strength characteristics of carbon nanotubes.

For this thesis, an AFM with lateral force mode capability was the main experimental apparatus. The work involved careful movements of the AFM tip followed by lateral force measurements, which were used to model the rope’s response. The AFM
tip was brought close to a nanotube rope that had been previously identified using a scanning electron microscope. The tip was allowed to slowly float off the surface and was then locked in place. The tip was slowly brought in towards the nanotube rope in spaced increments. It was allowed to scan repeatedly at each step to watch for breakage or deformation. Advances were made until a failure occurred. SEM images of the nanotube rope were captured before and after the experiment. The data was fitted to a model treating the nanotube rope as an elastic string. The model was found to be accurate and showed no plastic deformation throughout the tip advancement. Values for the strain-to-failure and yield strength were obtained, 5.9 ± 0.9% and 45 ± 7 GPa respectively.

These results are lower bound values for the mechanical properties of both individuals and ropes of single-wall carbon nanotubes. The strain-to-failure results agree with the theoretically predicted value of 5%, while the yield strength result provides further support as to the order of magnitude of its true value. The fact that intermolecular forces between individual nanotubes inside a rope hampered results strongly suggests that the true strain-to-failure and yield strength are actually higher than reported here. However, these results provide an excellent step towards realizing those true strength characteristics.
2. Carbon Nanotube Background

Carbon nanotubes were first discovered by Sumio Iijima of NEC Corporation in 1991 [3]. When voltage was applied between two carbon electrodes contained within an argon environment, carbon needles were observed on the negative electrode and examined by transmission electron microscopy. They appeared to be microtubules of graphitic carbon, most containing multiple shells, like concentric hollow cylinders. These macromolecules became known as carbon nanotubes.

2.1 Nanotube Synthesis

Due to experimental conditions, the first nanotubes produced and studied were predominantly multi-walled nanotubes (MWNTs). A year later, two independent research groups found that by adding small amounts of transition metals, namely cobalt, nickel, or iron, growth would favor single-wall carbon nanotubes (SWNTs) [4, 5]. The arc-discharge method of nanotube production resulted in nanotubes with few structural defects and is still widely used in the field of nanotube production. Its only disadvantage is its small yield.

Material used throughout this research was the product of the latest process for production, pulsed laser vaporization (PLV) [6]. A rotating target of pressed graphite containing small amounts of cobalt and nickel powder is subjected to nanosecond laser pulses on the order of 2.5W of power. The incident laser creates a plume of plasma, wherein the metal particles catalyze single-wall nanotube growth. The entire process
occurs in a sealed atmosphere of flowing argon. The product is then carried downstream and collected. The PLV process can produce an order of magnitude more nanotubes than current arc-discharge methods (order 10g vs. 1g) [7, 8]. A scaled version of the PLV technique plus various purification steps [7] has become the standard for Tubes@Rice, one of the major providers of nanotubes in the world.

2.2 General Properties of Carbon Nanotubes

A carbon nanotube can best be thought of as a sheet of graphite, which has been rolled into a narrow, long cylinder and then capped at either end by a hemisphere. Another appropriate visualization is that of a C_{60} sphere that has been cleaved in half and then elongated, with a graphite sheet of carbon atoms filling the gap between the two distanced halves. Either way, the end result is a nanotube, on the order of 150nm in length and 1.5nm in diameter.

Like graphite, nanotubes are comprised of interconnected six-member rings, or hexagons, of carbon atoms. These hexagons of carbon span the entire surface of a nanotube and are the source of many of the impressive qualities of nanotubes. The spatial orientation of the hexagon with respect to the nanotube's length is not fixed, resulting in three chirality classifications of nanotubes – armchair, zigzag, and chiral. Armchair and zigzag nanotubes are named after the pattern of bonds exposed on an open end. Chiral nanotubes are all other nanotubes. Figure 2.1, taken from Dresselhaus et al.'s Science of Fullerenes and Carbon Nanotubes [9], depicts the three types of nanotubes.
Figure 2.1: The three types of nanotubes are shown with their cross-sections exposed. Nanotubes were named after the general shape of their cross-section. Note the varying orientation of the hexagons with respect to the nanotube axis.

The novelty of carbon nanotubes extends well beyond an appreciation of physical uniformity and uniqueness. Theoretical predictions regarding all manner of properties have been proposed ever since their discovery — electrical conductivity better than copper, thermal conductivity better than diamond, strength characteristics better than steel. Experimental work, coupled with more elaborate theoretical research, has provided introductory glimpses into many of these properties.

Because of their impressive theoretical electronic properties, nanotubes are the primary contender for device elements in the next evolution of computers. Theoretical work predicted that nanotubes could be metallic or semi-conducting, depending on their chirality [10, 11]. Experimental work involving scanning tunneling microscopy and
spectroscopy has already confirmed these electronic properties [12, 13]. This variety of properties allows for all manner of electronic devices and systems to be based on nanotubes. Conductivity measurements for individual single-wall nanotubes have been made [14] and an effective field-effect transistor has been successfully engineered and demonstrated [15]. The high conductivity is the result of the unmodified bond structure running the length of the nanotube. The conductivity is reduced as more scattering sites are introduced, either through chemical or physical means [16]. The electronic properties of carbon nanotubes are inevitably linked to their strength characteristics — resistance measurements of strained nanotubes have shown a direct correlation between electrical conductivity and plastic deformation [17].

2.3 Strength Characterization of Carbon Nanotubes

Because of their uniform structure and strong carbon bonds, nanotubes have been expected to have high strength properties from their discovery. Their similarity to graphite fibers automatically makes them viable candidates for reinforcement of composite materials and super-strong wires or cables. Unfortunately, their small size has made direct characterization difficult. Whole technologies and approaches have been adopted for manipulation of nanotubes as a result of this challenge, such as the atomic force microscope [18 – 21] and Yu et al.’s nanostressing stage [22].
2.3.1 Previous Theoretical Strength Research

Theoretical calculations appeared almost immediately following Iijima’s discovery of nanotubes. Due to computational difficulties, theoretical work has focused almost entirely on single-wall nanotubes. Although this thesis does not rely on theoretical calculations, this research does provide a link between theory and experiment, a comparison between what is expected and what is reality. In addition, understanding mechanical activity on the molecular level, as described by theory, gives greater meaning to the observations described in this thesis. Theoretical research provides valuable insights, both in descriptions of the exact nature of nanotube mechanical failures and expected strength characteristics for single-wall carbon nanotubes (SWNTs).

Theoreticians have shown that the elastic limit for single-wall nanotubes and the mode of failure (ductile vs. brittle) are dependant on both chirality and radius [1, 23 – 25]. Molecular dynamics calculations revealed that a zigzag nanotube has nearly twice the elastic limit of an armchair tube of equal radius [25]. In ductile failure, according to theory, the diameter shrinks as defects are formed, thereby increasing the surface stress for a constant applied tension [23]. The formation barrier for such defects increases with increasing tube diameter, theoretically making larger diameter tubes more resistant to applied strains [24]. However, in this thesis research the nanotube ropes are a distribution of nanotube diameters and chiralities. Investigation of the mode of failure as a function of diameter or chirality is therefore not feasible.

While theoretical models governing the stress failure of nanotubes are illuminating, an understanding of key strength properties such as strain-to-failure and Young’s Modulus is essential. Engineering applications are primarily interested in when
a material breaks or deforms as opposed to how a material breaks or deforms. Materials are chosen to withstand stress and strain; accurate knowledge of mechanical properties allows the best material for the job to be used. Simulations have repeatedly shown that the formation of strain-related defects is energetically unfavorable below strains of 5%. Depending on the actual activation barriers of these defects, the strain-to-failure may be as high as 30% [1]. Most calculations of the Young’s modulus of SWNTs result in values close to that of in-plane graphite, namely 1 TPa [26, 27]. However, Yakobson et al. present a value of $Y = 5.5$ TPa, using the π orbital extension as the thickness of the nanotube (otherwise the various theoretical calculations are consistent) [26-28], and Gao et al. present a value of $Y \approx 0.65$ TPa using interaction potentials [29]. The former result is now considered incorrect because of its choice for the nanotube thickness, while the latter uses a conservative model. All this previous work provides a solid foundation and direction on which experimental research can build.

2.3.2 Previous Experimental Strength Research

Experimental carbon nanotube research has had two obstacles to-date: size and production of nanotubes. A typical single-wall nanotube rope is 1-10 microns in length and 10-100nm in diameter; however, individual single-wall nanotubes (SWNTs) are on the order of 100nm long and 1.5nm in diameter. Controlled manipulation and imaging of these objects is challenging, but has become more easily realized through technologies such as atomic force microscopy (AFM) [30].

The second complication is the production of usable amounts of defect-free SWNTs. Multi-wall nanotubes (MWNTs) have been easily obtained from the beginning,
through arc-discharge methods previously described. Much of the early experimental work in this field of nanotube research was first applied to MWNTs, allowing for an initial glimpse into the general order of nanotube strength. With the development of pulsed laser vaporization, high quality single-wall nanotubes (SWNTs) are now readily available [6, 7], allowing for more insightful and direct measurements of strength properties. This research [2] pre-dates some of the background work presented. While the research was published prior to some of the experiments, this thesis was written afterwards. These experiments [21, 31] are useful in the context of this thesis.

Although this thesis focuses exclusively on SWNTs, many of the experimental techniques were first developed using MWNTs and later applied to SWNTs. MWNTs are widely considered inferior to SWNTs for mechanical applications for a number of reasons. MWNTs have structural defects due to their large size and concentric nanotube composition. These defects serve as nucleation sites for strain failure, resulting in lower strain-to-failure and yield strength characteristics. MWNTs are also less flexible than SWNTs because of their larger diameter. The only advantage MWNTs have is their accessibility, both in cost from outside sources and in the simplicity of the synthesis apparatus necessary for in-house production.

Treacy et al. provided the first direct measurement of carbon nanotubes’ elastic modulus [32]. Freestanding multi-wall nanotubes were observed in a transmission electron microscope (TEM) under a controlled temperature environment. The thermal vibrations of freestanding rods gave direct measurements on the elastic modulus. An average value for the Young’s modulus, $Y = 1.8$ TPa, was obtained. Krishnan et al. repeated the same experiment some years later, this time involving SWNT and yielding
\( Y_{\text{exp}} = 1.25^{+0.45}_{-0.33} \text{TPa} \) [33]. This result is considered by many to be the most accurate value, to date, for the Young’s modulus of SWNTs. It is used in this research when a value for \( Y \) is necessary.

Although thermal vibrations led to the first values for the Young’s modulus of nanotubes, most experimental work has focused on more traditional methods of characterization, albeit on a much smaller scale. Early on, nanotubes were found to be very flexible and durable macromolecules. Iijima et al. presented TEM images of MWNTs captured in bent positions along with proof that such bending was reversible and elastic [34]. Further theoretical simulations showed that high degrees of repeated bending and torsion would not affect single-wall nanotubes [28]. Additional research groups have gone on to use an AFM tip to manipulate, bend, and rotate MWNTs with no failures or visible plastic alteration to the nanotubes’ structure [35, 36]. Such work showed the versatility, simplicity, and possibilities of the AFM as it relates to controlled manipulation of carbon nanotubes. Three types of experiments involving the use of atomic force microscopy to measure forces and apply controlled strains have been performed to date. Two of the three were first performed using MWNTs and then later applied to SWNT ropes or individuals.

One approach used an AFM tip to bend nanotubes secured on a substrate. By measuring the lateral forces on the tip, values for the Young’s modulus were obtained [18]. In Wong et al.’s research, MWNTs were dispersed on a low friction substrate of MoS\(_2\) and then pinned with pads of SiO\(_2\) using a shadow mask. For comparison, the same experiment was also performed on SiC nanorods. A Young’s modulus of \( Y = 1.28 \pm 0.59 \) TPa and \( Y \sim 600 \) GPa were determined for MWNTs and SiC nanorods.
respectively. To the author’s knowledge, these experiments have not been repeated on SWNTs.

A second set of experiments involving strength characterization of nanotubes focused on a custom-made nanometer-scale mechanical loading device. Yu et al. designed and implemented a “nanostressing stage” wherein a nanotube rope is mounted between two AFM tips inside a scanning electron microscope (SEM). The rope is secured to each tip by van der Waal forces between deposited carbonaceous material on the tip and the nanotubes. Controlled forces can then be applied to the system while being monitored via the SEM. This technique was first applied to MWNTs [22] and then to SWNT ropes [31]. The Young’s modulus for the outer sheath of MWNTs ranged from 270 to 950 GPa, while Y = 18 – 68 GPa was seen for entire MWNTs with strain-to-failure as high as 12% [22]. Although impressive at first glance, the 12% MWNT strain-to-failure result included telescoping strain where an outer sheath broke, but an inner nanotube held. SWNTs yielded Y_{avg} = 1.002 TPa, maximum strain-to-failure of 5.3%, and tensile strength of S = 13-52 GPa [31]. The experiments bear many of the same characteristics as this thesis work: SWNT ropes of comparable lengths are strained with no substrate involvement. Because of these similarities, the results mirror those of this thesis, namely, strain-to-failure of ~5% and tensile strength ~50 GPa.

The third, and more direct, approach involving AFMs to measure strength properties has the nanotube secured on both ends and stressed in the middle using an AFM tip. As supplemental research to the work involving catalyzed growth of nanotubes from metallic islands on a silicon substrate, Kong et al. measured the tensile strength of an individual single-wall nanotube that had bridged between two islands [19]. A value of
~280 GPa for the tensile strength was obtained and was the first strength characterization experiment where the nanotube was fixed at its ends. This result is promising, but it is still an unconfirmed value for an individual single-wall nanotube’s (SWNT) tensile strength.

Salvetat et al. eliminated the underlying surface by depositing MWNTs [20], and later, SWNT ropes [21] onto a porous alumina membrane. An AFM tip was then maneuvered directly above the center of a suspended nanotube. A controllable force was applied and the normal deflection was measured. The vertical displacement of the nanotube was calculated directly from the experiments, and the strength characteristics were determined. The average value of the elastic modulus for arc-discharge MWNTs was found to be \( E_{\text{avg}} = 810^{+430}_{-160} \text{ GPa} \) [20] while an elastic modulus of \( \sim 1 \text{ TPa} \) was deduced from SWNT experiments [21]. These experimental techniques are similar to those of this thesis, but because Salvetat et al. focused on different mechanical properties, a comparison of the results is not possible.

In summary, previous theoretical and experimental work has presented a strain-to-failure of at least 5% [1] and a Young’s modulus of \( \sim 1 \text{ TPa} \) [21, 33] for individual single-wall nanotubes (SWNTs), with a yield strength of \( \sim 50 \text{ GPa} \) for SWNT ropes [31]. By building on the use of the atomic force microscope to manipulate MWNTs on surfaces [18, 35, 36], this thesis research was able to contribute the first experimental evidence that the strain-to-failure of SWNTs is at least \( 5.9 \pm 0.9 \% \) with an accompanying yield strength of \( 45 \pm 7 \text{ GPa} \). Both of these mechanical properties support single-wall carbon nanotubes as a remarkable material of the future.
3. Thesis Research

This thesis research involved experimental measurements of nanotube rope strains in order to better characterize the strain-to-failure and the yield strength of SWNTs. This research’s approach took advantage of the physical geometry of an elastic string secured at both ends. Namely, the strain came solely from pushing the center of rope a certain distance. In this scenario, obtaining the diameter of the rope and calibrating the lateral force were not critical to the applied strain. Both of these tasks are difficult and have been important in other researchers’ strength experiments [18, 19, 21]. In contrast, this work used theoretical derivations of force vs. displacement based on the geometry of a suspended rope secured at both ends to fit atomic force microscope (AFM) lateral force data and obtain strain-to-failure and yield strength results.

3.1. Theoretical Thesis Research

To extract useful information from the atomic force microscope’s (AFM) lateral force measurements, this thesis’ theory needs to describe the strain applied to a suspended nanotube rope when an AFM tip pushes along its length a specified distance. The system can be modeled as an elastic string pushed at a fixed point parallel to the direction of the trench. Nanotube suspensions without any slack were chosen so as to simplify the required analysis of the acquired force data. Further discussion of this decision can be found in Section 3.2.4. Furthermore, there is no way to determine if a taut rope spanning the gap is strained or not prior to the experiment, so it is assumed that the elastic string is taut across the trench, but has not been stretched yet.
The first step is to describe the lengths of the nanotube rope, before and after stretching, in terms of the sample geometry. The unstretched nanotube has a length given by $L_0 = \frac{g}{\cos \alpha}$, where $g$ is the width of the trench and $\alpha$ is the angle the unstretched nanotube rope makes with the x-axis. The rope is then stretched a distance $y$ from its starting position. The resulting two lengths of the stretched rope are given by

$$L_1 = \frac{\left(\frac{g}{2} + x_0\right)}{\cos(\alpha + \theta_1)} \quad (3.1.1)$$

and $L_2 = \frac{\left(\frac{g}{2} - x_0\right)}{\cos(\theta_2 - \alpha)} \quad (3.1.2)$

Next, the strain experienced by the nanotube rope is calculated. The strain is the result of tension forces along its length. Expressions for these forces can be easily derived using Newton's Third Law. The tip translates back and forth in the y-direction, applying the maximal displacement of the nanotube at the turning points of motion, just before it reverses direction. It can be assumed that at that point, the tensions and the applied force are in equilibrium:
Figure 3.2: This figure shows the forces acting on a strained nanotube.

\[ \sum F_x = 0 \]
\[ \sum F_y = 0 \] (3.1.3)

\[ \sum F_y = F - T_1 \sin(\alpha + \theta_1) - T_2 \sin(\theta_2 - \alpha) \]
\[ \sum F_x = T_2 \cos(\theta_2 - \alpha) - T_1 \cos(\alpha + \theta_1) \] (3.1.4)

Because the nanotube is being modeled as an elastic string, the tension experienced can be expressed in terms of the change of length \((L - L_0)\) and the spring constant, \(k\), as follows:

\[ T = k(L - L_0) = k(L_1 + L_2 - \frac{g}{\cos \alpha}) \] (3.1.5)

Since the lengths are parts of the whole, the entire object must be experiencing the same tension throughout its length: \(T_1 = T_2\). Solving for the force from Eq. 3.1.3 and 3.1.4,

\[ F = T[\sin(\alpha + \theta_1) + \sin(\theta_2 - \alpha)] \] (3.1.6)

Using the Law of Cosines, one can then find relationships for the two lengths in terms of the other known angles and dimensions. The resulting equations express the lengths of
the strained nanotube rope in terms of measurable dimensions and angles as well as the distance the tip has moved:

\[ L_1 = \left( \frac{g + 2x_0}{2\cos\alpha} \right)^2 + y^2 - 2\left( \frac{g + 2x_0}{2\cos\alpha} \right)y\cos\left(\frac{\pi}{2} + \alpha\right) \]

\[ L_2 = \left( \frac{g - 2x_0}{2\cos\alpha} \right)^2 + y^2 - 2\left( \frac{g - 2x_0}{2\cos\alpha} \right)y\cos\left(\frac{\pi}{2} - \alpha\right) \]

\[ L_1 = \sqrt{\left( \frac{g + 2x_0}{2\cos\alpha} \right)^2 + y^2 - 2\left( \frac{g + 2x_0}{2\cos\alpha} \right)y\cos\left(\frac{\pi}{2} + \alpha\right)} \] \hspace{1cm} (3.1.6)

\[ L_2 = \sqrt{\left( \frac{g - 2x_0}{2\cos\alpha} \right)^2 + y^2 - 2\left( \frac{g - 2x_0}{2\cos\alpha} \right)y\cos\left(\frac{\pi}{2} - \alpha\right)} \] \hspace{1cm} (3.1.7)

Also note that \(\sin(\theta_1 + \alpha)\) and \(\sin(\theta_2 - \alpha)\) can be replaced by using simple trigonometric relations. This substitution eliminates the need for \(\theta_1\) and \(\theta_2\), both of which exist only in

![Diagram](image)

**Figure 3.3:** These diagrams show the relevant angles and nanotube lengths used to simplify Equation 3.1.6.
situ. The lower leg of the left triangle can be obtained as follows:

\[ \cos \alpha = \frac{g + 2x_0}{2} \cdot \frac{1}{h_1} \quad \text{and} \quad \sin \alpha = \frac{l_1}{h_1}, \]

where \( h_1 \) and \( l_1 \) are the hypotenuse and lower leg, respectively, of the smaller left triangle.

Substituting for \( h_1 \) and solving for \( l_1 \),
\[ l_1 = \frac{(g + 2x_0) \sin \alpha}{2 \cos \alpha}, \]

as shown in Figure 3.3. This development then leads to:

\[
\sin(\theta_1 + \alpha) = \frac{y + \frac{1}{2} g \cdot \sin \alpha}{L_1} \tag{3.1.8}
\]

and \( \sin(\theta_2 - \alpha) = \frac{y - \frac{1}{2} g \cdot \sin \alpha}{L_2} \),

where \( g := \frac{g \pm 2x_0}{\cos \alpha} \). \tag{3.1.9}

All the various equations can now be combined to form the final form of the equation for the force applied to the suspended nanotube rope:

\[
F = k \cdot \left( L_1 + L_2 - \frac{g}{\cos \alpha} \right) \cdot \left( \frac{y + \frac{1}{2} g \cdot \sin \alpha}{L_1} + \frac{y - \frac{1}{2} g \cdot \sin \alpha}{L_2} \right) \tag{3.1.11}
\]

where \( g := \frac{g \pm 2x_0}{\cos \alpha} \), \( L_1 = \sqrt{\left(\frac{g}{2}\right)^2 + y^2 + g \cdot y \sin \alpha} \), and \( L_2 = \sqrt{\left(\frac{g}{2}\right)^2 + y^2 - g \cdot y \sin \alpha} \).

Equation 3.1.11 was used to model the force data, so that values for \( y \) could be obtained. The angle of the rope, \( \alpha \); the equilibrium rope length, \( L \); and the gap distance, \( g \), were all obtained through direct SEM measurements. With the various lengths of the nanotube rope defined, an equation for the maximum strain applied to a given nanotube rope can be easily found:
\[ \varepsilon_{\text{max}} = \frac{(L_1 + L_2 - L_0)}{L_0}. \quad (3.1.12) \]

The above equations allow us to fit the AFM force data to equations that accurately describe what is occurring during the experiment, arriving at values for the maximum strain-to-failure for a given rope. Using the strain-to-failure and a known value for the Young's modulus, the yield strength can also be acquired. These theoretical developments set the stage for the actual experiment research to come.
3.2. Experimental Thesis Research

The experimental section of this work consisted of three steps: sample preparation, data acquisition, and data analysis. Sample preparation describes how the suspended ropes were created. Data acquisition discusses procedures and techniques developed for using the scanning electron microscope (SEM) and atomic force microscope (AFM) in this thesis work. Finally, the later sections present computational data analysis and results.

3.2.1. Sample Preparation

Single-wall carbon nanotube (SWNT) material was obtained from Tubes@Rice. The nanotubes were grown using a pulsed laser ablation process [6] and then purified [7]. The final product consisted of concentrated SWNTs suspended in an aqueous solution of Triton X-100, a common non-ionic surfactant.\(^1\) The solution was then filtered and washed repeatedly with water. The resulting wet paper of nanotubes was then placed in a vial of N,N-dimethylformamide (DMF)\(^2\) and sonicated vigorously, producing a well-suspended solution of nanotubes without any surfactant aid. With suspended defect-free SWNTs available, the experimental sample could be created.

The desired sample consisted of SWNT ropes freely suspended across a trench that is large enough to maneuver an AFM tip into, but as small as possible so as to minimize the number of nanotubes in the suspended rope. With this kind of sample, forces could be applied to SWNT ropes in a controllable manner without any surface

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\(^1\) Triton X-100, product# 23,472-9, available from Sigma-Aldrich (Milwaukee, WI).

\(^2\) N,N-Dimethylformamide, product# 27,054-7, available from Sigma-Aldrich (Milwaukee, WI).
effects from an underlying substrate. Creating the sample involved surface chemistry, controlled deposition, and semiconductor etchant technology. Sample creation involved three key steps – deposition, anchoring, and etching.

Deposition of monodispersed nanotube ropes onto a substrate was the first stage. A clean silicon substrate with a thermally grown oxide layer, approximately 100nm thick, was exposed to 3-aminopropyltriethoxysilane, creating a self-assembled monolayer of condensed amine groups [37]. These protocols are detailed in Appendix A. The silicon chip was then dipped into a DMF suspension of SWNTs, removed, and rinsed. Nanotubes adhered to the chip’s surface through strong surface-tube interactions [37]. This procedure produced a well-dispersed monolayer of nanotube ropes on the substrate (Fig. 3.4).

Figure 3.4: This figure shows an amine-terminated SAM exposed to nanotubes suspended in DMF at 50 mg/L for 15 minutes. The image is a 10μm² Tapping Mode™ AFM height scan. Note that the majority of nanotube ropes span less than 4μm, but that there are a couple in this scan region that are greater than 5μm in length, and thus longer than the created silicon trench.
The second preparative step was to anchor the nanotubes to the substrate. A small copper mesh, traditionally used as a transmission electron microscope support\textsuperscript{3}, was secured on top of the substrate with quick-drying glue.\textsuperscript{4} The smallest amount of glue necessary was used so as to minimize wetting the inner active region of the mesh. This left as much as possible of the nanotube-covered surface untouched by the glue and available for investigation. The copper mesh effectively acted as a lithographic shadow mask.

The sample was then placed in an evaporator. During this process, 2nm of chromium and 20-50nm of gold were sequentially deposited. The evaporator consisted of a sample, mounted upside-down, positioned above a small piece of pure metal. The metal was heated to boiling, evaporating atoms, and deposited on the sample. Due to the sensitivity of the apparatus, metal layers could be controllably deposited with angstrom accuracy. The copper mesh protected selected regions of the nanotube-covered sample from having metal deposited on it. The sample was then placed in a small acetone bath. The mask lifted off the sample, leaving only a metal structure and nanotube ropes on the silicon oxide substrate. Such soaking does not affect the deposited gold, nor does it affect the forces keeping the nanotubes stuck to the surface. Because of the copper mesh shadow mask, the resulting metal structure consisted of 10μm\textsuperscript{2} pads of chromium-gold with a 5μm spacing of open silicon oxide where the bars of the grid had blocked the evaporated metal.

At this stage in the preparation process, the sample had dispersed nanotubes and metal anchors securing them to the silicon oxide. All that remains is to create a trench,

\textsuperscript{3} Gilder New Revolutionary Specimen Support Grid, 2000 Mesh, CAT# T2000-Cu, Ted Pella Inc. (Redding, CA).
\textsuperscript{4} Loctite 495 Superbonder Cyanoacrylate Ester.
over which the nanotube ropes will span. First, the chip was dipped in 4.9%aq hydrofluoric acid (HF). The acid etched away the amine SAM and oxide layer. This etching occurred in all directions, both perpendicular and parallel to the plane of the sample, but the anchoring pads were chosen so as to be much larger than the oxide thickness of 100nm. Etching did occur under the metal anchors, but most of the oxide remained under the pad, pinning the nanotubes rope securely. A second etchant was used to anisotropically etch the silicon itself. Silicon was etched 0.5-1.5μm by dipping in 38 wt.% potassium hydroxide (KOH). KOH has the advantage that it etches preferentially along the (110) crystal plane [38]. The anchors were placed parallel to the (011) plane such that a trench would be etched that slopes away from the pads into the silicon in a "V" shape. As the final step, the sample was sequentially rinsed with liquids of decreasing surface tensions. The meniscus forces on the hanging ropes were reduced, thereby decreasing unwanted stress on the ropes. The sample was first rinsed with water, then isopropyl alcohol, acetone, and finally, tetramethylsilane.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Surface Tension (mN/M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.75 at 20°C</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>20.93 at 25°C</td>
</tr>
<tr>
<td>Acetone</td>
<td>23.46 at 20°C</td>
</tr>
<tr>
<td>Tetramethylsilane</td>
<td>10.2 at 20°C</td>
</tr>
</tbody>
</table>

Table 3.1: This table presents surface tension characteristics for solvents used in sample preparation [39].

This dehydration procedure is an alternative to critical point drying for biological samples [40]. This step was important for two reasons. First, it increased the number of nanotube ropes spanning trenches available for experimentation. Second, it helped support the
assumption made in the theory (Section 3.1) that the nanotube ropes had not experienced any strain prior to the AFM part of the experiment.
3.2.2. Atomic Force Microscopy (AFM)

At the nanometer scale, very few instruments use physical components for imaging or manipulation. The atomic force microscope (AFM) offers an easily controllable and modifiable apparatus that operates at the desired size level. Because the AFM is such an integral part of this research, a brief discussion of its basic operation is worthwhile.

An AFM consists of a small cantilever with an even smaller tip at its end positioned over a solid sample. A laser beam is reflected from the back of the cantilever to detect changes in position. As the tip scans parallel to the sample, changes in height produce changes in the atomic forces acting between the sample and the tip. Electronics provide a feedback circuit that adjusts the tip to maintain a constant height. The laser detects these changes and an image is produced that reflects the topography of the

![Diagram](image)

Figure 3.5: This figure shows the basic operation of an atomic force microscope.
sample. Figure 3.5 is taken from Digital Instruments’ *Multimode™ Scanning Probe Microscope Instruction Manual* [41]. A Nanoscope III AFM was used throughout these experiments.¹

An AFM has two available modes of operation – contact mode and Tapping Mode™, both of which are used in this research. In contact mode, the tip is kept at a fixed height. Changes in atomic force affect changes in the tip’s height. These changes are measured as a vertical deflection and are used as the feedback for adjusting the tip height. In Tapping Mode™, the tip is oscillating in resonance at a fixed amplitude, and changes in applied atomic force are measured as a damping force. Changes in the vibrational amplitude are used as feedback for adjusting the tip height. The feedback circuit then adjusts the height of the oscillating tip to restore the predetermined

![Diagram of AFM tip](image)

Figure 3.6: A typical silicon AFM tip is depicted. Dimensions were acquired through high magnification SEM imaging. Also depicted is the orientation of the tip during the force experiment and the direction axis consistent with the theoretical model of Fig 3.1.

¹ Atomic force microscope (AFM) manufactured by Digital Instruments (Santa Barbara, CA).
amplitude. Contact mode allows for increased imaging speeds (for comparable quality), but results in much greater force applied to the sample. Tapping mode is more sensitive to dramatic surface feature changes, but requires increased scanning time and involves an oscillating tip. However, the measurement of lateral forces is too sensitive to minor changes in tip position, and the signal is harder to relate to the applied forces for Tapping Mode™ to be viable in controlled force experiments.

While topographical information analysis is the primary application of an AFM, lateral forces applied to the tip can also be measured. Lateral force mode allows for nanoNewton magnitude forces to be measured on nanometer size objects in a controllable manner. Just as a laser is used to measure changes in height, the same laser can also be used to extrapolate lateral movement through torsion of the tip. This AFM feature is the critical component that allows the forces, and therefore strains, experienced by a nanotube rope to be measured. If, the tip scans horizontally across the sample it encounters a feature that blocks its movement, the feedback electronics will attempt to rapidly adjust the tip’s height so as to move over the obstacle. However, if the feedback circuitry is disabled, then the tip is left to push against the obstacle. As the tip pushes, it experiences a torque about the axis of the cantilever. The top plane of the cantilever rotates and the reflected laser beam is shifted. Figure 3.7 shows how the detectors are arrayed in relation to the cantilever and the laser beam. The position of the tip is determined through the position of the reflected beam spot. A detector array is present that can measure both vertical and lateral displacement of the tip. The spot is calibrated upon each use such that \( \frac{A-B}{A+B} \) and \( \frac{C-D}{C+D} \) are near zero volts [41]. The silicon AFM tips are manufactured from crystal silicon with known crystalline planes. Because of this, it is
Figure 3.7: (a) Quadrant detectors are used to measure lateral and vertical motion. The laser spot is calibrated in the center of the detectors. (b) If the tip is deflected vertically, the signal from the A detectors or the B detectors is greater than the other one. (c) If the tip is deflected laterally, the signal from the C detectors or the D detectors is greater than the other one.

assumed that the tip has a uniform plane along its entire length. If the tip deflects in the vertical direction, the signal in the A set of detectors is greater than the B set. If the tip experiences torsion, than the C and D set of detectors will have unequal signals and the lateral displacement is detected. Since the tip is a chemically homogeneous material (i.e. silicon nitride, silicon, etc...) with well-known structural and crystalline attributes, knowing the spring constant of the tip and the amount of laser deflection, the applied force can be determined. Knowing the force applied to the nanotube rope and the distance the tip traveled, the theoretical equations developed in Section 3.1 can be used to analyze and interpret the strain of single-wall carbon nanotube ropes.
3.2.3. Data Acquisition

Acquiring data on the strain of freely suspended nanotube ropes as a function of applied force involved three stages – locating a suspended rope in the scanning electron microscope (SEM), positioning the atomic force microscope (AFM) tip near that same rope, and measuring the lateral force on the tip while straining the nanotube rope. Each stage involved its own unique experimental obstacles and practices, and therefore warrants discussion.

Figure 3.8: A low magnification SEM image taken of the sample after extraction from tetramethyl silane. The image was taken at 70° stage tilt to improve contrast. The arrow on the top portion of the image is an artifact of the TEM mesh used and is useful for repeatable orientation. Because of the crude nature of superglue application, there are ample landmarks and perimeter variations for navigation.
3.2.3.1. Locating Suspended Ropes

After extraction through tetramethylsilane, the sample is ready to be investigated in the SEM. The nanotubes have no preferential alignment or regular dispersion spacing, and in fact, vary from 100nm single nanotubes to larger 5um bundles. For this experiment, the nanotube rope had to fulfill several requirements to be a viable specimen. Obviously, the rope had to be anchored on both ends by the pads and span the trench. From theory, the ropes also had to exhibit no slack, but instead be taut across the gap. The assumption, used in calculations, that the strain was distributed uniformly along its length required that the nanotube rope have a uniform diameter. Finally, anomalous contaminants on the rope were not desirable because they could complicate or corrupt the lateral force data by changing the tip properties or changing the way the tip strained the rope. All of these features were necessary in a located rope.

It was essential to locate well-suspended ropes and to be able to return to the same rope repeatedly, both in the SEM and the AFM. The system had unique landmarks from the nonuniform removal of the copper mesh. These sample flaws provided the means for repeatable navigation around the sample. Without such landmarks, using a located rope in the AFM would have been much more difficult.
Figure 3.9: A top-view (0° stage tilt) SEM image (250x, 12kV beam) used for relocation of specific ropes under the AFM. The "L" shaped gap created by removed pads is an example of the type of landmarks that are visible under SEM and AFM.

From SEM images, a sketch of the overall patterned region was made at low magnification (~50x), and a second sketch of the region to be investigated was made at an intermediate magnification (~500x). Both sketches were made at 0 deg sample rotation and were intended for reference while using the AFM. It was found that because of the background-nanotube contrast, it was easier to see nanotubes if the sample was rotated along an axis perpendicular to the trench that the user was looking along. Rotation angles of 45 to 70 degrees were typically used. To find a suitable nanotube rope, the user slowly translated parallel to one of the trenches, watching for a decent rope. When one was found, several images were taken of the rope at higher magnifications, both from above (i.e. 0 deg rotation) and along the trench (i.e. 70 deg). The location of the rope was
noted and local landmarks were recorded. This was done for each rope to be used under
the AFM.

![Image of a suspended nanotube rope anchored by gold pads. This image was taken at 70° stage tilt to improve contrast and resolution. This rope is a candidate for the experiment because it is taut, spans the gap, and has a relatively uniform appearance across its entire length.]

Figure 3.10: An SEM image of a suspended nanotube rope anchored by gold pads. This image was taken at 70° stage tilt to improve contrast and resolution. This rope is a candidate for the experiment because it is taut, spans the gap, and has a relatively uniform appearance across its entire length.

Once an experiment specimen had been identified and its location recorded, the
sample was taken to the AFM. This stage of the experiment involved many steps, all of
which played either a practical or theoretical role. To better aid the researcher’s memories
and for repeatability, an experimental protocol was developed. The steps are listed below
and their relevance to the experiment are described individually.
3.2.3.2. Sample Mounting and Alignment

The first part of the experiment involved mounting the sample in the atomic force microscope (AFM) and aligning the sample's grid pattern with the translation axes of the AFM stage.

1. The sample was mounted in the AFM and positioned such that the stage's translation axes were parallel to the geometric features on the sample. The tip needed to move at least 10\(\mu\)m in either direction with minimal change in position relative to the gold anchors. It was also important to know that the applied force was along the axis of the trench and not at an angle. The positioning was accomplished using the microscope's video display (~500x magnification). The sample was moved in both directions using the coarse stage movement. Only when no change was seen for multiple screens of movement was its position considered satisfactory.

2. The tip mount, with tip, was placed in the AFM. The cantilevers used were force modulated etched silicon probes (FESP\textregistered s). The back of the cantilever was coated with gold to minimize optical interference between back-reflected laser light from the sample and the tip. FESP\textregistered s were chosen over more common Tapping Mode\textsuperscript{TM} etched silicon probes (TESP\textregistered s) because of their lower force constant. FESP\textregistered s would be less likely to cause damage to the gold anchors during imaging.

3. The tip was navigated near the active region. The same landmarks seen from the top view in the SEM were visible with the video microscope display attached to the AFM. This allowed the tip to be maneuvered with \(\pm 5\mu\)m accuracy. The tip was maneuvered in the same column as the suspended rope and approximately 1.5
rows above the active row (i.e. 10 \( \mu \text{m} \) in the negative \( y \) direction, as described by Fig. 3.1).

4. The laser spot was positioned on the back of the cantilever as per standard AFM use. The AFM was set to Tapping Mode\textsuperscript{TM} and the output signal was zeroed and the signal sum maximized, as per standard Tapping Mode\textsuperscript{TM} use.

5. The AFM was set to contact mode and the horizontal deflection signal was calibrated to zero. This adjustment allowed for more accurate lateral force measurements.

6. The contact mode interference was minimized. A false engage was initiated, wherein the tip approached the sample, but was made to start imaging well above the surface. The measured lateral force was observed and the position of the laser spot on the back of the cantilever was then adjusted in minor increments to minimize the peak-to-peak friction and deflection signals. The signals are not real forces, but are caused by the interference between the light reflected off the tip and the sample. The maximum calibrated signals allowed for the friction and the deflection were set at 0.2 \( V_{pp} \) and 0.05\( V_{pp} \) respectively. The tip was then withdrawn.

7. The scan angle was set to 90°. The tip's motion was now perpendicular to the trench as opposed to parallel to it, making the lateral force the force applied to the suspended ropes. Figure 3.11 shows the orientation of the tip with respect to the suspended SWNT rope.
3.2.3.3. Tapping Mode™ Initial Contact

The second part of the experiment involved navigating towards the nanotube rope of interest, using Tapping Mode™ imaging to reduce damage to the anchors.

1. The engage setpoint was set at 1.03 to minimize the force applied to the sample in the $z$ direction. We wanted to minimize any possible damage the engaging tip might cause to the gold features.

2. The AFM was returned to Tapping Mode™ and the drive frequency found.

3. The sample was legitimately engaged and the tip navigated towards the region containing the rope of interest. High-resolution images (0.5Hz, 256 lines/sample) of the surface floor were taken, both an overview image that included the edges of the anchors ($8\mu m$ scan size) and more magnified images ($4\mu m$ and $2\mu m$ scan sizes). These were used to position the tip in the center of the trench. The offset position values were noted for future use. Note that at this point, a small region in
the center of the trench floor away from the edges of the anchor was being scanned.

4. The video camera was moved away from the AFM and a vibration isolation hat was placed over the AFM to reduced extraneous noise. The tip remained engaged with the surface to detect any shifts in position.

3.2.3.4. Contact Mode Experiment

The last stage of data acquisition involved collecting the lateral force data while straining a suspended nanotube rope with an AFM tip.

1. The AFM was switched to contact mode.

2. The sample was engaged. A high-resolution image (4Hz, 256 lines/sample) was taken of the same region last captured in Tapping Mode™ (2μm scan size or less). The position offset values were noted for later maneuvering. Care was taken to increase the setpoint only when the anchor pads were not included in the imaging. The scan size was then adjusted to the final experimental size. This value varied from experiment to experiment during the evolution of the research, ranging from 0.5 to 1.5 μm.

3. The bidirectional scan feature was turned on. The scan line shift was calibrated so as to optimize the image quality on the edge of the image where the rope was expected to arrive. Bidirectional scanning means that the signal was being measured in both the positive and negative y direction, as opposed to only the positive direction.
Figure 3.12: This figure is an example of how surface images taken in Tapping Mode™ (Section 3.2.3.3, Step 3) and contact mode (Section 3.2.3.4, Step 2) were used to navigate toward the suspended nanotube rope. Identical features helped the researcher to locate the tip on the surface, without imaging the gold pads, as well as to identify any shifts in tip position when switching to contact mode (Section 3.2.3.4, Step 1).

4. Force Calibration Mode was used to determine a conversion constant (the Deflection Sensitivity) between the voltage signal and tip deflection distances. Typical deflection sensitivity values were approximately 80 nm/V.

5. The slope of the sample’s surface was determined. The Scope Mode showed a cross sectional slice of the sample at the full range of the scan size. The slope displayed was the slope the sample makes with the horizontal \( \frac{dz}{dy} \) in Fig. 3.1).

6. The experiment called for force to be applied to the center of the suspended nanotube rope. Therefore, the slow scan was disabled when the tip was at the
center of the trench, thereby limiting the tip’s motion to 1 dimension. A landmark on the silicon surface was used to gauge when the center was reached. The tip was now scanning in the y-direction only. The accuracy of this step was estimated at ±100nm based on the resolution of previous images and the sporadic distribution of surface features, both used for determining the center of the trench.

7. The z sensitivity was recorded. This number described the conversion of volts to nanometers for the motion of the translation piezos in the z-direction.

8. The displayed contact mode image was set to Deflection and Friction with 1.0μm and 0.1V scales, respectively. Offline Planefit was set to “None” and Realtime Planefit was set to “Offset.”

9. The tip was locked, floating above the sample. The slope of the sample was taken into account so that there was no danger of running the tip into the surface. The setpoint was decreased slightly until the tip was seen lifting off the sample, as evident in the setpoint monitor. The tip was then locked above the sample by monitoring its position and setting the Integral Gain and Proportional Gain to 0.0 when it had reached a height of 100-200nm (depending on surface features and sample slope). The z sensitivity was used here to translate the displayed voltage signal of the tip z position into actual distances of nanometers.

10. The tip was allowed to stabilize for 10 minutes. Sometimes following tip movement, the tip’s position can shift slightly as the piezos find their equilibrium state for a given applied voltage. This step was born out of experience and caution since such shifts were rare in practice.
11. The tip was moved to the rope using the y-offset to control its motion. The tip was advanced at a steady pace, in 25nm steps, until some deflection signal was detected. The tip was then retreated from the rope 100nm because this distance was found to be sufficient such that drift in the piezo positions would not bring the tip back into contact with the ropes.

12. The actual force experiment was started. If, at any time, we were suspicious of the results, the tip would be retreated a couple microns and Steps 9-12 of Section 3.2.3.4 were repeated.

Figure 3.13: SEM images of before and after an experiment show the single-wall nanotube rope failing at one of its anchors.

Once the tip had been carefully maneuvered to the suspended rope, it was time to strain the nanotube rope. The tip was advanced a single 25nm increment and allowed to scan back and forth several times (typically 4-8). This step was repeated until the
nanotube rope failed. Each time, the tip was allowed to scan the full scan range. In each experiment, multiple data files were necessary due to scanning size limits. Efforts were taken not to advance the tip between images, so that events could be observed. During contact with the nanotube rope, the tip was sometimes retreated incrementally and then advanced back into the rope to investigate plastic deformation versus elastic deformation. The applied strain was incrementally increased until the rope broke and the signal suddenly returned to zero deflection. This usually occurred immediately after the tip was advanced. The deflection data (normal and lateral) was saved as a binary file and used for computational data analysis and modeling.
3.2.4. Data Processing

The AFM data files described the tip deflection (normal and lateral) as a function of displacement along the y-axis. Before a meaningful result could be obtained, the data was taken through several steps. These files were in a binary number format unique to the NanoScope IIIa AFM and required processing steps to extract the simple two-dimensional plot of the deflection vs. displacement. Once extracted and presented in a standard graphical format, the data was fitted to the theoretical equations developed in Section 3.1 to determine several experimental characteristics. The resulting fit parameters were then used to calculate the maximum strain experienced by the suspended nanotube rope. The graphical analysis software package, Igor Pro 3.13, was used throughout the research's analysis.¹

Several computer procedures were written to fulfill the necessary data manipulation and analysis requirements of this thesis research. The application of these procedures fell into one of two categories: manipulation of data for presentation purposes, or calculations involving data to provide an experimental result. The computer code along with line comments is provided in Appendix B for reference, but discussion of the procedures' roles in the data analysis is included in the method of analysis.

Due to the number of steps and complexity of the data manipulation, each experiment² was analyzed in the same manner for consistency and as a check for erroneous assumptions. The steps are discussed, in both execution and motive.

¹ Software program produced by WaveMetrics, Inc. (Lake Oswego, Oregon).
² The term experiment is used from this point on to describe a specific incident wherein an atomic force microscope tip strained a suspended single-wall carbon nanotube rope (i.e. the 07NOV98 experiment vs. the 15DEC98 experiment).
1. Top-view scanning electron microscope (SEM) images, in conjunction with Atomic Force Microscope (AFM) images of the trench floor, were analyzed to determine the gap distance, \( g \), and the position offset from center, \( x_0 \). These parameters were necessary for the computer analysis involving the force vs. displacement equation, Equation 3.1.11. The SEM images were taken while searching for usable nanotube ropes, as discussed in Section 3.2.3.1. The AFM images were taken during the experiment, during Tapping Mode™, in Section 3.2.3.3 Step 3, and contact mode, in Section 3.2.3.4 Step 2. Landmarks, common to images in both steps, were used to correlate AFM images taken in different steps and at different scan sizes. The measurement of the gap had a ±3% error and the offset measurement had an error of ±0.1 \( \mu \text{m} \). These errors were determined through experimental observations and experience.

2. SEM images taken in Section 3.2.3.1 were used to determine the angle the single-wall carbon nanotube (SWNT) rope made with the x-axis, \( \alpha \). Because \( \alpha \) is used only in trigonometric functions, the error was negligible compared to the distance measurements in the previous step.
3. The IGOR procedure, *LoadNS4_3Dual* was used to import the last binary data file of an experiment before a failure occurred. This procedure accepts a Nanoscope IIIa data file for a dual AFM image and displays it as a three-dimensional image plot. The friction output of *LoadNS4_3Dual* is shown in Figure 3.14. A similar plot is produced for the vertical tip deflection vs. displacement signal; however, the friction signal is the force applied to the nanotube rope and is therefore more useful.

![Figure 3.14: *LoadNS4_3Dual* produces a 3D plot of the friction signal as a function of tip movement. The AFM tip scans perpendicular to the nanotube rope (left to right in this figure). A force is displayed above as a gray signal, with darker shades representing larger forces. The tip scans back and forth at one position for several scans and is then incremented towards the nanotube rope, to the right. Note that the force experienced by the tip increases, as it is incremented closer to the rope and also increases as it scans from left to right.](image-url)
4. A second procedure, *Separate Trace Retrace*, was used to separate the trace signal from the retrace signal in the combined friction image. The trace signal measured data (friction, deflection, etc...) as the AFM tip scanned from left to right. The retrace signal measured the same data type, but as the tip scanned in the opposite direction. This step allowed the progression of the tip, as it was incremented towards the nanotube rope, to be studied more clearly. The trace and retrace signals represented different parts of the tip-rope interaction. The trace described the tip as it approached the rope, initiated physical contact, and started straining the rope. The retrace described the tip as it retreated from the tip, reducing the strain, and breaking contact with the rope. For example, if there had been adhesion between the tip and the rope, the effect would not be seen in the trace signal, but only in the retrace signal.

![Graphs showing friction trace and retrace signals](image)

*Figure 3.15: This figure shows the separated trace and retrace friction signals for the image plot of Figure 3.14. The incremental tip movement is more visible in these plots and there are subtly differences in the tip-rope interaction.*
5. The trace rows, corresponding to the farthest tip increment without any failure, were extracted using the AnalyzeRows procedure. Data from an increment without a failure was selected to insure that the strain was real and unaffected by whatever initiated the rope’s failure.

6. One of the trace rows was selected for detailed analysis based on its low noise, level baseline near the origin, and normal looking curve (i.e. no strange anomalies during straining). BackgroundSubtraction was performed on the selected wave, using the first 50 data points to calculate the linear subtraction. This procedure subtracted a line from all of the friction data extrapolated from the data near the beginning of the scan. The data at the beginning of a scan represented force information before the tip reached the suspended SWNT rope. Figure 3.16 shows raw data from one of the successful experiments along with the data after background subtraction.

7. A curve fit was performed using the ForceAngleNotCenter function on the data after the 50th point. The function was a computer code of Equation 3.1.11, describing the force applied to the rope as a function of tip displacement. Data used for the background subtraction was not included in the fit so as to not prejudice the fit results. The gap, angle, and xoffset were held constant while the spring constant, $k$, and $\gamma$ were allowed to vary. Values for the adjustable variables as well as a fitted plot were produced. The contact point, $\gamma$, between the tip and the nanotube rope was checked to make sure that the linear background fit included only out-of-contact data. If the background fit did include data where the nanotube was being strained, Steps 6-7 were repeated with fewer
than 50 data points. Figure 3.16 shows the background-subtracted data along with the fitted curve.

![Graph showing force signal (volts) vs. tip displacement (micrometers)](image)

Figure 3.16: This graph shows the raw friction data, the background-subtracted friction data, and the curve fitted friction data as a function of tip displacement. The background-subtracted plot appears the same, but shifted vertically and made level. Note that the curve fitted data follows the background-subtracted data well along their entire lengths, as evident in their behavior near a tip displacement of 1 μm.

8. Finally, the strain was calculated using *FindStrain* and the parameters from the curve fit. This procedure used the equations for the rope lengths (strained and unstrained), as derived in Section 3.1, to calculate the maximum strain on the nanotube rope, as described by Equation 3.1.12. The strain was also calculated by hand for a couple of the experiments to independently verifying the computer results.

At first, the slack in the suspended nanotube rope was accounted for in the analysis. With slack, the AFM tip would touch the rope, but would not apply any force until it had moved some fixed distance. Thereafter, the slack would be taken up and the discussed model (Section 3.1.) would accurately describe the exhibited behavior. It would be too complicated to attempt to describe the slack relative to the nanotube or gap dimensions,
so instead it was described as the distance the tip needed to move in the y direction before the force experienced by the nanotube was non-zero.

Two problems were quickly identified involving the inclusion of slack. The first was that small changes in the initial slack variable used for the curve fitting produced noticeably different results, sometimes even nonsensical ones. The second problem was that, with slack, the resulting curve fit had a sharp corner. This curve shape was indistinguishable from the curve produced by a stiff beam, which would have higher strains than an elastic string at a given tip displacement. If the systems believed to be elastic strings with slack were in fact acting like stiff beams, then erroneous strain results would be reported. In the end, attention was focused on those experiments that displayed zero slack, as seen in SEM images. Such results might underestimate the strength characteristics of single-wall carbon nanotubes, but they would not represent falsely optimistic claims.
3.2.5. Analysis and Results

Analysis of the results followed data processing. This research demanded several criteria be met before an experiment was considered useful: the suspended single-wall carbon nanotube (SWNT) rope exhibited no slack, the data showed no anomalies or irregularities, and the final strain-to-failure was noteworthy (i.e. order of ~1%). Four successful experiments remained after applying these conditions. The curves from each one and the resulting fit parameters are provided. The variables listed are those used to determine the maximum strain experienced by the nanotube rope. The elastic spring constant is \( k \), the width of the trench is \( gap \), the angle that the rope makes with the \( x \) axis is \( angle \), the \( xoffset \) is the distance from the center of the trench that the tip makes contact with the rope, and the \( yshift \) is the distance the tip displaced from the beginning of data acquisition to where the force was non-zero. The raw strain is the maximum strain experienced by the nanotube rope before any corrections due to experimental considerations.

3.2.5.1. Presentation of Raw Results

In each of these experiments, the force is roughly proportional to \( y^3 \). The force increases gradually as the tip begins to push on the rope. The tip movement is perpendicular to the rope, so the stretching of the rope contributes a factor of \( y^2 \). As the rope deflects, the force balance changes, contributing an additional factor of \( y \). All four curves follow this cubic behavior, which is consistent with an elastic string rather than a stiff beam. The bending of a stiff beam is described by \( F \propto y \) [42], while an
intermediary state with properties of both models would have both a cubic and a linear term. Appendix C discusses the mathematical derivation of $F \propto y^3$ for an elastic string strained at its center.

**Figure 3.17:** This figure shows the curve and fit parameters for experiment 1, 07NOV98. The dotted line is the AFM data, while the solid line is a curve fitted using Equation 3.1.11.

**Figure 3.18:** This figure shows the curve and fit parameters for experiment 2, 04DEC98. The dotted line is the AFM data, while the solid line is a curve fitted using Equation 3.1.11.
Figure 3.19: This figure shows the curve and fit parameters for experiment 3, 15DEC98. The dotted line is the AFM data, while the solid line is a curve fitted using Equation 3.1.11.

Figure 3.20: This figure shows the curve and fit parameters for experiment 4, 16DEC98. The dotted line is the AFM data, while the solid line is a curve fitted using Equation 3.1.11. Because of the anomalous behavior near zero, raw data from 0.6 to 0.8 μm was used for the linear background subtraction (Section 3.2.4, Step 6).
3.2.5.2. Elastic vs. Plastic Deformation

Several possible complications needed to be eliminated before the results could be accepted. The first was plastic deformation during repeated straining at a stationary position. Elastic deformation was a necessary assumption made in the theoretical development of Section 3.1. The equation describing the tension (Eq. 3.1.5) and the subsequent force vs. tip displacement equation (Eq. 3.1.11) were based on elastic behavior of the nanotube rope:

\[(\text{maximum strain}) \times (\text{Young's modulus}) = (\text{maximum stress})\]

Furthermore, elastic behavior is of fundamental and practical interest because in applications, stresses are usually kept below the threshold for plastic deformation, to insure durability and an extended lifetime.

For each of the experiments, traces immediately before those displayed in Figures 3.17 – 3.20 were captured. In each case, the curves overlaid each other almost exactly. If

![Experiment 1](image_url)

Figure 3.21: This figure shows sequential tip traces (background-subtracted) at the same increment from experiment 1. The traces are shown with an artificial offset as well as in their normal form.
plastic deformation were occurring, the point of tip-rope contact would be farther along the \( +y \) direction as the tip permanently stretched the rope. This effect would be observed most directly both in the shape of the curve, but also in the \( y_{shift} \) variable.

The curves showed the same interaction between the tip and the rope, with no permanent change. The tip was scanning during this entire time: advancing into the rope, stretching the rope to a maximum distance of 1.0 \( \mu \text{m} \), withdrawing and reducing the strain, moving away from the rope entirely, and then repeating the processes. Further proof that no plastic deformation occurred can be seen in the fit parameters and subsequent maximum strain.

<table>
<thead>
<tr>
<th></th>
<th>Trace 123</th>
<th>Trace 124</th>
<th>Trace 125</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K (V/\mu\text{m}) )</td>
<td>10.8</td>
<td>10.7</td>
<td>10.9</td>
</tr>
<tr>
<td>( \text{Gap*} (\mu\text{m}) )</td>
<td>4.3</td>
<td>4.3</td>
<td>4.3</td>
</tr>
<tr>
<td>( \text{Angle* (degrees)} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{Xoffset* (\mu\text{m})} )</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>( \text{Yshift (\mu\text{m})} )</td>
<td>0.46</td>
<td>0.45</td>
<td>0.46</td>
</tr>
<tr>
<td>( \text{Raw Strain (%)} )</td>
<td>3.2</td>
<td>3.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 3.2: This table presents fit parameters and calculated raw strain for three sequential traces in experiment 1. The parameters marked with "*" were held constant during the curve fitting because they were measured from AFM and SEM images.

Both of the variable parameters and the resultant strains agree. These results do not rule out transient plastic deformation that relaxes completely between scans, or slow plastic deformation that requires applied force for a long time (creep). However, there was no evidence of either of these effects. The other three experiments show similar results. Therefore, only elastic deformation is occurring during a given tip increment.

A second possible event that would make the results erroneous was plastic deformation occurring as the tip advances to the next increment. While it was unknown if
this type of event would differ from repeated straining at the same increment, it was important to investigate nonetheless.

These three traces show the tip-rope interaction at different tip increments. The curves all start as a baseline near zero, but begin their cubic increase in force at slightly farther distances for each increment. The dip in the data for trace 74 near 1.2 μm is an anomaly caused by some unknown rope behavior. The tip could slip a little in the z-direction, which would show a decrease in lateral force, or perhaps the rope shifted along its axis exposing a different cross-section to the tip. Corrections for tip torsion and deflection were performed on the final results and are discussed in Section 3.2.5.3.
Table 3.3: This table presents fit parameters and resulting strain from traces from three sequential tip displacement increments. The variables marked with "*" indicate held variables that were determined from AFM and SEM images.

<table>
<thead>
<tr>
<th></th>
<th>Trace 54</th>
<th>Trace 64</th>
<th>Trace 74</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (V/μm)</td>
<td>1.8</td>
<td>2.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Gap* (μm)</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Angle* (degrees)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Xoffset* (μm)</td>
<td>0.67</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Yshift (μm)</td>
<td>1.28</td>
<td>1.25</td>
<td>1.20</td>
</tr>
<tr>
<td>Raw Strain (%)</td>
<td>0.6</td>
<td>0.8</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The traces show a steady change in both yshift and raw strain. As the tip was incremented towards the rope, it would take less distance from the far withdrawn position to encounter the rope. This can be seen in a decreasing yshift. The theoretical increment distance was 50 nm, which is the change in yshift from one trace to the next shown above. The strain is also seen to increase as the tip was advanced closer to the rope, which is expected. Since the strain and yshift are consistent with expected behavior, there was no plastic deformation during tip incrementation.

3.2.5.3. Data Corrections

The strain obtained from the curve fitting of the force vs. tip displacement equations requires correction for two known inaccuracies. The two corrections come from the geometry and behavior of the atomic force microscopy (AFM) tip during use.

The first correction accounts for tip deflection. The side of the tip that pushed against the nanotube ropes was sloped, 17° from the vertical axis of the tip. Because the contact face of the tip was not perfectly vertical, the tip could slide up the rope, appearing to move forward, but with the rope remaining stationary. It was also possible when combined with torsion of the tip along its axis, or some other unknown phenomena, that
Vertical AFM Tip Deflection

![Diagram](image)

Figure 3.23: This figure illustrates AFM tip deflection. The dimension markers show a significant change in horizontal distance resulting from vertical deflection. The units are arbitrary and the figure is not to scale.

the tip deflected towards the surface. To account for this, vertical deflection data was captured along with the friction data used for curve fitting. This data revealed how far the tip was flexed vertically during the experiment. The traces used for the raw strains for each experiment were looked at and the maximum deflection signal noted. The deflection sensitivity is known for the AFM which, when coupled with the geometry of the tip, provided a correction to the maximum tip displacement:

\[
\text{Displace. Correction (nm)} = [\text{Deflection (V)}][\text{Deflection Sensitivity (nm/V)}][\tan (17^\circ)]
\]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Deflection (volts)</th>
<th>Deflection Sensitivity (nm/V)</th>
<th>Displacement Correction (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.693</td>
<td>70.83</td>
<td>15.00</td>
</tr>
<tr>
<td>2</td>
<td>0.161</td>
<td>70.73</td>
<td>3.47</td>
</tr>
<tr>
<td>3</td>
<td>-0.01</td>
<td>84.21</td>
<td>-0.19</td>
</tr>
<tr>
<td>4</td>
<td>-0.13</td>
<td>77.01</td>
<td>-3.01</td>
</tr>
</tbody>
</table>

Table 3.4: This table presents relevant deflection correction data from the four experiments.

The second necessary strain correction results from torsion of the tip along its long axis. The tips will inevitable twist some because a torque is being applied to the
AFM Tip Torsion

![AFM Tip Torsion Diagram](image)

Figure 3.24: This figure illustrates AFM tip torsion. The dimension markers show a significant change in horizontal distance resulting from torsion. The units are arbitrary and the figure is not to scale.

shaft of the tip by the tip/rope interaction. First, a calibration constant must be determined to relate the friction voltage signal with a horizontal displacement due to torsion.

In contact mode, a tip was pressed hard into a silicon oxide surface. The slow scan axis was disabled so that the tip was scanning only in one direction. Then the tip was scanned over a small distance of 20nm and the trace and retrace friction signals captured. The maximum signals for each trace and retrace were averaged to produce a known friction signal for a given displacement distance. This calibration constant was determined to be 44 ± 15 mV/nm.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Maximum Friction Signal (volts)</th>
<th>Displacement Correction (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.77</td>
<td>17 ± 6</td>
</tr>
<tr>
<td>2</td>
<td>0.09</td>
<td>2.1 ± 0.7</td>
</tr>
<tr>
<td>3</td>
<td>0.06</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>3 ± 1</td>
</tr>
</tbody>
</table>

Table 3.5: This table presents relevant torsion correction data from the four experiments.
With both corrections calculated, the maximum effective tip displacement used in Step 8 of Section 3.2.4 could be adjusted and a new strain calculated.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Total Correction (nm)</th>
<th>Raw Strain</th>
<th>Corrected Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32 ± 6</td>
<td>3.2 %</td>
<td>2.8 %</td>
</tr>
<tr>
<td>2</td>
<td>5.6 ± 0.7</td>
<td>6.0 %</td>
<td>5.9 %</td>
</tr>
<tr>
<td>3</td>
<td>1.1 ± 0.4</td>
<td>1.2 %</td>
<td>1.2 %</td>
</tr>
<tr>
<td>4</td>
<td>0.5 ± 1</td>
<td>1.1 %</td>
<td>1.1 %</td>
</tr>
</tbody>
</table>

Table 3.6: This table presents the corrected strain values from each experiment.

3.2.5.4. Error Analysis

The error analysis of the corrected strains gives a sense of how accurate the findings are. Given only four experiments, a lack of accuracy would greatly diminish any significance to be drawn from this research.

Several sources of error contribute to the overall strain uncertainty. The measurements of the gaps from AFM and SEM images were estimated to have an error of ±1-3%. The xoffset variable has an error of ±100nm. The error for yshift is the 5% non-linearity error in the AFM’s piezoelectric transducers. Finally, the correction displacements introduced an uncertainty from the calibration constant of 44 ± 15 mV/nm. The angle plays a negligible role because it is near zero. For each source, the maximum uncertainty in both the positive and negative direction was applied to its corresponding variable and the strain recalculated. The changes in strain were then added in quadrature to produce an independent positive and negative final uncertainty for the corrected strain.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Corrected Strain</th>
<th>Strain $\pm \sigma_{app}$</th>
<th>Strain $\pm \sigma_{offset}$</th>
<th>Strain $\pm \sigma_{yshift}$</th>
<th>Strain $\pm \sigma_{corrections}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.813%</td>
<td>+0.176%</td>
<td>+0.036%</td>
<td>+0.302%</td>
<td>+0.067%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.162%</td>
<td>-0.024%</td>
<td>-0.288%</td>
<td>-0.066%</td>
</tr>
<tr>
<td>2</td>
<td>5.850%</td>
<td>+0.495%</td>
<td>+0.483%</td>
<td>+0.588%</td>
<td>+0.014%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.438%</td>
<td>-0.389%</td>
<td>-0.563%</td>
<td>-0.014%</td>
</tr>
<tr>
<td>3</td>
<td>1.205%</td>
<td>+0.085%</td>
<td>+0.046%</td>
<td>+0.123%</td>
<td>+0.003%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.076%</td>
<td>-0.036%</td>
<td>-0.117%</td>
<td>-0.003%</td>
</tr>
<tr>
<td>4</td>
<td>1.102%</td>
<td>+0.073%</td>
<td>+0.025%</td>
<td>+0.113%</td>
<td>+0.003%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-0.065%</td>
<td>-0.019%</td>
<td>-0.107%</td>
<td>-0.003%</td>
</tr>
</tbody>
</table>

Table 3.7: Errors from all relevant sources. The corrected strain is the raw strain corrected for vertical deflection and torsion of the AFM tip as discussed in Section 3.2.5.3.

To arrive at a final uncertainty for each experiment’s corrected strain, the positive and the negative errors were added in quadrature, separately. The greater of the two errors, for each experiment, was adopted as the overall uncertainty. The final results, making appropriate significant digits simplifications, were as follows:

- Experiment 1: $2.8 \pm 0.4\%$
- Experiment 2: $5.9 \pm 0.9\%$
- Experiment 3: $1.2 \pm 0.2\%$
- Experiment 4: $1.1 \pm 0.1\%$

The uncertainty was low for all of the experiments. Even taking the worst result and assuming maximum error, the strain-to-failure was still 1%. Now that the uncertainty in each of the strain results has been calculated, the values for strain-to-failure can be discussed, with a focus on whether the results are representative, reasonable, and valuable.
3.2.5.5. Discussion

Table 3.6 presents the maximum strain experienced by the nanotube rope in each of the experiments. These values are lower bounds on the yield strength of an individual nanotube and not direct measurements, in either an analytical or statistical interpretation, of the true strength of nanotubes. In any physical system subjected to strains, the weakest component or location will fail first. This failure could be the result of intrinsically lower local structural characteristics, or because of a disproportionate amount of the overall strain. The latter possibility is due to its position and interactions with neighboring components. In the system studied throughout this research, the latter was almost definitely the case – some portion of the nanotubes experienced a higher than average strain, thereby breaking.

Nanotubes are predicted to withstand plastic deformation well beyond 5% strain and, depending on their diameter and chirality, strains in the range of 10-20% [1]. There is no experimental evidence or any theoretical calculations that predict the strain-to-failure of single-wall carbon nanotubes to be less than 5%. However, there are several reasons why suspended nanotubes anchored by gold pads would fail below 5% strain.

The gap distance, across which the nanotube ropes span, is on the order of 4\mu m, with the shortest distance being 3.7\mu m. Research to date on the type of nanotubes produced by the Tubes@Rice laser vaporization apparatus strongly suggests that the average single nanotube length is approximately 200nm with very few as long as 500nm. Even assuming all four experiments’ ropes contained a nanotube twice that length, the gap is still much larger. Therefore, no single nanotube spans the length of the gap, and
van der Waal forces between adjacent nanotubes will limit the maximum strain experienced before two or more nanotubes slip across one another.

The anchors provided by the layer of deposited chromium and gold are assumed fixed, able to resist all forces applied to the suspended nanotube rope. However, the strength of the anchor is variable and indeterminable prior to experimentation. The security of the chromium / nanotube interaction depends on how much of the rope is pinned by the anchor as well as any weaknesses in the anchoring layer and nanotube. It is quite possible for the anchor to fail before the nanotube does, especially for nanotubes that do not travel far under the metal layer. Experiment 2 displayed just such a failure.

After comparing before and after images, no evidence of any section of the nanotube rope weakening or deforming was found, suggesting that the failure at the point of attachment is the primary contributor to the maximum strain value obtained.

Figure 3.25: This figure shows the rope from Experiment 2 after failure. The right anchor broke before the suspended section of the nanotube.
The nanotube ropes were not of a uniform diameter across the entire gap. None of the four was abnormally thinner in a specific location, but variations in diameter were easily noticeable in the SEM. Assuming that the force applied to the rope was constant along its length, the stress experienced across the thinner sections would be greater than that of the average. Since the maximum strain previously calculated in this research was an average strain across the rope's entirety, higher local strains would have occurred. Because of this, the true maximum strain at the points of failure along the length could easily be greater than the strains reported herein.

Finally, when the AFM tip stretches the nanotube rope, there are key locations at the point of contact and at the anchors where the rope bends significantly. While the majority of the rope's length experienced only axial stretching, the combination of stretching and bending could have nucleated defects in some of the nanotubes, expediting the rope's overall failure. This type of failure would be indistinguishable from failure due to pure axial stretching.

So while there are many explanations for failure, the values for maximum strain obtained are still very valuable. It is in fact because of these errors that the results must be considered a lower bound on the strain-to-failure of perfect nanotubes. All of these possible events existed in each of the four experiments, and so each experiment represents an independent investigation of strain. Therefore, this thesis reports a lower bound on the strain-to-failure of single wall carbon nanotubes of 5.9% ± 0.9%.
3.2.5.6. Yield Strength

Armed with the Young's modulus of single-wall nanotubes and the strains presented previously, one can calculate the yield strength of SWNTs. The yield strength is defined as the stress at which the linear relationship between stress and strain fails. This relationship is described by \( Y = \frac{S}{\varepsilon} \), where \( Y \) is the Young's modulus, \( S \) is the tensile stress, and \( \varepsilon \) is the resulting tensile strain. The tensile stress is defined as the applied force divided by the cross sectional area, \( S = \frac{F}{A} \). The tensile strain is defined as the change in length in the direction of the applied force, \( \varepsilon = \frac{\Delta L}{L} \).

The Young's modulus has been relatively well studied, resulting in an average value of \( Y_{\text{avg}} = 1.25^{+0.45}_{-0.35} \) TPa, using a nanotube wall thickness equal to the graphite interlayer spacing, \( G = 0.34 \text{ nm} \) [33]. The tensile strain is the maximum strain found as a result of this research, \( \varepsilon = 5.9 \pm 0.9 \% \). The resulting yield strength is not the product of these values however.

The system being studied is not simple individual single-wall carbon nanotubes. Instead, it is a rope comprised of dozens of nanotubes formed through van der Waal forces. Because of the empty space in a nanotube rope, the volume averaged Young's modulus is effectively lower than if the entire object was solid nanotube. The majority of nanotubes obtained from Tubes@Rice have a radius of \( r = 1.2 \text{ nm} \) [7]. The nanotube thickness can be estimated by the graphite interlayer spacing, \( G = 0.34 \text{ nm} \) [33]. The ratio of the area occupied by nanotubes to open area is the fraction of the Young's modulus applicable for these yield strength calculations.
Figure 3.26: This figure depicts a small rope of three nanotubes. A triangle marks a unit cell for a rope of any size. The tube thickness is given by $G$ and the radius given by $r$.

The total area of the triangular unit cell is given by $A_r = \frac{\sqrt{3}}{4} (2r + G)^2$. The area occupied by graphene is the perimeter of the three nanotube sections multiplied by the differential thickness, or $A_{nr} = n\pi G$. Using $r = 1.2$ nm and $G = 0.34$ nm results in a ratio of nanotube area to total area of ratio = 0.62. Note that this is the same definition of "nanotube area" used by Krishnan et al. [33]. The yield strength is then the product of the tensile strain, Young's modulus, and the area ratio: $S = 45 \pm 7$ GPa. Similar to the tensile strain, this value is a lower bound on the yield strength of single-wall carbon nanotubes. In contrast, the yield strength of typical high-strength steels is 20 times lower [43].
4. Conclusion

Even with the level of engineering knowledge and experience today, the characterization of carbon nanotubes has been a slow one. Single-wall nanotubes are on the order of 1 nm in diameter and 100 nm in length, dimensions that defy almost all existing techniques and apparatuses used in engineering to determine mechanical properties. And yet, SWNTs are viewed as having exceptional promise as a structural material, both as a stand-alone object in the form of cables and as reinforcement in composite materials. Because of a nanotube’s size, advances and refinements in the understanding of its properties, mechanical and otherwise, have been achieved in small steps. Taken out of context, all of these experiments are interesting, but not profound; however, each step forward inspires new approaches and solidifies existing theories and proposals. This research is just such a stepping-stone. This research provides the first experimental confirmation of nanotube strain-to-failure over 5% and presents yield strength results 20 times stronger than current high-strength steels [43].

Yakobson et al.’s theoretical work (1998) stated that single-wall nanotubes are expected to be resistant to plastic deformation up to 5% strain and possibly as high as 20-30% [1]. As far as this author is aware, this thesis’s result of $5.9 \pm 0.9\%$ strain-to-failure as a lower bound was the first experimental evidence that supports a strain-to-failure as high as 5% [43]. Yu et al. (2000) have since provided further experimental work involving SWNT ropes on a nanostressing SEM stage that supports this research’s findings of a lower bound strain-to-failure on the order of 5% [31]. Since SWNT ropes
are more easily manipulated than individual nanotubes, both in suspension and physically, these values are directly relevant to future applications.

In addition to strain-to-failure results, this research also presents a lower bound tensile strength for single-wall carbon nanotubes. The tensile strength value in this thesis research was calculated using an accepted Young's modulus for individual single-wall carbon nanotubes, \( Y = 1.25 \) TPa [33], this research's experimental strain-to-failure, and a simplified model of a nanotube rope: \( S = 45 \pm 7 \) GPa. This work's yield strength result provides both a lower bound on the yield strength of individual SWNTs as well as a value for the yield strength of SWNT ropes. Two other experimental groups have published tensile strength results: Kong et al. reported a yield strength of \( \sim 280 \) GPa for an individual SWNT [19] while Yu et al. reported \( S = 13 \) to \( 52 \) GPa [33]. Yu et al.'s results support this research's findings, while Kong et al.'s results provide a preliminary comparison between the yield strength of individual nanotubes and nanotube ropes.

Overall, this work further promotes carbon nanotubes as the next evolution in high-strength materials. Since the findings are the result of SWNT ropes and not individuals, much work still remains before full characterization. However, because this research's strain-to-failure and yield strength are already well beyond those of steel, this research gives great hope to those who will build on this work.
Bibliography


Appendix A: Amine-Terminated Self-Assembled

Monolayer Silicon Substrate Preparation Protocol

Silicon is a commonly used substrate for atomic force and scanning electron microscopy because of its availability, smooth surface, and susceptibility to micro-machine techniques. However, use with either microscopy technique, requires a clean silicon sample. With the scanning electron microscopy, surface contaminants can introduce noise and decrease imaging resolution. In atomic force microscopy, surface contaminants can conceal important sample features and adversely affect tip movement.

For this research, a silicon sample was cleaned to provide a smooth surface for the condensation of an amine SAM. Nanotubes readily adhere to an amine SAM [39]. The mechanism of the tube-surface interaction is speculated to be van der Waal forces, but this has not been experimentally verified. Regardless, an amine SAM serves the goals of this thesis research well by dispersing single-wall carbon nanotubes (individuals and ropes) onto a substrate without involving meniscus drying forces.

1. A diamond scribe was used to cut a silicon chip from a wafer of silicon. The silicon had a thermally grown oxide layer approximately 100nm in thickness. The cut chip was approximately 4mm x 6mm. The oxide layer was necessary for the condensation of the amine self-assembled monolayer (SAM). This thickness allowed several nanometers to be etched away, while still maintaining a uniform oxide layer.

2. The silicon chip was then placed under an ultra-violet lamp, in air, for 30 minutes. In this environment, the ultra-violet light created ozone, and an additional oxide
layer was deposited on the chip’s surface. This layer covered any organic contaminants that might have been on the surface with an oxide layer, allowing for more efficient etching by acid in the following step.

3. Next, the silicon chip was dipped in a 4.9%aq hydrofluoric acid solution for 10 seconds. The chip was rinsed with filtered water\(^1\) and blown dry using inert nitrogen gas.

4. The chip was then placed back under the ultra-violet lamp for 30 minutes. This step deposited a uniform oxide layer on the silicon-oxide surface, minimizing any surface feature anomalies.

5. The chip was placed in a 3-aminopropyltriethoxysilane (APTES)/chloroform solution for 20 minutes. The solution consisted of 4-6 drops of APTES in a 60mL bath of chloroform. In this step, amine groups condensed onto the silicon-oxide surface, creating a self-assembled monolayer.

6. Next, the chip was placed in a 100mL bath of pure chloroform. This step helped rinse away any excess APTES that might have been transferred out of the solution bath with the silicon chip.

7. The chip was rinsed with chloroform, isopropyl alcohol, and filtered water. The order of rinsing was established to fully remove excess APTES: chloroform is a good solvent for APTES, isopropyl alcohol is a good solvent for chloroform, and water is a good solvent for isopropyl alcohol. Finally, the silicon chip was blown dry with inert nitrogen gas.

\(^1\) Filtered using a NANOpure Ultrapure Water System, manufactured by Barnstead-Thermolyne (Dubuque, IA), with a minimum conductivity of 18 \(\Omega\text{cm}\).
Appendix B: IGOR Data Analysis Procedures

NS4_3Procs Procedure

The first program that was written took Nanoscope 4.3 data files as input and converted them into two-dimensional waves for manipulation in Igor. Both the template for this macro, as well as some of the subordinate functions, came from pre-existing programs designed for manipulating earlier versions of Nanoscope files in Igor [44]. These functions are included for reference and easier interpretation of the larger macro, LoadNS4_3Dual. The procedure files are listed separately with their corresponding functions and macros.

The first two functions, JEG_StrByKey, and JEG_NumByKey, were written by J. Guyver and D. Vezenov as part of JEG Tools. JEG_StrByKey parses a given list for a specific string key. It then returns a string that follows a given field separator. JEGNumByKey searches in a similar manner, but returns the numeric value that follows the field separator.

Function/S JEG_StrByKey(key,list,fieldSep,recordSep)
    String key,list,fieldSep,recordSep
    key += fieldSep
    Variable pos= strsearch(list, key, 0)
    if( pos < 0 )
        return ""
    endif
    pos += strlen(key)
    Variable pos2= strsearch(list,recordSep,pos)
    if (pos2 == -1)
        pos2 = strlen(list)
    endif
    return list[pos,pos2-1]
Function/D JEG_NumByKey(key,list,fieldSep,recordSep)
    String key,list,fieldSep,recordSep
    String s = JEG_StrByKey(key,list,fieldSep,recordSep)
    if( strlen(s) == 0 )
        return NaN
    endif
    return str2num(s)
End

ScaleBin2Real takes a wave with binary data and scales it according to a given scale
range. This procedure allows raw NanoScope AFM data to be scaled according to a linear
conversion factor.

Function ScaleBin2Real(binwave,scale)
    Variable scale
    Wave binwave
    return (binwave*scale/66536)
End

LoadNS4_3Dual takes in a binary data file from the NanoScope 4.3 AFM program and
produces image plots. It was written assuming that the input would be a data file
containing dual images. Due to the macro’s size and complexity, comments are
interspersed to explain various sections.

Macro LoadNS4_3Dual()
    Variable aspectratio, numlines, zscale0, zscale1, scansize
    String messageStr="Please select a Nanoscope 4.3x file:"
    String filename = ""
    Variable dummy, dummy2
    String lf = num2char(10)
    String crlf = "\r" + lf
    String ctrlZ = num2char(26)
    String theHeader = ""

The following line opens a dialog box and asks for the binary file to be input by the user:

    Open /D /R /M=messageStr dummy
    filename = S_fileName
The file is opened and the header read:

    Open/R dummy2 as filename
    FReadLine /T=ctrlZ dummy2, theHeader

The number of lines in the images is determined:

    numlines = JEG_NumByKey("Samps/line", theHeader, ":", crlf)

The scan size of the images is determined:

    scansize = (JEG_NumByKey("Scan size", theHeader, ":", crlf)) / 1000
    String str_aspectratio = JEG_StrByKey("Aspect ratio", theHeader, ":", crlf)

This line reads in the aspect ratio. It assumes that the aspect ratio is n:1 where n < 10:

    aspectratio = str2num(str_aspectratio[1])

The scale of the first (i.e. left) image is determined:

    String str_zscale0 = JEG_StrByKey("@2:Z scale: V [Sens. Deflection]", theHeader, ":", crlf)
    Variable zscale0start, zscale0end
    zscale0start=strsearch(str_zscale0, ","), 0)
    zscale0end=strsearch(str_zscale0, "V", zscale0start)
    zscale0=str2num(str_zscale0[zscale0start + 2, zscale0end - 2])

The scale of the second (i.e. right) image is determined:

    Variable zscale1start, zscale1end
    String str_zscale1 = JEG_StrByKey("@2:Z scale: V [Sens. Friction]", theHeader, ":", crlf)
    zscale1start=strsearch(str_zscale1, ","), 0)
    zscale1end=strsearch(str_zscale1, "V", zscale1start)
    zscale1=str2num(str_zscale1[zscale1start + 2, zscale1end - 2])

If the image types are not Deflection/Friction, then the scaling won't be found and a
"NaN" value will result. The following code tests for that contingency:

    if (numtype(zscale0)>=1)
       zscale0=66536
    endif
    if (numtype(zscale1)>=1)
       zscale1=66536
endif
Close dummy2

This part cleans up the binary dos filename for later wave naming. The resulting waves have meaningful names based on the binary file name.

String tempname=CleanupName(filename,0)
String temp0=tempname + "0"
String temp1=tempname + "1"
Make/O/N=(numlines, numlines/aspectratio) $temp
Make/O/N=(numlines, numlines/aspectratio) $temp1
PauseUpdate
GBLoadWave/O/B/N=name/T={16,16}/S=20480/W=2/U=(numlines* numlines/aspectratio) filename

The following line produces two waves called "name0" and "name1" which contain the image data. The 1D waves are turned into 2D waves using the meaningful names.

Redimension/N=(numlines, numlines/aspectratio) name0, name1
$temp0=name0
$temp1=name1
KillWaves name0, name1

The binary data is scaled to volts:

$temp0=ScaleBin2Real($temp0, zscale0)
$temp1=ScaleBin2Real($temp1, zscale1)

The scan size is scaled:

SetScale/L x 0,scansize,"", $temp0
SetScale/L x 0,scansize,"", $temp1

Image plots of the two AFM images are then produced. The first image is assumed to be the deflection signal and the second the friction signal. The x-axis is scaled using the image scan size and labels are added for reference:

Display;AppendImage $temp0
Label bottom "Displacement (micrometers)"
Textbox/N=text/A=MB "Deflection Signal"
ModifyGraph height={Aspect, 1/aspectratio}
Display;AppendImage $temp1
The second program used in the analysis is *SeparateTraceRetrace*. This macro is used to separate the two signals of a bidirectional scanned image. The macro accepts the scanning direction and the data's file name as inputs. Since macros cannot accept waves as input, the image's file name is instead input as a string and later used in the code to reference the data file. The up direction was arbitrarily chosen to be "1" with down assigned "0."

**Macro SeparateTraceRetrace(direction, prewave)**

Variable direction
String prewave
Variable index, nrows, ncols

The number of datapoints in a row and column of the combined image is defined:

```
nrows=DimSize($prewave, 1)
nrows=DimSize($prewave, 0)
```

Waves for the separated images are created:

```
Make/N=(nrows, ncols/2)/O tracewave, retracewave
index=0
```

This if statement tests for which direction (up or down) the image was scanned:

```
if (direction <= 0.4)
do
```

Data is transferred in pairs into the trace and retrace waves:

```
tracewave[][((index/2)]==$prewave[p][index]
retracewave[][((index/2)]==$prewave[p][index+1]
```

The index is incremented to the next pair of scans:

```
index += 2
while (index <= (ncols-2))
```
else
do
    tracewave[][(index/2)]=prewave[p][index]
    retracewave[][(index/2)]=prewave[p][index+1]
    index += 2
while (index <= (ncols-2))
endif

String temptrace, tempretrace
temptrace= prewave + ",_trace"

Meaningful names for the traces are created based on the original wave's name and then extraneous waves are killed off:

    tempretrace= prewave + ",_retrace"
Make/N=(nrows, ncols/2)/O $temptrace, $tempretrace
$tempretrace=tracewave; KillWaves tracewave
$tempretrace=retracewave; KillWaves retracewave

The trace and retrace image are scaled to the same scan size as the original image:

    SetScale/1 x 0,(DimDelta($prewave, 0)*nrows),"", $tempretrace
SetScale/1 x 0,(DimDelta($prewave,0)*nrows),"", $tempretrace

The trace and retrace waves are displayed with the x-axis labeled accordingly:

    Display; AppendImage $tempretrace
Label bottom "Displacement (micrometers)"
Textbox/N=text/A=MB "Trace Signal"
ModifyGraph height=\{Aspect, ncols/nrows\}
Display; AppendImage $tempretrace
Label bottom "Displacement (micrometers)"
Textbox/N=text/A=MB "Retrace Signal"
Modifygraph height=\{Aspect, ncols/nrows\}

END

The AnalyzeRows macro is used in a graph marquee to select a series of rows from a 2D wave. The user draws a marquee on an image plot created by LoadNS4_3Dual and selects this macro. The macro then retrieves information about the overall displayed 2D wave as well as specific information about the 1D subwaves inclusive in the drawn
marquee. Each subwave of data is then displayed as a 2D graph in a separate graph. The scaling of the original 2D wave is preserved.

Macro AnalyzeRows() : GraphMarquee

The following lines grab information about the size and position of the drawn marquee. If no marquee has been drawn, an error message is displayed.

    GetMarquee left, bottom
    if (V_Flag == 0)
        Print "There is no marquee"
    Else

This line determines how many rows were selected:

    Variable numwaves=(trunc(V_top)) - (trunc(V_bottom))
    Variable currentrow, numlines
    String str_currentrow, activenname

This section grabs the name of the active 2D wave:

    GetWindow kwTopWin wavelist
    activenname = W_WaveList[0][0]
    KillWaves W_WaveList

The number of data points per row is determined:

    numlines=DimSize($activenname, 0)

A graph is created in which to display the selected data to be displayed in. An iterative loop is then used that transfers the data to individual waves instead of subwaves of the parent wave. These new waves are then appended to the freshly created graph:

    Display
    do
        currentrow = trunc(V_bottom) + numwaves -1
        str_currentrow = num2str(currentrow)
        Make/O/N=256 $(activenname + "_row" + str_currentrow)
        = $activenname[p][currentrow]

This line preserves the scaling of the parent wave:
Force_vs_Displace Procedure

The second procedure that was developed fit the force vs. tip displacement data to the theoretical equations developed in Section 3.1. Namely,

\[
F = k^*(L_1 + L_2 - \frac{g}{\cos \alpha})^*\left(\frac{y + \frac{1}{2} g \cdot \sin \alpha}{L_1} + \frac{y - \frac{1}{2} g \cdot \sin \alpha}{L_2}\right),
\]

where \( g' = \frac{g \pm 2x_0}{\cos \alpha} \), \( L_1 = \sqrt{\left(\frac{g'}{2}\right)^2 + y^2 + g' y \sin \alpha} \), and \( L_2 = \sqrt{\left(\frac{g'}{2}\right)^2 + y^2 - g' y \sin \alpha} \).

The main code included in this procedure was the function \textit{ForceAngleNotCenter}. A function was required so as to allow for curve fitting analysis in Igor Pro. The function took as input a set of sample parameters as well as a tip displacement. It then produced the appropriate force experienced by the nanotube rope.

Function ForceAngleNotCenter (prms, x)

Variable x

The wave, \textit{prms}, is the set of undetermined constants to be used in the fit:

Wave prms
Variable length1, length2, gap, slack, angle, gminus, gplus, force, k, xoffset, yshift, yposition
The variable, \( k \), is the lateral spring constant of a cantilever. It is the same in both this function and the theoretical equations.

\[
k = \text{prms}[0]
\]

The gap distance between anchoring pads is given by \( \text{gap} \) in \textit{ForceAngleNotCenter} and \( g \) in the theory.

\[
\text{gap} = \text{prms}[1]
\]

Slack in the nanotube rope was initially modeled in both the theory and the computer analysis. It was impossible to measure relative to the tube, but was instead defined, as the distance the tip must move after touching the rope before any force is applied. Experiments, which displayed zero slack, as measured from SEM imaging, were eventually chosen due to the greater reliability of the fits.

\[
\text{slack} = \text{prms}[2]
\]

The next variable is the angle the nanotube rope makes with the x-axis. It is \textit{angle} here and \( \alpha \) in the theory.

\[
\text{angle} = \text{prms}[3]
\]

The \textit{xoffset} is called \( x_0 \) in theory. It is the distance from the point of contact to the midpoint of the rope. The experimental steps in Section 3.2.3.4 attempted to align the tip near the center of the trench. However because landmarks are relied upon to position the tip, the position was not perfectly centered.

\[
\text{xoffset} = \text{prms}[4]
\]

The \textit{yshift} is the distance from the tip's position at the beginning of an experimental run to the point of non-zero force. When the tip's position was incremented towards the rope, the experimenter did not have an accurate measure of how far it would have to go before
the rope was encountered. This vagary occurred because the tip never encountered the rope during the positioning and imaging steps of the experiment for fear of influencing the rope through stretching in either the Y or Z directions, or weakening the anchor points.

\[
yshift = \text{prms}[5]
\]

The measured displacement of the rope is equal to the distance it took for the tip to approach the rope, plus the actual displacement of the rope:

\[
yposition = x + yshift
\]

This section is included so that the function can be used to create data. This allows simulations of various conditions.

\[
\text{if } (yposition \leq 0) \\
\quad yposition = 0 \\
\text{endif}
\]

The following lines are the equations listed at the beginning of this section and derived in the theory, Section 3.1.

\[
\text{gminus} = \frac{\text{gap} - 2 \times \text{offset}}{\cos(\text{angle})} \\
\text{gplus} = \frac{\text{gap} + 2 \times \text{offset}}{\cos(\text{angle})} \\
\text{length1} = \sqrt{yposition^2 - (\text{gplus}/2)^2 + (yposition \times \text{gplus} \times \sin(\text{angle}))} \\
\text{length2} = \sqrt{yposition^2 - (\text{gminus}/2)^2 - (yposition \times \text{gminus} \times \sin(\text{angle})))} \\
\text{force} = k \times (\text{length1} + \text{length2} - (\text{gap}/\cos(\text{angle})) - \text{slack}) \times (((yposition + 0.5 \times \text{gplus} \times \sin(\text{angle}))) / \text{length1}) + (((yposition - 0.5 \times \text{gminus} \times \sin(\text{angle}))) / \text{length2}))
\]

The final line returns the calculated force:

\[
\text{return force}
\]

END

The \textit{BackgroundSubtraction} macro accepts a 1D wave and subtracts a linear background signal, changing the values in the original wave. The linear function to be
subtracted from the overall wave is extrapolated from data points in the wave at the
beginning of the tip approach. The number of data points to be used in determination of
the background line is passed as an input variable.

    Macro BackgroundSubtraction(prewave, fitend)
        String prewave
        Variable fitend

The macro fits a line to the first fitend data points.

    CurveFit line $prewave(0,DimDelta($prewave, 0)*fitend)

Appending a suffix to the end of the original wave’s name creates a new, meaningful
wave name:

    String newname
    newname = prewave + "_nb"
    Make/N=(DimSize($prewave, 0), DimSize($prewave, 1))/O $newname

The background-subtracted wave is scaled to the same dimensions as the raw data wave:

    SetScale/I x 0,(DimDelta($prewave, 0)*DimSize($prewave, 0)), "", $newname

Finally, the background line is subtracted from all data points in the wave:

    $newname = $prewave - (W_coef[0] + W_coef[1]*x)

End

The final data analysis program calculates the strain on a given rope. FindStrain
accepts the same parameters as ForceAngleNotCenter and the maximum tip displacement
as input. It returns the maximum strain experienced by the rope.

    Function FindStrain (prms, maxdisplace)
        Variable maxdisplace
        Wave prms

This section calculates the maximum strain from the input parameter wave:

    Variable length0, length1, length2, gap, slack, angle, gminus, gplus, force,
k, xoffset, yshift, strain
k=prms[0]
gap=prms[1]
slack=prms[2]
angle=prms[3]
oxoffset=prms[4]
yshift=prms[5]

These equations are the same as in *ForceAngleNotCenter* and in Section 3.1.

\[
g_{\text{min}} = \frac{\text{gap} - 2 \times \text{oxoffset}}{\cos(\text{angle})}
g_{\text{plus}} = \frac{\text{gap} + 2 \times \text{oxoffset}}{\cos(\text{angle})}
\text{length}_0 = \frac{\text{gap}}{\cos(\text{angle})} - \text{slack}
\text{length}_1 = \sqrt{((\text{maxdisplace} + \text{yshift})^2 + (g_{\text{plus}}/2)^2 + ((\text{maxdisplace} + \text{yshift}) \times g_{\text{plus}} \times \sin(\text{angle})))}
\text{length}_2 = \sqrt{((\text{maxdisplace} + \text{yshift})^2 + (g_{\text{minus}}/2)^2 - ((\text{maxdisplace} + \text{yshift}) \times g_{\text{minus}} \times \sin(\text{angle})))}
\]

From theory, the strain in the nanotube rope is given by Eq. 3.1.12: 
\[
\varepsilon_{\text{max}} = \frac{(L_1 + L_2 - L_0)}{L_0}
\]

strain = (length1 + length2 - length0)/length0
return strain

END
Appendix C: Elastic String vs. Flexed Beam Models

Two models exist which could describe the behavior of a suspended single-wall carbon nanotube (SWNT) rope strained at its mid-point. One models the rope as a stiff beam, which flexes in its center when strained. The second models the rope as an elastic string, which stretches as it is strained. Both are reasonable models, but describe drastically different behavior.

A stiff beam with a center load is described in the first order of \( y \), \( F \propto y \). The exact equation is given by \( F = \frac{192EI}{(L_0)^2} y \), where \( y \) is the displacement of the center of the beam, \( E \) is the Young’s modulus, \( I \) is the moment of inertia, and \( L_0 \) is the unstrained length of the beam [44].

An elastic string with a force applied at its center produces a different relation between \( F \) and \( y \). For these order of magnitude derivations, a simpler scenario of a nanotube rope perpendicular to the gap, strained at its center suffices. Figure C.2 shows the elastic string model, as used in this thesis work and developed in Section 3.1.
The tension in the stretched nanotube rope is given by

$$T = \Delta L \ast k = (L - L_0)k .$$  \hspace{1cm} (C.1)

The equilibrium force diagram yields equations for the force in terms of the rope tension,

$$\sum F_x = F - 2T \sin \theta = 0$$

$$F = 2T \sin \theta .$$  \hspace{1cm} (C.2)

Combining Equations C.1 and C.2 and using the geometry of the sample, $\sin \theta = \frac{2y}{L}$,

then yields:

$$F = 4 \frac{(L - L_0)ky}{L} .$$  \hspace{1cm} (C.3)

Also note that the original rope’s length, $L_0$, can be expressed as the gap width, $g$, and the

stretched rope’s length can be expressed in terms of known quantities using the

Pythagorean theorem:

$$\left(\frac{L}{2}\right)^2 = y^2 + \left(\frac{g}{2}\right)^2$$

$$L = 2 \sqrt{(y^2) + \left(\frac{g}{2}\right)^2} .$$  \hspace{1cm} (C.4)
Equation C.4 can be substituted into Eq. C.3 to provide the full equation for the force, $F$, in terms of the displacement, $y$, and known quantities:

$$ F = 4 \frac{(L - L_0)ky}{L} $$

$$ F = 4 \frac{[2\sqrt{(y^2)} + (\frac{g}{2})^2 - g]ky}{2\sqrt{(y^2)} + (\frac{g}{2})^2} \quad (C.5) $$

This equation can be reorganized as

$$ F = 8ky \frac{\frac{g}{2} \sqrt{\left(\frac{2y}{g}\right)^2 + 1} - \frac{g}{2}}{\frac{g}{2} \sqrt{\left(\frac{2y}{g}\right)^2 + 1}}. \quad (C.6) $$

Note that for when the rope is initially displaced, $y \ll \frac{g}{2}$. Taking this relation into account, a binomial expansion centered around $y_0 = 0$ yields:

$$ F = 8ky \left[\frac{g}{2} \left[1 + \frac{1}{2} \left(\frac{2y}{g}\right)^2 - \ldots\right] - \frac{g}{2} \right] \times \frac{2}{g} \left[1 - \frac{1}{2} \left(\frac{2y}{g}\right)^2 + \ldots\right] $$

$$ F = 8ky \left[\frac{g}{2} + \frac{y^2}{g} - \frac{g}{2}\right] \times \left[\frac{2}{g} - \frac{4y^2}{g^3}\right]. \quad (C.7) $$

In Eq. C.7, the last term has $g^3$ in the denominator, which makes it much smaller than the other terms. The equation simplifies to

$$ F = \frac{16k}{g^2} y^3, \quad (C.8) $$

which is third order in $y$, or $F \propto y^3$ for the elastic string model.