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Neat Macroscopic Membranes of Aligned Carbon Nanotubes

by

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

Doctor of Philosophy

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April, 2002

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ABSTRACT

Neat Macroscopic Membranes of Aligned Carbon Nanotubes

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This work reports the successful production of neat macroscopic membranes of aligned single-walled carbon nanotubes (SWNTs) via filtration in intense magnetic fields of 25 Tesla and 7 Tesla. These membranes comprise a novel material that allows an unprecedented capability to characterize and manipulate aligned SWNTs, providing access to the more remarkable properties of SWNTs. Surface areas in excess of 100 cm² and thickness in excess of seven microns were produced. A density within a factor of two of close packing was achieved. These assemblies exhibit anisotropy in Raman resonance, electrical transport, thermal transport, and reflection of polarized light. These samples provide a macroscopic window to exploring the properties of SWNTs and pave the way for many potential applications. The successful extension of this process to 7 Tesla provides a more pragmatic path towards aligned assemblies of carbon nanotubes. Variations in the properties of the materials made under different magnetic field intensities were observed.

Acknowledgements

I am grateful to my advisor, Dr. Richard E. Smalley for providing me with a unique opportunity to work in such an important and cutting edge area of science; the unusually high level of scientific resources that Dr. Smalley provided was a great boon. The team of post docs and students he has assembled have helped me and taught me a great deal as well. Drs. Deron A. Walters, Jie Liu, and, for the short time I knew him, Andrew G. Rinzier, have helped me develop a greater pragmatism in my experiments. The many hours I spent working with them helped me refine my judgment of how to pursue an experimental goal. Dr. Walters was a valuable colleague in executing experiments. Dr. Angelo Benedetto patiently listened to countless hours of griping and applied his remarkable skills of proofreading to this thesis; he was also a good friend and colleague. Speaking of friends, Lars M. Ericson had to put up with me more than most and was still always willing to listen or help out. Chad Huffman fielded numerous questions and requests from me with exceptional patience. I would also like to acknowledge the help of my many other coworkers over the years: Yuhuang Wang, Michael Strano, Dr. Robert Hauge, Jake Schmidt, Michael J. O'Connell, Peter Boul, XiaoChuan Qin, and Pavel Nikolaev. I would also like to thank Dr. Alex Rimberg and Wei Lu for their help on various projects leading up to this work. The staff at the National Magnetic Field Lab was pivotal in completion of this project, especially Dr. Bruce Brandt, Mrs. Merry Ann Johnson, Dr. Vincent Salters, and Dr. Ted Satezlo. Dr. Jack Fischer, Dr. Dave Luzzi, Dr. Charlie Johnson, James Hone, and Brian Smith collaborated with us on analysis of the filtration material and were great collaborators to work with. Above all, I would like to thank my wife, Reema. Her love, unfaltering support, and faith in me have helped keep me going through good times and bad.

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1 – Introduction

It is an exciting time to be a researcher in nanoscale science and technology. The global community has started to look towards nanotechnology for the current and future needs of the world's population. Funding initiatives are springing up from all sides to help support work in a variety of related disciplines. The potential for new medicine, materials, and entirely new scientific paradigms is thrilling. However, as with any science, fundamental investigations need to be completed to give the scientific community the building blocks to construct a bright new future.

The carbon nanotube promises to be one such building block, but to use it effectively, new ideas and techniques are needed. One such technique is the capability to align carbon nanotubes and fabricate material from aligned nanotubes. This is needed to access the remarkable properties of nanotubes, which are constrained by the orientation of the nanotube axis; this is a natural consequence of the tubular geometry of a carbon nanotube. This thesis reports the successful creation of such a technique and material, sheets of magnetically aligned single walled nanotubes created via filtration in 25 Tesla and 7 Tesla magnetic fields.

This accomplishment is but one stepping-stone to achieving practical applications of carbon nanotubes in the macroscopic world. Many more advances are needed, such as the ability to sort the tubes by type and size. These are worthwhile goals, based upon the mounting experimental evidence and predicted applications.

The materials produced in this work hold the promise of some applications of their own; they exhibit anisotropic mechanical, electrical, and thermal characteristics that may prove to be useful in transmission and management of heat and electricity, to include

power lines, heat pipes, insulation, and jet turbine blades. With further work, their strength could be exploited to provide remarkably strong and lightweight materials that could revolutionize construction, paving the way to better armor, lighter spacecraft, and artificial muscles. This technology is not yet a reality, but the work in this thesis reports one more step towards the goal and some ideas of how progress might continue.

1.1 Naming Conventions

Before continuing, it is helpful to address some commonly used jargon. In the field of carbon nanotubes, certain terms take on very specific meanings. When the words *tube* or *nanotube* are used in this thesis, they will refer to SWNTs, unless otherwise noted. Clusters of SWNTs aligned along their length, i.e. parallel, will be called *ropes*. Clusters of SWNT ropes will be called *bundles*. These terms will be listed in the Appendices, along with other terms and abbreviations as well, but this terminology is adequate to discuss carbon nanotubes in more detail, beginning with the history of carbon nanotubes.

1.2 Carbon Nanotubes

In 1985, a new allotrope of carbon, Buckminsterfullerene, was discovered by Drs. Richard E. Smalley, Robert F. Curl, and Harry Kroto [1]. Buckminsterfullerene, which is commonly referred to as the *buckyball*, earned its name for its geometric similarity to the geodesic dome designed by the architect Buckminster Fuller for the Expo '67 in Montreal. The structure of a buckyball is akin to a graphite sheet into which has been introduced pentagons to induce curvature. The most common form, C_{60} , has a structure

that matches the geometry of the edges and vertices of a soccer ball and was actually referred to as *footballene* by some researchers [2]. With the discovery of this zero-dimension allotrope and the two and three dimensional allotropes of graphite and diamond already established, it was not long before thoughts turned to a one-dimensional allotrope of carbon.

In 1990, Dr. Richard E. Smalley speculated on the possibility of such a one-dimensional allotrope, a fullerene tube. This was quickly followed by a theoretical treatment by Dr. Mildred Dresselhaus, who proposed the physical and electronic structure of a carbon nanotube [3]. Within a year, Dr. Sumio Iijima reported the observation of “Helical microtubules of graphitic carbon” [4].

What Iijima had discovered are what are now known as *multi-walled nanotubes*, or simply MWNTs. These structures were nested versions of what had been predicted, encased one within the other, not unlike a Russian matreshka doll. There are a number of references that discuss MWNTs in detail [3,5,6], but the original speculations about carbon nanotubes had been about a single-shelled structure.

In 1993, this single-shelled structure, the *single-walled carbon nanotube*, or SWNT, was discovered [7,8], fulfilling the speculations of Smalley and the theories of Dresselhaus. Compared to the MWNT, it was smaller, had fewer defects, and would later be found to have remarkable properties. SWNTs were used for all of the work in this thesis.

After their discovery, scientific exploration of SWNTs was dramatically limited by their supply. Production methods yielded impractically small amounts, only a few percent yield [7,8]. Laser ablation methods improved on this, yielding >70% SWNTs.

This process is slow and only produces milligram quantities [9], but it is still used actively in research. Industrial-scale production efforts are maturing rapidly with a promising gas-phase process [10] that, as of 2001, was reportedly producing quantities of up to 10 grams per day [11]. This promises to provide an excess of SWNTs for research and possibly enough for wide-scale industrial use. This flow of nanotubes has allowed the scientific community to explore the properties of these remarkable structures vigorously and, although much is not known, a great deal has been explored and reported already.

1.3 Carbon Nanotube Structure & Properties

The properties of nanotubes that have drawn the most attention are those qualities closely tied to applications of nanotubes, such as their mechanical, electronic, and thermal properties. The context in which these topics can be discussed begins with the geometry of nanotubes. Nanotubes, like any molecule, are defined most fundamentally by their chemical structure and physical geometry.

1.3.1 Chemical Structure

Physically, a nanotube is essentially a rolled up graphitic sheet. Not surprisingly, the general chemical structure of nanotubes is similar to graphite in many regards. The overall structure is aromatic and the walls are composed completely of benzene rings, barring defects. Accordingly, the carbon atoms in the lattice are sp^2 hybridized in a *trigonal* structure. As with a typical benzene ring structure, there are pi electrons shared between the various carbon atoms. In SWNTs, this propagates across the whole

nanotube and, as with benzen this *closed bonding shell* contributes to the remarkable stability of the carbon nanotubes [12].

However, the ends of nanotubes tend to be more reactive, whether they are open or closed. The curvature necessary to cap a closed end is provided by the presence of pentagons in the end cap structure. This high degree of curvature, combined with the graphitic nature of the walls, leads to an expectation that the ends of a nanotube are more reactive. Open ends do not experience the same ring strain due to curvature, yet they are still the ends of a graphitic sheet and thus dangling bonds are present, which will be more reactive than those within the sheet.

Although these characteristics communicate the chemical nature of carbon nanotubes, they do not tell the whole story. The fundamental physical structure of a carbon nanotube is also needed to accurately describe a carbon nanotube.

1.3.2 Nanotube Geometry

The basic structure of a SWNT is very simple to describe. It is essentially a rolled up graphite sheet, a graphitic tube. As discussed above, the ends may be open, like a pipe, or closed by a hemispherical cap; such a cap would be geometrically akin to half of a buckminsterfullerene molecule. However, the fundamental geometry of a SWNT depends upon the geometry of the tube proper.

The graphitic sheet comprising the walls of the tube can be rolled a variety of ways to achieve a tube shape. The only requirement is that the hexagonal lattice edges are in good registry, which is to say that they match up exactly with each other. The simplest way to accomplish this is to line up the edges directly; however, a twist can be

induced in the roll and still achieve the desired registry. This twist is referred to as *chirality*, from the Greek word for handedness, and is an important metric for categorizing SWNTs. This chirality is different than the typical use of the term in reference to stereoisomers, in which the handedness derives from differences in molecular structures when mirror images of the molecule are laid one over the other. Due to the cylindrical symmetry of a SWNT, handedness only manifests when the axis of the tube is rotated 180 degrees.

This nanotube chirality can be explicitly defined in terms of vectors, and a quantitative treatment of chirality is a straightforward affair. First, a set of basis vectors needs to be defined, as in Figure 1.1.

Figure 1.1 Basis Vectors

General vectors can then be defined in terms of these basis vectors [6]. The chiral vector, C_h , is defined in terms of integer multiples, n and m , of the basis vectors, a_1 and a_2 , respectively, as follows:

$$C_h = na_1 + ma_2 \equiv (n, m) .$$

Eq. 1.1

To reduce the set of possible chiral vectors to a one-to-one correspondence, the values of n and m are constrained to integer values with a relationship as follows:

$$0 \leq |m| \leq n . \quad \text{Eq. 1.2}$$

Additionally, constraining m to positive values reduces confusion by eliminating superfluous redundant indices. Some of the (n, m) pairs generated by the basis vectors are shown in Figure 1.2 below:

Figure 1.2 Sample Values for n and m

With this chiral vector approach, SWNTs can be specifically designated by their chiral indices, n and m .

To generate an (n, m) tube, start in the $(0,0)$ hexagon and draw the chiral vector to the appropriate (n, m) hexagon. Align the $(0,0)$ hex with the (n, m) hex for the desired nanotube. The chiral vector should be perpendicular to the cylinder axis, producing an equator of sorts. The resulting tube can then be quickly and distinctly described by its

chiral vector indices, e.g. a “(10, 10) tube.” This chiral vector approach requires that the underlying structural geometry is a hexagonal lattice. SWNT walls have this geometry, and thus we can directly apply this model to them. As a result, references to integer pairs of the form “(n, m)” throughout this thesis should be assumed to refer to chiral vector indices unless otherwise noted.

There are two special cases of (n, m) pairs that fall out of this vector model. These cases are when $m = n$ and when $n = 0$, called *armchair* tubes and *zigzag* tubes, respectively; these names derive from the shape of the tube edges, as shown in Figure 1.3.

Figure 1.3 Zigzag and Armchair Tubes

The 30° angle shown in the armchair tube can be related back to the chiral vectors and thus is called its *chiral angle*. This line traces a twisting corkscrew pattern around the tube as it travels down the length of the tube. For 30°, there is no real handedness, as the tube would look the same if flipped end for end; such tubes are generally called *achiral tubes*. However, for chiral angles other than 30° or 0°, the twist in the tube structure would look different if the tube were flipped end for end; such tubes are generally called *chiral tubes*. The chiral angle θ can now be defined as the angle

between $\mathbf{a}_1$ and $\mathbf{C}_h$, constrained because of the symmetry of the hexagonal lattice such that $0^\circ \leq \theta \leq 30^\circ$. The inner product of $\mathbf{C}_h$ and $\mathbf{a}_1$ can be used to derive a formula for computing this chiral angle [6] as follows:

$$\cos \theta = \frac{\bar{\mathbf{C}}_h \bullet \bar{\mathbf{a}}_1}{|\bar{\mathbf{C}}_h| |\bar{\mathbf{a}}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}} . \quad \text{Eq. 1.3}$$

These properties allow for unique definitions of a specific nanotube and enable a more coherent and concise exploration and discussion of their properties.

1.3.3 Electronic Structure and Properties

Electronic properties are often among the first to be explored in a new material. This is due in part to the ability of physics to predict electronic properties based upon a material's structure. Nanotubes are no exception. Within a year of their discovery, a host of articles appeared to predict and describe their electronic properties [13-16].

It became readily apparent in these reports that the chiral vectors and the indices they generate dramatically facilitated the discussion of the electronic properties of SWNTs, which is not surprising, since the electronic properties of a system depend upon the boundary conditions imposed by the structure. The chirality and diameter of SWNTs provide adequate boundary conditions for assessment of their electronic properties [13]. Conveniently, SWNTs can be categorized electronically by their chirality, specifically the n and m indices of the basis vectors.

The general rule for categorizing by (n, m) pairs is that metallic tubes have chiral indices, n and m , such that the difference $(n - m)$ is a multiple of three, including zero; all

other SWNTs are semiconducting. This results in armchair nanotubes always being metallic while zigzag tubes are either metallic or semiconducting, depending upon their indices. These predictions and calculations have been corroborated by experiment [17-19].

The calculations of possible chiral combinations produce fractions of one-third metallic and two-thirds semiconducting nanotubes [20] from a simple assessment of the permutations. However, further theoretical and experimental work suggests that for the nanotubes produced, metallic tubes are the dominant fraction [21,22], which may suggest that the synthesis of metallic tubes are favored in the current production methods.

In addition to simple qualitative determinations of electronic character, the electron transport properties of nanotubes have also been investigated, and SWNTs have been shown to exhibit ballistic conduction [6,23]. In a typical material, an electron would encounter a great deal of scattering as it moved through the material, a.k.a. *resistance*. With a nanotube, the electron encounters resistance only when entering or exiting the tube; there is no resistance encountered along the length of the tube, it essentially travels straight down the nanotube from one end to the other. This effect earned the nanotube the name *quantum wire* because this effect was associated with discrete levels imposed by the finite length and one-dimensionality of a nanotube. This effect has only been reported to propagate over microns thus far [6,23].

While “quantum wire” may sound sexy to researchers, and ballistic conduction measurements are important to fundamental understanding of the nanotube, most practical applications will be concerned with the properties of bulk nanotubes such as resistivity. Multiple sources have reported resistivities that agree with the theoretical

model of metallic and semiconducting SWNTs, with reports of values of 10^{-6} to 10^{-5} $\Omega\cdot\text{m}$, indicating metallic materials, and 10^{-1} $\Omega\cdot\text{m}$, indicating semiconducting material [6,23]. Metallic resistivity has also been confirmed for crystalline ropes of SWNTs [24].

Anisotropy in electrical properties with respect to the orientation of the tube has also been explored. It has been confirmed that a randomly oriented bulk material exhibits a resistivity roughly 50 times greater than that measured along crystalline ropes of nanotubes [24]. The materials measured were notably different in structure, though. For a more direct comparison and better understanding, a bulk aligned sample of SWNTs is needed, like those produced by this work.

Another obvious candidate for anisotropic behavior is electric polarizability. Calculations of the static electric polarizabilities [25] of SWNTs have yielded dramatically anisotropic results. For metallic SWNTs, the static electric polarizability along the tube axis has been calculated to be effectively infinite compared to insignificant radial polarizabilities. Although not as anisotropic as metallic nanotubes, semiconducting nanotubes considered have been found to have their dominant polarizability along their tube axis; the relative ratios for semiconducting nanotubes were within two to three orders of magnitude of each other [25].

1.3.4 Mechanical Properties

Although electrical properties are of great interest, the most common questions concern the mechanical properties of carbon nanotubes. This is not surprising since most of the other allotropes are seen more frequently in mechanical applications. People have

come to associate graphite with lightweight strong materials and look to nanotubes to provide similar applications.

Graphite's reputation is well-deserved; it is in fact the stiffest material known with respect to its in-plane elastic modulus [26]. It is reasonable to predict that nanotubes, which also have a graphitic structure and thus benefit from strong in-plane trigonal sp^2 bonding described above, will have similarly noteworthy mechanical properties.

Scores of reports on theory and experiments pertaining to the mechanical properties of SWNTs and MWNTs have been published [3,5,6]. The highest Young's modulus reported for SWNTs thus far is 1.25 TPa [27] (cf. graphite, 1.02 TPa). The highest reported yield strength is 45 ± 7 GPa [28] (graphite whiskers, ~ 20 GPa [3]). It is worth noting that the yield strength of an SWNT is well over an order of magnitude greater than high-strength, construction, or special heat-treated steels, which have yield strengths of 0.3 to 1.5 GPa [29]. Predictions that nanotubes should have remarkable buckling tolerances [30] have been verified experimentally [31,32].

MWNTs have also been found to have remarkable mechanical properties. Atomic force microscope (AFM) deflection experiments have discovered a Young's modulus of 1.3 TPa [31] and transmission electron microscope (TEM) measurements of thermal vibrations of MWNTs have shown an average Young's modulus of 1.8 TPa [33].

The remarkable mechanical properties discussed so far are for an individual carbon nanotube. Current production methods result in nanotubes with lengths on the order of only microns and many processing methods further reduce these lengths to tens or hundreds of nanometers [34]. As with graphite and tube-shaped structures in general,

the mechanical properties of carbon nanotubes might be expected to depend upon the orientation of the nanotube. For bulk samples, the intermolecular forces will become significant. The dominant intermolecular forces between nanotubes are simple van der Waals interactions, which are generally only on the order of 1 kJ/mole.

It is worth pursuing such a bulk nanotube material as a potential structural replacement for other current materials. The density of bulk SWNTs is 1.3 g/mL, compared with the typical density of steel, which is 7.9 g/mL [35]. Thus, a nanotube holds the promise of a material one-sixth the density of steel and potentially orders of magnitude stronger.

Even if a bulk nanotube material could only provide similar strength to steel or other high strength materials it would be a significant breakthrough, as the typically high density of high strength materials continues to be a limiting factor; the material's own weight is a significant fraction of its load-bearing capability. Lower density is also crucial in space technology applications. Simply reducing the weight of a launch vehicle would translate into remarkable savings. However, once again the anisotropic nature of SWNT strength suggests that an aligned nanotube structure is needed to exploit these properties fully.

1.3.5 Thermal Conductivity

While graphite stimulates consideration of mechanical properties, graphite and diamond similarly stimulate the consideration of the thermal conduction of carbon nanotubes because of their remarkable thermal properties. Combined with the structure of nanotubes and the presence of semiconducting and metallic behavior, this leads to the

notion of a material that is at once a thermal conductor and a thermal insulator, depending upon the structure and orientation of the material.

These properties alone could make SWNTs valuable, as the distribution of thermal energy is a critical technology, whether it is the reduction of heat buildup, retention of heat via insulation, or transport of thermal energy where it is needed. The buildup of heat on the leading edge of jet turbines continues to be a concern and a limiting design factor. Efficient dissipation of heat from the central processing units of computers continues to be a problem for the computer manufacturing industry. Efficient transport of thermal energy, e.g. in heat pipe, with minimal loss is a daily concern. An aligned carbon nanotube structure might provide the versatility to address all of these needs in a single material.

Some measurements have already been made and extrapolations of thermal transport measurements on unaligned SWNT materials have yielded a value for room temperature longitudinal thermal conductivity for SWNTs, $17.5 \text{ W cm}^{-1} \text{ K}$ to $58 \text{ W cm}^{-1} \text{ K}$ [36]. For comparison, consider some of the most conductive materials, listed below [35]:

Material	Thermal Conductivity (W/cm K)	Material	Thermal Conductivity (W/cm K)
Aluminum	2.37	Gold	3.17
Copper	4.01	PG*, in-plane	19.5
Diamond type I	8.95	PG*, normal to plane	0.0570
Diamond type IIa	23.0	Silver	4.29
Diamond type IIb	13.5	SWNT	17.5 - 58

* - pyrolytic graphite

Table 1.1 Sample Room Temperature Thermal Conductivities

This places SWNTs as one of the most thermally conductive materials. However, this extrapolation was made for a theoretical aligned SWNT mat. Randomly-oriented mats of SWNTs have a thermal conductivity of merely 0.35 W/cm K. As with electrical conductivity, to fully take advantage of the anisotropic thermal conductivity of SWNTs, an aligned sample of SWNTs is needed. Such an aligned mat should facilitate more rigorous measurements of thermal conductivity, and some thermal transport measurements will be include in the Analysis chapter.

1.4 Previous Alignment Work

In light of the discussion above, it is not surprising that this work is not the first attempt at creating aligned nanotube structures; numerous attempts have been reported.

The simplest method was that of aligning nanotubes by stroking with a Teflon scraper [37]. This method, while interesting, did not produce a functional or useful material. The reported “alignment” achieved was a sparse monolayer of nanotubes oriented in the direction of scraping. This method is inadequate in that the depth of alignment effect is impractically shallow and does not produce an independent material that can be used; rather it is a smear on a substrate.

A very common sense approach would appear to be the use of a polymer matrix. Nanotubes have been successfully suspended in polymer matrices and some degree of alignment was achieved by subsequent cutting [38] or stretching [39] of the polymer matrix. In both cases the result is a relatively localized effect and the nanotubes are not in a state that allows the alignment to be retained after the removal of the polymer matrix. These approaches do not provide a pathway towards a neat, aligned nanotube material.

A few other approaches demonstrated good control over tube orientation, but they were localized to nanometer or micron-sized regions. Molecular combing, the use of a receding wetting line, was reported to align nanotubes in suspension [40], but the resulting alignment was of sparse tubes in poorly controlled placements.

Finally, there is a method reported that involves “wrapping” the tubes in a polymer and then assembling them [41]. Unfortunately, the polymer interferes with accessing the remarkable nanotube properties. Until such a method can accommodate the removal of the polymer without loss of alignment, it is an impractical technology.

Not all reports concerned mechanical approaches. The use of electric fields to align nanotubes is a natural path to explore. Metallic nanotubes should have some properties of a simple conducting rod. This, combined with their high static electric polarizability, makes an excellent rationale for using an electric field for alignment. Our previous work explored this to an extent. Although we were able to achieve some gross transport, alignment effects due to electric fields were never remarkable [42].

Since nanotubes are typically suspended or dispersed into a liquid medium, surface tension is another viable candidate for alignment forces. Some tiny effects were observed with experiments related to the controlled deposition of nanotubes using oxidative lithography and self-assembled monolayers (SAMs) [43].

A more dramatic effect was seen with a more recent experimental report which combined an electric field and surface tension forces. A large number of nanotubes were attracted to a conducting wire by an electric field while being withdrawn from a nanotube suspension [44]. This process produced a very rough, coarse material that was reported to have regions with clear anisotropy and postulated a mosaic angle of 62 degrees [44].

Thus far, that result is the only published one that competes with the scale and quality of alignment of the material created with this work.

1.5 Alignment by Magnetic Fields

While the above approaches all have merit for specific reasons, they are not a complete solution. Magnetic fields were investigated as a cleaner, larger scale, and more reproducible alignment tool. Magnetic fields are superior to electric fields in that they penetrate many materials quite readily and are not constrained by the myriad of complications in an electric cell, such as contamination by the electrodes, double layer screening, electrolyte maintenance, and unwanted chemical reactions at the electrode interface.

A magnetic field can thus produce a more homogenous effect throughout a system with less extraneous effects. There is also the capability to separate the geometry of the deposition surface from the geometry of the magnet, two things that tend to be inextricably intertwined with electrode setups.

However, these advantages are for naught unless a magnetic field can align a nanotube. Theoretical predictions have shown that SWNTs should have an anisotropic magnetic susceptibility [45-49]. This forms the basis of the case for using magnetic fields, as it is necessary to achieve an alignment effect, but it begs the question of whether or not the effect will be adequately large. Experimental results show that nanotubes have a greater magnetic susceptibility than buckyballs, diamond, carbon black and highly ordered pyrolyzed graphite (HOPG) [50]. This should mean that magnetic

field alignment effects should be most efficacious in nanotubes, among the other carbon allotropes, but it does not guarantee success, so some calculations are in order.

Thanks to the marvelous conceptual waltz in which electricity and magnetism are perpetually engaged, magnetic susceptibility in magnetic fields is somewhat analogous to electric polarizability in electric fields. Magnetic dipole moments are somewhat analogous to electric dipole moments. The energy of a given magnetic moment, $\vec{m}$, in an external magnetic induction field, $\vec{B}$, that does not vary much over the material is

$$U_{\text{magnetic}} = -\vec{m} \cdot \vec{B} [51]. \quad \text{Eq. 1.4}$$

This is also called the *orientational energy* to stress its nature as a potential energy.

To arrive at a relation in terms of the molar magnetic susceptibility, some substitutions need to be made. We can simplify things by considering only orientations of the moment parallel and perpendicular to the magnetic field axis. Given the magnetic field, $\vec{H}$, the molar magnetic susceptibility, $\chi_{\parallel}^m$, and the number of moles, n , we obtain:

$$\vec{m}_{\parallel} = \chi_{\parallel} \cdot \vec{H} \cdot V = \chi_{\parallel}^m \cdot \vec{H} \cdot n, \text{ and thus} \quad \text{Eq. 1.5}$$

$$U_{\text{magnetic},\parallel} = -\chi_{\parallel}^m \cdot n \cdot \vec{H} \cdot \vec{B}. \quad \text{Eq. 1.6}$$

Realizing that $\chi \ll 1$ and thus

$$\vec{B} = \mu \vec{H} = (\chi + 1) \vec{H} \approx \vec{H}, \quad \text{Eq. 1.7}$$

the relation for the difference in energy for parallel and perpendicular orientations can be determined to be:

$$\Delta U = n \cdot (\chi_{\text{parallel}}^m - \chi_{\text{perpendicular}}^m) \cdot \tilde{H}^2. \quad \text{Eq. 1.8}$$

The primary result of this relation is that a transition to a more positive value for molar magnetic susceptibility results in a decrease in energy, and is thus favorable. Given the molar magnetic susceptibility values shown in Figure 1.4 [52], the lowest energy orientation for all SWNT types is parallel to the magnetic field, regardless of whether they are paramagnetic or diamagnetic.

Figure 1.4 Angular Dependence of Nanotube Magnetic Susceptibilities

Based upon these predictions, it should thus be possible to orient nanotubes in a liquid suspension, analogous to the magnetic orientation of liquid crystals [53]. This has been experimentally demonstrated for small quantities of multi-wall nanotubes [54]. The calculated susceptibilities [45-49] predict an observable alignment of SWNTs at fields on the order of 10 T at room temperature. This was experimentally confirmed by measuring the optical transmittance of an SWNT suspension as a function of polarization angle and magnetic field [55]. The results of that experiment are summarized in Figure 1.5.

Figure 1.5 Experimental Verification of Nanotube Alignment in Magnetic Fields

Note the minima in Figure 1.5 at the points where the axis of the polarization vector is parallel or antiparallel to the magnetic field axis. A nanotube is a remarkably long thin object, having a length to width aspect ratio of at least 100:1. It is therefore

easier for incident light to drive the motion of free electrons along the tube axis. This allows the absorption and scattering of incident radiation. If nanotubes are the entities responsible for the data in Figure 1.5, this is clear proof of alignment with the tube axis along the magnetic field. However, in spite of the predictions and expectations of the results in Figure 1.5, it is possible that the effects seen were due to magnetic particles aligning with the field. As will be shown by the experimental data, it was verified that nanotubes are in fact aligning in the field.

An important piece of information to take away from these results is that between 8 Tesla and 19 Tesla there is a diminishing return, as the magnetic field effect appears to reach saturation. The 6 Tesla line is believed to be in error due to the lack of a sinusoidal dependence on angle. Regardless, the results of Figure 1.5 suggest that a magnetic field on the order of 7 Tesla should be adequate to achieve alignment. Based on a model of the saturation behavior, it was inferred that, at 19 T, 90% of the tubes lay within $17 \pm 1^\circ$ of the magnetic field axis and the alignment energy was on average 28 ± 3 times kT , where k is the Boltzmann constant and T is the temperature in Kelvin [55].

Finally, theory also predicts that the molar magnetic susceptibility is a weak magnetic field effect that scales linearly with diameter [52]. As a weak magnetic field effect, the interaction with the nanotubes will not significantly diminish the magnetic field. Scaling linearly with diameter is encouraging since most of the SWNTs in the SWNT colloid are likely to be bundles of at least a few ropes and as suspension is broken, the SWNT structures should increase in diameter.

In summary, the theoretical expectations are that:

- **magnetic fields on the order of 7 Tesla or higher should align SWNTs,**
- **the alignment torque should act to orient the nanotubes into a position coaxial with the magnetic field axis, and**
- **the effect should increase with larger diameter SWNT structures.**

2 Materials & Methods

Preliminary investigations that prompted this work were reported in my Masters thesis [42], which covered controlled chemical deposition of SWNTs, electrical deposition of SWNTs, most of the work performed with a syringe filter apparatus, and the preliminary investigations that led up to this work, using the cylindrical filter apparatus to create macroscopic neat membranes with smoother surfaces, larger surface areas, and under more pragmatic magnetic field strengths. Many of the materials and methods are similar or unchanged from that work. Some brief synopses from that work are included in this chapter as necessary. To facilitate comparisons, this chapter begins with a quick overview of the syringe filter apparatus.

2.1 Syringe Filter Fabrication

The purpose of the syringe filter apparatus was the demonstration of concept that bulk aligned nanotube materials could be created. Although successful, the process was small scale and impractical, and produced an awkward surface geometry in the resulting material due to the filter membrane. However, it provided the basis of this work.

2.1.1 Apparatus & Filtration Method

The syringe filter apparatus is explained in great detail in my Master's Thesis [42]. Its design is the basis for the cylindrical filter apparatus, and thus a brief overview is in order to facilitate the discussion of the current work as well as to enable the reader to make more complete conclusions about the work presented here. The schematic of the syringe filter system is reproduced below.

Figure 2.1 Schematic of Filtration Apparatus

The design of this apparatus was dominated by the filtration process requirements. Rather than pulling a vacuum on the filter membrane, the system was pressurized throughout the process. This was cleaner than a pump and safer around the high intensity magnetic field. The first step was passing nanotubes suspended in 0.05% aqueous TX100 through the filter, in the presence of a 25 Tesla magnetic field. Without allowing the filter to become dry, a rinse solution of 0.05% aqueous TX100 was then passed through the system. Finally, isopropyl alcohol (IPA) was introduced. The mixing chamber facilitated a more gradual transition in concentration from the aqueous TX 100 to the IPA. The result was a gradual shift from well-dispersed nanotubes to an aligned

mat of nanotubes. The system was pressurized to 20 psi, and the weight of the filtrate was used to monitor mass flow. The schematic above is simplified in that it shows only one filter. Two filters, connected in parallel, were used for each run. The specific materials and vendors are detailed thoroughly in my Masters thesis [42].

2.2 Cylindrical Filter Apparatus Design Overview

In contrast to the syringe filter apparatus, which was intended for the quickest possible successful result using the least amount of material, the cylindrical filter apparatus was designed to provide the largest filter surface area within experimental constraints. Chief among these constraints were the magnetic field itself as well as the two-inch diameter bore and vertical orientation of the 27-Tesla magnet used at the National High Magnetic Field lab. To provide a reference frame for discussions of the apparatus, the designs and design process notes have been reproduced in Appendix A from my Master's thesis [42]; however, a brief overview is useful.

The fundamental concept is a vertical coaxial double cylinder system that supports a tube-shaped nylon filter membrane. Fluid flows in from the top of the cylinders, is diverted to the outer walls, and passes down the sides to the filter membrane surface. Filtration occurs as the fluid passes through the filter membrane into the center of the system and the remaining fluid passes out through the bottom of the system.

Filtration is driven by a pressurized reservoir similar to that used in the Syringe Filter apparatus, but a more sturdy system, capable of sustaining 200 psi, is used. Non-magnetic metal tanks replace the Nalgene bottle; and sturdy Teflon tubing and metal quick connects replace Tygon tubing and plastic Luer locks. The design rationales and

further details are covered in much greater depth in my Master's thesis [42]; details essential to the use of the are addressed as needed in section 2.5 Filtration Procedure.

2.3 Modifications for 7 Tesla Work

The filtration apparatus was not the only change made in this work; a lower, more accessible magnetic field intensity was investigated, 7 Tesla. This field was provided by a custom made superconducting magnet from Oxford Systems. The bore was six inches in diameter and had a horizontal orientation. The field was essentially uniform over a length of about 15 cm from the center of the field, or a total of about 30 cm [56].

Figure 2.2 Superconducting 7 Tesla Magnet

While these parameters could accommodate a new apparatus, they were adequate for the cylindrical filter apparatus and this apparatus was used in order to facilitate reproducible work and timely execution of the experiments. However, there was a slight modification necessary to accommodate a 2-in apparatus in a 6-in bore. Providing a well-centered orientation for the apparatus within the magnet bore was accomplished with a spacer. A series of 6-in diameter, 1-in thick discs of expanded polystyrene were glued together and sanded until they fit snugly in the magnet bore. These had the benefit of being readily modified, discarded, and/or replaced. They provided the desired coaxial position and snug fit within the magnet bore without adding significant mass or complexity to the system.

Figure 2.3 Spacer Mount for Positioning Cylindrical Apparatus in 6" bore

Another chief difference was the magnet technology itself. The 27-Tesla magnet was a direct current resistive Bitters design electromagnet. The 7-Tesla magnet was a superconducting system. Whereas the 27-Tesla magnet was operated for up to 7.5 hours at a time, being ramped up from zero applied field, the 7-Tesla magnet resided at 7 Tesla continuously once brought up to field.

One characteristic both magnets had in common were significant cooling needs. The 27-Tesla magnet had incredible cooling requirements, but only during operator times. However, the 7-Tesla magnet required continuous cooling to prevent quenching of the field. This cooling was provided by routinely replenished cryogenics, specifically liquid helium and liquid nitrogen. The procedures settled on for cryogen maintenance of the 7-Tesla magnet can be found in Appendix B.

The final chief difference in the magnet setups was the available workspace. The area dedicated to the 7-Tesla magnet was significantly smaller than the “cell” used for the 27-Tesla magnet. Care was taken to keep electronics outside of the 100 Gauss line and a perimeter barrier was set up at the 5 Gauss line to obstruct foot traffic, and warning signs were posted around the area as well, in accordance with OSHA guidelines.

2.4 Nanotube Colloid Material

A magnetic field alone was not adequate for success in this work; the SWNTs needed to be in a form that allowed for the magnetic field to align them. This required a stable colloid of free-floating nanotubes, ropes, and bundles, with minimal or no disordered floccules present to sabotage alignment.

Producing such a colloid started with SWNTs produced by the laser oven method [57]; the source of these tubes was Tubes@Rice, Houston, TX, which has since ceased operations. The material was purified and filtered via a process detailed in my Master's thesis [42]. What is important to the discussion of this work is that the final material used was single walled carbon nanotubes in a colloid of water and 0.05% by weight Triton X 100.

Triton X 100 (TX100) is a nonionic detergent/surfactant. It has a density of 1.07 g/mL and is miscible with water, alcohol, acetone, benzene, and toluene. Its chemical structure is shown in Figure 2.4.

Figure 2.4 General Chemical Structure of Triton X

Typically, the number of repeating units, denoted by the subscript n in Figure 2.4, is nine to ten. TX100 has an unusual structure for a detergent. The hydrophobic portion of TX100 is the head and the long tail is the hydrophilic region, the opposite of common detergents. The chemical structure of TX100 is shown in Figure 2.5 below:

Figure 2.5 Hydrophobic and Hydrophilic Groups of an $n=10$ TX100 Molecule

TX100 aids colloidal dispersal of SWNTs via the same mechanism by which typical detergents suspend any hydrophobic entities. TX100 forms a micelle with the SWNTs, facing its hydrophobic portion towards the SWNT and the hydrophilic region pointing out. This allows the SWNTs to remain in a colloid form in water, typically in very small ropes of a few SWNTs each. The end result is a reasonably stable colloid that allows nanotubes the freedom to respond to the applied magnetic field and pass through the filtration system.

2.5 Filtration Procedure

The filtration procedure used resembled typical chemistry lab filtration in many regards. The process consisted of readying the solutions for filtration, pressurizing the system, priming the system filtering, rinsing, and finally removing the deposited material. However, before filtration was started, data acquisition was set up.

2.5.1 Data Acquisition Setup

The acquisition of drainage mass data was computerized using LabVIEW 5.1 and an Ohaus scale [58] with a serial port output. The time and mass were recorded at user-defined intervals, typically five seconds between each data point. Filtration system pressure data was also acquired.

To provide some real-time feedback data, the mass data was buffered and used to estimate current flow rates. The accuracy of the real-time flow rate estimates varied with the size of the buffer.

The pressure data was logged using standard LabVIEW solutions, but the Ohaus scale required a custom setup. The *virtual instrument* code, or VI, for the Ohaus scale data acquisition and real time flow rate estimation is included schematically in Figure 2.6. A soft copy of the VI can be found with this thesis.

Figure 2.6 Schematic Diagram of VI Code Used for Data Acquisition from Ohaus Scale.

2.5.2 Nanotube Colloid Preparation

With the data acquisition in place, preparation for filtration began, typically at least one day prior to the filtration run. The first step was preparation of the SWNT colloid which was generally not stable for more than a few hours or days. The nature of these suspensions is covered in greater detail in my Master's thesis [42]. Due to concerns over flocculation of the colloid, its preparation immediately preceded filtration. This step required a minimum of about 14 hours to complete.

It began with stock solutions of aqueous SWNT material and aqueous TX100 solution. A portion of aqueous SWNT material, typically with a density of 4.38 g/L, was combined with a portion of 5% aqueous Triton X 100 (TX100) stock. This was further diluted with added water, typically to 145 (+/-15) mL, and sonicated for at least eight hours, usually overnight, in a 5.5 gallon Bransonics B8510MT [59]. This stock colloid was then diluted with water as required by the experiment, typically to a mass of 4 kg, and sonicated for at least four more hours right up until the filtration run was about to start. The result of the process was a well-dispersed colloid with the desired concentration of SWNTs and typically 0.05% TX100 by weight.

2.5.3 Filter Apparatus Preparation/Assembly

As the colloid preparation drew to a close, usually during the last hour of sonication, the filter membrane was secured on the filter support core of the cylindrical filter apparatus. This step began with the securing of a sleeve of polypropylene (PP) mesh around the Delrin filter core, which was perforated with holes to facilitate passage of fluid. The sleeve was cut from a sheet and joined into a cylindrical sleeve shape by

matching the edges and melting them together with a soldering iron. The PP sleeve could be re-used from run to run, and is shown in the top of Figure 2.7, with the weld line visible near the top (w.r.t. the picture) of the sleeve.

Figure 2.7 Filter Assembly (top: PP sleeve, bottom: complete assembly)

The filter membrane was then wrapped around the PP sleeve. The filter membrane was cut from a 293-mm diameter 0.22-micron pore size Osmonics Magna membrane, a nylon membrane with a polyester support mesh. This was wrapped around the PP sleeve and welded in place by melting with a soldering iron, using 3 weld lines. It was found by experimentation that one weld line was not adequately robust, two were reliable, and three never failed. The ends of the filter sleeve were then secured with rings of 1.5" diameter heat shrink material. O-rings and wire were also tested as alternatives, but both were found to perform significantly poorer. The advantage of the heat shrink material was the uniform seal; other sealing methods tended to crease and mangle the end

of the membrane and create unwanted pathways for fluid flow. The final filter assembly is shown in the bottom of Figure 2.7, above. A summary of the process is detailed schematically in Figure 2.8.

Figure 2.8 Filter Mesh and Paper Assembly Process

This filter assembly was then inserted into the Lexan housing and the ends of the apparatus were closed. The source and drainage tubes were attached by quick connects and then the apparatus was placed inside the magnet bore. In the case of the 7-Tesla magnet, the filter apparatus was first placed in the spacer mount, shown in Figure 2.3.

2.5.4 Fluid Staging

With the filter apparatus assembled and data acquisition ready, the fluids were then staged. A cylinder of compressed prepurified nitrogen was attached to the system to provide a positive pressure on the source side of the filtration system, removing the need for a pump on the drainage side of the system. This provided two chief advantages, operation at higher pressure and greater safety. Typically, when a pump or other suction system is used in room air, there is an inherent limit of 15 psi, atmospheric pressure to the suction provided. With the compressed air approach the system was only limited by the source pressure and mechanical limit of the apparatus, which was 200 psi (with a safety factor of 2). The high magnetic fields required create a safety issue regarding pumps; they are more likely to fail and, because they are large ferromagnetic objects, they present a hazard to users.

With the positive pressure source in place, the staging of the liquids began. 8 L of isopropyl alcohol (IPA) was poured into a high-pressure canister. A second high-pressure canister was filled with 4 L of 0.05% TX100 in water. Finally, a third was filled with the SWNT/TX100 colloid. The removal of the SWNT from sonication and subsequent filling of the SWNT colloid container was delayed until immediately before

the run to minimize the danger of premature flocculation of the colloid; because of this danger, once the fluids were staged and the canisters sealed, things proceeded at a brisk pace.

Figure 2.9 High Pressure Tanks Used With Cylindrical Filter Apparatus

2.5.5 Filtration

With the fluids staged and canisters sealed, the system was pressurized with Nitrogen to a low pressure, typically 1 to 5 psi. The system was then primed with aqueous 0.05% TX100. The filter housing was removed and manipulated as needed to remove bubbles from the system, then returned to the magnet bore. Once the priming was finished, the scales were zeroed and the flow of SWNT colloid into the system started.

First, 75%-80% of the SWNT colloid was passed through the system. This was followed, without interruption, by a rinse with 1 kg of aqueous 0.05% TX100. Finally, again without interruption, IPA was passed through the system. In the more successful alignment runs, 4 L (or more) of IPA was passed through the system. In all cases, IPA began to drain from the system after 0.3 kg of IPA passed through; this was determined from the smell of IPA in the drainage.

During the filtration, the pressure was steadily increased. The initial pressure ranged from 1 to 5 psi and the final pressure was variously ~100 psi or ~175 psi. Slow ramping of the pressure was used in the successful runs.

2.5.6 Disassembly

With the filtration complete, the apparatus was removed from the magnet bore and then the filter core was removed from the apparatus and drained of any remaining liquid. The heat shrink was then carefully cut away and discarded. Finally, the filter membrane was carefully pulled off the core, dried, and stored flat. Once dry, the paper was ready for analysis.

2.6 Analytical Tools

Analysis of alignment was measured by Raman spectroscopy, x-ray diffraction (XRD), and measurement of thermal and electrical properties. Raman spectroscopy data was used as the primary data and was complemented by the XRD.

Carbon nanotubes have a distinct resonance Raman spectrum with well-characterized features [60-64], making Raman spectroscopy an ideal tool for confirming

the presence of nanotubes. Samples from the various runs were extensively analyzed with a Renishaw Raman microscope. The preliminary experiments performed with the syringe filter apparatus are covered in adequate detail in my Master's thesis and will only be used for comparison in this work. The primary samples examined in this work are the large neat membranes created with the cylindrical filter apparatus in magnetic fields of 25 Tesla and 7 Tesla.

The Raman microscope is an analytical tool that has only truly come of age in the last quarter century. Raman and Krishnan first observed the Raman effect in 1928, using sunlight as the radiation source and their eyes as the detectors. It remained a minor player in analytical spectroscopy, playing second fiddle to infrared (IR) spectroscopy.

The invention of the laser unlocked the potential of Raman. Within a few years, laser excitation had become an ideal source for producing the Raman effect. It took a little over a decade for optics and instrumentation technologies to catch up, but by 1975 the Raman spectrometer was mated with a microscope and Raman microscopy had begun to take its place as a valuable and widely used analytical tool.[65]. This created a powerful analytical tool that was greater than the sum of its parts.

Raman microscopy takes Raman spectroscopy one step farther by combining a confocal microscope with a Raman spectrometer. This not only provides a powerful combination of analytical tools, confocal microscopy and Raman spectroscopy, it also enhances the capabilities of the Raman spectrometer by facilitating analysis of a sample beyond the diffraction limit of the spectrometer alone.

The physical phenomenon measured by a Raman microscope is Raman scattering. Raman scattering is an inelastic scattering of light that results from interactions of

electromagnetic radiation with the vibrational and/or rotational modes of a molecule. This interaction can produce a photon with a lesser energy or a higher energy, a.k.a. *Stokes Raman scattering* and *anti-Stokes Raman scattering*, respectively. Stokes Raman scattering is the preferred regime of Raman spectroscopy.

The energy loss of a photon to a given molecular species from Stokes Raman scattering will produce a distinct spectroscopic fingerprint. The laser provides a coherent source of photons of similar energy. The Raman spectrum is obtained by irradiating the sample with this beam, collecting the scattered photons, and recording the energy shift of the scattered photons.

The micro Raman microscope used for this work was a Renishaw micro Raman 3000[66]. It consisted of a Raman spectrometer using one of two lasers focused through a Leica DMLM Microscope; this combination allowed it to image samples less than one micron across. The two lasers available were a 780 nm red diode laser (near-IR, 1.59 eV, 50 mW max CW) and a 514 nm Argon ion laser (green, 2.42 eV, 25 mW). The system was driven by the Renishaw WiRE™ 1.2 Raman software package on a Dell personal computer running Windows 98™. This Raman apparatus is reputedly easier to use, more stable, and less likely to damage samples than a typical Raman system.

The laser light that impacted the sample was polarized. This was specifically used in this work to compare the quality of alignment in some samples by assessing the dependence of scattering intensity on the angle between the polarization axes of the sample and the incident beam. This application was pioneered in my Master's work and reported on syringe filter samples [55]. Similar application of Raman microscopy has

been reported for assessing the alignment of drawn columnar aggregates of carbon nanotubes [44].

3 Run Data

To understand and explore the parameters that define a successful filtration run, data was acquired regarding the system pressure and drainage mass during the runs. The mechanisms for the acquisition of the pressure and mass data taken during the runs are explained in subsection 2.5.1, Data Acquisition Setup. The experimental data are sorted on a run-by-run basis. An overview of the runs will be addressed in the Discussion chapter. The raw data files are included on the CD-ROM with this thesis.

The execution of the runs was guided primarily by estimations of the flow rate of the filtration fluids, based upon real time calculations of the flow rate. The sheer volume of data points acquired renders the direct differential of the mass data cluttered and potentially confusing. The flow rate data was imported into Origin 7.1 and processed via a smoothed first order differential plot of the data, using the maximum of 25 points (left and right) for smoothing; this dramatically improved the readability of the data. The g/s units selected for the flow rate are a result of the units found to be most practical during the runs.

The pressure plots were processed as necessary to convert them from raw voltage data to pressure values. There was some slight variation in the arithmetic from plot to plot to arrive at values that agree with readings taken during the experiment; the pressure values are accurate to within ± 0.2 psi.

3.1 Run 1 (25 Tesla Field)

Run 1 was performed with a mixture of solutions M5J (36.51 g of 4.38 g/kg SWNT stock + 40.10 g of 5% TX100 stock) and M5K (36.50 g of 4.38 g/kg SWNT stock + 39.64 g TX100 stock); this was diluted to 8 kg to achieve a SWNT concentration of 0.04 g/kg. The data files for mass and pressure data for this run are *Run01_Weight.txt* and *Run01_Pressure.txt*, respectively.

The pressure and mass flow rates for Run 1 are shown in Figure 3.1.

Figure 3.1 Run 1 Pressure and Mass Flow

This preliminary run was characterized by flow rates that dramatically exceeded control experiment values. As a result, the pressure was increased only as needed to maintain a flow rate of approximately 1 g/s.

	Nanotubes	Aqueous TX100	IPA
Initial amounts (kg)	≈ 8	≈ 3.5	≈ 7.6
Total drainage (kg)	3.856	3.926	5.6
Step drainage (kg)	3.856	0.07	1.674
Flow rate (g/s)	0.8-1.2	0.6	0.5
Pressure (Torr)	4.7-39.2	39.1	38.9

Table 3.1 Run 1 Reagent, Pressure, Flow, and Drainage Mass Summary

The filter core was scraped slightly during removal from the filter housing. The liquid outside the core was grossly flocculated, with visible floccules greater than 2 mm in diameter. There were no obvious leak points in the filter welds or the heat shrink seals. The floccules were rinsed off of the core with isopropyl alcohol (IPA), and the core was kept moist with IPA until the filter and SWNT paper were removed from the core.

Once dry, the paper had a matte appearance. The paper did not exhibit obvious preferential cleaving, although there was a slight tendency for the material to part along the applied magnetic field axis during removal. The flakes were somewhat stronger when pulled by hand along the applied magnetic field line than when pulled perpendicular.

3.2 Run 2 (25 Tesla)

Run 2 was performed with the same mixture of solutions from Run 1, M5J (36.51 g of 4.38 g/kg SWNT stock + 40.10 g of 5% TX100 stock) and M5K (36.50 g 4.38 g/kg SWNT stock + 39.64 g TX100 stock); as noted in Run 1, this was diluted to 8 kg to achieve a SWNT concentration of 0.04 g/kg. The data files for mass and pressure data for this run are *Run02_Weight.txt* and *Run02_Pressure.txt*, respectively.

Due to the flocculation from Run 1, the mixing chamber and tubing were rinsed thoroughly with aqueous 0.05% TX100 to remove residual IPA, a known flocculant for SWNT/TX100 colloids.

The pressure and mass flow rates for Run 2 are shown in Figure 3.2.

Figure 3.2 Run 2 Pressure and Mass Flow

Due to concerns of premature flocculation of SWNTs, the amount of aqueous TX100 stock rinse used in Run 2 was increased. After the filtration was complete and the filter core removed, significant flocculation was seen, but slightly less than with Run 1.

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 8 - Run 1	≈ 3.5 - Run 1	≈ 7.6 - Run 1
Total drainage (kg)	3.50	3.71	5.61
Step drainage (kg)	3.50	0.21	1.9
Flow rate (g/s)	0.4-1.8	0.9	0.8-1.0
Pressure (Torr)	5.2-97.5	97.5	97.3-97.2

Table 3.2 Run 2 Reagent, Pressure, Flow, and Drainage Mass Summary

The dried paper had a matte appearance. There was a slight tendency to part along the axis of the applied magnetic field. There was a spotty gray residue left behind on the filter-side surface of the paper when it was removed from the filter.

3.3 Run 3 (25 Tesla)

Run 3 was performed with solution M5L (36.6 g of 4.38 g/kg SWNT stock + 39.94 g of aqueous TX100 stock); this was diluted to 4 kg to achieve a SWNT concentration of 0.04 g/kg. The data files for mass and pressure data for this run are *Run03_Weight.txt* and *Run03_Pressure.txt*, respectively. A plot of pressure data is uninformative and thus is not included here.

During this run, it was immediately obvious there was a complication, as the drainage was slightly darker than before and the flow rates started at 2.4 g/s and kept rising. When the run was stopped, it was found that the welds on the filter membrane had ruptured and the core was full of IPA. Noticeable floccules were present, similar to Runs 1 and 2. Large particles readily washed away from the core when rinsed with IPA.

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 4	> 1 kg	> 4 kg
Total drainage (kg)	0.940	1.986	4.614
Step drainage (kg)	0.940	1.046	2.628
Flow rate (g/s)	2.4	3.0-3.4	“Too high”
Pressure (Torr)	19.4-19.8	19.3-19.4	~19?

Table 3.3 Run 3 Reagent, Pressure, Flow, and Drainage Mass Summary

The dry paper had a matte appearance and exhibited some creases. There was no remarkable polarization effect. The paper could be removed freely from the filter and no preferential cleavage of the material was observed.

3.4 Run 4 (25 Tesla)

Run 4 was performed with solution M5M (36.59 g of 4.38 g/kg SWNT stock + 39.96 g of aqueous TX100 stock); this was diluted to 4 kg to achieve a SWNT concentration of 0.04 g/kg. The data files for mass and pressure data for this run are *Run04_Weight.txt* and *Run04_Pressure.txt*, respectively.

In assembling the filter membrane for this run, it was found that spinning the filter core on a rod while heating the heat-shrink material resulted in a better seal. The O-ring spacers were omitted during assembly. The pressure and mass flow rates for Run 4 are shown in Figure 3.3.

Figure 3.3 Run 4 Pressure and Mass Flow

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 4 - ~0.2 prime & spill	> 1kg	>4 kg
Total drainage (kg)	3.54	4.102	6.246
Step drainage (kg)	3.54	0.562	2.144
Flow rate (g/s)	0.2-1.6	0.2	0.13-0.43
Pressure (Torr)	0.7-4.5	4.4	4.4-16.5

Table 3.4 Run 4 Reagent, Pressure, Flow, and Drainage Mass Summary

The flow rates were adjusted to match those of a previously successful syringe filter run, run #6 of that series of experiments [42]. The flow rate was allowed to dip to 0.2 g/s and was maintained at that rate during deposition.

Upon removal of the filter apparatus from the magnet bore, floccules were found again, but almost exclusively located between the heat-shrink and housing wall. The dried paper had a matte appearance similar to Runs 1-3, but exhibited the greatest degree of cleavage thus far, cleaving within 30 ° of the applied magnetic field axis, occasionally peeling off in long strips. However, the top layer was poorly consolidated.

3.5 Run 5 (25 Tesla)

Run 5 was performed with solution M5N (36.54 g of 4.38 g/kg SWNT stock + 40.40 g of aqueous TX100 stock); this was diluted to 4 kg to achieve a SWNT concentration of 0.04 g/kg. The data files for mass and pressure data for this run are *Run05_Weight.txt* and *Run05_Pressure.txt*, respectively.

The pressure and mass flow rates for Run 5 are shown in Figure 3.4. This run was the first in which multiple small incremental pressure increases were used to maintain a minimum flow rate. The target in this run was 0.30 g/s; it was maintained by incremental pressure increases until the maximum pressure of 175 psi was reached.

Figure 3.4 Run 5 Pressure and Mass Flow

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 4	$> 1 \text{ kg}$	$> 5 \text{ kg}$
Total drainage (kg)	2.866	3.636	8.366
Step drainage (kg)	2.866	0.77	4.73
Flow rate (g/s)	0.25-1.8	0.18-0.25	0.22-0.64
Pressure (Torr)	1.0-175.0	~ 175	~ 174

Table 3.5 Run 5 Reagent, Pressure, Flow, and Drainage Mass Summary

The amount of IPA rinse was once again increased in this run, as shown in Table 3.5. This increase was based upon a concern that the TX100 was not being adequately rinsed away in previous runs.

When the filter apparatus was removed from the magnet bore, almost no free-floating floccules were present. Once dried, the paper was visibly glossier than the papers produced by Runs 1-4, exhibiting a satin sheen, distinctly different from the appearance of Runs 1-4. There was a more obvious preferential cleavage along the applied magnetic field line, almost as much as that achieved with the syringe filter apparatus runs [42]. There was noticeable dimpling in the paper, consistent with the pattern of holes in the Delrin filter core support.

3.6 Blank Runs (25 Tesla)

Two runs were performed as controls to examine how the system behaved in the bore with an applied magnetic field but without a filter membrane in place. The pressures and weights are not addressed here, but the data files for mass and pressure data for this run are still included on the CD-ROM with this thesis, the file names are *BlankRun_Weight.txt* and *BlankRun_Pressure.txt*, respectively.

Flow rates of 0.2 g/s and 1.0 g/s were employed. No flocculation was seen in the system throughout the run (this does not account for flocculation once the IPA mixed with the SWNTs in the drainage vessel). The solution color visibly darkened, consistent with SWNTs present in the system, after 0.1 ($\pm$ 0.02) kg had collected in the drainage vessel.

3.7 Run 6 (25 Tesla)

Run 6 was performed with solution M5P (36.71 g of 4.38 g/kg SWNT stock + 39.9 g of aqueous TX100 stock); this was diluted to 4 kg to achieve a SWNT concentration of 0.04 g/kg. The data files for mass and pressure data for this run are *Run06_Weight.txt* and *Run06_Pressure.txt*, respectively.

The pressure and mass flow rates for Run 6 are shown in Figure 3.5.

Figure 3.5 Run 6 Pressure and Mass Flow

As with Run 5, this run was performed with small incremental pressure increases aimed at maintaining a certain minimal flow rate. However, an attempt was made to

reserve the bulk of the pressure increases for the end of the run, and so a lower minimum flow rate of 0.25 to 0.27 g/s was the target for this run.

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 4	> 1 kg	> 4 kg
Total drainage (kg)	2.868	3.667	7.664
Step drainage (kg)	2.868	0.799	3.997
Flow rate (g/s)	0.23-1.6	0.20-0.23	0.20-0.60
Pressure (Torr)	0.9-173	~ 173	~ 171

Table 3.6 Run 6 Reagent, Pressure, Flow, and Drainage Mass Summary

The dried paper had a satin sheen similar to Run 5 and exhibited a distinct preferential cleavage along the applied magnetic field axis. Peeled pieces possessed a ribbon-like character similar to that seen in the syringe filter material. As with Run 5, there was dimpling in the filter paper consistent with the pattern of holes in the Delrin filter support core.

3.8 Run 7 (25 Tesla)

Run 7 was performed with solution M5Q (36.44 g of 4.38 g/kg SWNT stock + 40.21 g of aqueous TX100 stock); this was diluted to 4 kg to achieve a SWNT concentration of 0.04 g/kg. The data files for mass and pressure data for this run are *Run07_Weight.txt* and *Run07_Pressure.txt*, respectively. The pressure and mass flow data are shown in Figure 3.6. The pressure was adjusted for Run 7 to maintain a flow rate of 0.27 g/s to 0.30 g/s.

Figure 3.6 Run 7 Pressure and Mass Flow

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 4	> 1 kg	> 5 kg
Total drainage (kg)	2.866	3.888	8.796
Step drainage (kg)	2.866	1.022	4.908
Flow rate (g/s)	0.23-1.1*	0.22-0.25	0.25-0.62
Pressure (Torr)	1.1-47	~47	46-98

* - flow rate was ~0.27 to 0.30 g/s until ~1.202 kg

Table 3.7 Run 7 Reagent, Pressure, Flow, and Drainage Mass Summary

The dried paper exhibited dimpling similar to those from Runs 5 and 6, but to a lesser degree. The paper cleaved preferentially along the applied magnetic field axis. Of the seven cylindrical filter apparatus runs performed in the 25-Tesla magnetic field, the material produced in Run 7 was distinctive in its luster. It was the shiniest material produced, having a slick appearance similar to that of a pool of oil.

3.9 Run 8 (7 Tesla)

Run 8 was performed with solution M6A, diluted to 0.4 g/kg. The mass data file for this run is *Run08_Weight.txt*; the pressure data was acquired manually. Run 8 was the first run in which the filtration system was operated in the 7-Tesla magnet. Based upon the results of the 25-Tesla runs, pressure was adjusted via small incremental changes to maintain a specific range of flow rate; the target rate for Run 8 was 0.15 g/s. The pressures and mass flow rates are shown in Figure 3.7.

Figure 3.7 Run 8 Pressure and Mass Flow

The initial pressure for this run was 0.8 psi. The system limit of 175 psi was reached at 210 minutes, 60 minutes before the SWNT solution was depleted. The aqueous TX100 rinse began at 270 minutes and the IPA final rinse began at 450 minutes.

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 4	> 1 kg	> 5 kg
Total drainage (kg)	2.866	3.890	8.938
Step drainage (kg)	2.866	1.024	5.048
Flow rate (g/s)	0.12-0.5	0.10-0.13	0.12-0.47
Pressure (Torr)	0.6-175	~175	~175

Table 3.8 Run 8 Reagent, Pressure, Flow, and Drainage Mass Summary

Upon removal of the apparatus from the bore there were some small bubbles present, but no floccules were visible in the system. The filtration apparatus was left overnight in IPA. When it was opened and the filter core removed, the top portion of heat shrink was swollen and no longer provided a secure seal. It was not clear if this had happened during the run or overnight.

The filter and paper were held flat and left to dry; the paper immediately cracked in a few places along the applied magnetic field axis. The paper had a glossy sheen; it was glossier than Runs 5 and 6 but flatter than the sheen of Run 7. The dimpling of the paper was consistent with that seen with Runs 6 and 7, which also topped out at 175 psi. Under a confocal microscope, some irregularities were evident. It appeared as if a more ordered and smooth surface was covered with globs of more amorphous material.

3.10 Run 9 (7 Tesla)

Run 9 was performed with solution M6B, diluted to 0.6 g/kg. The mass data file for this run is *Run09_Weight.txt*; the pressure data was acquired manually. Run 9 was the first cylindrical filter run in which the concentration of SWNTs exceeded 0.4 g/kg.

The mass flow rates and pressures of Run 9 are shown in Figure 3.8.

Figure 3.8 Run 9 Pressure and Mass Flow

This run was started at 0.5 psi, as reflected by the initial spike in mass flow in Figure 3.8. The flow was switched to aqueous TX100 at 357 minutes, by which time the system pressure had stabilized at 5.1 psi. One kilogram of aqueous TX100 was rinsed

through the system. The IPA rinse started at 557 minutes. The system was left running without pressure increase; Figure 3.8 reflects a slight but steady decrease in mass flow rate throughout this step. At the start of the IPA rinse, the system had stabilized at 4.3 psi, and at the very end of the run the system was at 4.0 to 4.1 psi. By 660 minutes, the system began to experience a steady increase in flow rate to 2 g/s. Upon completion, the system was left in the magnet overnight (about 8 hours).

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 2.1	> 1 kg	> 5 kg
Total drainage (kg)	2.1	3.168	8.108
Step drainage (kg)	2.1	1.068	4.94
Flow rate (g/s)	0.07-0.34	0.07-1.0	0.07-0.23
Pressure (Torr)	0.5-4.9	4.6-4.9	4.0-4.6

Table 3.9 Run 9 Reagent, Pressure, Flow, and Drainage Mass Summary

Upon removal, the filter housing exhibited visible floccules, especially around the source-side heat shrink seal. Once the filter core was removed it was apparent that the heat shrink had expanded as before. Floccules were rinsed off the surface of the paper with IPA. There was a thin line of disk-shaped pits in the paper, aligned with the central axis of the assembly; this may correspond to the topmost region of the filter.

Once dry, the paper had a dull sheen and spontaneously peeled off the filter paper. There was no gray residue visible on the filter-side surface of the paper. The paper was 15 microns thick, or 50% thicker than previous runs, as might be expected from the 50% increase in concentration of nanotubes.

3.11 Run 10 (7 Tesla)

Run 10 was performed with solution M6C, diluted to 1 g/kg. This is the highest concentration of SWNTs that was attempted. The file for mass data for this run is *Run10_Weight.txt*; the pressure data was acquired manually. The mass flow rates of Run 10 are shown in Figure 3.9.

Figure 3.9 Run 10 Pressure and Mass Flow

This run started at 0.5 psi. The flow of aqueous TX100 started at 292 minutes. The last adjustment to pressure occurred at 310 minutes, when it was raised to 41.6 psi; the flow rate remained relatively constant, decreasing very slightly until the flow of IPA

was started at 724 minutes. The flow rate more than tripled within 15 minutes of the start of the IPA and continued to increase. This proved to be problematic as the system was left overnight and the fluid ran out due to a dramatic spike in flow rates. As a result, the material dried in the bore.

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 0.08	> 2.2 kg	> 10 kg
Total drainage (kg)	0.114	2.284	11.742
Step drainage (kg)	0.114	2.170	9.458
Flow rate (g/s)	0.04-0.24	0.04-0.05	0.05-1.6
Pressure (Torr)	0.5-0.6	0.5-41.6	41+

Table 3.10 Run 10 Reagent, Pressure, Flow, and Drainage Mass Summary

When the filter core was removed there was a dark stain visible in the region that was at the bottom while in the magnet bore. The resulting paper had a satin sheen and split spontaneously and dramatically along the applied field axis, up to two or three splits per 1 mm width. It was generally more brittle than previous material.

3.12 Run 11 (7 Tesla)

Run 11 was performed with 200 g of solution M6G, diluted to 0.93 g/kg. This is the second highest concentration of SWNTs that was attempted. This run was distinguished by the presence of an inline sonicator emplaced in an attempt to improve the quality of colloidal suspension immediately before it entered the magnetic field. This was accomplished by passing the fluid through a coil inside an ultrasonic bath. The file for mass data for this run is *Run11_Weight.txt*; the pressure data was acquired manually. The mass flow rates of Run 11 are shown in Figure 3.10.

Figure 3.10 Run 11 Pressure and Mass Flow

The filter core was dampened before applying the filter membrane and a controlled temperature soldering iron was used, set at 600 ° F, to melt the welds of the filter membrane; a long Weller ETK soldering iron tip was used. The heat shrink bands used were cut 1 1/8 in wide.

The run was started with a pressure of 1.4 psi. The aqueous TX100 rinse was started at 9 minutes. The IPA rinse was started at 336 minutes.

	Nanotubes	Aqueous TX100	IPA
Beginning amounts (kg)	≈ 0.08	> 2.2 kg	> 10 kg
Total drainage (kg)	0.114	3.616	12.722
Step drainage (kg)	0.114	3.502	9.106
Flow rate (g/s)	0.05-0.46	0.02-0.35	0-1.26
Pressure (Torr)	1.4-1.9	1.9-16.6	15.8+

Table 3.11 Run 11 Reagent, Pressure, Flow, and Drainage Mass Summary

Upon removal, there was no cracking or floccules. Some fine ribbons peeled up spontaneously and preferentially along the applied magnetic field axis. The sheen of the material was irregular. A thin region down the length of the filter that corresponded to the topmost surface inside the bore was glossier than the rest of the paper, which had a satin sheen to it.

4 Analysis

Once the membranes were fabricated, the primary analytical tools used to assess their alignment were Raman spectroscopy and X-ray diffraction (XRD). Transport measurements were also conducted; the resulting data demonstrated anisotropic thermal and electronic transport. In practice, Raman microscopy was the most heavily used of these tools for measuring and verifying the anisotropic properties of the aligned sheets.

4.1 Quantitative Use of the Renishaw Raman Microscope

Raman microscopy is of greatest utility when used for qualitative analysis of a sample, specifically the confirmation of the presence of a specific Raman resonant material. Quantitative analysis outside the bounds of a single collection of a single spectrum requires more care and some additional considerations.

Inconsistent focusing was found to skew data, as shown in Figure 4.1. A shift of as little as 2-microns in the elevation of the focal plane can modify the collected counts by $\pm 10\%$. Figure 4.1 shows an initial increase in intensity, which, although interesting, was not too surprising as this particular plot was a deviation of the focal plane into the sample surface.

The focus mechanisms of the microscope also exhibited obvious hysteresis. In practice it was found that consistency and reproducibility were greatest if the final focus adjustment was always performed such that the stage was moving downward in a smooth motion. This also minimized errors due to the tendency of the stage to settle downward after adjustment. Settling was dramatically exacerbated when the system was experiencing noticeable vibration, which was a problem of its own.

Figure 4.1 Sensitivity of Collection Efficiency to Focal Plane Deviation

Vibration of the microscope introduces randomness into the collection of scattered light from the sample spot. This tends to reduce the collection efficiency and thus the overall counts collected. If the vibration is minimal and consistent in character, then it is not generally an issue; however, sporadic and/or dramatic vibration in the system can compromise reproducibility by variably reducing Raman intensities up to 50%.

Non-mechanical considerations can be problematic as well. Extended irradiation of a sample with laser light can cause changes in the data acquired. This can be due to

simple desorption and adsorption of species, thermal effects, and possibly even chemical reactions in the beam spot. It has been reported that permanent modification of the Raman spectrum of a sample of SWNTs can result from intense laser irradiation [67]. All of the samples produced by the runs described in Chapter 3 exhibited anywhere from 5% to 20% increases in intensity if irradiated for one to ten minutes before collection of a spectrum. To minimize this effect, the laser shutter was only opened immediately before the collection of a spectrum and was closed immediately afterwards.

Irregularities in the surface of the sample can also effect the efficient collection of scattered photons. To minimize this, the samples were affixed to a flat mount, typically a microscope slide. Once mounted, the samples were affixed to a rotating stage to facilitate assessment of the angular dependence of Raman intensity. Samples were cut such that the magnetic field axis was obvious, but this still only gave a gross indication of the axis direction after cutting and mounting. There was generally as much as a 10-degree variation introduced by the cutting and mounting process; this was accounted for in the analysis techniques, discussed later in this section.

The simplest approach to take in analyzing an aligned sample is the comparison of counts collected with just two orientations: the applied magnetic field axis parallel and perpendicular to the polarization vector of the laser. While this is quick and informative, it is still crude and can be misleading. Rather, measuring and analyzing the incremental change in counts and its angular dependence obtains a more accurate and reliable assessment of the character of a sample's alignment, or lack thereof.

For simple acquisition of a single spectrum alone for the purposes of qualitative consideration, the extended grating was used with a single accumulation of 60 to 90

seconds in duration and cosmic ray reduction turned on. The more quantitative goal of assessing the alignment of the samples with the Raman microscope was accomplished with two different methods, which will be called the *survey method* and the *point method* for the purposes of this discussion.

The first approach, the survey method, was aimed at assessing the general character and reproducibility of the surface. Preliminary data was acquired to fine tune the alignment of the applied magnetic field of the sample with the polarization vector of the laser beam; these data were quick samples taken with single accumulations lasting 10 seconds with a static grating and cosmic ray reduction (CRR) turned off. Once aligned, five data points, spaced 1 mm apart were acquired for each angular orientation. The sample was exposed only during active collection to reduce skewing of the spectrum with long term irradiation. After each translation to a new location, the stage was moved up slightly and the sample brought back into focus once again so as to ensure a consistent focal plane. Data were acquired at a given point using either a static grating or an extended spectrum, with a single accumulation of 60 seconds in duration; cosmic ray reduction was turned off. After five points had been collected at a given orientation, the sample was rotated 15 degrees, then the sample was translated to roughly the same starting location, and collection of five more data point ensued. This was repeated until five points had been collected at 15, 30, 45, 60, and 90 degrees. The data acquired with this method showed that the samples created were remarkably uniform, as illustrated in Figures 4.2 and 4.3.

Figure 4.2 Plot of Data Showing Uniformity of Raman Signal Across Surface

Figure 4.3 Standard Deviation of Mean Across a Surface

This uniformity of Raman signal across the sample surfaces justified the transition to a different approach that focused on a more localized region.

The second approach, the point method, was simpler and quicker than the survey method. It consisted of collecting data in ten-degree increments over a sufficiently broad range of angles to ensure the inclusion of the maxima and minima angles in the acquired data set. Again, care was taken to irradiate the sample with the laser beam only during active collection to reduce skewing of the spectrum with long term irradiation. Also, as with the survey method, the stage was moved up slightly and the sample brought back into focus once again after each rotation to a new angle, so as to ensure a consistent focal plane. Data were usually acquired over a range starting 20 or 30 degrees before the minima and ending 20 or 30 degrees after the maxima. At each orientation, a single accumulation of 30 seconds duration was made using the static grating and with cosmic ray reduction turned off. The sample stage was configured such that the central point of rotation was approximately 5-10 microns off center, to minimize prolonged laser irradiation effects while still imaging essentially the same area.

There are distinct advantages and disadvantages to each method. The survey approach has the advantage of creating more accurate data for a given point, but is significantly more time consuming; the average time to acquire data from 0 to 90 degrees in 15-degree increments for a single sample was approximately 1.5 hours. This made the exploration of numerous angles impractical and the initial time spent aligning the axis with the polarization vector essential. On the other hand, the point approach is a very fast method that facilitates data acquisition at multiple angles and also minimizes the danger of prolonged laser irradiation effects. The numerous angles facilitate data fitting and give

a clearer picture of the angular dependence of the signal intensity. However, the data for a given angular orientation is necessarily less accurate than if it had been acquired via the survey method.

4.2 Analyses of Selected Papers

All of the papers were examined via Raman microscopy. Initial assessments were made using the survey method, but the point method was used for the bulk of the data presented here, once the uniformity of the samples had been established and comparable information obtained from the point method. Figure 4.4 shows a representative spectrum.

Figure 4.4 Representative Raman Spectrum of Fabricated SWNT

4.2.1 Runs 1-4 (25 Tesla)

As discussed in the run data of Sections 3.1-3.4, these preliminary runs produced dull sheets with unremarkable physical characteristics; the exception to this was Run 4, which exhibited a slight preference in cleaving with respect to the applied magnetic field axis.

A representative plot of the spectra maxima at various angles from Run 1 is shown in Figure 4.5. Although this plot was taken with the survey method, the resulting data was scattered and inconsistent with a smooth angular dependence in intensity. No further assessment of Run 1 was made.

Figure 4.5 Run 1 Raman Spectrum Maxima at Various Angles (survey method)

Run 2 was assessed with the point method. A plot of the spectra maxima at various angles is shown in Figure 4.6. The quality of the data is marginally better than Run 1, although still quite poor.

Figure 4.6 Run 2 Raman Spectrum Maxima at Various Angles (point method)

Run 3 was the failed run in which the welds burst. A plot of Raman data was found to be more erratic than the Run 1 and 2 data. No plot of this data is included.

Run 4 was the most successful of Runs 1-4, based upon simple observation unaided by instrumentation. A plot of the spectra maxima at various angles is shown in

Figure 4.7. This data is on par with the quality of the Run 2 data. Although distinct points of inflection seem to become visible, there is not a clear 90-degree difference between the minimum and maximum of the plot, and the generally erratic intensities in general make the results ambiguous.

Figure 4.7 Run 4 Raman Spectrum Maxima at Various Angles (point method)

4.2.2 Runs 5-7 (25 Tesla)

Run 5 was the first of the runs that exhibited gross physical characteristics that suggested the presence of alignment in the material produced. Similar results were achieved with Runs 6 and 7. Plots of the spectral maxima at various angles for these three runs follow in Figures 4.8 - 4.11. Based upon the results of the analyses, additional data was taken on Run 5, hence the presence of data from the survey methods and point methods for Run 5.

Figure 4.8 Run 5 Raman Spectrum Maxima at Various Angles (survey method)

Figure 4.9 Run 5 Raman Spectrum Maxima at Various Angles (point method)

Figure 4.10 Run 6 Raman Spectrum Maxima at Various Angles (point method)

Figure 4.11 Run 7 Raman Spectrum Maxima at Various Angles (point method)

A sample of Run 7 material was baked in a thermogravimetric analysis system (TA Instruments SDT 2960) in an attempt drive off possible residue. The temperature was ramped at a rate of 5 °C/min until 400 °C was reached and then the system remained isothermal. The results are shown in Figure 4.12. Mass loss was 25% and stabilized at approximately 50 minutes and 250 °C.

After the bake was finished, the sample was analyzed via Raman microscopy again; the results are shown in Figure 4.13. Note that the sample was rotated 90 degrees on the microscope slide, hence the differences in the position of maxima and minima with respect to the unbaked sample analysis. To assess the inner surface, the top layer was sheared off and the sample was analyzed again; this plot is shown in Figure 4.14.

Sample: run7
Size: 0.1861 mg
Method: mjc

n.bt

TGA-DTA

Figure 4.12 Thermogravimetric Analysis of Run 7

Figure 4.13 Run 7 Raman Maxima After Baking at 400 °C

Figure 4.14 Run 7 Raman Maxima After Baking at 400 °C and Tape-Shearing

In the end, baking and shearing had little effect on the Raman data. Shearing to expose the inner surface raised the total counts by about 50%, but the relative peak heights and anisotropy remained essentially unchanged.

4.2.3 Runs 8-11 (7 Tesla)

Of the runs 8-11, only 8 and 11 exhibited remarkable anisotropy. Raman spectral analyses of Run 8 and 11 are shown in Figure 4.15 and Figure 4.16, respectively.

Figure 4.15 Run 8 Raman Spectrum Maxima at Various Angles (point method)

Figure 4.16 Run 11 Raman Spectrum Maxima at Various Angles (survey method)

Due to an irregular surface on the Run 11 sample, it was sheared with tape. It split into somewhat equal portions and both exposed faces were analyzed. The data taken from both faces are plotted in Figure 4.17.

Figure 4.17 Run 11 Raman Spectrum Maxima, Sheared Faces (point method)

The data have remarkable agreement except in the intensity of the signal. Both sets of data were acquired with the same parameters, were mounted on the same microscope slide, and were acquired back to back. The “lower” surface was the one that was already adhered to the slide. The “upper” surface was the exposed surface of the material that peeled away with the tape during shearing. As a result, the upper surface experienced significant plastic deformation forces.

4.2.4 Comparison of Annealed 25 Tesla Material and 7 Tesla Material

Figure 4.18 depicts a comparison of material from the 25 Tesla and 7 Tesla runs after undergoing a 1200 °C vacuum anneal.

Figure 4.18 Comparison of Annealed Samples from 25-T and 7-T Runs

These plots show a remarkable similarity in anisotropy in spite of the differing magnetic fields. The implications of this will be discussed further in Chapter 5.

4.3 XRD Analyses

Additional characterization of our membranes was performed at the University of Pennsylvania. The results of XRD and Raman analyses of alignment of Run 5 and Run 11 samples are shown in Table 4.1.

	XRD	Raman
7 T Mosaic angle	38 °	36°
7 T Unaligned Fraction	0.58	0.28
25 T Mosaic angle	34°	42°
25 T Unaligned Fraction	0.60	0.20

Table 4.1 Combined XRD and Raman Data of 25 T and 7 T Samples

4.4 Thermal and Electrical Transport

Measurements were made at the University of Pennsylvania that showed a distinct anisotropy in thermal and electrical transport [68]. A summary of the resistivity measurements is shown in Table 4.2.

	7 TESLA	25 TESLA
ρ	0.9 m Ω cm.	0.9 m Ω cm.
$\rho(//)/\rho(\text{perp.})$	8	6

Table 4.2 Resistivity of Aligned Samples

A sample of the resistivity data is shown in Figure 4.19.

Figure 4.19 Electrical Transport Anisotropy of 7 Tesla Sample

4.5 Relative Packing of Filter Paper Assemblies

Given the calculated density of 1.34 for a close-packed structure of nanotubes, the ideal thickness of the assemblies can be calculated based upon the mass of nanotube suspension deposited. If $m_{deposited}$ is the mass of SWNTs deposited, and $A_{membrane}$ is the area of the filter membrane upon which the SWNTs are deposited then t_{ideal} , the thickness of an ideal SWNT paper with closest packed structure, can be estimated:

$$t_{ideal} = \frac{m_{deposited}}{1.34 \cdot \frac{g}{mL} \cdot A_{membrane}} \quad \text{Eq. 4.1}$$

For the syringe filters created in the previous work [42], the thickness was roughly measured as 2 to 3 microns thick. The cylinder apparatus papers were measured as 7-8 microns thick. A comparison of ideal versus experimental values for the thickness and packing of the materials examined is shown in Table 4.2.

Quantity	Syringe	Cylinder
Mass* (mg)	0.40 (0.66)	68.4 (114)
Area in (cm ²)	3.5	130
Ideal Thickness (μm)	0.85 (1.42)	3.93 (6.55)
Actual Thickness (μm)	2-3	7-7.9
% of close-packed	30-40%	50-60%

* - the adjusted mass assumes 40% by weight of residual contaminants in assembly

Table 4.2 Thickness Values for Filter Papers Produced

5 Discussion

5.1 Magnet Run Results

5.1.1 Runs 1-4

All of the samples from Runs 1-4 had a matte black appearance and were generally unremarkable in their degree of alignment. A brief discussion follows on what may have caused the failure in each case.

Run 1 exhibited unusually high flow rates at low pressures, and had relatively low maximum pressure. There were visible floccules around the filter upon removal. The anisotropy of the sample by Raman analysis was unremarkable. However, the filter membrane showed no signs of leaks and the outflow was only fairly clear. It is most likely that the system did in fact leak, possibly due to inadequate tightening of the filter housing which would have compromised the seal at the base of the filter housing.

Run 2 was similar to Run 1 in that it was unremarkable and produced floccules. Based upon the flow rates for the successful runs, the relatively high flow rates suggest that leaking may have been a significant problem in this run.

Run 3 was clearly a failure due to ruptured welds in the filter membrane. The subsequent difficulty with removing the SWNT paper from the filter was most likely due to inadequate material necessary to form a continuous sheet and robust enough to peel off of the filter.

Run 4 was an attempt to match the flow rates of a previously successful syringe filter run, Run #6 of that series of experiments [42]. The flow rate was allowed to dip to 0.2 g/s and was maintained at that rate during deposition. Based upon the syringe filter Run #6 result, the final rinse rate should have been 0.33 to 0.4 g/s; however, the final

rinse rate was in fact 0.43 g/s. The more preferential cleavage in spite of a poorly consolidated top layer suggested that a longer IPA rinse was necessary, and possibly even higher pressures to pack down the material.

5.1.2 Runs 5-7 (25 Tesla)

Runs 5 through 7 produced distinctly anisotropic material. There were some common parameters in all three runs.

- The flow rate was maintained at ~ 0.2 g/s
- The amount of TX100 rinse was 0.7 to 1 kg
- The amount of IPA rinse was > 4 kg
- The ultimate pressures were in excess of atmospheric pressure
- The sheen was lustrous to some degree, ranging from satin to glossy

The sheen of the sample is a simple and quick, albeit crude, way to assess alignment. Smoother and more ordered surfaces tend to have a greater luster. This is true with graphite, which has a dull black luster in its natural form but a silvery luster when created in a highly oriented pyrolyzed form. The same has been observed with SWNT membranes, as was demonstrated with the syringe filter samples. This gives a simple, if crude, qualitative indicator for comparison of relative alignment of samples. Runs 1-4 possessed a dull luster and unremarkable alignment, whereas runs 5-7 were distinctly more shiny and possessed appreciable alignment.

5.1.3 Runs 8-11 (7 Tesla)

The 7-Tesla superconductor magnet provided a greater freedom for experimentation. It was continuously available, easily accessible, and required very little maintenance beyond refilling of cryogenics. This facilitated greater variation of experimental parameters. More importantly, it is a more practical magnetic field to use. A 7 Tesla magnet is available at most research institutions, making this a more viable technique. The 7 Tesla work demonstrated that the 7-Tesla field is capable of creating aligned materials of SWNTs comparable to 25-Tesla materials.

5.2 Parameters of a Successful Deposition

Based upon the results in the 7-Tesla and 25-Tesla magnetic fields, the following can be reasonably concluded about the parameters of a successful filtration deposition of aligned SWNTs. Assuming similar amounts of SWNT colloid are being deposited, one should

- Try to maintain a flow rate of 0.1-0.2 g/s,
- Rinse with at least 0.5 kg of TX100,
- Rinse with at least 4 kg of IPA,
- Ramp pressures as needed to maintain the desired flow rate,
- Ensure adequate drainage from the system, and
- Remove the filter core from the apparatus immediately after the run ends.

The cylindrical filter apparatus is best used with a vertical bore. If further work with horizontal bore magnets is performed, an apparatus designed with good drainage for that orientation is needed.

5.3 Alignment

The data clearly shows that there is alignment in the materials produced. The remarkable similarities seen in the Raman anisotropy of the annealed and unannealed materials illustrates the comparable effectiveness of the 7-Tesla magnetic field with respect to the 25-Tesla results. The vacuum annealing results show that there was essentially no effect on the anisotropy of the Raman intensities.

Raman and XRD clearly indicate aligned structures. Electron diffraction studies of these samples show a structural anisotropy [69]. Reports of anisotropy in thermal and electrical transport confirm changes in properties that theory would predict for an aligned structure [68].

The combination of XRD and Raman suggests a number of things. XRD shows a similar alignment for both fields and a similar unaligned fraction. Raman shows better alignment in the 25 Tesla field and a lower fraction of unaligned tubes. At first glance, this may appear to be incongruous, but it is not necessarily so.

The theory which this work, and the work before, was based upon called for larger diameter tubes to be more readily aligned. Consider a medium-sized SWNT rope of a hundred tubes. Given the equations presented in the Introduction, the energy reduction for alignment of such a rope in a 7 Tesla field is almost an order of magnitude greater than ambient thermal energy, so one might expect that such a rope would readily align in a 7 Tesla field. On the contrary, a 300 nm long tube with a (10,10) diameter, the dominant diameter fraction in the tubes used, would require at least 15 Tesla for a similar effect. This means that one should expect that a sample aligned under 7 Tesla would

have similar alignment to 25 Tesla in large ropes or bundles, but have poorer alignment in individual tubes or thin ropes composed of very few tubes. Comparison of XRD and Raman data is an excellent tool for assessing the alignment of SWNT structures. Table 4.1 is reprinted for easy reference.

	XRD	Raman
7 T Mosaic angle	38 °	36°
7 T Unaligned Fraction	0.58	0.28
25 T Mosaic angle	34°	42°
25 T Unaligned Fraction	0.60	0.20

Table 4.1 (reprint) Combined XRD and Raman Data of 25 T and 7 T Samples

5.3.1 XRD vs. Raman

XRD is a technology that assesses crystal structure. As such, it will be more sensitive to ropes and bundles than tubes. Raman, on the other hand, is distinguished by a sensitivity that can provide spectral data for very small sample sizes, especially in the Raman microscope configuration [65]. This makes the combination complementary and informative.

5.3.2 XRD Results for 25 Tesla and 7 Tesla

The XRD showed almost identical results for 25 Tesla and 7 Tesla in terms of mosaic angle and unaligned fraction. This suggests that both fields are resulting in the same degree of alignment in SWNT structures that the XRD is sensitive to, larger bundles with sufficient crystallinity to register on XRD. Therefore, as predicted, a 7-Tesla magnetic field is adequate to provide a significant alignment effect.

5.3.3 Raman Results from 25 Tesla and 7 Tesla

The Raman results show a better mosaic angle, but greater unaligned fraction at 7 Tesla. Recall from the theory that there is a dramatic difference in the alignment effect on different types of nanotubes. This result can be explained by the greater magnetic field intensity at 25 Tesla causing poor alignment of SWNT structures that would not otherwise align. This causes a smearing of the mosaic angle as the mosaic angle of the more responsive, better-aligned SNWT structures is spoiled by the less responsive, poorly-aligned SWNT structures.

5.3.4 XRD and Raman for 25 Tesla and 7 Tesla

The direct comparison of Raman and XRD can be tricky. Conservatively, it can be said that there is an underlying alignment of SWNT structures of small bundles that is not be detected by XRD. Also, while a similar amount of the larger structures appear to be aligned at both fields, more of the smaller structures are being aligned at 25 Tesla.

Therefore, the data reflects exactly what the theory predicts. At 7 Tesla, tubes, ropes, and bundles alike are aligned and both analytical techniques confirm this. At 25 Tesla, more small ropes are aligned, but bundles and larger ropes are still well aligned; Raman is sensitive to the decrease in aligned tubes and small ropes, but the entities that XRD detects are still experiencing a similar degree of alignment, in accord with the theoretical predictions presented in Chapter 1.

5.4 Future Directions

There are a number of future projects that could be explored using this method as well as using the materials already produced. The term “membranes” was not chosen lightly, and one interesting path of exploration is analyzing the SWNT membranes produced by this process as membrane entities. Studies of liquid and gas flow, adsorption, and a whole host of other membrane properties can be investigated with these materials. The filtration process could also conceivably be exploited to complement SWNT separation technologies in sorting by size and type by exploiting the constraining effect of the magnetic field as well as its preferential effect on metallic tubes. It is indeed an exciting time to be a researcher.

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Appendix A – Design Notes and Drawings of Cylindrical Apparatus

Consider a cross-section of the assembled apparatus, oriented vertically:

Figure A.1 Assembled Apparatus

Figure A.1 shows the o-rings, spacers, and gaskets in place. The dimensions shown do not account for gasket compression or slop. Given that I allowed 0.030 inches for these factors, so the housing length should be 3.566 inches greater than the filter support length. The topmost piece, labeled A, is a Delrin end piece. Below that is a spacer, labeled B, with channels to allow fluid flow through and around it. Beneath the spacer is a Teflon disk to facilitate rotation of the spacer and top piece. The spacer is considered to be rotated in Figure A.1 such that the cross-section is a channel, hence the void around it (see the spacer design below). Beneath the Teflon disk is a disk of fluorosilicone gasket material to prevent slipping and friction at the filter support and to provide some strain relief when the pieces are tightened. Beneath the gasket is the filter element, labeled C, held away from the walls of the main housing by a ridge on the spacer (not seen in this cross-section) and centered by nubs on the bottom end piece, labeled D. A ring gasket of fluorosilicone fits snugly around the nubs on the bottom end pieces, providing a static face seal between the filter element and bottom end piece. The nubs allow for more precise centering and thus a greater tolerance in the system for a small dead space between the filter and the inner wall of the housing. The filter support is rotated in this cross-section to illustrate the holes through which liquid would flow. Note that the mesh support screen and filter paper are not shown in this picture.

The top and bottom end pieces were designed to seal the system, allow fluid entry and outflow, and hold the internal components in place. Sealing of the end pieces was provided by an o-ring made of Viton and rated to 75 °C. The end pieces drilled and tapped down their center to accommodate 1/8-27 NPT fittings for fluid flow. The top piece and end piece are shown in Figures A.2 and A.3, respectively:

Figure A.2 Drawing: Top End Piece

Figure A.3 Drawing: Bottom End piece

The spacer design was engineered to be easy to machine while still achieving two specific goals; it had channels to accommodate fluid flow and a ridge on its bottom to help keep the filter support, and thus filter membrane, away from the filter housing. The channels were machined by three passes with a standard 1/8-inch diameter end mill with 60-degree offsets. The joining of the spacer and filter support, along with the Teflon disk and gasket, is shown in Figure A.4. The spacer design is shown in Figure A.5.

Figure A.4 Cross-section of Spacer, Teflon Disk, Gasket and Filter Support

Figure A.5 Drawing: Top Spacer

Below the spacer was the filter support. This piece was designed for use with two over layers of a 105-micron opening polypropylene mesh, secured around the support, with a filter membrane over the mesh. Heat shrink bands were used to seal the ends of the filter paper, as described in Chapter 2. The design is shown in Figure A.6.

Figure A.6 Drawing: Filter Support Element

The ring gasket sealed the bottom of the filter support. This geometry forced liquid to pass through the filter, enter through the sides of the filter support, and exit out the bottom of it. The dimensions of the Teflon and fluorosilicone disks and the fluorosilicone ring gasket are illustrated in Figure A.7.

Figure A.7 Disk and Ring Gasket Dimensions

With the component designs above, the housing length is constrained. Excluding the filter support element and accounting for reasonable compression of the gasket material, the housing needs to be 3.566 inches longer than the filter support. In this case, it was 11.556 inches long. The dimensions of the main housing transverse cross-section follow in Figure A.8; a cross-section of the element is included to convey the housing's tolerance.

Figure A.8 Transverse Cross-section of Main Housing

Appendix B – Cryogen Maintenance of Smalley Lab 7 Tesla Magnet

The 7 Tesla magnet maintained in the Smalley lab is a custom made superconducting magnet with a 6” diameter horizontal bore. It requires regular cryogen replenishment to prevent quenching of the magnetic field.

B.1 Maintaining Cryogen Supplies

Nitrogen – This magnet requires its own supply of Liquid Nitrogen (LN2) and the large tanks needed require the use of an elevator and at least a two business day lead time for an order. It is critical that the magnet remains supplied with adequate cryogen levels; this requires some planning such as stocking an extra tank, depending on the scheduled outage. Realize that cryogenics will leak from their storage vessel. To avoid unreasonable waste, a tank of LN2 should not be ordered or stored for more than a few weeks in advance. The purpose of the LN2 is to provide a thermal blanket of 77 Kelvin to shield the Helium layer from 300 K room temperature.

Helium – Liquid Helium (LHe) cannot be stored on hand, as it leaks too quickly. At room temperature and pressure, a tank loses about 1 liter per day. Ideally, you should order 60 L of LHe when the Dewar reaches 60%, and refill at 40%. Once the level gets below 10%, the magnet has to be powered down, which means six months and ~\$100,000 to get it going again. Because of this, it is crucial that the operators of the magnet stay keenly aware of the constraints on delivery of liquid helium. Typically, two business days is the minimum, as limited by the refilling process.

B.2 Transferring Nitrogen (refill at 20% on our fluid level gauge)

1. Record the cryogen boil-off flow rates and fluid levels.
2. Assemble the necessary equipment:
 - a. An LN2 source (*****use the shiny, steel colored tanks, they are non-magnetic*****),
 - b. The LN2 transfer hose,
 - c. The LN2 transfer fixture,
 - d. A pair of appropriate gloves, and
 - e. The black vinyl cap for the end of the overflow tube of the transfer fixture.
3. Connect the transfer hose to the LN2 source liquid outlet. Be careful to keep a firm grip on the wrench at all times around the magnet. *Whether or not it is a magnetic wrench, treat it as though it is.*
4. Don the protective gloves.
5. Disconnect the LN2 boil-off tubing from the flow meter. Leave the tubing connected to the LN2 manifold (the fixture with black vanes that the tubing leads from).
6. Remove the LN2 manifold and quickly replace it with the LN2 transfer fixture.
7. Rotate the fixture so the overflow tube is placed conveniently.
8. Slide the L-shaped metal tubing down until it stops, then screw it firmly in. Do not over tighten it or under tighten it. The former could disable the LN2 system, the latter will compromise filling. *Err on the side of under tightening until you are comfortable with the procedure.* The tube needs to be facing such that the transfer hose can be connected to it.
9. Tighten the seal around the metal tube of the fixture.

10. Connect the transfer hose to the L-shaped metal tube.
11. Gently and slowly open the LN2 source until a small plume, about 30 cm long, is seen.
12. Maintain this small plume until the transfer fixture and tubing has developed a coating of frost.
13. Increase the flow rate as desired, and let it run until liquid pours from the overflow.
14. Turn off the LN2.
15. Verify that the LN2 is full. The meter should read ~70%. If it is not full, but you saw liquid pour from the overflow, then the L-shaped metal tube is probably not screwed in far enough. Allow the system to defrost, tighten the tube, and try again.
16. Cap the end of the overflow tube with the black vinyl cap.
17. Wait for the transfer apparatus to defrost for about 30 minutes.
18. Disconnect the transfer hose from the transfer fixture.
19. Loosen the seal on the metal tube.
20. Unscrew the metal tube and lift it up a few inches to ensure it is free of the thread.
21. Make sure the manifold is nearby.
22. Quickly and smoothly remove the transfer fixture and replace it with the LN2 manifold.
23. Reconnect the boil-off tubing.
24. Remove the black vinyl cap from the overflow tube and store the transfer fixture in a position that facilitates drainage of fluids from the various tubings.
25. Wait about five minutes, then record the cryogen boil-off rates and fluid levels.

B.3 Transferring Helium (requires two people)

The transfer of LHe is a little more difficult than the transfer of LN₂. A dry run prior to performing the actual transfer is advisable the first few times you do it. You must have two people to do this well. A third person can be useful for random emergencies, but is not necessary.

Generally, the overall process is to “push” LHe from the source tank into the magnet using compressed high-purity helium. This should occur at a pressure of between 2 to 5 psi. A pressure higher than 5 psi is progressively more dangerous and a pressure lower than 2 psi can result in backflow of air into the magnet Dewar.

The recommended refill point is 40% LHe. At 10% or below, the magnet may need to be de-energized, which will incur the loss of ~\$100,000 and months of time (that’s a bad thing).

1. Record the cryogen boil-off flow rates and fluid levels.
2. Assemble the necessary equipment:
 - a. An LHe source containing at least 50 L of LHe (source),
 - b. The LHe transfer tube (TT),
 - c. A regulated source of compressed Helium, ***placed outside the 5 gauss line (any closer could get someone killed)***, to maintain the LHe flow rate, and appropriate tubing and connections to attach it to the LHe source tank.
 - d. A pair of appropriate gloves,

- e. The black vinyl cap for the opening on the magnet where the transfer tube inserts, and
 - f. The black rubber stopper to temporarily cap the check valve opening.
3. Switch He level monitor to “High” sample rate (1 sample per ~10 seconds).
 4. Disconnect the tubing from the He boil-off flow meter.
 5. Ensure that the brass end piece is affixed to the shorter of the insertion tubes on the TT. This is the end that will go into the magnet.
 6. Position the source tank conveniently for transfer, as close as possible to the TT port on the magnet Dewar.
 7. Purge the Tygon tubing from the high purity He cylinder. Listen for the transition from air to He.
 8. Open the gas vent valve of the source tank slightly to purge the gas vent line. This takes a few seconds.
 9. Connect the tubing to the gas vent line via the gas adapter and then close the gas vent valve. Adjust the pressure of the gas until it is about 3 psi.
 10. Remove the cap from the magnet Dewar TT port and slide the o-ring and black collar onto the Dewar end of the TT. This will allow for an easier insertion of the Dewar end of the TT later. Slide the o-ring and black collar almost all the way up the Dewar end of the TT.
 11. Check that the brass collar and o-ring are on the source tank end of the TT.

WARNING: when holding the Dewar end of the TT, be aware that the fitting on the end will vent LHe back towards the holder, so be sure to hold the tube high enough to avoid

injury. Read over steps 12 through 16 before continuing. You should have two people to do this, Person "A" and Person "B". Person A should be at the source tank ready to insert the TT into the source tank and Person B should be on the magnet cart, ready to insert the TT into the magnet Dewar. Also, be sure to handle the tubing with a proper glove.

12. **Person "A"** inserts the source tank side of the TT.

- a. Release the source tank pressure by opening the top valve (liquid).
- b. Close the safety valve.
- c. Insert the source end (longer rigid tube) of the TT into the source tank's liquid port, lowering the TT slowly but steadily to avoid excess boil off (too fast) or visible icing (too slow).
- d. Tighten down the brass-collar and o-ring to seal the connection.

13. **Person "A"** opens the gas vent valve to provide pressure to push the LHe out of the source tank and then prepares to remove outlet check valve.

WARNING: the check valve clamp has magnetic components, maintain a firm grip on it when it is near the magnet and do not set it down near the magnet.

14. **Person "B"** inserts the magnet Dewar side of the TT.

- a. After about 30-40 seconds, a white plume of vapor should jet from the ports on the brass fitting at the end of the magnet Dewar end of the TT.

- b. After about 20 more seconds, a blue tongue of vapor should be seen; this is LHe.
 - c. (The manual refers to quickly releasing the pressure on the source tank before this, but we do not do that; if we did, we would do so by temporarily closing the gas vent valve and opening the safety valve) Insert the TT into the magnet Dewar port as far as it will go into the magnet Dewar TT port, and then pull it back up about 5 cm. Simultaneously, Person A should the remove outlet check valve as the TT is being inserted into the magnet Dewar.
15. A plume should jet from the opening where the check valve was located.
 16. Maintain a plume length of about 0.5 m by regulating the pressure in the source tank.
 17. Wait until the magnet Dewar is full. Note that this will be beyond the 100% mark on the fluid level monitor. When the plume spontaneously elongates and turns more opaque, the magnet Dewar is full.
 18. Vent the Dewar pressure by closing the gas vent valve and opening the safety valve.
 19. Immediately plug the outlet (where the check valve normally rests) with the black rubber stopper.
 20. Remove the TT from source tank.
 21. Remove the TT from the magnet Dewar and cap the Dewar immediately with the black vinyl cap. The black vinyl cap is used as an intermediate measure to allow time to remove the o-ring and black collar from the TT carefully.
 22. Warm up the o-ring and black collar, slide them off the TT, remove the black vinyl cap, and affix the o-ring and black collar to the magnet Dewar opening.

23. Insert the proper cap into the magnet Dewar TT port (it looks approximately like a black peg) and tighten the black collar such that the o-ring is just barely snug.
24. Remove the black rubber stopper, reattach the check valve to the Dewar (clean off frost as needed), and loosely secure the clamp, just enough to hold the check valve in place.
25. Reconnect the tubing to the boil-off flow meter.
26. Set the LHe fluid level monitor to “Low” (1 sample per ~100 seconds).
27. As they warm up, retighten the check valve clamp and the black collar of the transfer tube port.
28. Wait about five minutes then record the cryogen boil-off rates and fluid levels.
29. Make sure that the gas adapter (connects the He cylinder to the source tank vent valve) is not left on the source tank vent valve, nor the brass collar and o-ring left on the liquid valve.

Appendix C - Abbreviations

Bundle – I will use this to refer primarily to a cluster of parallel SWNT ropes.

DMF – N,N-dimethylformamide, an organic solvent.

k – Boltzmann constant, 1.38×10^{-23} J/K.

LDPE – low-density polyethylene.

IPA – isopropyl alcohol, a.k.a. 2-propanol.

mil – a thousandth of an inch. A measure used in machining.

MWNTs – Multi-walled carbon nanotubes*.

rope – a cluster of parallel SWNTs.

RT – room temperature

SWNTs – Single-walled carbon nanotubes*

T – temperature

tube – SWNT

***** - The term “nanotubes” implies carbon nanotubes unless otherwise stated.