STUDY OF THE MECHANICAL PROPERTIES AND THE ELECTRICAL PROPERTIES OF SINGLE-WALLED CARBON NANOTUBES THROUGH FINITE ELEMENT ANALYSIS AND MOLECULAR DYNAMIC SIMULATIONS

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ABSTRACT OF THE THESIS

Study of the Mechanical Properties and the Electrical Properties of Single-Walled Carbon Nanotubes through Finite Element Analysis and Molecular Dynamic Simulations

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The primary motivation of the current research focuses on the ability to create simplified models that can accurately predict the response of carbon nanotube structures undergoing different types of loading conditions. Moreover, the conductivity characteristics of these structures under different geometrical arrangements are investigated. In this way, the mechanical characteristics regarding single-walled carbon nanotubes (SWCNTs) through finite element modeling are computed. This is followed by the determination of the electrical properties of carbon nanotubes through molecular dynamic simulations.

A simplified finite element model is created for different types of SWCNTs with varying input parameters. An input array for the elastic modulus and load is generated to control the physical effects of these parameters in the nanotube structure. The geometries of the nanotubes are altered through various thicknesses employed for the construction of the C– C bonds. The current work contributes to the generation of different model responses to monitor the stress distribution employing a wide range of parameter values. The ability to introduce variability in the parameters and boundary conditions without altering the capabilities and computational time in the model represents the main contribution of the thesis from the mechanical component. The electrical aspects of the simulations are carried using simple molecular dynamics schemes taking into consideration finite and infinite SWCNTs modeled as isolated tubes, triangular lattice configurations, and both curved and non-purified structures. Through optimized molecular models, the total energies of the carbon nanotubes are obtained along with the virtual and occupied energy eigenvalues. From this analysis, the carbon nanotube band structures can be computed to determine its conductivity capabilities.

Findings explaining the output from the mechanical and electrical simulations are summarized. Furthermore, conceptual contributions for future work are listed to develop models capable of physically interpreting the characteristics of single-walled carbon nanotubes.

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Dedication

Dedicado a mi mayor inspiración, mi madre, Miryam Cienfuegos de Jaramillo. Siempre serás mi ángel.

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Chapter 1

Introduction

The scope of this research work can be divided into two main parts. First, the mechanical characteristics regarding single-walled carbon nanotubes (SWCNTs) are examined through finite element modeling. Second, the electrical properties of carbon nanotubes assuming infinite length and different types of configurations are studied through molecular dynamic simulations.

For the mechanical modeling, a simplified finite element model is created for different types of SWCNTs with varying input parameters. An input array for the elastic modulus and load is generated to control the physical effects of these parameters in the nanotube structure. In addition, the geometries of the nanotubes are altered through various thicknesses employed for the construction and characterization of the C-C bonds.

The parameters considered in the current work are obtained from literature. The works of Chen and Cao [8], Yakobson et al. [9], Kudin et al. [10], Pantano et al. [11], Tserpes and Papanikos [12], and Ogata et al. [13] are employed to create simplified finite element models. The current work contributes to the generation of different model responses to monitor the stress distribution throughout the carbon nanotube structures employing a wide range of parameter values. From a mechanical perspective, the ability to introduce variability in the parameters and boundary conditions without altering the capabilities and computational time in the model represents the main contribution of the thesis.

Additionally, the electrical aspects of the simulations are carried using simple molecular dynamics schemes considering finite and infinite SWCNTs modeled as isolated tubes, triangular lattice configurations, and both curved and non-purified structures. Through optimized molecular models, the total energies of the carbon nanotubes are obtained along with the virtual and occupied energy eigenvalues. From this analysis, the carbon nanotube band structures can be computed to determine conductivity capabilities. Consequently, the findings obtained from these virtual experiments provide a preliminary picture that is not only employed to predict simple carbon nanotube studies, but also more complex configurations with greater computational demands. In addition, identical carbon nanotubes are simulated under different geometrical configurations so as to monitor the effects of conductivity characteristics. This represents the most important contribution in the current study of the electrical characteristics found in SWCNTs.

The current work is presented by elaborating on a background review in Chapter 2 that summarizes the key aspects of the structure of SWCNTs, including their geometry, strain energy, and growth. In addition, Chapter 2 provides a detailed review of atomistic simulation methods and their implementation through different approaches in determining the mechanical properties of SWCNTs from these simulations. Next, both a conceptual and mathematical approach are presented including several different models, which provide distinctive geometric configurations when describing the characteristics of SWCNTs through finite element analysis.

Following the mechanical aspect of this review, an overview regarding the electrical properties of carbon nanotubes is presented in Chapter 3 by providing a mathematical interpretation of molecular dynamic concepts including density functional theory and basis sets. A process is followed to calculate the total energy in these systems. In this way, relevant features are explained in the field of condensed matter physics by giving emphasis to the Brillouin zone, band theory, and energy dispersion.

Concluding the background review, the contribution of the current research is explained. The finite element procedure is outlined in Chapter 4 containing details about the model geometry, assumptions, and boundary conditions. This is followed by presentation of the results obtained from the finite element model. Moreover, Chapter 4 discusses the results gathered from loading the carbon nanotube structures by tension (linear and multilinear), bending, and torsion.

Continuing to Chapter 5, the setups for the molecular simulations are discussed along with the results obtained from these virtual experiments. Firstly, graphical representation of the energy per atom is presented for all the case studies. This is followed by similar representation of the energy bands and the electronic density of states.

Finally, conclusions (in Chapter 6) explaining the output from the mechanical and electrical simulations are summarized, along with conceptual contributions for future work that may enhance the capabilities of the finite element model. For instance, proposed case studies are given associating the molecular simulations output to mathematically-obtained, input mechanical parameters required for the finite element model. In this way, more elaborate models can accurately determine the characterization properties of SWCNTs through the manipulation of parameters such as temperature and Poisson's ratio.

Therefore, the primary motivation to develop the current research deals with the ability to create simplified models that can accurately predict the response of carbon nanotube structures undergoing different types of loading conditions. At the same time, the conductivity characteristics of these structures under different geometrical arrangements are investigated. As a result, the current work explains the physical behavior of specified SW-CNTs while carrying on simplified modeling considering the most critical characteristics that can affect the structure.

Chapter 2

Literature Review of the Mechanical Properties of Carbon Nanotubes

Carbon nanotubes are composed of C-C covalent bonds, which are the strongest bonds found in nature. Hence, carbon nanotubes are identified as the "ultimate fiber" due to their great strength in the direction of the nanotube axis and their ability to enhance the elastic properties of materials [1]. The first indications of synthesizing carbon nanotubes date back to 1952. Russian scientists Radushkevich and Lukyanovich [14, 15] were able to produce nanosized hollow carbon filaments. Nevertheless, it was until 1991 that multi-walled carbon nanotubes (MWCNTs) were discovered by Sumio Iijima at NEC Corporation Lab, which was followed by his study and synthesis of single-walled carbon nanotubes (SWCNTs) in 1993 [16, 17].

Since their discovery, there has been a constant pursuit to understand the properties and identify the optimal applications of these structures. The importance of carbon nanotubes relies on their ability to enhance the mechanical and electrical properties of other materials due to their unique elastic properties and conductivity characteristics. Additionally, carbon nanotubes can improve the capabilities and properties of other materials, like polymer composites [1]. Currently, there is an ongoing process to accurately understand the fundamental characteristics of these structures, in particular, to develop the governing laws necessary to control, predict, and manipulate these properties. This will eventually have an impact on the bulk properties of materials where carbon nanotubes may be incorporated.

2.1 Structure of SWCNTs

Carbon nanotubes are created by rolling a graphene sheet to form either MWCNTs, which are composed of coaxially situated SWCNTs of different radii, or SWCNTs, created by rolling the graphene sheet once [1, 12]. Thus, carbon nanotubes are viewed as hollow cylinders consisting of sp^2 bonds. The curvature presented in these structures causes $\sigma - \pi$ rehybridization where the three σ bonds are considerably out of plane causing the π orbital to be more delocalized outside the tube. As a result, carbon nanotubes are mechanically stronger, electrically and thermally more conductive, and chemically and biologically more active than graphite.

SWCNTs can be viewed as hollow cylinders composed of a carbon hexagon pattern replicated throughout the entire structure. They are characterized by the chiral vector \mathbf{C}_h defined by two integers (n, m) that are related to graphite vectors \mathbf{a}_1 and \mathbf{a}_2 as described by Eqn. 2.1. The atomic structure of carbon nanotubes depends on tube chirality¹ [19]. The chiral vector \mathbf{C}_h is defined as

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m). \tag{2.1}$$

The structure of the carbon nanotube, as displayed in Fig. 2.1, is determined by the equator of the nanotube, that is, vector **OA**, which lies perpendicular to the tube axis. Conversely, the vector **OB** lies in the direction of the nanotube axis. By rolling the equivalent sites O, A, B, B' so that the points O and A as well as B and B' coincide allows the carbon nanotube structure to be created [1].

The carbon nanotube has a diameter specified by:

$$D = |\mathbf{C}_h| / \pi = \mathbf{a}(n^2 + nm + m^2)^{1/2} / \pi, \qquad (2.2)$$

where $\mathbf{a} = |\mathbf{a}_1| = |\mathbf{a}_2|$ and refers to the lattice constant of graphite. SWCNTs are classified in three different types: (1) armchair (n, n), (2) zigzag (n, 0), and (3) chiral (n, m) [19]. Examples of SWCNTs types are presented in Fig. 2.2, which are defined distinctively by the chiral angles. For the armchair and zigzag carbon nanotubes, the chiral angle θ equals 30° and 0° , respectively, where $n \geq m$. For the chiral SWCNT, θ is defined by

$$\theta = \tan^{-1}[3^{1/2}m/(m+2n)]. \tag{2.3}$$

The translation vector \mathbf{T} is defined as the unit vector of a 1D carbon nanotube. \mathbf{T} is

¹By chirality, it is meant that a molecule is not superimposable on its mirror image regardless of how it is contorted [18].



Figure 2.1: Unrolled lattice of a nanotube displaying the vectors **OA** and **OB**, which define the chiral vector \mathbf{C}_h and translational vector \mathbf{T} . \mathbf{R} denotes the symmetry vector and rectangle OAB'B represents the unit cell of the nanotube [1].



Figure 2.2: Classification of carbon nanotubes generated in GaussianTM simulation package. Figures (a)-(c) represent zigzag, armchair and chiral SWCNTs, respectively.

parallel to the nanotube axis and perpendicular to the chiral vector \mathbf{C}_h , as specified in Fig. 2.1. \mathbf{T} can be expressed in terms of basis vectors \mathbf{a}_1 and \mathbf{a}_2 as

$$\mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2 \equiv (t_1, t_2), \tag{2.4}$$

where t_1 and t_2 are integers determined by complying to orthogonality rules between **T** and **C**_h, that is, from **C**_h · **T** = **0**. These integers are defined as

$$t_1 = \frac{2m+n}{d_R}, \ t_2 = -\frac{2n+m}{d_R},$$
 (2.5)

where d_R represents the greatest common divisor of (2m + n) and (2n + m). Additionally, the length of the translational vector **T** is given by

$$T = |\mathbf{T}| = \frac{\sqrt{3L}}{d_R}.$$
(2.6)

When the area of the nanotube unit cell $|\mathbf{C}_h \times \mathbf{T}|$ is divided by the area of the hexagon $(|\mathbf{a}_1 \times \mathbf{a}_2|)$, the number of hexagons per unit cell N is given as a function of n and m by

$$N = \frac{|\mathbf{C}_h \times \mathbf{T}|}{|\mathbf{a}_1 \times \mathbf{a}_2|} = \frac{2(m^2 + n^2 + nm)}{d_R} = \frac{2L^2}{a^2 d_R} = \frac{2LT}{\sqrt{3}a^2},$$
(2.7)

where L is the circumferential length of the carbon nanotube. The parameters L and d_R are governed by [1]:

$$L = 2\pi d_t, \tag{2.8}$$

$$d_R = \left\{ \begin{array}{l} d \text{ if } n - m \text{ is not a multiple of } 3d \\ 3d \text{ if } n - m \text{ is a multiple of } 3d \end{array} \right\},$$
(2.9)

where d_t is the nanotube diameter and d is the greatest common divisor. The symmetry vector \mathbf{R} (see Fig. 2.1) is another relevant component for the coordinate generation of carbon nanotube structures. Vector \mathbf{R} is expressed in terms of its projections on the orthogonal vectors \mathbf{C}_h and \mathbf{T} of the nanotube unit cell. It can also be defined in terms of basis vectors \mathbf{a}_1 and \mathbf{a}_2 by

$$\mathbf{R} = p\mathbf{a}_1 + q\mathbf{a}_2 \equiv (p, q), \tag{2.10}$$

where p and q are the selected coefficients of the symmetry vector such that $(t_1q-t_2p=1)$.

Other important parameters for the generation of carbon nanotubes are the lattice constant and intertube spacing, which depend on the tube diameter or radial direction. Experimental and theoretical measurements agree that for a C-C bond length, $d_{C-C} =$ $0.142 \text{ nm or } \mathbf{a} = |\mathbf{a}_1| = |\mathbf{a}_2| = 0.246 \text{ nm}$, and intertube spacing $d_f = 0.34 \text{ nm}$ [19].

2.2 Strain energy of SWCNTs

The strain energy E_{σ} of a SWCNT is related to the curvature of the nanotube. That is, the strain energy increases with decreasing d_t :

$$E_{\sigma} = \frac{\pi E T d_f^3}{6d_t},\tag{2.11}$$

where E is the elastic modulus of the sheet, T is the length of the carbon nanotube in the direction of the nanotube axis, and the interplanar distance between two graphene layers $d_f = 0.34$ nm.

The unit cell of the 1D carbon nanotube can also be related to the strain energy per carbon atom. There are 2N carbon atoms in each unit cell of the carbon nanotube. Hence, the strain energy per carbon atom is inversely proportional to d_t^2 through the relation

$$\frac{E_{\sigma}}{N} = \frac{\sqrt{3}d_f^3 a^2}{24d_t^2}.$$
(2.12)

Currently, an overview of the key parameters characterizing the SWCNT structure has been explored. A summary describing the key methods for growth, synthesis, and purification of carbon nanotubes is described in the following section.

2.3 Growth and synthesis of SWCNTs

SWCNTs are characterized by being sensitive to variations in the process parameters, including light intensity, process temperature, geometry, carrier gas type, pressure and flow conditions. Growth time for SWCNTs produced in laser and arc processes is about 10 ms under optimal conditions. Both arc ablation and laser processes produce carbon in the form of spallated graphitic particles and single-walled nanohorn aggregates. These factors directly affect the yield and properties of SWCNTs. The growth of carbon nanotubes can be accomplished through three methods: carbon vapor generated by arc discharge of graphite, carbon vapor generated by laser ablation of graphite, and the vapor growth method. The arc discharge method remains the easiest and most inexpensive method to obtain significant quantities of SWCNTs; however, the nanotubes are less pure than those produced by the laser ablation method.

2.3.1 Arc discharge method for producing SWCNTs

SWCNTs are produced via the arc process using covaporization of graphite and metal in a composite anode, commonly made by drilling an axial hole in the graphite rod and densely packing it with a mixture of metal and graphite powders. Ni/Y and Co/Ni are the most common catalysts utilized in SWCNT production. Thermogravimetric analysis (TGA) and near-infrared (NIR) spectroscopy are utilized to accurately determine the metal and SWCNT content in the arc material. These methods appear to be the most useful for analyzing arc-product composition and structure.

SWCNTs are generally organized in bundles consisting of a few dozen tubes, tightly compounded in a honeycomb lattice with an average separation between tube axes of approximately 1.7 nm. Bundles are covered with an amorphous carbon layer of approximately 2–5 nm thick, which contains embedded fullerenes. The majority of tubes have diameters in the range of 1.2–1.5 nm and lengths reaching up to 5 μ m in the Ni/Y system and 20 μ m in the Co/Ni system. SWCNT diameters depend on the temperature of the catalytic site at which growth occurs. This temperature is regulated by many factors, including heating of the reaction zone with an externally controlled heat source. The mean diameter of the SWCNTs increases with the environment temperature [20].

2.3.2 Laser ablation method of carbon-metal target for producing SWC-NTs

Implementing laser techniques for the production of SWCNTs can yield up to 70–90% by conversion of graphite [1]. There are two methods to scale up the SWCNT production using laser ablation: (1) the continuous wave laser-powder method of SWCNT synthesis, and (2) the ultrafast pulses from a free electron laser (FEL) method. The SWCNT abundance in a soot product is 20–40% while the tube diameter range from 1.2–1.3 nm.

For the second method, light pulses at a repetition rate of 75 MHz are generated to vaporize the graphite-metal target. The SWCNT soot is collected on a cold surface at a rate of 1500 mg/h. As a result, SWCNT bundles are produced from 8–200 nm thick with diameter and length ranging from 0.4 - 1 nm and $5-20 \mu \text{m}$, respectively.

Transmission electron microscope (TEM) is employed to verify the presence of ropes of SWCNTs consisting of bundles aligned along an axis. The SWCNTs are held in bundles by the van der Waals forces forming a 2D triangular lattice with a lattice constant of 1.7 nm, and an inter-tube separation of 0.315 nm [1].

2.3.3 Vapor growth method

The vapor growth method is beneficial since it is a continuous production of carbon nanotubes, which at optimal conditions can produce large quantities of these structures under relatively controlled conditions. The equipment necessary for the synthesis of carbon nanotubes is analogous to that used for vapor-grown carbon fibers. Carbon nanotubes generated by the vapor-growth method show poor crystallinity, which is improved after a heat treatment at $2500-3000^{\circ}C$ in argon gas.

Other methods have been developed for the synthesis of carbon nanotubes, including the use of carbon ion bombardment to create carbon whiskers, and the use of solar energy to achieve temperatures of 3000 K. Nevertheless, development of optimal and control synthesis process is required for the higher production of purified SWCNTs.

2.4 Purification of SWCNTs

Carbon nanotubes, produced by any method, contain impurities. These impurities are mostly catalyst metal particles and different forms of amorphous carbon. There have been developed several postprocessing purification methods with the goal of removing the metal catalysts and other impurities.

The major impurity in carbon nanotubes are iron particles, which can be up to 30% by weight. The most effective procedure has been reported by Cinke et al. [21] by applying the high pressure CO disproportionation (HiPco) process [1]. The (HiPco) process is based on the decomposition of $Fe(CO)_5$ to form iron clusters for the catalytic production of SWCNTs from CO at about 1000 °C. The procedure consists of an acid treatment by removing the metal filtration, washing with water, and drying in vacuum. It has been found that high vacuum heat treatment of HiPco tubes reduces Fe content to 2% while the diameter of SWCNTs increases substantially. Cinke et al. [21] utilize a two-step purification process for the HiPco SWCNTs, which reduces the iron content to less than 1%. Through this approach, a high resolution transmission electron microscopy (HRTEM) is implemented in the purification process to monitor the quality of SWCNTs.

Another technique to enhance the purification process in SWCNTs has been performed by Laborde-Lahoz et al [22]. The authors execute a two-step reflux process, which eliminates the catalytic particles in the SWCNTs, optimally disperse the carbon nanotubes, and oxide them through the addition of carboxylic functional groups, which help the SWCNTs adhere to the polymer matrix using covalent bonding.

Providing an overall explanation about the structure and formation of carbon nanotubes enable the study of simulation methods that are able to resemble and quantify the properties by these structures. As a result, the two following sections provide a detailed overview of the different atomistic simulations and finite element methods employed for the study of the SWCNT properties.

2.5 Atomistic simulation methods applied in SWCNTs

In exploring the mechanical and electrical properties of SWCNTs, there exist a variety of molecular approaches that may be used for the atomistic investigation relating to these structures. Two broad areas in computational chemistry are devoted to the molecular structure and reactions, that is, molecular mechanics and electronic structure theory. Both methods can be employed in energy computation and its properties, geometry optimizations due to energy minimization, and computation of vibrational frequencies of molecules.

Molecular mechanics apply the laws of classical physics to predict the structures and properties of molecules employing specific force fields. Force field refers to the functional form and parameter sets used to describe the potential energy of a system of particles, typically but not necessarily atoms. Force field functions and parameter sets are derived from both experimental work and high-level quantum mechanical calculations [18]. Three components are required in the force field: (1) equation set describing potential energy variation of atoms, (2) definition of element characteristics within a specific chemical context, and (3) one or more parameter sets fitting the equations and atom types to experimental data. These sets define the force constants, which are values relating the atomic characteristics to energy components and structural data.

The computations in molecular mechanics are based on the interactions among the nuclei, and include the electronic effects implicitly in the force fields through parametrization [23]. This technique is highly developed in the exploration of the mechanical properties of carbon nanotubes since it is computational inexpensive as well as applicable to large systems. The applicability of molecular mechanics in the study of SWCNTs can be found in references [24–31].

Nevertheless, there exist some limitations when performing simulations in molecular mechanics. First, the force field achieves accurate results for the limited class of molecules for which it is parametrized. Also, the exclusion of electrons indicates that these methods are unable to handle the electronic aspects regarding any structure. For these reasons, molecular mechanics is not considered in the development of the present research [23].

On the other hand, the electronic structure methods such as molecular dynamics, apply the laws of quantum mechanics as the basis of the computations. Quantum mechanics states that the energy and its properties in a molecule are obtained by solving the Schrödinger equation:

$$\mathbf{H}\Psi = E\Psi; \tag{2.13}$$

however, exact solutions of Eqn. 2.13 are not computational practical. Hence, the electronic structure methods represent approximations to the Schrödinger solution.

There are three main classes of electronic structure methods:

- (1) Semi-empirical methods consider the parameters to be derived from experimental data and an approximate solution of Eqn. 2.13 is solved considering the appropriate parameters for the chemical system. Different semi-empirical methods are characterized by the different parameter sets.
- (2) Ab initio (also known as first principles) methods consider no experimental parameters in the computations. These methods are based on the laws of quantum mechanics and on the value of physical constants, such as the speed of light, masses and charges

of electrons and nuclei, Planck's constant. Solutions of the Schrödinger equation are developed through extensive mathematical approximations.

(3) Density functional methods² may be regard as another method to approximate solutions for the Schrödinger equation. These are similar to the ab initio methods, including the high computation demands. These methods include the effects of instantaneous electron correlation, which causes it to be a very accurate electronic structure method [23].

2.5.1 Study of the mechanical properties in SWCNTs

Atomistic simulations are performed to identify the stress-strain behavior, and in turn, the elastic modulus of the carbon nanotube structure. Liu et al. [32] considers the secondgeneration reactive empirical bond order³ (REBO) potential to determine correlations between the diameter, helicity, and the tensile deformation of SWCNTs. The procedure requires end atoms to be displayed along the axial direction by small time steps. Relaxation of the entire tube through a velocity damping method allows the atoms to achieve a mechanical equilibrium state with fixed boundary conditions at the other end. The stress on each atom in the SWCNT is determined from Eqn. 2.14:

$$\sigma_{ij}^m = \frac{1}{\Omega_0} \frac{\partial U_m}{\partial \varepsilon_{ij}^m},\tag{2.14}$$

where σ_{ij}^m is the first Piola-Kirchhoff stress, U_m refers to the potential energy, ε_{ij}^m equals the Lagrange strain of atom m, and Ω_0 is the atomic volume at the reference state. As a result, the stress and elastic modulus depend on the value of Ω_0 . This value is given by Eqn. 2.15:

$$\Omega_0 = \frac{3\sqrt{3}a_0^2 b_0}{4},\tag{2.15}$$

²There exits a debate on whether or not density functional methods represent another kind of atomistic simulation rather than part of the ab initio methods. In this work, the method will be explained separately from ab initio methods following the GaussianTM manual explanation Any debate on this issue is out of the scope of this work [23].

³The improved REBO is a second-generation form of hydrocarbon potential energy expression, which includes both modified analytic functions for the intramolecular interactions and fitting database. As a result, an enhanced description of bond energies, lengths, especially C-C bonds, as well as forces associated with rotation about dihedral angles for C-C bonds and angular interactions are developed [33].

where a_0 refers to the C-C bond at the reference state and $b_0 = 0.34$ Å indicates the wall-wall separation. The Lagrange strain is determined by Eqn. 2.16:

$$\varepsilon_{ij}^m = \frac{\left(F_{ik}^m F_{kj}^m - \delta_{ij}\right)}{2},\tag{2.16}$$

where F_{ij}^m is the deformation gradient of atom m and δ_{ij} is the Kronecker symbol. The deformation gradient is calculated from Eqn. 2.17:

$$F_{ij}^m = \sum_{n=1}^N \left(\frac{r_i^{mn}}{R_j^{mn}}\right),\tag{2.17}$$

where r_i^{mn} and R_j^{mn} are the distance between atoms m and n in the deformed and reference state, respectively. N refers to the total number of atoms within the cut-off distance of atom m.

Through this atomistic approach, a uniform deformation results in a uniform stress and uniform strain distribution for armchair, zigzag, and chiral SWCNTs. The simulations are performed keeping a 3 : 1 length to diameter ratio. Liu et al. [32] research draw some important conclusions regarding the helicity and diameter effects on SWCNTs. First, the helicity factor is significant since it is noticed that the elastic moduli, tensile strength, and stress-strain curves are higher for armchair SWCNTs than zigzag nanotubes. Second, the nanotube diameter does not play any significant role in the mechanical parameters. The simulations calculate an elastic modulus range of 0.68–1.30 TPa, and tensile strength range of 0.066–0.131 TPa.

In the same way, Agrawal et al. [34] incorporate second-generation REBO with van der Waals (vdW) interactions between two carbon atoms, as quantified in the Lennard-Jones (LJ) interaction potential. The Hamilton equations are solved through an integration method for SWCNTs (14, 14), which comprises 1372 atoms. The structures are simulated using five different methods to determine the elastic modulus, Y: (1) determination of strain for a fixed stress, (2) determination of stress for a fixed strain, (3) determination of strain energy for a fixed strain, (4) longitudinal vibration method, and (5) transverse vibration method.

Methods (1)–(3) are computed under fixed-free boundary conditions, assuming thickness t = 3.4 Å, and applied external force. Eqns. 2.18-2.19 indicate the formulations used in

these methods,

$$\sigma = \frac{F}{\pi D t},\tag{2.18}$$

$$Y = \frac{1}{v} \left(\frac{d^2 V_c}{d\varepsilon^2} \right) \text{ and } v = \pi D t L, \qquad (2.19)$$

where Eqn. 2.18 corresponds to methods (1) and (2). F is the external force, D is the diameter, and t = 3.4 Å. In the same manner, Eqn. 2.19 corresponds to method (3). V_c refers to the configuration energy of the system, which is a function of strain ε , v is the volume, and L denotes the length of the nanotube.

Methods (4)–(5) consider the measurement of natural frequencies based on a uniform rod. Formulations specified in Eqns. 2.20-2.21 are employed in these methods, respectively

$$f_n = \frac{(2n-1)}{4L} \sqrt{Y/\rho} \text{ and } \rho = \left(\frac{M}{\pi D t L}\right),$$
 (2.20)

$$f_n = \left(\frac{\beta_n^2}{2\pi L^2}\right) \sqrt{YI/\rho A} \text{ and } I = \pi \left(a^4 - b^4\right)/4, \qquad (2.21)$$

where *n* corresponds to the mode of vibration, f_n is the natural frequency, *M* is the mass, ρ equals the mass density of the nanotube, and *I* is the second moment inertia of the crosssectional area *A*. Finally, the outer and inner radii correspond to *a* and *b*, respectively [34].

From these simulations, the elastic modulus ranges from Y = 0.55-0.76 TPa [34]. As in the work of Liu et al. [32], Y for the zigzag tube is higher than that for an armchair SWCNT. In addition, these methods are very dependent on the nanotube diameter.

A short-range second generation REBO potential and a long-range LJ 12-6 potential are assumed by Liew et al. as specified in Eqn. 2.22

$$E_{REBO} = V_R(r_{ij}) - \bar{b}_{ij}V_A(r_{ij}), \qquad (2.22)$$

where $V_R(r)$ and $V_A(r)$ are the repulsive and attractive potential pair terms, and \bar{b}_{ij} is the reactive empirical bond order between atoms. As a result, the total energy E_{TOT} becomes

$$E_{TOT} = \sum_{i} \sum_{i>j} \left[E_{REBO} + E_{vdW} \right], \qquad (2.23)$$

where E_{vdW} is defined as

$$E_{vdW} = \left\{ \begin{array}{ccc} 0 & :r_{ij} < r'_s, \\ c_{3,k}(r_{ij} - r_k)^3 + c_{3,k}(r_{ij} - r_k)^2 & :r'_s \le r_{ij} \le r'_m, \\ 4\xi \left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^6 \right] & :r'_m \le r_{ij} \le r'_b, \end{array} \right\},$$
(2.24)

where E_{vdW} represents the van der Waal interaction potentials mathematically corresponding to cubic splines.

Simulations are conducted for (5,5), (7,7), (10,10), and (12,12) SWCNT bundles to solve for the Hamiltonian equations assuming t = 0.34 nm. The nanotubes are subjected to axial tension and compression at a constant rate 20 m/s at both ends (free-free boundary conditions). Total failure loads and critical strains are determined for both types of simulations. From these simulations, Liew et al. [35] determined that the SWCNT bundles are directly proportional to the average critical failure load per nanotube and the critical strains are independent of the bundle size. On the other hand, the critical buckling load increases exponentially with the increment of the individual SWCNT diameter size.

Considering a more classical approach, Cornwell et al. [36] perform MD simulations using the Tersoff-Brenner potential, which accurately describes the bonding energies and elastic properties of hydrocarbons. SWCNTs radius range from 5.56 Å–16.63 Å. The process utilizes the Verlet algorithm and subjects the structures to a quasi–static compression under free-free boundary conditions. A critical strain is calculated once the structure buckles, and Hooke's law is used to provide a good approximation for the tube's response in axial compression. As a result, a least squares curve-fitting calculates the elastic modulus as a function of the nanotube radius.

Ab initio methods present another reliable approach to explore the mechanical properties of SWCNTs. The main challenge regarding these computations relies on the large computational demand in solving the Schrödinger equation. Zhou et al. [37] employ a molecular orbital cluster model, that is, the linear combination of atomic orbitals (LCAO-MO) method. The authors focus on the study of geometrical structure and mechanical properties, i.e, elastic modulus, theoretical tensile strength and Poisson's ratio of the carbon nanotube. The simulation is conducted using an armchair SWCNT comprising 156 Catoms attached to an H terminal to prevent the boundary effects. The variational basis sets employed are 2s2p and 1s for C and H, respectively. Additionally, the von Barth-Hedin exchange-correlation potential is adapted for the calculations.

An optimized geometrical structure through energy minimization is obtained. The C-Cbond lengths become 1.466 Å. The elastic modulus and tensile strength are calculated as Y = 0.764 TPa and $\sigma_{tensile} = 6.249$ GPa, while the Poisson's ratio is $\nu = 0.32$.

Many techniques have been developed with the purpose of integrating molecular mechanics, molecular dynamics and continuum modeling. In the case of Chen and Cao [8], a multiscale model relates these methods. The authors generate nine molecular dynamic simulations for SWCNTs using COMPASS force field. These include four zigzag, (10,0), (12,0), (14,0), (16,0), four armchair, (5,5), (6,6), (7,7), (8,8), and one chiral SWCNT, (8,4). All nanotube lengths are set approximately equal to $L \approx 12.6$ nm. The structures are first optimized through molecular mechanics so that the total potential energy is minimized and the interatomic forces are zero at 0 K [8]. The nanotubes experience uniaxial tension, bending and torsion under fixed-free boundary conditions and controlled displacement, so as to optimize the structure for each displacement increment and minimize the potential energy of the system. The strain energy-deformation relationship obtained in the simulations is then compared with continuum models to fit the key parameters.

The space-frame model is constructed using two different types of circular beams. The primary beams (r_1, E_1) refer to the C-C bond model which considers the bond stretching energy, while the secondary bonding (r_2, E_2) link the nearest carbon atoms to represent the potential energy associated with angle variation. Different beam parameters are employed so as to adequately match the strain energy-deformation relationship with the molecular dynamics simulations. The primary and secondary beams are isotropic and Poisson's ratio is set to zero. All the calculations were carried out using ABAQUS [38] software. The space-frame models are subjected to uniaxial tension, bending and torsion under fixed-free boundary conditions. Poisson's ratio of the space-frame SWCNT model is found to be approximately $\nu \approx 0.19$, as in graphite. The optimal beam parameters are determined to be r_1 , = 0.05 nm, E_1 = 31.7 TPa and r_2 = 0.04 nm, E_2 = 86.5 TPa.

Additionally, a shell model is constructed and subjected to the same loads and boundary conditions. This model approaches the behavior of beams by neglecting stress concentrations near the ends. Poisson's ratio, $\nu \approx 0.19$, and averaged elastic modulus-thickness factor, Et = 548 Pam, are determined to agree with the other two concept models. Finally, SWCNT (5,5) is subjected to vibrational study by applying axial and transverse vibration frequencies under fixed-free boundary conditions for the three conceptual models.
The molecular dynamic simulation is carried out under a temperature of 800 K. All three models agree consistently with each other, which indicates a successful study of the dynamic behavior of SWCNTs.

Ogata et al. [13] employ density functional theory based on local density approximation as well as tight-binding calculations for three zigzag (8,0), (9,0), (10,0); and one armchair SWCNTs, (8,8). The simulations investigate the structures under uniaxial tension and compression. The relaxed ideal tensile strengths, defined as the maximum axial tensile strength σ_{zz}^{Y} , are evaluated. The axial stress σ_{zz} is indirectly calculated from the axial force and the interlayer distance of graphite, t = 3.35 Å. The density functional calculations are performed using the Vienna ab initio simulation package along with the Cepley-Alder local density approximation functional. The structures are relaxed before applying the axial strains.

The elastic moduli are found to have an averaged value of Y = 972 GPa and Y = 1000 GPa for nanotube simulations performed using tight-binding and local density functional, respectively. It is found that at 20% tensile strain, the SWCNTs in both simulations become unstable. From the stress-strain curves, ideal tensile strength values, σ_{zz}^{YC} and σ_{zz}^{YT} , are determined for compression and tension corresponding to the critical strain calculations ε_{zz}^{crit} . However, the elastic modulus predictions from these results are only reliable for the tensile cases.

At the same time, the electronic properties such as band gaps correlate with the fixed strains undergone by these nanotubes. Very ductile behavior is observed in SWCNT (8,8), and zigzag nanotubes change their properties from metallic to semiconductor or vice versa within the range of stable deformation [13].

Carbon nanotubes are also studied beyond the elastic range, focusing on the consequences of permanent deformation. Work by Srivatasa et al. [39] explore the concept of nanoplasticity of SWCNTs. This is studied under axial compression through the molecular simulation of finite (8,0) SWCNTs. The structures are compressed via the quantum generalized tight-binding molecular dynamics scheme. In this simulation, the edge atoms of the nanotube are moved axially inward at a fixed rate to compress the structure. Once elastic limit is reached, at 12% in compression, the relaxation causes plastic collapse. Plasticity of the structure through this strain relaxation triggers the localized deformations that result in the inward collapse. Additionally, it is observed through these deformations that the axial strain is primarily affecting the bonds parallel to the tube axis, followed by the change in the bond angle and increment of the tube radius. The strained bonds reduce in length from 1.42 Å to 1.33 Å. And so, the inward collapse transforms the structure from sp^2 to sp^3 type reconstruction at the location of the collapse. The calculated Young's modulus from this method is 1.8 TPa, considering t = 3.4 Å for the nanotube.

Griebel and Hamaeckers [40] simulate carbon nanotube reinforcing polyethylene composite. The simulation is conducted under normal conditions with no external stress applied. The systems studied by the authors include

- a polyethylene matrix consisting of 1330 CH₂ units.
- a (10, 10) capped SWCNT embedded in 1420 CH₂ units.
- a periodic (10, 10) SWCNT embedded in 1095 CH₂ units.

Griebel and Hamaeckers concluded from the molecular simulations that the SWCNTs do not provide reinforcement via transverse stiffness to the matrix. The rationale is that the Young's modulus of the composite is only in the range of the modulus of the polyethylene matrix [40].

Altogether, these methods provide an extensive and thorough explanation for the mechanical properties observed in the atomistic scale. The output of these simulations enable the further study of the carbon nanotube structure via finite element analysis, which represents the main focus of the current work.

2.6 Structural mechanics analysis approach for modeling SWCNTs

The urge to develop simplified structural methods to simulate the mechanical properties of carbon nanotubes has created the need for hybrid modeling simulations combining molecular methods such as molecular mechanics for the advance of nanoscale continuum models in solid mechanics. The continuum structures are modeled in terms of bond energies and different assumed force fields.

2.6.1 The finite element method

The finite element method provides an approximate solution to the equations of the theory of elasticity. The main concept of this method is to divide the body into small parts named elements. The displacement field is then approximated in each element through interpolation between the values of the displacement at specific points on the element called nodes. The displacement field, which is assumed to be continuous, is then substituted into the potential energy expression. This condition generates a set of linear algebraic equations for the nodal displacements through the condition of minimum potential energy. The elements are numbered e = 1, 2, 3, ..., N.

Consider one element and one displacement component u_i within an element. The component u_i is dependent on the nodal displacements D_K for that element. However, the dependency relies only on the displacements at nodes falling within the element or on its boundary. The displacement component is described through the linear relation

$$\mathbf{u}_i(\mathbf{x}) = \sum_{K \in I_m} \mathbf{N}_{iK}(\mathbf{x}) \mathbf{D}_K, \qquad (2.25)$$

where I_m refers to the set of nodal displacements for the m^{th} element, i = 1, 2, 3 for 3D problems, and N_{iK} are the shape functions for the element.

The shape functions must provide continuity to the generated displacement field, and be approximated to the true solution so that the error tends to zero as the element size tends to zero. Therefore, these functions must comply with the following:

- (1) element boundary continuity for arbitrary nodal displacements
- (2) exact representation of constant strain in the element.

Through the shape functions, the strains are determined by

$$\varepsilon_{ij} = \sum_{\mathbf{K} \in \mathbf{I}_m} \mathbf{A}_{ijK} \mathbf{D}_K, \tag{2.26}$$

where A_{ijK} refers to

$$A_{ijK} = \frac{1}{2} \left(\frac{\partial N_{iK}}{\partial x_j} + \frac{\partial N_{jK}}{\partial x_i} \right).$$
(2.27)

The calculated stress is given by

$$\tau_{ij} = l_{ij} + \sum_{\mathbf{K} \in \mathbf{I}_m} \mathbf{B}_{ijK} \mathbf{D}_K, \qquad (2.28)$$

where the coefficient B_{ijK} is described as

$$\mathbf{B}_{ijK} = \mathbf{c}_{ijkm} \mathbf{A}_{kmK},\tag{2.29}$$

where c_{ijkm} and l_{ij} are characteristic of the structure.

For each element a function $\mathcal{A}(\boldsymbol{\varepsilon})$ is defined as

$$\mathcal{A}(\boldsymbol{\varepsilon}) = \frac{1}{2} c_{ijkm} \varepsilon_{ij} \varepsilon_{km} + l_{ij} \varepsilon_{ij}$$
(2.30)

$$= \sum_{\mathbf{K}\in\mathbf{I}_m} \sum_{\mathbf{M}\in\mathbf{I}_m} \frac{1}{2} \mathbf{A}_{ij\mathbf{K}} \mathbf{B}_{ij\mathbf{M}} \mathbf{D}_{\mathbf{K}} \mathbf{D}_{\mathbf{M}} + \sum_{\mathbf{K}\in\mathbf{I}_m} l_{ij} \mathbf{A}_{ij\mathbf{K}} \mathbf{D}_{\mathbf{K}}, \qquad (2.31)$$

in which indices K and M range over the index set for the particular element.

Considering the potential energy, the elements divide the region \mathcal{V} into sub-regions \mathcal{V}_m . Let \mathcal{S}_m indicate the part of the boundary of the sub-region \mathcal{V}_m position on the loaded exterior surface. Then, the potential energy becomes

$$\mathcal{P} = \sum_{m=1}^{M} \mathcal{P}_m = \sum_{m=1}^{M} \left(\int_{\mathcal{V}_m} \left[\mathcal{A}(\boldsymbol{\varepsilon}) - b_i \mathbf{u}_i \right] d\mathbf{V} - \int_{\mathcal{S}_m} \mathbf{T}_i^{\mathbf{o}} \mathbf{u}_i d\mathbf{A} \right),$$
(2.32)

where b_i represents the body forces per unit mass and T_i^o is the stress tensor.

Replacing Eqns. 2.25 and 2.31 in Eqn. 2.32, the potential energy for the element becomes

$$\mathcal{P} = \sum_{\mathbf{I}, \mathbf{J} \in \mathbf{I}_m} \frac{1}{2} \mathbf{k}_{IJ}^m \mathbf{D}_I \mathbf{D}_J - \sum_{\mathbf{I} \in \mathbf{I}_m} \mathbf{f}_I^m \mathbf{D}_I, \qquad (2.33)$$

where \mathbf{k}_{IJ}^m and \mathbf{f}_I^m are defined as

$$\mathbf{k}_{IJ}^{m} = \int_{\mathcal{V}_{m}} \mathbf{B}_{kiI} \mathbf{A}_{kiJ} d\mathbf{V}$$
(2.34)

$$\mathbf{f}_{I}^{m} = -\int_{\mathcal{V}_{m}} l_{ki} \mathbf{A}_{kiI} d\mathbf{V} + \int_{\mathcal{V}_{m}} \mathbf{b}_{k} \mathbf{N}_{kl} d\mathbf{V} + \int_{\mathcal{S}_{m}} \mathbf{T}_{k}^{\mathbf{o}} \mathbf{N}_{kI} d\mathbf{A}.$$
 (2.35)

As a result, the potential energy of the body becomes a summation as shown in Eqn. 2.33. I and J depends on the element m. To perform the sum on m, Eqn. 2.33 can be extended to all displacement parameters by defining k_{IJ}^m to be zero for all I and J not included in the set I_m . Combining Eqn. 2.32 and Eqn. 2.33, the total potential equation simplifies to

$$\mathcal{P} = \sum_{I=1}^{N} \sum_{J=1}^{N} \frac{1}{2} K_{IJ} D_I D_J - \sum_{J=1}^{N} F_J D_J, \qquad (2.36)$$

where K_{IJ} and F_J represent the stiffness and force matrix for N degrees of freedom, respectively. These are defined as

$$K_{IJ} = \sum_{m=1}^{M} \mathbf{k}_{IJ}^{m} \tag{2.37}$$

$$F_{I} = \sum_{m=1}^{M} f_{I}^{m}.$$
 (2.38)

The system equations are solved by minimizing the potential energy, that is, $\frac{\partial \mathcal{P}}{\partial D_I} = 0$. By applying this condition, a set of N equations is generated with N unknowns:

$$\sum_{J=1}^{N} K_{IJ} \mathcal{D}_J = F_I. \tag{2.39}$$

Eqn. 2.39 is solved numerically for D_J . Therefore, displacement, strain, and stress fields for an element are calculated using Eqns. 2.25-2.28 [41].

Through the solution of this system of equations, carbon nanotube structures are modeled in a continuum environment, which focuses on developing a nanoscale continuum model to simulate the mechanical behavior of these structures.

2.6.2 Molecular-continuum model

Kalamkarov et al. [42] presents two different continuum models to investigate the mechanical properties of carbon nanotubes, including single-walled, double-walled and multiwalled nanotubes. Focused will be given only to the SWCNTs. The first model analytically develops the constitutive relations for predicting the effective mechanical properties of SW-CNTs. The second model is a finite element approach to determine the effective properties of these carbon nanotubes.

For the analytical model, SWCNTs are formed as a cylindrical network shell with a hexagonal periodicity cell. This method is employed for the analysis of composite and smart composite shells and plates. The shell is assumed to be a heterogeneous thin 3D layer with no elastic properties in areas of perforation.

In the finite element approach, the C atoms are represented as material points connected by load carrying beam elements. Correlations are established between molecular mechanics and finite element analysis. Hence, atoms are treated as forces acting between two junctions separated by structural beam or spring elements. To determine the force constants of these covalent bonds, the potential energies of the individual bonds are equated with the adequate beam model. The beam elements are assumed to be isotropic with length L, cross-section area A, and moment of inertia I.

The strain energies of the elements under pure axial load P, bending moment M, and twisting moment T are denoted respectively by

$$U_P = \int_0^L \frac{P^2}{2EA} dL = \frac{EA}{2L} \left(\Delta L\right)^2$$
 (2.40)

$$U_M = \int_0^L \frac{M^2}{2EI} dL = \frac{EA}{2L} (2\alpha)^2$$
 (2.41)

$$U_T = \int_0^L \frac{T^2}{2GJ} dL = \frac{GJ}{2L} (\Delta\beta)^2.$$
 (2.42)

According to this approach, a direct relationship exists between the parameters from structural mechanics and those of molecular mechanics, k_r , k_{θ} , k_{ϕ} , as described in Eqn. 2.43:

$$k_r = \frac{EA}{L}, \quad k_\theta = \frac{EI}{L}, \quad k_\phi = \frac{GJ}{L}.$$
 (2.43)

The beam elements are assumed isotropic. The covalent bonds are modeled using a 3D beam element. The beam contains six degrees of freedom at every node, three translations (x, y, z) and three rotations about (x, y, z). The nonlinear spring elements refer to the noncovalent interactions between carbon atoms able to undergo tension and compression. This element type has three degrees of freedom, that is, translations at (x, y, z) at each node.

The results from this method generate a relationship for the effective elastic and shear moduli with respect to the material and geometric parameters, as described in Eqns. 2.44-2.45:

$$E_{SWCNT} = \frac{\pi}{6\sqrt{3}} \left(\frac{\delta E}{l}\right) \tag{2.44}$$

$$G_{12} = \frac{\pi}{32\sqrt{3}} \left(\frac{\delta E}{l}\right), \qquad (2.45)$$

where $E = 5.488 \times 10^{-6} \text{ N/ nm}^2$, $\delta = 0.147 \text{ nm}$, L = 0.142 nm. By employing Kalamarov et al. [42] parameters, the results become $E_{SWCNT} = 1.71$ TPa and $G_{SWCNT} = 0.32$ TPa.

The finite element method assumes a wall thickness t = 0.68 nm. The results obtained from this method produce an elastic modulus ranging from 0.96–1.04 TPa, as the diameter varies from 4 Å to 35 Å. Similarly, the shear moduli are found to be in the range 0.14–0.47 TPa.

Again, molecular mechanics and nanoscale continuum theory are incorporated in the SWCNT model. In this case, Natsuki et al. [43] relates both methods through the Morse potential by considering the atoms as individual bodies connected with bond energy. For the model, the wall thickness is regarded as zero since the authors assume this parameter does not affect the governing equations. Stress and strain equations are then formulated for the continuum theory, specifically for armchair and zigzag nanotube. These equations are functions of the force, bond length, angle variation, and bond deformation.

The computer simulations are conducted for nanotubes (10, 10) and (17, 0). The results for both structures indicate the elastic modulus is E = 0.94 TPa. The maximum stress for the zigzag nanotubes is predicted at approximately 70 GPa with 11% failure strain. The armchair nanotube has a maximum stress of 80 GPa at 15% failure strain. Similarly, the compressive stresses are predicted to range from 110–125 GPa at the elastic limit of 12% compression.

The approach for the carbon nanotube analysis developed by Li and Chou [44] presents a geometrical frame-like structure, which employs molecular mechanics from AMBER force field parameters. As in the work of Kalamkarov [42], Eqns. 2.40-2.43 are valid in representing a relation between molecular mechanics and structural mechanics. The method simulates armchair and zigzag carbon nanotubes under fixed-free conditions by applying two different loads: a tensile force and a torsional moment to the structures. A fixed wall thickness is assumed as t = 0.34 nm. The elastic and shear moduli range are determined, which display dependency on the nanotube diameter ranging from D = 0.4 to 2.0 nm. The elastic modulus range for armchair and zigzag SWCNTs are $E_a \approx 0.95$ -1.02 TPa and $E_z \approx 0.90$ -1.03 TPa. Similarly, the shear modulus range for armchair and zigzag SWCNTs are $G_a \approx 0.23$ -0.48 TPa and $G_z \approx 0.28$ -0.48 TPa.

A slightly different kind of approach is employed in the work of Gao and Li [45]. Here, the continuum model is developed for the computation of SWCNT strain energies as well as the estimation of the elastic modulus through the incorporation of molecular structures. The concept of these properties is derived from a graphite sheet, which is represented by a thin plate. The thin plate is then rolled to form the continuum model for the carbon nanotube. Kinematic and constitutive relations at the continuum level are determined.

The strain energy, Π_s , is determined from the governing equation as

$$\frac{\Pi_s}{2L} = \frac{4\pi}{3} E\left[r_i^2 \ln\left(\frac{\pi}{W}r_i\right) + \frac{1}{4}(r_o^2 - r_i^2)\right]$$
(2.46)

$$dV = (2L)(2\pi r)dr, \qquad (2.47)$$

where dV refers to the volumetric element and W refers to the width of the continuum plate. The strain energy and potential energy are determined and set equal to satisfy energy equilibrium. An equation for the elastic modulus is analytically determined and a parametric study is conducted. The elastic modulus determined is 5.5 TPa for radius 0.0375 nm. It was determined that there exists a dependency on the nanotube diameter r_{nt} . In addition, the elastic modulus is determined assuming plane strain case and dependence on Poisson's ratio. As a result, the elastic modulus determined is E = 7 TPa independent of r_{nt} . Therefore Gao and Li concluded that there is an inverse proportionality between the cross-sectional area of the tube and the elastic modulus [45].

From the work of Saito et al. [1], the Young's modulus for carbon nanotubes is, in general, 1500 G Pa. Values vary from 500 G Pa to 1500 G Pa, depending on the potential model and the estimation of the cross-section. For calculations, a wall thickness is assumed to be 0.344 nm, which is the interlayer separation. When the diameter of the SWCNT increases, the nanotube becomes unstable and is prone to failure. The authors measure Young's modulus by determining the amplitude of a thermal vibration of a nanotube in terms of the temperature. By this method, the estimated values for Y are approximately 1000 G Pa [1].

Griebel and Hamaeckers [40] determine the Young's modulus and the Poisson's ratio via molecular simulation for a polyethylene matrix embedded in SWCNTs and also established the properties of a (10, 10) SWCNT. The results for the Young's moduli and the Poisson's ratios range from 395.04 G Pa-410.18 G Pa and 0.22–0.24, respectively.

Experimental and theoretical models are employed by Laborde et al. [22] to identify

the tensile strength and Young's modulus of SWCNT/epoxy composite systems. For the latter, the authors apply four models to approximate the properties of the systems including, Poisson's ratio contractions, three dimensional effects, and the mixture law. According to Laborde et al. [22], all the results obtained to determine the Young's modulus are excellent approximations to the experimental results with a low error of 2.3%.

A review referring to the different methods has been presented highlighting the atomistic and finite element approaches as well as hybrid scheme models relating both methodologies. The main focus is to identify the mechanical properties characterizing SWCNTs. Subsequently, the overview presented in the following chapter aims to provide the key methods to characterize the electrical properties of SWCNTs.

Chapter 3

Overview of the Electrical Properties of Carbon Nanotubes

By exploring the electrical properties of carbon nanotubes, it is possible to explore the noticeable distinctions regarding conductivity between metals and semiconductors presented in carbon nanotube structures. Electrons in a crystal are arranged in energy bands separated by regions in energy where there are no electron orbitals. These are known as band gaps, which form through the interaction of the conduction electron waves with the ion cores of the crystal. The definition of an energy band gap for insulators and semiconductors refer to the difference between the top of the valence band and the bottom of the conduction band in which electrons are able to jump from one band to another [18]. It is possible to observe the band gap differences between metals and semiconductors. For instance, in metals, 10%–90% of bands are partially filled. On the other hand for semiconductors, one or two bands are slightly filled (or empty) [5].

In this chapter, a general overview of concepts associated with the electrical properties of carbon nanotubes will be provided. This synopsis focused on the fundamentals and applications of the numerical analysis done with the goal of determining the energy band gap and the density of state (DOS) of several SWCNTs. By DOS, it is referred to the property in statistical and condensed matter physics that quantifies how closely packed energy levels are in some physical system. It is often expressed as a function $\mathbf{g}(\mathbf{E})$ of the internal energy \mathbf{E} , or a function $\mathbf{g}(\mathbf{k})$ of the wavevector \mathbf{k} [18].

3.1 Brillouin zones in SWCNTs

The Brillouin zone is defined as a primitive cell in the reciprocal lattice, specifically the Fourier space. It provides a geometrical interpretation of the diffraction condition as well as exhibits all the wavevectors \mathbf{k} which can be reflected, assuming Bragg Law, by the crystal. The construction of the Brillouin zone produces a set of planes perpendicular to the reciprocal lattice vectors satisfying the laws of diffraction. The planes divide the Fourier space of the crystal into fragments. The first Brillouin zone is the smallest volume entirely enclosed by these planes that are the perpendicular bisectors of the reciprocal lattice vectors. Their importance rely on the analysis of the electron energy band in a crystal structure.

There are 2N carbon atoms in the SWCNT unit cell so that there exist N pairs of π bonding represented by the valence bands and π^* anti-bonding representing the conduction energy bands. The phonon dispersion consists of 6N branches resulting from a vector displacement of each carbon atom in the unit cell. The reciprocal lattice vectors \mathbf{K}_1 and \mathbf{K}_2 , as presented in Fig. 3.1, are obtained from the relation $\mathbf{R}_i \cdot \mathbf{K}_j = 2\pi \delta_{ij}$, where \mathbf{R}_i and \mathbf{K}_j are the lattice vectors in real and reciprocal space, respectively. The expressions for \mathbf{K}_1 and \mathbf{K}_2 are given by

$$\mathbf{K}_{1} = \frac{1}{N}(-t_{2}\mathbf{b}_{1} + t_{1}\mathbf{b}_{2}) \quad and \quad \mathbf{K}_{2} = \frac{1}{N}(m\mathbf{b}_{1} - n\mathbf{b}_{2}), \tag{3.1}$$

where \mathbf{b}_1 and \mathbf{b}_2 are the reciprocal lattice vectors of graphite. The first Brillouin zone is depicted in line segment WW'. Furthermore, \mathbf{K}_1 gives discrete k values represented by the parallel lines in the \mathbf{C}_h direction as indicated in Fig. 3.1. The N parallel lines conformed through the quantization of wave vectors associated with the periodic boundary conditions on \mathbf{C}_h . Hence, for the N parallel lines, there are N energy bands [1]. These energy bands provide a description regarding the electrical properties of SWCNTs, which can be assessed through the molecular dynamics method.

3.2 Density Functional Theory

Carbon nanotubes can be either metallic or semiconducting, depending on its chirality. The electronic structure of a SWCNT is analyzed implementing molecular dynamics (MD) through the Density Functional Theory method (DFT). The DFT method is a ground-state theory used in first-principle calculations, which models the electronic structure of many-body systems. By the Hohenberg- Kohn theorem [23,46], it is possible to determine one external potential V(r) yielding the density charge n(r). This charge density n(r) is



Figure 3.1: The Brillouin zone of a carbon nanotube conformed by line segment WW'. Vectors \mathbf{K}_1 and \mathbf{K}_2 represent the reciprocal lattice vectors corresponding to \mathbf{C}_h and \mathbf{T} , respectively [1].

defined as

$$n(r) = N \int |\Psi(r, r_2, r_3, \dots r_N)|^2 dr_2 \dots dr_N.$$
(3.2)

The ground state energy E is determined by the ground-state charge density. Assuming E is a functional E[n(r)]. It can be defined as

$$E[n(\mathbf{r})] = \langle \Psi | T + U + V | \Psi \rangle = \langle \Psi | T + U | \Psi \rangle + \langle \Psi | V | \Psi \rangle = F[n(\mathbf{r})] + \int n(\mathbf{r}) V(\mathbf{r}) d\mathbf{r}, \quad (3.3)$$

where T is the kinetic energy, U is the electron-electron interaction, V is the potential energy, Ψ is the ground-state wavefunction, F[n(r)] is the universal functional of charge density n(r). In this way, DFT optimizes the N-body problem to the 3-D function n(r) so as to minimize the functional E[n(r)].

Kohn and Sham (KS) reformulated the problem to provide applicability to DFT. For this case, a system of interacting electrons is mapped on an auxiliary system of non-interacting electrons, which remains constant. For the non-interacting system, the electrons groundstate charge density are represented as a summation over one electron orbital, the KS orbitals, $\psi_i(r)$; as displayed in Eqn. 3.4:

$$n(\mathbf{r}) = \mathbf{2} \sum_{i} |\psi_i(\mathbf{r})|^2, \qquad (3.4)$$

where $\psi_i(r)$ are the solutions to the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\mathbf{r})\right)\psi_i\left(\mathbf{r}\right) = \epsilon_i\psi_i\left(\mathbf{r}\right),\tag{3.5}$$

obeying orthonormality constraints

$$\int \psi_i(\mathbf{r}) \,\psi_j(\mathbf{r}) \,d\mathbf{r} = \delta_{ij},\tag{3.6}$$

where $V_{KS}(r)$ represents a unique potential with n(r) as its ground state charge density. $V_{KS}(r)$ is determined through the variational property of energy. From this assumption, it follows that the Schrödinger equation can be re-expressed as

$$\left(\frac{\hbar^2}{2m}\nabla^2 + V_H(\mathbf{r}) + V_{xc}[n(\mathbf{r})] + V(\mathbf{r})\right)\psi_i(\mathbf{r}) = \sum_j \lambda_{ij}\psi_j(\mathbf{r}), \qquad (3.7)$$

Local Density Approximation (LDA) method, developed by Hohenberg & Kohn, provides an approximation of this energy term in an electronic system. In LDA, the exchangecorrelation is obtained by assuming that the exchange-correlation energy of an electronic system per electron at point r, $E_{xc}(r)$, equals the exchange-correlation per electron in a homogeneous electron gas, $E_{xc}^{\text{hom}}[n(\mathbf{r})]$. That is, both have the same density at point r

$$E_{xc}[n(\mathbf{r})] = \int E_{xc}(\mathbf{r})n(\mathbf{r})d^{3}\mathbf{r}, \text{ and}$$
$$\frac{\partial E_{xc}[n(\mathbf{r})]}{\partial [n(\mathbf{r})]} = \frac{\partial n(\mathbf{r})E_{xc}(\mathbf{r})}{\partial n(\mathbf{r})},$$

where $E_{xc}(r) = E_{xc}^{\text{hom}}[n(r)].$

In general, LDA provides simple computational and good accuracy of results since it permits a single well-defined global minimum for the energy of a non-spin system of electrons in a fixed potential. In this way, any energy minimization scheme produces the global energy minimum of the electronic system [3]. On the other hand, DFT band gaps may be underestimated since there is a reliance on the exact energy functional as well as the inability to adequately estimate these functionals. The following detailed procedure is outlined for the DFT calculations to solve the Kohn-Sham equations self-consistently since the Kohn-Sham eigenvalues represent the derivatives of the total energy with respect to the occupation number of states.

3.3 DFT Calculations

The atomic DFT calculations assume a spherical averaged charge density; therefore, the Kohn-Sham equations have spherical symmetry and can be separated into radial and angular parts.

To determine the solution for the KS equations, the following procedure is engaged:

- (1) for a given electronic configuration, an initial guess of KS potential is assumed.
- (2) radial KS equations are solved for those radial orbitals corresponding to occupied states.
- (3) the spherical averaged charge density is recalculated.
- (4) a new KS potential is determined from step 3.
- (5) process is iterated until self-consistency has been reached.

From this process, minimum energy is obtained for the ground state electronic configuration of all atoms. In molecules, the KS equations are solved by expansion of KS orbitals $\psi_i(r)$ into a suitable basis set. Localized basis sets are atomic-like wavefunctions centered on atoms. Most common basis sets are linear combinations of atomic orbitals (LCAO), Gaussian-type Orbitals (GTO), Slater-type Orbitals (STO), and atomic-independent Plane Waves (PW) basis sets, just to mention a few [46].

3.4 Basis Sets

A basis set is the mathematical description of the orbitals in a system, which estimates the electronic wavefunction of the entire system. The standard basis sets apply linear combinations of the Gaussian functions to configure the orbitals [23, 47]. The two most common choices of basis function are plane waves and Gaussian type orbitals. The functions ϕ_i are Cartesian Gaussian function consisting of polynomials of the position vector **r** shown in Eqn. 3.8:

$$\phi_i(\mathbf{r}) = (x - R_{ix})^{n_1} (y - R_{iy})^{n_2} (z - R_{iz})^{n_3} e^{-\alpha_i (\mathbf{r} - \mathbf{R}_i)^2}, \qquad (3.8)$$

where n_1, n_2, n_3 are the integers. Linear combinations of these Cartesian Gaussian functions can be chosen to form functions that transform into spherical harmonics under rotation.

Using basis sets and generating localized orbitals result in a very efficient technique applicable to all elements without any dependence on pseudopotentials¹ [48]. There are different types of basis sets used in the Gaussian 03^{TM} package. For this current work, basis set $3-21G^*$ has been utilized to generate the total minimum energy of the system. $3-21G^*$ is considered a partially polarized split valence basis set as it has two sizes of basis function for each valence orbital. For instance, carbon, the element conforming SWCNTs, is represented as [23]:

$$C: 1s, 2s, 2s', 2p_x, 2p_y, 2p_z, 2p'_x, 2p'_y, 2p'_z,$$

where the primed and unprimed orbitals refer to different sizes. A graphical representation of basis set $3-21G^*$ is found in Fig. 3.2.

Two parameters are needed for the specification of a Gaussian basis per atom, that is, the coefficients of the functions and their exponents. Using basis sets for all electron calculation can be very demanding for tightly bounded core states since it requires a large amount of Gaussian orbitals to describe them accurately. Similarly, basis sets are typically optimized for atoms and not solids or molecules. The addition of d or p-type functions may improve the description of atoms such as carbon or silicon in a molecular or solid state environment.

Another important criteria is the optimization of the structure, which is achieved by moving atoms to minimize the total energy. A common approach is the use of the Conjugate Gradient method. The Conjugate Gradient method is an effective scheme for symmetric positive definite systems. This procedure generates vector sequences of iterates (i.e., successive approximations to the solution), residuals corresponding to the iterates, and search

¹Pseudopotential approximations are pseudo wavefunctions replacing the core electrons with ionic potential in the system [3].



Figure 3.2: The linear combination of Gaussians is indicated by the row of dots (coming out of paper). The dots indicated the basis function [2].

directions used in updating the iterates and residuals. For each iteration of the method, two inner products are performed in order to compute update scalars that are defined to make the sequences satisfying orthogonality conditions. On a symmetric positive definite linear system these conditions imply that the distance to the true solution is minimized in some norm [49]. For instance, assuming a force f_{am}^n of atom a under direction m in the n^{th} iteration of structural optimization, the first conjugate direction d_{im}^n is described by

$$d_{am}^n = f_{am}^n - x d_{am}^{n-1}, \text{ where}$$

$$(3.9)$$

$$x = \frac{\sum_{am} f_{am}^{n} (f_{am}^{n} - f_{am}^{n-1})}{\sum_{am} (f_{am}^{n-1})^{2}} \quad (\text{when } n = 1, \text{ then } x = 0).$$
(3.10)

At this point, the key elements employed to perform molecular dynamic simulations have been defined. The following is a mathematical representation of the molecular dynamics methodology for calculating the total energy of the SWCNT structure.

3.5 Density Functional Theory and Molecular Dynamics

The MD method is a dynamical method, which applies to the variational principle in order to determine the eigenstates of all the lowest-energy electronic states [3]. Assumed ions behave as classical particles and electrons are in the ground-state corresponding to their instant positions. Using classical Lagrangian to describe the dynamical behavior or ions, it follows:

$$L = \frac{1}{2} \sum_{i} M_i \dot{\mathbf{R}}_i^2 - E_{tot}(\{\mathbf{R}\})$$
(3.11)

where M_i are the mass of ions. The equation of motion becomes:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\mathbf{R}}_i} - \frac{\partial L}{\partial \mathbf{R}_i} = 0; \text{ in particular}, \qquad (3.12)$$

$$\sum_{i} M_{i} \ddot{\mathbf{R}}_{i} - \frac{\partial E_{tot}(\{\mathbf{R}\})}{\partial \mathbf{R}_{i}} = 0.$$
(3.13)

In classical MD, consider a mechanical system of N atoms enclosed in a volume constraint by periodical boundary conditions.

The system contains mechanical energy $E = T + E_p$, where $T = \frac{1}{2} \sum M_i \dot{R}_i^2$ (kinetic energy) and $E_p = E_p\{R\}$ (interatomic potential). To solve the equation of motion numerically, the Verlet algorithm is employed. The Verlet algorithm is a finite difference algorithm



Figure 3.3: Simulation of the evolution of coefficients $\{c\}$, KS Hamiltonian H, and the total energy, in the final two time steps of the MD method. The final time step reaches self consistency [3].

for integrating the equation of motion. It is derived from second-order differential equation. Therefore, it provides the value of the i^{th} electronic state at the next time $\psi_i(\Delta t)$ defined as

$$\psi_i(\Delta t) = 2\psi_i(0) - \psi_i(-\Delta t) + \Delta t^2 \dot{\psi}_i(0), \qquad (3.14)$$

where Δt is the length of the time step, $\psi_i(0)$ is the value of the state at current Δt and $\psi_i(-\Delta t)$ refer to the last time step [3].

And so, the Verlet algorithm becomes

$$\psi_i(\Delta t) = 2\psi_i(0) - \psi_i(-\Delta t) - \frac{\Delta t^2}{\mu} [H - \lambda_i] \psi_i(0), \qquad (3.15)$$

where the wave functions in Eqn. 3.15 approach the Kohn-Sham eigenstates to recalculate the potentials. In this way, the coefficients λ_i reach self-consistency, as in Fig. 3.3. In summary, the Verlet algorithm is very efficient and numerically stable since it produces accurate energy outputs in comparison to other higher-order schemes.

Another widely used approach is the Car-Parinello dynamics approach [3]. This method

also applies MD through first-principle interatomic potential calculated from DFT. A Lagrangian is introduced as

$$L = \frac{\mu}{2} \sum_{k} \int d\mathbf{r} |\dot{\psi}_{k}(\mathbf{r})|^{2} + \frac{1}{2} \sum_{i} M_{i} \dot{\mathbf{R}}_{i}^{2} - E_{tot}(\{\mathbf{R}\}) + \sum_{k,l} \Lambda_{kl} \left(\int \dot{\psi}_{k}^{*}(\mathbf{r}) \psi_{l}(\mathbf{r}) d\mathbf{r} - \delta_{kl} \right),$$
(3.16)

which generates the equation of motions:

$$\mu \ddot{\psi}_k = H \psi_k - \sum \Lambda_{kl} \psi_l, \qquad (3.17)$$

$$M_i \ddot{\mathbf{R}}_i = -\frac{\partial E_{tot}}{\partial \mathbf{R}_i,} \tag{3.18}$$

where μ represents a fictitious electronic mass, and Λ_{kl} represents the Lagrange multipliers.

Most Car-Parrinello calculations are used for aperiodic systems as well as systems with a large unit cell [46]. For the latter, it is imperative to handle the infinite number of non-interacting electrons moving in the static potential of the infinite number of nuclei or ions.

The Car-Parrinello method used to calculate the KS eigenstates of a system works through a series of iterations to generate the wave functions. These iterations occurred until the wave functions converge to the KS eigenstates [3].

The molecular dynamic method enables the determination of the energy bands characterizing the different SWCNTs. The next section summarizes the main points in band theory of solids.

3.6 Band theory of solids

The band gap, E_g , is the energy difference between the conduction band and the valence band, as shown in Fig. 3.4. E_g varies depending whether the solid is an insulator, semiconductor, or metal as shown in Fig. 3.5. Electrons occupy energy levels from the lowest energies upward. As a result, the allowed energy levels form bands. The highest filled level (at 0 K) is the valence band. The electrons in the valence band do not participate in the conduction process. The first unfilled level above the valence band is the conduction band. Thus, electrons are excited from the valence band to the conduction band. This contribution promotes electrical conductivity.



Figure 3.4: Energy gap representation of a semiconductor [4].



Figure 3.5: Schematic electron occupancy of allowed energy band gaps for an insulator, semiconductor, and metal [4].

Band structure is explained by the Nearly Free Electron model, which suggests that allowed energies are distributed continuously from zero to infinity. The free electron wavefunctions are of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r}),\tag{3.19}$$

where $\psi_{\mathbf{k}}(\mathbf{r})$ represent the running waves and carries a momentum $\mathbf{p} = \hbar \mathbf{k}$. The model is governed by

$$\boldsymbol{\epsilon}_{F} = \frac{\hbar}{2m} (k_{x}^{2} + k_{y}^{2} + k_{z}^{2}), \qquad (3.20)$$

along with the respective boundary conditions. Band electrons are perturbed only by the periodic potential of the ion cores. The energy gaps, as shown in Fig. 3.6, occurred by the Bragg reflection of the electron waves. Each subsequent Bragg reflection generates time-independent standing waves of the form $\exp(\pm i\pi x/a)$. The origin of the energy gap develops as the standing waves assemble large amounts of electrons at different regions, which allows for different values of potential energy [5].



Figure 3.6: (a) Plot of energy ϵ vs. k for a free electron. (b) Sample of energy band for an electron in a monoatomic linear lattice of lattice constant a. First gap is associated with the Bragg reflection at $k = \pm \frac{\pi}{a}$ [5].

3.6.1 Fermi level

Electrons are fermions. In addition, the Fermi-Dirac distribution function follows:

$$f(E) = \frac{1}{\exp((E-\mu)/k_B T) + 1},$$
(3.21)

where μ is the fermi energy, ϵ_F , or the chemical potential. The fermi function f(E) provides the probability that an available electron energy state will be occupied at a given T.

For semiconductors, the fermi level is the energy at which the probability of occupation by an electron is exactly 1/2. At the energy gap, there are no electrons because the density of states (DOS) is zero. This is illustrated in Fig. 3.7. Consequently, ϵ_F becomes the sea where no electrons have enough energy to rise above the surface.

In metals, ϵ_F provides information about the velocities of the electrons involve in electrical conduction. The electrons close to ϵ_F participate in the conduction process. The conductivity characteristics for both types of solids is presented in the following two sections.

3.6.2 Metals

Metals have the ability of easily conducting electricity since the conduction band and the valence band are closely packed with more available energy levels, or because there are more energy levels available than electrons to fill them. In metals, there is no band gap, E_g , since the conduction band and the valence band overlap so as to allow free electrons to



Figure 3.7: Band gap for a semiconductor solid [6].

participate in the conduction process.

The electrical properties of metal are determined by the shape of the fermi surface. The fermi surface separates the unfilled orbitals from the filled orbitals at 0 K. In addition, these free electron fermi surfaces are developed from spheres of radius k_F determined by the valence concentration.

3.6.3 Semiconductors

Semiconductors have a band gap, E_g , approximately of 1–2 eV. There are two types of semiconductors:

- (1) intrinsic (pure) semiconductors, and
- (2) extrinsic (added impurities) semiconductors.

The resistance of a semiconductor decreases with temperature. That is, as T increases, the thermal energy of valence electrons increases; therefore, breaking the gap into conduction band. When an electron (n) has enough energy to escape electrostatic attraction it creates a hole (p). Holes are vacant orbitals in a conduction band.

For intrinsic semiconductors, n = p, the total number of charge carriers per unit volume. On the other hand, extrinsic semiconductors can be formed by doping an intrinsic semiconductor. The dopants, which creates holes and contributes to the conduction band are known as p-type or acceptor semiconductor. Dopants which add electrons are known as n-type or donor semiconductor [6].

The overall explanation regarding band structure in terms of SWCNTs with metallic or semiconductor characteristics is explore in the next section of this chapter.

3.7 Energy dispersion of SWCNTs

Energy bands of SWCNTs can be acquired through two-dimensional graphite under appropriate periodic boundary conditions in the direction of the chiral vector \mathbf{C}_h . At the same time, the direction of the translational vector continues along the nanotube axis. As a result, the energy bands become sets of one-dimensional (1*D*) energy dispersion relations, which in turn are cross sections of the ones from two-dimensional (2*D*) graphite.

The 1D energy dispersion relations are given by

$$\mathbf{E}_{\mu}(\mathbf{k}) = \mathbf{E}_{g2D}\left(\mathbf{k}\frac{\mathbf{K}_{2}}{|\mathbf{K}_{2}|} + \mu\mathbf{K}_{1}\right), \quad \left(\mu = 0, \dots, N-1, \text{ and } -\frac{\pi}{T} < k < \frac{\pi}{T}\right), \quad (3.22)$$

which corresponds to the energy dispersion relations of a SWCNT. The N pairs associated with Eqn. 3.22 represent the cross sections of the 2D energy dispersion surface of graphite as shown in Fig. 3.8. The cutting lines in Fig. 3.8 represent the 2D Brillouin zone. If the line passes through a K point of the 2D Brillouin zone in which π and π^* energy bands of 2D graphite are degenerate by symmetry, then the 1D energy bands have zero energy gap and a finite Fermi level value making the nanotube metallic. Conversely, if the line does not pass through a K point, then the nanotube will show semiconducting behavior. That is, a finite energy gap between valence and conduction bands.

The condition for obtaining a metallic energy band relies on the ratio of the vector length \overrightarrow{YK} to that of \mathbf{K}_1 is an integer. The vector \overrightarrow{YK} is defined as

$$\overrightarrow{YK} = \frac{2n+m}{3}\mathbf{K}_1,\tag{3.23}$$

where the condition for metallic nanotubes relies on the result of (n-m) being a multiple of 3. Therefore, the armchair nanotubes (n, n) are always metallic while the zigzag nanotubes are only metallic when n is divisible by 3. A complete picture of the energy bands for



Figure 3.8: Graphite energy bands dispersion for σ and π bands [1].

semiconducting and metallic carbon nanotubes are shown in Fig. 3.9. These are generated from a Gaussian03TM output in MATLABTM.

3.7.1 Energy Dispersion of Two Types of Single-Walled Carbon Nanotubes

The energy dispersion of SWCNTs is mainly focused on two types of nanotubes: armchair and zigzag. Both are highly symmetric which constitutes a simple case to examine the energy dispersion.

For armchair carbon nanotubes $\mathbf{C}_h = (n, n)$, the allowed wave vectors $k_{x,q}$ in the circumferential direction are given by:

$$n\sqrt{3k_{x,q}}a = 2\pi q, \quad (q = 1, ..., 2n).$$
 (3.24)

Using Eqn. 3.24, the energy dispersion relations $E_q^a(k)$ for the nanotube become

$$E_q^a = \pm t \left\{ 1 \pm 4 \cos\left(\frac{q\pi}{n}\right) \cos\left(\frac{ka}{2}\right) + 4 \cos^2\left(\frac{ka}{2}\right) \right\},\tag{3.25}$$

where $ka = (-\pi, \pi)$, q = 1, ... 2n, and k is in the 1D direction $\mathbf{K}_2 = (\mathbf{b}_1 - \mathbf{b}_2)/2$. For all armchair nanotubes, the energy bands display large degeneracy at the boundary zone (ka =



Figure 3.9: Band structures of single-walled carbon nanotubes for (a) (7,0), with the distinctive gap between the virtual and occupied bands signifying that it is a semiconductor, while (b) (5,5) displays no gap and contact between both bands.

 π). In general, the armchair carbon nanotubes generates 4n energy subbands comparable to Eqn. 3.25, with 2n conduction and 2n valence bands. All armchair nanotubes have a band degeneracy between the highest valence band and the lowest conduction band at $k = \pm 2\pi/(3a)$, at which the bands cross the Fermi level. For this reason, all armchair nanotubes display metallic behavior similar to the graphene sheet.

For the zigzag carbon nanotubes $\mathbf{C}_h = (n, 0)$, the energy dispersion $E_q^z(k)$ is obtained by using the periodic boundary conditions on k_y :

$$nk_{y,q}a = 2\pi q, \ (q = 1, ..., 2n).$$
 (3.26)

Consequently, the 1D energy dispersion for the 4n states of the (n, 0) zigzag nanotube becomes:

$$E_q^z(k) = \pm t \left\{ 1 \pm 4 \cos\left(\frac{\sqrt{3}ka}{2}\right) \cos\left(\frac{q\pi}{n}\right) + 4 \cos^2\left(\frac{q\pi}{n}\right) \right\}^{\frac{1}{2}}, \qquad (3.27)$$

where $ka = \left(-\frac{\pi}{\sqrt{3}}, \frac{\pi}{\sqrt{3}}\right)$, and q = 1, ..., 2n.

The energy gap depends on the chirality of the zigzag nanotube as governed by Eqn. 3.23. That is, when n is divisible by 3, the energy gap at k = 0 becomes zero. On the contrary, when n is not divisible by 3, the energy gap opens at k = 0 [1].

3.8 Density of states of SWCNTs

The Density of states (DOS) outputs the number of orbitals per unit energy range. Its importance relies on using this information as a tool to calculate the number of available states per unit volume per unit energy. First, the available states in k-space are determined. Then, employ energy-momentum relation to determine DOS in terms of energy [4].

For all metallic carbon nanotubes, regardless of diameter and chirality, the density of states per unit length along nanotube axis is a constant given by:

$$N(\epsilon_F) = \frac{8}{\sqrt{3\pi a|t|}},\tag{3.28}$$

where a is the lattice constant of the graphene layer and |t| is the nearest-neighbor C-C tight binding overlap energy. DOS has a nonzero value for metallic nanotubes, but not for semiconductors at the fermi level ϵ_F .

Experimental methods to calculate DOS have been conducted very accurately through scanning tunneling spectroscopy (STS). Scanning tunneling spectroscopy (STS) studies the local electronic structure of a sample's surface. The electronic structure of an atom depends upon its atomic species and also upon its local chemical environment. STS generates "topographic" (constant-current) images using different bias voltages and comparing them, taking current (constant-height) images at different heights, and ramping the bias voltage with the tip positioned over a feature of interest while recording the tunneling current.

STMs can be set up to collect I-V curves at every point in a data set, providing a threedimensional map of electronic structure. With a lock-in amplifier, dI/dV (conductivity) or dI/dz (work function) vs. V curves can be collected directly. All of these are ways of probing the local electronic structure of a surface using a scanning tunneling microscope. As a result, STS is able to validate the fact that in nanotube bundles, there are about 1/3 SWCNTs that are metallic while 2/3 are semiconducting [1].

Currently, the background review highlighting the major components of the mechanical and electrical properties about SWCNTs have been explained. The subsequent chapters will concentrate on the contribution developed from this research work. Chapter 4 is mainly focused on presenting the finite element simulations done in ANSYSTM. First, the procedure for two finite element models are explained along with the graphical representation of its results. The ANSYSTM output is discussed starting with the linear model for the case of loading by tension followed by the cases of bending and torsion. Next, the multilinear model is introduced for the loading by tension to study the elastic–plastic response of the SWCNTs. Thus, these simulations encompass the study of the mechanical characteristics observed in carbon nanotubes.

Chapter 4

Single-walled carbon nanotube (SWCNT) representation using finite element analysis

Finite element analysis is employed to simulate the carbon nanotube structure under different types of loading conditions. By inputting adequate average parameters, the model can be used to model the mechanical behavior of the structure as well as the interaction of more complex nanostructure configurations. The following chapter describes the details regarding the finite element modeling of the SWCNTs for two types of models.

4.1 Finite element analysis

4.1.1 Linear Model

SWCNTs (5,5), (7,7), (10,0), and (12,0) are represented in ANSYSTM as space-frame structures. The elements comprising the structure correspond to the C-C bonds propagated in a carbon nanotube structure, as shown in Fig. 4.1. The depiction of each carbon nanotube in ANSYSTM varies according to the chirality of the carbon nanotube, which in turn affects the number of elements in the finite element analysis representation as specified in Table 4.1 and displayed in Fig. 4.2.

The C-C bond elements are modeled using BEAM4 [7] element. BEAM4 is a uniaxial element with tension, compression, torsion, and bending as well as stress stiffening and large deflection capabilities. The element has six degrees of freedom at each node: x, y, znodal translational directions and rotations about the nodal x, y, z axes [7]. The specifics of BEAM4 are displayed in Fig. 4.3. In the analysis, the nodes become the carbon atoms while the elements represent the bonds. For this reason, the elements are meshed with zero divisions.



Figure 4.1: SWCNTs (5,5) and (12,0) space-frame representation in ANSYSTM. Elements represent C-C covalent bonds while the nodes represent the C atoms.

Five different sets of input parameters are considered to model these structures. The parameters are gathered from published literature, which vary depending on the approach used and the representation of the carbon nanotube structure. Table 4.2 lists the input data acquired for the finite element simulations. At the same time, the values for density, $\rho = 2.68 \times 10^{-27} kg/\text{ Å}^3$, and the Poisson's ratio, $\nu = 0.19$, remain constant through the different simulation runs. It is imperative to highlight the fact that the thicknesses employed from the different input sets directly affect the diameter as well as the cross-sectional area of the C-C bond. Nevertheless, the C-C length remains constant in the structure for which $C-C|_{length} = 1.4210 \text{ Å}.$

The constraints applied to the SWCNT structures are fixed-free. For the fixed-free boundary conditions (BCs), there are three different types of loading imposed on the structure: tension, bending, and torsion. Table 4.3 presents a tabulated specification of the different simulations that have been performed in this analysis. Eqns. 4.1–4.3 characterize the properties of the elements since the beam formulations relating the strain energy Uand the elongation δ , displayed in Figs. 4.4(*a*)–(*c*), are employed to calculate the input parameters of the elastic modulus for the finite element model.

SWCNT	No. of elements
(5,5)	290
(7,7)	406
(10, 0)	580
(12, 0)	696

Table 4.1: Number of elements employed to configure model in $\mathbf{ANSYS}^{\mathrm{TM}}$



Figure 4.2: Representation of C-C bond in a molecular simulation as well as finite element modeling.



Figure 4.3: Geometric characteristics presented in element BEAM4 employed in ANSYSTM to construct the space-frame elastic SWCNT model [7].

Author	Tkz=Tky (Å)	Area (\AA^2)	\mathbf{Izz} (Å ⁴)	$Iyy (Å^4)$	\mathbf{Ixx} (Å ⁴)
Chen & Cao [8]	0.500	0.1963	0.003068	0.003068	0.006136
Yakobson et al. [8],	0.660	0.3421	0.009314	0.009314	0.01863
[9]					
Kudin et al. [8],	0.890	0.6221	0.03080	0.03080	0.06160
[10]					
Pantano et al. [8],	0.750	0.4418	0.01554	0.01554	0.03106
[11]					
Tserpes & Pa-	1.470	1.6972	0.2292	0.2292	0.4584
panikos [8], [12]					

Table 4.2: Tabulated data set inputs for the ANSYSTM parameters in the configuration of the different carbon nanotube simulations.

Linear model	Loading			
	BCs	Tension	Bending	Torsion
(5,5)	fixed-free	\checkmark		\checkmark
(7,7)	fixed-free	\checkmark	\checkmark	
(10,0)	fixed-free	\checkmark		\checkmark
(12,0)	fixed-free			

Table 4.3: Diagram of finite element simulation analyses performed in ANSYSTM.

$$U_{tension} = \pi \delta^2 E t \frac{R}{L} \tag{4.1}$$

$$U_{bending} = \frac{\pi}{8} \theta^2 E t \frac{R}{L} (4R^2 + t^2)$$
(4.2)

$$U_{torsion} = \frac{\pi}{8(1+\nu)} \phi^2 E t \frac{R}{L} (4R^2 + t^2)$$
(4.3)

4.1.2 Multilinear Elastic Model

The multilinear elastic (MELAS) model [7] approach represents a nonlinear relationship allowing the structure's stiffness to change at different load levels. The behavior of this material property assumes a conservative, path-independent response in which unloading follows the same stress-strain path as loading. To construct the solid model in ANSYSTM, tabulated data points are entered to approximate a curve with linear interpolation between the points. In this way, the stress-strain curve of the material is used in ANSYSTM to accurately model the plastic deformation of the material.

Using the total strain components $\{\varepsilon_n\}$ provided as input data an equivalent total strain,







Figure 4.4: Strain energy - deformation relations from Chen and Cao: molecular dynamics and space-frame model results. (a) tension results, (b) bending results, and (c) torsion results [8].

 ε_e^t , is computed

$$\varepsilon_e^t = \frac{1}{\sqrt{2}(1+\nu)} \left[(\varepsilon_x - \varepsilon_y)^2 + (\varepsilon_y - \varepsilon_z)^2 + (\varepsilon_z - \varepsilon_x)^2 + \frac{3}{2} (\varepsilon_{xy})^2 + \frac{3}{2} (\varepsilon_{yz})^2 + \frac{3}{2} (\varepsilon_{xz})^2 \right]^{\frac{1}{2}}.$$
(4.4)

Next, ε_e^t along with the stress-strain curve similar to the one presented in Fig. 4.6 is employed to compute the equivalent total stress σ_e . Then, the elastic (linear) component of the strain, $\{\varepsilon_n^{el}\}$, and plastic (nonlinear) part, $\{\varepsilon_n^{pl}\}$, are determined as:

$$\left\{\varepsilon_n^{el}\right\} = \frac{\sigma_e}{E\varepsilon_e^t}\left\{\varepsilon_n\right\},\tag{4.5}$$

$$\left\{\varepsilon_n^{pl}\right\} = \left\{\varepsilon_n\right\} - \left\{\varepsilon_n^{el}\right\}.$$
(4.6)

Therefore, the ANSYSTM MELAS model is employed to simulate SWCNTs (8, 0), (8, 8), (9, 0), and (10, 0) as continuum model structures. An example is displayed in Fig. 4.7. In this case, the SWCNTs are hollow cylinders with constant thickness. The different diameter input values, density ρ , and Poisson's ratio ν are also determined from Table 4.2.

The element type applied is SOLID45 [7], which is used for the 3D modeling of solid structures. The element is defined by eight nodes, as displayed in Fig. 4.5 having three degrees of freedom at each node: translations in the nodal x, y, z directions. The element has plasticity, creep, swelling, stress stiffening, large deflection, and large strain capabilities. For these simulations, the stress-strain behavior is controlled from input data obtained in Ogata et al. [13].

Although the data employed for both models, linear and multilinear, were previously developed in other simulations, the carbon nanotube model responses are not been compared to each other. The space-frame and hollow cylinder model exemplify a SWCNT, but the schemes do not present the same fundamental characteristics. It is imperative to emphasize that the space-frame model based its parameters in the characteristics of the C-C bonds. On the other hand, the hollow cylinder treats the nanotubes as homogeneous and continuous bodies. Therefore, every point in the enclosed system contains the same mechanical properties. In the following sections of this chapter, it is the goal of the current work to look for consistency and/or discrepancies in both simulations, but not to develop any comparisons between the two systems.



Figure 4.5: Geometric characteristics presented in element SOLID45 utilized in ANSYSTM to construct the multilinear elastic SWCNT structure [7].



Figure 4.6: Stress-strain curve of the multilinear elastic material behavior (MELAS) assumed for the modeling of SWCNT in $ANSYS^{TM}$ [7].

Multilinear model	BCs	Tension
(8,0)	fixed-free	\checkmark
(8,8)	fixed-free	\checkmark
(9,0)	fixed-free	
(10,0)	fixed-free	\checkmark

Table 4.4: Diagram of finite element simulation analyses performed in $ANSYS^{TM}$.



Figure 4.7: Scheme of the continuum model used in the multilinear elastic model for the SWCNTs (8,0), (8,8), (9,0), and (10,0).

4.2 Loading by axial tension via linear model

SWCNTs (5, 5), (7, 7), (10, 0), and (12, 0) are modeled in ANSYSTM. For the simulation, a more elaborate model is required due to the complexity of the system. Hence, each model is configured using a space-frame structure that is a mechanical model of the characteristics found in the C-C bond structure. Input arrays of the elastic modulus and tension load are applied tin the system to determine the maximum axial stresses generated in the elements conforming the space-frame structure. For the elastic modulus, the array values are called before creating the geometry of the carbon nanotube. Once the nodes and elements are generated in 3D space, the tension load array values are applied at the end nodes located in the +z direction. For each of the four SWCNTs, a different tension load array is employed. The different tensile loading values are shown in Fig. 4.8. Detailed FORTRAN-based code is attached in Appendix B.

The elastic modulus array is derived from Eqns. 4.1–4.3. The values of the strain energy U and elongation δ are assumed from Fig. 4.4(a). The tension load array values,

as displayed in Fig. 4.8, are arbitrarily selected for each carbon nanotube. The loads vary between chiralities, but not significantly since these are in the order of 10^{-9} with a maximum value approximately of 8×10^{-9} kg Å/s². The small tension loads are applied to track the carbon nanotube response for each element under the five different models logged in Table 4.2. Each carbon nanotube is simulated in ANSYSTM five times. In this way, sets of 50 simulations are developed for each carbon nanotube to observe the effects of the structure's output.

The maximum stress distribution for every element is determined by applying Eqn. 4.7:

$$\sigma_{axial}^{\max} = \frac{F_x}{A} + \left|\frac{M_y z}{I_y}\right| + \left|\frac{M_z y}{I_z}\right|,\tag{4.7}$$

where F_x refers to the force component in the x, A is the cross-section area, M and I are the moment component and moment of inertia, respectively, for y and z. In order to determine the maximum element stress output using ANSYSTM, an element solution is computed for each C-C bond. The data is gathered through element tables so as to calculate the maximum stress distribution in each element. Element tables are a feature created in ANSYSTM to access element results data that are not otherwise directly accessible. In this case, element forces F_x , and element moments in the y and z direction M_y and M_z are output in a log file to compute the maximum axial stresses for each element.

The tabulated output for the different SWCNTs, σ_{axial}^{\max} , is plotted per element for each elastic modulus and tensile loading pair. As a result, 200 finite element simulations have been performed. A representation set is shown in Figs. 4.10–4.14 while the other results are displayed in Appendix A. The results indicate that the space-frame structure is essential for a finite element method simulation of the carbon nanotube structure. The stress distribution results between the two armchair nanotubes: (5,5) and (7,7), and zigzag nanotubes: (10,0) and (12,0) reflect a uniform and distinctive pattern when undergoing the same type of loading. Regardless of the geometric parameters input from the different sources, as tabulated in Table 4.2, each SWCNT behaves in the same manner throughout the five different finite element simulations done per structure. For instance, the elements enduring most of the loading in the SWCNTs remain consistent as the forces vary in the different simulation runs, as shown in Figs. 4.10–4.14. Table 4.5 describes the elements
undergoing the maximum amounts of stress in the system.

Referring to Figs. 4.10(a)-4.12(b), SWCNT (5, 5) has the highest maximum axial stress for the case when t = 0.50 Å where $\sigma_{axial}^{\max} = 4 \times 10^{-7}$ kg Å/s². The highest peaks observed are at the end of the structure since it can be tracked by the element numbers as seen in Fig. 4.10(a). Elements lying on the xy plane at z = 0 were constrained with zero degrees of freedom. The fixed boundary conditions affected elements 1 to 100 consistently for the five cases with very low stress output. Furthermore, the maximum axial stress tend to decrease as the thickness of the C-C bond increases. This is observed in the stress value range variations of the peaks for the five cases, where the lowest maximum axial stress is found for the case t = 1.47 Å where $\sigma_{axial}^{\max} = 20 \times 10^{-9}$ kg Å/s². The last case presented in SWCNT (5, 5) as displayed in Fig. 4.15(b), allows the C-C bond to be represented as a disk rather than a cylinder. The input criteria employed by the model underestimated the C-C bonds maximum axial stresses in the order of 10^{-9} , when compared to the other thicknesses.

For the case of SWCNT (7,7), the constraint elements at the xy plane for z = 0 responded slightly different to the tensile load when compared to SWCNT (5,5). More than half of the carbon nanotube elements remained constant at a steady maximum axial stress output. Two peaks were observed near the free end of the nanotube where the tension load was applied. The five different cases for SWCNT (7,7) are displayed in Figs. 4.13(a)– 4.15(b). Furthermore, the maximum axial stress values decreased as the thickness value of the C-C bond incremented. As in SWCNT (5,5), the maximum axial stress output for t = 1.470 Å was the lowest in the order of 10^{-9} .

The characteristics found in armchair SWCNTs (5,5) and (7,7), present a very similar output to the axial loading as it is expected due to their chirality. The average maximum axial stress range for both nanotubes is approximately $\sigma_{axial}^{\max} = (0.72-3.80) \times 10^{-7} \text{ kg/ Å s}^2$. The lower stresses are obtained from t = 0.89 Å [10], while the higher stresses are obtained employing t = 0.50 Å [8]. Considering the C-C bond length (L = 1.42 Å) Table 4.6 indicates the t : L ratio for the computational characterization of the nanotube structure properties. The highest stresses for the armchair SWCNTs are obtained from the lowest ratio (t : L = 0.352), while the lowest stresses are determined from the highest ratio (t: L = 0.627), without considering the case for t: L > 1 for which t = 1.47 Å as tabulated in Table 4.6. The beam-column assumption predominates in the characterization of the C-C bonds since the last case for both simulations t: L > 1 resembled a disk of constant thickness. In general, the maximum axial stress values obtained for SWCNTs (5,5) and (7,7) are adequately represented as beam columns rather than disks since the higher stress values are expected for these carbon structures. Having the C-C bond being represented by the criteria set from Tserpes and Papanikos [12] hinders its ability to simulate higher axial stresses in the finite element model.

For the zigzag SWCNTs (10,0) and (12,0), shown in the Appendix A (Figs. A.1–A.6), the stress responded in a similar trend. For these structures, the average maximum stress range is approximately $\sigma_{axial} = (0.098-2.30) \times 10^{-7} \text{ kg/ Å s}^2$. In these cases, the lower stress is for t = 1.47 Å, whereas the higher stress is for t = 0.50 Å. Furthermore, for these simulations the maximum axial stresses also decreased as the thickness of the C-Cbond increased as shown in Figs. A.1–A.6. The simulation for the two zigzag nanotubes produced very low stress values at approximately 200 elements approaching the xy plane at z = 0. For the SWCNT (10,0), elements greater than 200 and up to 580 underwent a somewhat uniform stress, as shown in Figs. A.1(a) to A.3(b). At the same time, slight peak values were observed in the middle and end of structure where the tension load in the z direction was applied. Similarly, for SWCNT (12,0) elements displayed very low stress values approximately for the first 400 elements. The element numbers greater than 400 and up to 696 remained at constant maximum axial stress as can be observed in the Appendix A Figs. A.4–A.6.

One of the simulations carried out for SWCNT (12,0) was not considered in the generation of Fig. A.4(b) for t = 0.66 Å, which employs Yakobson et al. [9] criteria. The axial stress output response is plotted in Fig. 4.16. The decision for removing the results from Fig. A.4(b) is due to numerical discrepancies in the output of this particular simulation. In this way, skewed results were avoided since the axial output to tensile load $F_9 = 0.015 \times 10^{-7} \text{ kg/ Å s}^2$ unexpectedly generated maximum axial stresses in the order 10^{-6} . Moreover when applying tensile loads greater than F_9 to the SWCNT (12,0) structure, the axial responses remain closely to the order of 10^{-7} . As a result, to count this simulation run as part of the ten simulations performed for this case would have affected the validity of the whole finite element case model.

In conclusion, the average values for maximum axial stresses observed in the four carbon nanotubes demonstrated a correlation between the carbon nanotube diameter and the axial stress output. More specifically, there exists an inverse proportionality between the structure's diameter and the axial stress determined from the finite element models. Furthermore, there are also differences presented in the simulations performed for armchair and zigzag carbon nanotubes. The number of elements significantly affected by the tensile load is higher for zigzag than for armchair carbon nanotubes. As a result, the maximum axial stress output is higher for SWCNTs (5,5) and (7,7) when compared to SWCNTs (10,0) and (12,0). Nevertheless, SWCNTs as observed in Figs. 4.10–4.15 and Figs. A.1–A.6 still displayed similar inverse proportionality trends between the increased thickness values and the maximum axial stress output per element calculated from the simulations.

The differences in the response behavior of both types of carbon nanotubes, armchair and zigzag, reflect once again the importance of the geometric differences between the two models. For instance, the impact of the stress distribution in the models is clearly distinguishable and can be observed in the member of elements affected by the axial load. Overall, the behavior observed for both armchair and zigzag SWCNTs is expected due to geometric differences, specifically regarding the orientation of the hexagonal unit cell observed in Fig. 4.9. As pointed out by Liu et al. [32], in armchair nanotubes 1/3 of the bonds are perpendicular to the loading direction which causes a stronger resistance to lateral deformation. On the other hand, for zigzag nanotubes 1/3 of the bonds are aligned with the loading direction so that all the bonds are stretched and the lateral resistance is mainly caused by bond angle variation in the structure. In summary, greater deformations of the elements representing C-C bonds occur in the armchair nanotubes when compared to the zigzag nanotubes so the chiral differences between these structures predominate in their mechanical properties. Therefore, modeling carbon nanotube structures in a finite element package requires understanding regarding the properties and interactions of the C-C bonds. From the space-frame finite element model, different trends distinguished the stress output between armchair and zigzag carbon nanotubes. In addition, correlations between the



Figure 4.8: Tensile loading on SWCNTs (5,5) to (12,0) for the finite element simulations of the space-frame structure.

SWCNT	Elements with σ_{axial}^{\max}	Average $\sigma_{axial}^{\max} \times 10^7 (\text{kg}/\text{\AA s}^2)$
(5,5)	174,290	2.88
(7,7)	254-278,384	1.45
(10, 0)	363 - 380, 578	0.93
(12, 0)	628-630, 640-665	0.88

Table 4.5: Tabulated results for the average maximum stresses obtained from the different finite element simulations for SWCNTs (5,5) to (12,0)

SWCNT diameter and axial stress were identified. For this reason, employing uniform hollow cylinders to represent carbon nanotube structures does not adequately deliver the information regarding the stress distribution between bond interactions and the effects of these stresses in the whole system.

4.3 Loading by bending via linear model

For this finite element study, SWCNTs (7,7) and (12,0) are modeled in ANSYSTM under fixed-free boundary conditions. The structures are simulated experiencing flexure loads to determine the maximum axial stress distribution in the carbon nanotubes under these conditions. The flexure loads, as displayed in Fig. 4.17, are created by imposing a counterclockwise moment about the x-axis at the free end of the structure while restricting all degrees of freedom at z = 0. The nanotubes are modeled as space-frame continuum



Figure 4.9: Scheme of a hexagon cell resembling an armchair (n, n) and a zigzag (n, 0) nanotube orientation.

Thickness	t:L
0.500 [8]	0.352
0.660 [9]	0.465
0.750 [11]	0.528
0.890 [10]	0.627
1.470 [12]	1.035

Table 4.6: Values for the t:L ratio used in the different finite element cases for SWCNTs (5,5)-(12,0)



Figure 4.10: Maximum axial stress response as a function of elements for SWCNT (5,5). The maximum stress output is plotted for (a) t=0.50 Å and (b) t=0.66 Å.



Figure 4.11: Maximum axial stress response as a function of elements for SWCNT (5,5). The maximum stress output is plotted for t=0.75 Å.

structures for which five different case studies are compared through variations of geometric parameters, flexural modulus and bending loads. The flexural moduli for these simulations are obtained from the strain energy relations determined in Eqn. 4.2.

The different case studies are indicated in Table 4.2 for which the results are plotted in Figs 4.18–4.23. The goal of these simulations is to understand the characteristic of two different types of SWCNTs under flexural loading through the calculations of the maximum axial stresses as functions of the structure's elements.

The behavior of SWCNT (7,7), as described in Figs. 4.18–4.20, for the different case studies presents the same trend of behavior observed in all plots. There are two critical areas with high stress peaks, pk1 and pk2, tabulated in Table 4.7. The critical high stresses are affecting the same elements in the structure; that is, element range 250–285 and 375–400 approximately. The peaks, as expected, are caused by the highest load applied $M_{10} = 6.85 \times 10^{-10} \text{ kg Å}^2/\text{ s}^2$ from Fig. 4.17.

As noticed in the tensile load case, there is also an inverse proportionality presented between the axial stress output and the thickness of the C-C bond. However, in this case



Figure 4.12: Maximum axial stress response as a function of elements for SWCNT (5,5). The maximum stress output is plotted for (a) t=0.89 Å and (b) t=1.47 Å.



Figure 4.13: Maximum axial stress response as a function of elements for SWCNT (7,7). The maximum stress output is plotted for (a) t = 0.50 Å and (b) t = 0.66 Å.



Figure 4.14: Maximum axial stress response as a function of elements for SWCNT (7,7). The maximum stress output is plotted for t=0.75 Å.

the highest stresses occurred for two simulation case studies at t = 0.50 Å and t = 0.66 Å in Figs. 4.18(a)-(b), where the stress peak values are almost identical. Furthermore, there is a significant drop in the stress values from models employing t = 0.66 Å to t =0.75 Å, as noted in Fig. 4.19(a) having peak values $pk1 \sigma_{\text{max}}^{axial} \approx 2.34 \times 10^{-8} \text{ kg/ Å s}^2$ and $\sigma_{\text{max}}^{axial} \approx 1.54 \times 10^{-8} \text{ kg/ Å s}^2$. This abrupt jump validates the importance of identifying the proper characteristics to model C-C bonds in the space-frame structure through finite element analysis. Although the difference between t values is 0.09, the impact of the stress responses in the structure remains very significant as observed in the axial stress values found in Table 4.7.

The lowest stress peak values $\sigma_{\text{max}}^{axial} = 0.30 \times 10^{-8} \text{ kg/ Å s}^2$ and $\sigma_{\text{max}}^{axial} = 0.20 \times 10^{-8} \text{ kg/ Å s}^2$ are found in the simulations using t = 1.47 Å as displayed in Fig. 4.20. The same case is observed for the tensile load in SWCNT (7,7). Comparing the axial stress output of SWCNT (7,7) due to tensile and bending loads, the peak stress values are concentrated in the same range of elements. The pattern is noted in Figs. 4.13–4.15 and Figs. 4.18–4.20. Therefore, the different loading type conditions observed for the maximum element stress



Figure 4.15: Maximum axial stress response as a function of elements for SWCNT (7,7). The maximum stress output is plotted for (a) t = 0.89 Å and (b) t = 1.47 Å.



Figure 4.16: Maximum stress distribution as a function of elements for SWCNT (12,0) considering the case for t=0.66Å.

distributions are located in the same critical areas of the structure. The distribution of the stress output throughout the entire carbon nanotube remains constant.

The stress distribution presented in SWCNT (12,0), as plotted in Figs. 4.21–4.23 presents two distinctive stress peak values caused by the bending moment M_{10} , as in SW-CNT (7,7). The elements affected by these high peak stress values range between element numbers 200–250 and 600–675 approximately for the five case studies. The highest stress peaks are obtained for the case t = 0.50 Å (Fig. 4.21(*a*)) while the lowest stress peaks remain for t = 1.47 Å (Fig. 4.23). In this way, the inverse proportionality between axial stress output and C-C bond is also applicable for these cases. Furthermore, a significant jump in the peak stress values is observed between t = 0.50 Å and t = 0.66 Å for the bending load as displayed in Figs. 4.21(*a*)–(*b*). When compared to the tensile load cases, the stress differences between the two cases deliver similar results.

Thus, both types of carbon nanotubes responded similarly to bending loads regardless of their chirality. Similar stress distributions were obtained from these simulations in terms of the C-C bonds comprising the structure. At the same time, the variations of the C-Cbond thickness also poses a problem for this type of loading conditions. As in the tensile load cases, there is a need to acquire better accuracy in the values that will be able to



Figure 4.17: Plot of moment input array to cause flexural loading at end of the space-frame SWCNTs (5,5) to (12,0).

Thickness (Å)	$pk1, pk2 \sigma_{axial}^{\max} \times 10^8 (kg/ \text{ Å s}^2)$	Elements with σ_{axial}^{\max}
0.500	7.98, 5.23	258, 382
0.660	7.97, 5.21	258, 382
0.750	2.34, 1.54	258, 382
0.890	1.40, 0.92	258, 382
1.470	0.30, 0.20	258, 382

Table 4.7: Tabulated peak stress data output for cases applying SWCNT (7,7) in ANSYSTM under bending loads.

accurately quantify the characteristics observed in the C-C bonds.

4.4 Loading by torsion via linear model

The last finite element analysis is conducted for SWCNTs (5,5) and (10,0). The structures are modeled in ANSYSTM under fixed-free boundary conditions. The carbon nanotubes are simulated by applying torsion loads at the end structure. The torsion loads, as plotted in Fig. 4.24, are caused by a counterclockwise moment about the z-axis. In this way, the maximum axial stress distribution of the carbon nanotubes is determined under these boundary conditions. The nanotubes are again modeled as space-frame structures



Figure 4.18: Maximum axial stress response as a function of elements for SWCNT (7,7). The maximum stress output is plotted for (a) t = 0.50 Å and (b) t = 0.66 Å.



Figure 4.19: Maximum axial stress response as a function of elements for SWCNT (7,7). The maximum stress output is plotted for (a) t = 0.75 Å and (b) t = 0.89 Å.



Figure 4.20: Maximum axial stress response as a function of elements for SWCNT (7,7). The maximum stress output is plotted for t = 1.47 Å.

Thickness (Å)	$pk1, pk2 \sigma_{axial}^{\max} \times 10^8 (kg/ \text{\AA s}^2)$	Elements with σ_{axial}^{\max}
0.500	7.58 - 5.30	218 – 240,665
0.660	3.30-2.32	218 – 240,665
0.750	2.25–1.58	218 - 240,665
0.890	1.35 - 0.95	218 - 240,665
1.470	0.30-0.22	218 – 240, 629

Table 4.8: Tabulated peak stress data output for cases applying SWCNT (12,0) in $ANSYS^{TM}$ under bending loads.



Figure 4.21: Maximum axial stress response as a function of elements for SWCNT (12,0). The maximum stress output is plotted for (a) t=0.50 Å and (b) t=0.66 Å.



Figure 4.22: Maximum axial stress response as a function of elements for SWCNT (12,0). The maximum stress output is plotted for (a) t=0.75 Å and (b) t=0.89 Å.



Figure 4.23: Maximum axial stress response as a function of elements for SWCNT (12,0). The maximum stress output is plotted for t=1.47 Å.

for which five different case studies are compared through variations of the geometric parameters, torsional modulus and loading caused by a moment about the z-axis. The flexural moduli for these simulations are obtained through strain energy relations from Eqn. 4.3. The different case studies are indicated in Table 4.2 for which the results are plotted in Figs. 4.25–4.30. The goal of these simulations is to understand the characteristic of two different types of SWCNTs under torsional loading in order to calculate the maximum axial stresses generated for each C-C bond represented by elements.

The results gathered from SWCNTs (5, 5) display two distinctive peaks of maximum stress values conformed by a total of 38 elements. The highest maximum stress peak values are obtained for the case t = 0.50 Å as shown in Fig. 4.25(*a*) followed by a decay of the peak stress values for t = 0.66 Å until very low peak stresses are determined for the case t = 1.47 Å in Fig. 4.27. The peaks observed in these simulations are similar to those found in the finite element analysis undergoing tensile loads. The values of the maximum stress peak values are documented in Table 4.9.

The main remark observed for the maximum axial stress outputs found in SWCNT (5,5)

emphasizes on the inverse proportionality between the C-C bond thickness and the maximum stress distribution of the carbon nanotube structure. This assumption is sustained for the tensile and bending load cases. When comparing the stress peak outputs between Figs. 4.25–4.27, the continuous decay of the peak values are clearly displayed in the plots.

At the same time, the case for SWCNT (10,0), shown in Figs. 4.28–4.30, presents a similar outcome to the outputs described in SWCNTs (5,5). In these cases, the peak stress values range from $\sigma_{\text{max}}^{axial} = 1.32 \text{ kg}/\text{ Å s}^2$ for the case t = 0.50 Å to $\sigma_{\text{max}}^{axial} = 0.0531 \text{ kg}/\text{ Å s}^2$ for the case t = 1.47 Å. The stress has dropped significantly when comparing the limiting values.

The main observation regarding the axial stress output to torsion loading refers to the applicability of the correlation between C-C bond thickness and axial stress output. As in the previous models considering tension and bending load, the assumption indicating inverse proportionality between the thickness and the maximum axial stress is sustained for the torsion load cases. For these particular simulations, the decline of the peak stress values continue through the rest of the simulations for both SWCNTs. The results of the peak values are logged in Tables 4.9 and 4.10.

An important difference between armchair (5, 5) and zigzag (10, 0) involves the amount of elements subjected to the peak maximum axial stresses. As mentioned earlier, an approximate total of 38 elements are subjected to the two peaks characterizing SWCNTs (5, 5)for all the five cases. However, for SWCNT (10, 0) only a total of 16 elements are subjected to the peak stress values. For the case of the finite models undergoing bending loads, the amount of elements enduring peak stress values was very different between armchair and zigzag carbon nanotubes. For this type of analysis, SWCNT (7, 7) involved approximately 28 elements in the peak stress outputs, while SWCNT (12, 0) comprised approximately 58 elements for the two peak values. This presents a very contradictory result regarding the response of armchair and zigzag carbon nanotubes, which suggests that there is no association between the chirality of the nanotube and the type of loading applied under fixed-free boundary conditions.

Consequently, the analysis of the nanotubes under torsional loading contributes to a better understanding of the characteristics of the structure which are quantified by the input



Figure 4.24: Torsional loading values for SWCNTs (5,5) and (10,0) input in ANSYSTM finite element simulations [7].

Thickness (Å)	$pk1, pk2 \sigma_{axial}^{\max} (kg/ \text{\AA s}^2)$	Elements with σ_{axial}^{\max}
0.500	1.39, 1.62	91–99, 171–201
0.660	0.602, 0.707	91–99, 171–201
0.750	0.409, 0.483	91 - 99, 171 - 201
0.890	0.243, 0.291	91 - 99, 171 - 201
1.470	0.0524, 0.0664	91–99, 171–201

Table 4.9: Tabulated data output from case studies of SWCNT (5,5) in ANSYSTM.

parameters and the effects of the elements (C-C bonds) under torsional loading. Along with tension and bending finite element models, the simplified models and its assumptions provided more information regarding the variability of the bond characteristics as well as the modulus. Nevertheless, the response of the carbon nanotube structures establishes the need for a mechanical representation, such as the space-frame model, to be employed as a configuration of carbon nanotube structures when performing finite element calculations.

Following the study of SWCNTs through finite element analysis employing space-frame structures, a graphical representation of the strain effects is also reported in the following section of this chapter. For these results, SWCNTs (5,5) in tension, SWCNT (7,7) in bending, and SWCNT (10,0) in torsion are displayed in the deformed state.



Figure 4.25: Maximum axial stress response as a function of elements for SWCNT (5,5). The maximum stress output is plotted for (a) t=0.50 Å (b) t=0.66 Å.



Figure 4.26: Maximum axial stress response as a function of elements for SWCNT (5,5). The maximum stress output is plotted for (a) t=0.75 Å (b) t=0.89 Å.



Figure 4.27: Maximum axial stress response as a function of elements for SWCNT (5,5). The maximum stress output is plotted for t=1.47 Å.

Thickness (Å)	$pk1, pk2 \sigma_{axial}^{\max} (kg/As^2)$	Elements with σ_{axial}^{\max}
0.500	1.32, 1.28	374,579
0.660	0.575, 0.556	374,579
0.750	0.393, 0.378	374,579
0.890	0.236, 0.226	374, 579
1.470	0.0531, 0.0493	374,579

Table 4.10: Tabulated data output from case studies of SWCNT (10,0) in $ANSYS^{TM}$.



Figure 4.28: Maximum axial stress response as a function of elements for SWCNT (10,0). The maximum stress output is plotted for (a) t=0.50 Å (b) t=0.66 Å.



Figure 4.29: Maximum axial stress response as a function of elements for SWCNT (10,0). The maximum stress output is plotted for (a) t=0.75 Å (b) t=0.89 Å.



Figure 4.30: Maximum axial stress response as a function of elements for SWCNT (10,0). The maximum stress output is plotted for t=1.47 Å.

4.5 Graphical representation of the strain effects for the space-frame model

An example of the case studies performed for SWCNTs (5,5), (7,7), and (10,0) are employed to graphically represent the strain distribution, specifically for the thickness t = 0.66 Å. Figs. 4.31(a)-(c) are the strain outputs reflected in the finite element models. For the case of SWCNT (5,5) in tension, the peaks observed in Fig. 4.10(a) are not clearly distinguished in Fig. 4.31(a) since all the higher strains are represented by the color red. However, when comparing the information from both graphical representations and magnifying the output in ANSYSTM, the strain peak ranges are located close to the tension load in the structure. The calculated maximum strain value for this case is $\varepsilon_{xx} = 0.259 \times 10^{-8}$. Strain response behaviors are also observed for the cases of bending and torsion. Both cases present maximum strains close to the load end. For the case of bending, maximum strain values are located at the top surface of the SWCNT as observed in Fig. 4.31(b) depicted by the color yellow. The maximum strain value for this case is $\varepsilon_{xx} = 0.205 \times 10^{-12}$. For the case of torsion, the structure deformation behavior starts approximately from the middle to the load end of the structure. This is observed in Fig. 4.31(c) by the diameter increment of the carbon nanotube. In addition, the average strain values are observed for C-C links positioned perpendicular to the torsion load, as these elements are depicted by the color green. The maximum strain value is also located close to the load and the strain value obtained is $\varepsilon_{xx} = 0.178 \times 10^{-8}$.

The outputs for the maximum stress distribution for all space-frame models as well as the graphical representation of the strain behavior in the structure reinforce the relevance of understanding the behavior and response of the carbon nanotube structures when undergoing different types of loading. All three samples behave differently. This is observed in the stress distribution plots as well as the GUI strain plots.

Following the study of SWCNTs through finite element analysis employing space–frame structures, a continuum model is developed also in ANSYSTM for the next section of this chapter. The solid hollow cylinder model complies with stress-strain curves determined through molecular dynamics by Ogata et al. [13]. Thus, the simplified model analyzes the elastic and plastic behavior of the continuum carbon nanotube representation to follow the deflection of the model undergoing a tension load.

4.6 Loading by tension via the multilinear elastic model

Continuum schemes of the carbon nanotubes are specified in ANSYSTM. The models are defined as having multilinear elastic behavior, which implies a path independent response in which unloading follows the same stress-strain path as loading (see Fig. 4.6). The conservative material model, similar to the multilinear isotropic hardening option, allows for the appropriate use of large step loads [7]. The models are created as specified in Fig. 4.7. Using experimental data from Ogata et al. [13], SWCNTs (8,0), (8,8), (9,0) and (10,0) are simulated as hollow cylinders under fixed-free boundary conditions. These are then subjected to axial tension for comparison and observation of the elastic and plastic behavior.



Figure 4.31: Results graphically representing the elastic strain in ANSYSTM for (a) SWCNT (5,5) in tension, (b) SWCNT (5,5) in bending, and (c) SWCNT (10,0) in torsion. All these cases are for t=0.66 Å.

4.6.1 Specifications of the SWCNT setup using ANSYSTM

The carbon nanotubes are modeled while keeping in mind an approximate length for a SWCNT configuration range of 200–250 atoms. The length varies slightly depending on the chirality and number of atoms conforming the structure. The element selected for this simulation is SOLID45¹, as specified in [7]. The solid structure is meshed keeping in mind the length of the hexagon as displayed in Fig. 4.33. Nevertheless, for SWCNTs (9,0) and (10,0), the *hex_length* is selected to be larger to prevent wedge formation during meshing at the edges of the structure. This decision guarantees no distortion in the system. An example of the meshed continuum model with appropriate boundary conditions is displayed in Fig. 4.34. The density ρ and Poisson's ratio ν are the same as the space-frame model, that is, $\rho = 2.68 \times 10^{-27} \text{ kg}/\text{Å}^3$ and $\nu = 0.190$.

A total of 19 ANSYSTM simulations are generated. The material geometric parameters are specified employing data from Chen and Cao [8], Yakobson et al. [9], Kudin et al. [10], Pantano et al. [11], and Tserpes and Papanikos [12] as in the space-frame model. Tabulated data of these runs are displayed in Tables 4.11–4.14. The multilinear material behavior displayed in Fig. 4.6 is employed for the finite element analysis to model the elastic and plastic behavior. The stress-strain curves are obtained through molecular dynamic simulations by Ogata et al. [13].

The simulations are done under a static analysis and the force is applied through loadsteps until reaching convergence of the structure. The axial loading F_z for SWCNTs (8,0) and (8,8) are constant throughout the nine different schemes. The loading F_z applied for the SWCNTs (9,0) and (10,0) increases proportionally with the thickness of the structure. The purpose of these loading variations are to study the linear and nonlinear deflections of the nanotube structure through the elastic and plastic behavior of the different SWCNT structures.

The loading specifications are displayed in Fig. 4.35. For the SWCNTs (8,0) and (8,8), the tension applied to the structure is constant at $F_z = 80 \text{ kg}/\text{ Å s}^2$ in all the case studies. The loads applied to nanotubes (9,0) and (10,0) are variable for each case study since the

¹Details of the SOLID45 properties are found in Section 4.1.

increment of the thickness ranging from t = 0.50 Å to t = 1.47 Å requires higher applied loads to cause nonlinear effects in the model. The loads for all cases are applied in 100 load steps. In addition, the small increments do not cause any distortion in the model. In this way, the elastic–plastic phase of the SWCNTs are graphically analyzed. The elastic– plastic region refers to an intermediate state where the deflections are not entirely elastic or entirely plastic since both effects are present. The output explained in the following sections of this chapter refer to the deflection as well as the stress-strain response of the SWCNT continuum models.

4.6.2 Deflection output of the continuum models

The linearity of the deflections observed in Figs. 4.36-4.37 is indicative of the model's elastic behavior for SWCNTs (8,0) and (8,8). The deflections observed in both models are different given that SWCNT (8,0) displaces approximately twice as much as SWCNT (8,8). Through the multilinear model and the input characteristics from stress-strain relations [13], the variability of the force and displacement response between armchair (8,8) and zigzag (8,0) are validated. In this way, a continuum model is useful since it complies to the criteria of the input stress-strain multilinear scheme determined through first principles. Without the input stress-strain parameters, the continuum models for SWCNTs (8,0) and (8,8) would have not presented significant differences in their response values expected for zigzag and armchair carbon nanotubes.

For the continuum model, the cross-sectional differences, which can be deduced from Tables 4.11-4.12, between zigzag SWCNT (8,0) and armchair SWCNT (8,8) also contribute to the displacement differences of the structure in the z direction. In general, all the deflection outputs gathered from these structures reveal that regardless of the thickness range assumed from t = 0.50 Å–0.89 Å, the higher displacements are observed for SWCNT (8,0). Nevertheless, there are no correlations identified between the thicknesses assumed and the displacements u_z . From Fig. 4.36, t = 0.66 Å output the highest deflection in SWCNT (8,0) while t = 0.89 Å remains the lowest. On the other hand, Fig. 4.37 shows that for SWCNT (8,8), the highest deflections are obtained for t = 0.50 Å and t = 0.66 Å, whereas the lowest values are found at t = 0.75 Å. Consequently, the continuum model employed for these mechanical analysis lacks information concerning the bond characteristics and its effects when undergoing tension.

Continuing to the structures (9,0) and (10,0), higher load steps are considered for each different thickness case to observe nonlinearity responses in terms of the displacement and force in the z direction. The loads considered varied depending on the thickness to achieve nonlinear behaviors in the structure. Figs. 4.38–4.39 explicitly display the nonlinear deflections of SWCNT (9,0) and (10,0). The larger displacements for SWCNT (9,0) are observed for the cases t = 0.50 Å and t = 1.47 Å at $u_z \simeq 7.00$ Å. SWCNT (10,0) presents the largest displacement also for the case t = 1.47 Å at $u_z \simeq 7.00$ Å; however, for t = 0.89 Å deflections remain linear. Thus, plasticity behavior is achieved through these nonlinearities but there are no correlations between the load increments and the different thicknesses employed in the ANSYSTM models.

4.6.3 Stress-strain analysis of the single-walled carbon nanotube

Elastic behavior of SWCNTs (8,0), (8,8), (9,0), and (10,0) are displayed in Figs. 4.40– 4.41. The structures (8,0) and (8,8) present a maximum elastic strain for the load condition specified at approximately 6%, both for the case t = 0.50 Å. The highest elastic strain response for SWCNT (8,0) remains closely at 6% for the five different thicknesses applied. On the other hand, the maximum elastic strains for SWCNT (8,8) are inversely proportional to the thickness of the C-C bond as presented in Table 4.15. The case for t = 1.47 Å is not considered for SWCNT (8,8) since the mesh imposed to represent the C-C hexagon ring produced distortion in the model, which incur erroneous calculations in the finite element analysis. SWCNTs (9,0) and (10,0) show maximum elastic strains at approximately 13%. No inverse correlation is observed between the thickness and the elastic strain of the different simulation cases. The largest strains are presented at t = 1.47 Å for SWCNT (9,0) and at t = 0.50 Å for SWCNT (10,0).

Although the multilinear model imposed in the finite element method is obtained from molecular dynamic simulations by Ogata et al. [13], the lack of information regarding the C-C bond properties in these models question the accuracy of the output obtained from the multilinear model. On the other hand, the adopted space-frame model continuously demonstrates a correlation between the stress response of the nanotube and the thickness of the C-C bond which strengthens the validity of the model.

The thicknesses assumed for these simulations are within a range of 0.50 Å-1.47 Å. Nevertheless, other sources [24, 44, 50] assumed an approximate thickness of 3.40 Å, which can alter significantly the axial stress output. For this work, the latter thickness is not assumed since the modeling is performed in a finite element package (ANSYSTM). The reason for such thickness relies on the distance between stacked graphite sheets [1], taking into consideration the electron interaction potential and its effects on the structure. These conditions can be assumed in a molecular dynamic simulation, but not in finite element analysis. Therefore, modeling a structure in molecular dynamics and in a finite element software cannot be equally represented from a physical perspective. The modeling parameters should be considered accordingly as it is attempted in this current work.

The plasticity effects are highlighted in Fig. 4.42 for SWCNTs (9,0) and (10,0). For both structures the higher plastic strain values occurred for thicknesses t = 0.50 Å and t = 1.47 Å. SWCNT (9,0) presented higher average plastic strain and stress values at approximately $\varepsilon_{zz}^{pl} = 2.65\%$ and $\sigma_{zz}^{pl} = 10.4$ kg/Å s² for the cases simulated under the same loading conditions. There is no correlation observed between the C-C bond and the strain of the structure. This is corroborated through the similar behavior observed in SWCNT (10,0). In this structure, the higher strain values also occurred for thicknesses t = 0.50 Å and t = 1.47 Å. The higher average strain and stress values are $\varepsilon_{zz}^{pl} = 3.40\%$ and $\sigma_{zz}^{pl} = 9.82$ kg/Å s². In both models the parameters specified from Kudin et al. [10] (t = 0.89 Å) presented only elastic behavior regardless of the specified loading conditions.

The observed elastic and elastic-plastic behaviors from these structures largely depend on the nonlinear specifications input in the model used in the ANSYSTM software. For the multilinear model, the density functional theory is considered for the determination of the mechanical properties of the SWCNTs; however, there are other methods including tightbinding and Hartree–Fock, which can explore the nonlinear behavior of these structures. The key is to find consistency within these methods. At the same time, the geometric modeling requires to be more specific as well as consistent to develop a reliable model as observed in the space-frame structure. Assuming a constant thin hollow cylinder is



Figure 4.32: Stress-strain curve obtained computationally from molecular dynamics using Density Functional Theory in VASPTM software.

not sufficient to physically simulate and visualize the mechanical differences within the parameters assumed for the SWCNT structure. Moreover, the large range of the thickness values, densities, and Poisson's ratios also poise a problem when representing the structure in ANSYSTM finite element software since it strengthens error in the results and hinders the optimization of a reliable structural design.

Concluding the study regarding the mechanical properties of the specified SWCNTs, the following chapter focuses on the analysis of the electrical properties, specifically the electrical conductivity presented in the SWCNT structures. To perform these calculations, molecular dynamic simulation is employed for different SWCNT configurations and chiralities.

CNT (8,0) in Tension					
EX $(kg/ Å s^2)$	77.8475				
Author	Tkx=Tky(Å)	radius $\phi_i(\text{\AA})$	radius $\phi_o(\text{\AA})$	length(Å)	
Chen & Cao [8]	0.500	3.1355	3.6355	42.00	
Yakobson et al.	0.660	3.1355	3.7955	42.00	
[8], [9]					
Kudin et al. [8],	0.890	3.1355	4.0255	42.00	
[10]					
Pantano et al. [8],	0.750	3.1355	3.8855	42.00	
[11]					
Tserpes et al. [8],	1.470	3.1355	4.6055	42.00	
[12]					

Table 4.11: Input parameters for simulations of CNT (8,0) used in $ANSYS^{TM}$.

CNT (8,8) in Tension					
EX $(kg/ Å s^2)$	76.9856				
Author	Tkx=Tky (Å)	radius ϕ_i (Å)	radius ϕ_o (Å)	length(Å)	
Chen & Cao [8]	0.500	5.4240	5.9240	23.39	
Yakobson et al.	0.660	5.4240	6.0840	23.39	
[8], [9]					
Kudin et al. [8],	0.890	5.4240	6.3140	23.39	
[10]					
Pantano et al. [8],	0.750	5.4240	6.1740	23.39	
[11]					

Table 4.12: Input parameters for simulations of CNT (8,8) used in ANSYSTM.

CNT (9,0) in Tension					
EX $(kg/ Å s^2)$	77.9894				
Author	Tkx=Tky(Å)	radius $\phi_i(\text{\AA})$	radius $\phi_o(\text{\AA})$	length(Å)	
Chen & Cao [8]	0.500	3.523	4.023	41.97	
Yakobson et al.	0.660	3.523	4.183	41.97	
[8], [9]					
Kudin et al. [8],	0.890	3.523	4.413	41.97	
[10]					
Pantano et al. [8],	0.750	3.523	4.273	41.97	
[11]					
Tserpes et al. [8],	1.470	3.523	4.993	41.97	
[12]					

Table 4.13: Input parameters for simulations of CNT (9,0) used in $ANSYS^{TM}$

CNT (10,0) in Tension					
EX $(kg/ Å s^2)$	88.2318				
Author	Tkx=Tky(Å)	radius $\phi_i(\text{\AA})$	radius $\phi_o(\text{\AA})$	length(Å)	
Chen & Cao [8]	0.500	3.914	4.414	41.96	
Yakobson et al.	0.660	3.914	4.574	41.96	
[8], [9]					
Kudin et al. [8],	0.890	3.914	4.804	41.96	
[10]					
Pantano et al. [8],	0.750	3.914	4.664	41.96	
[11]					
Tserpes & Pa-	1.470	3.914	4.384	41.96	
panikos [8], [12]					

Table 4.14: Input parameters for simulations of CNT (10,0) used in $ANSYS^{TM}$



Figure 4.33: Scheme of the hexagonal unit cell for the space frame representation and the unit cell brick resulted from the volume mesh in the continuum model.



Figure 4.34: SWCNT represented as a continuum model with fixed-free boundary conditions under axial tension.


Figure 4.35: Loading conditions for the SWCNT structures simulated in the continuum multilinear elastic model in $ANSYS^{TM}$.

t	$\% \varepsilon_{elastic}$
0.50	6.1
0.66	4.5
0.75	4.0
0.89	3.4

Table 4.15: Maximum elastic strain percent results obtained for different carbon nanotube thicknesses for the case of SWCNT (8,8).



Figure 4.36: ANSYSTM plot results of linear deflections (elastic regime) as a function of the reaction force in the z direction for SWCNT(8, 0).



Figure 4.37: ANSYSTM plot results of the linear deflections (elastic regime) as a function of the reaction force in the z direction for SWCNT (8,8).



Figure 4.38: ANSYSTM plot results of the nonlinear deflections (elastic and plastic regime) as a function of the reaction force in the z direction for SWCNT (9, 0).



Figure 4.39: ANSYSTM plot results of the nonlinear deflections (elastic and plastic regime) as a function of the reaction force in the z direction for SWCNT (10, 0).



Figure 4.40: ANSYSTM stress-strain behavior of the nodal solution in the elastic regime for (a) SWCNT (8,0) and (b) SWCNT (8,8) under tensile load-step.



Figure 4.41: ANSYSTM stress-strain behavior of the nodal solution in the elastic regime for (a) SWCNT (9,0) and (b) SWCNT (10,0) under tensile load-step.



Figure 4.42: ANSYSTM stress-strain behavior of the nodal solution in the plastic regime for (a) SWCNT (9,0) and (b) SWCNT (10,0) under tensile load-step.

Chapter 5

Molecular dynamic simulation results using Gaussian

Aside from the mechanical properties of SWCNTs explored in the previous chapter, there is a great motivation to determine the electrical properties of SWCNTs; that is, regarding the electrical conductivity of the structure. For this reason, semiconductor and metallic SWCNTs are generated through Gaussian 03^{TM} [23] in order to identify computationally the key properties and main differences between the behavior of metallic and semiconducting SWCNTs. Additionally, different configurations are simulated, specifically triangular lattices and curved carbon nanotubes, so as to observe the variability of the electrical properties through these arrangements in the structures.

5.1 Energy dispersion for metallic and semiconductor SWCNTs

For the electronic properties of SWCNTs, a wide range of the structures are simulated in Gaussian 03^{TM} . The main objective of these simulations rely on analyzing the electrical conductivity of the SWCNTs in terms of the band structure and density of states. In this way, infinite SWCNTs versus complex configurations of SWCNTs may be compared to study the changes in the conductivity characteristics. Simulated SWCNTs are listed in Table 5.1.

The isolated SWCNTs are modeled as having infinite length for the Gaussian03TM simulations. The number of atoms per structure vary according to the chirality of the carbon nanotube. Nevertheless, carbon nanotubes are not simulated above 300 atoms due to computational limitations. All calculations are performed using DFT-LSDA as well as assuming a 3-21G* basis set. DFT refers to Density Functional Theory, which is a ground-state theory used in first-principle calculations assuming the electronic structure of many-body systems and the optimization of the ground state energy. In turn, LSDA

approximates the ground state energy through the assumption of an exchange-correlation term so that it results in a good estimate of energy minimization. Illustration of these structures are displayed in Figs. 5.1(a)–(h). The more complex configurations include triangular lattices of infinite length for SWCNT (5,5) and (5,0), finite SWCNT (5,5) with curvature $\rho = 50$ Å, and infinite impure SWCNTs (5,0) and (5,5) with carboxyl groups attached. These schemes are shown in Figs. 5.2(a)-(d).

The total energy per atom of the carbon nanotubes are obtained, as displayed in Fig. 5.3. The energy per atom remains stable at around $E \approx -1020 \,\text{eV}$; however, it drops significantly for the triangular lattice configuration of SWCNT (5,5) as well as for impure SWCNTs (5,0) and (5,5) with attached carboxyl groups. The energy change presented in the triangular lattice is not expected since the model encompasses three infinite and straight SWCNTs, more specifically SWCNTs (5,5). Nevertheless, the result demonstrates that network of nanotubes hinder their electrical capabilities when compared to the results from the isolated models. For the case of impure SWCNTs, the functionalization of these structures also affects the stability of the energy minimization which originates a change in the conductivity of the system.

On the other hand, the curvature nanotube (5,5) as displayed in Fig. 5.2(b) does not display an effect in the total energy per atom on the system. That is, the curvature imposed on the structure does not cause instability in the strained SWCNT. Nevertheless, it has been found from scanning electron microscope (SEM) that twisting maximize the bonding interactions [51]. The energy minimization of the system would have not converged to produce a solution. It can be speculated that the strained atoms in the structure were only close to the instability limit since convergence of the simulation required more computation time when compared to its corresponding straight SWCNT. Therefore, a more prominent curvature requires the evaluation of an optimal length proposed for C-C bonds in the system to guarantee adequate energy minimization and, in turn, convergence of the system.

The overall results demonstrate the relevance of imperfections presented in SWCNTs as well as the need to produce highly purified nanotubes that may adequately improve conductivity [1, 20, 52, 53]. In this manner, the applications of nanotube meshes can be controlled and manipulated to the functions of the system.

5.1.1 Energy bands

Energy bands are calculated for **N** wave vectors $\mu \mathbf{K}_1$ where $\mu = 0, ..., N - 1$. N discrete **k** vectors in the circumferential direction are produced. In this way, for each μ discrete value there is a 1D electronic band [51].

The metallic conduction in carbon nanotubes occurs when **k** wave vectors pass through the K-point of the 2D Brillouin zone. As the nanotube increases, there are more wave vectors for the circumferential direction that causes the band gap to disappear. Therefore metallic SWCNTs present a distinctive pattern in the band structure as observed in Figs 5.4-5.6. To produce the band structures from Gaussian03TM output, a MATLABTM [54] code is generated to display the bands for the carbon nanotube structures. The simulated metallic nanotubes contain virtual and occupied bands which overlap each other across their fermi level, E_F . This is clearly observed for SWCNTs (5,5), (9,0) and (9,9) in Figs. 5.4-5.5 For the case presented in SWCNT (30,0) in Fig. 5.6, both band types convene at E_F as well despite the pronounced gap observed with the increment number of k points.

The band structure pattern for semiconductor SWCNTs presents a gap between the virtual and occupied bands which can be manipulated through temperature changes. However, the simulations performed in Gaussian03TM are assuming 0 K. The band structure is corroborated through Fig. 5.8 for SWCNT (7,0) and (10,0). As expected in the band structure of semiconductors, the virtual and occupied bands do not interact with each other. The gap observed is more prominent in SWCNT (10,0) which validates a possible correlation between chirality and semiconductivity. Nevertheless, there always exists a band gap to prevent delocalized electrons from transferring between bands. A noticeable difference is observed between the band gaps generated from semiconductor triangular lattice (5,0) and SWCNTs (7,0) and (10,0). The gap observed in Fig. 5.7 for triangular lattice (5,0) is very minimal which demonstrates instability in its conductivity properties. This may be caused by the electron interactions between surrounding neighbor unit cells in the triangular lattice as displayed in Fig. 5.2(a), which attract neighbor electrons in the structure.

Band structure of impure SWCNTs (5,0) and (5,5) as displayed in Fig. 5.9 present small band gaps although SWCNT (5,5) is considered a metallic nanotube. The gap generated between the virtual and occupied bands in Fig. 5.9(b) is very minimal so the electronic conductivity properties are inconclusive from these results. Nevertheless, the addition of functional groups such as carboxyl groups causes the nanotube to respond differently to conductivity that can be verified through the electronic density of states (DOS).

In conclusion, the band structure of metal and semiconductor SWCNTs are identified and validated through the comparative behavior of both types of band structures. However, changes in configuration, imperfections and chirality play a role in the conductivity of the results as previously identified in the output models.

5.1.2 Electronic density of states (DOS)

The electronic DOS are generated for single-walled metallic and semiconducting nanotubes, as specified in Table 5.2. The DOS graphs are created through MATLABTM [54] and GaussSumTM [55], which read the output eigenvalues from the Gaussian03TM log file.

In general, defined van Hove singularities [56] are observed in the results represented by the peaks displayed in the Figs. 5.10–5.16. The singularities are caused by logarithmic peaks due to the existence of saddle points for each subband energy function. The band gap energy is calculated from the difference between the van Hove singularities. Moreover, the peaks represent critical points at which all derivatives vanish.

Comparing the semiconductor SWCNTs (5,0), triangular lattice (5,0), (7,0), and (10,0) in Figs. 5.10–5.15, the DOS Fermi energy level location are approaching zero. As a result, a gap is observed between the band energies of the structures. On the contrary, the metallic SWCNTs (5,5), triangular lattice (5,5), (7,7), (9,0), (9,9), (10,10), (15,15) and (30,0) in Figs. 5.11–5.16 display a nonzero Fermi energy level for DOS.

Fig. 5.12 displays the DOS for SWCNT (5,5) with curvature as well as graphite (5,5). The curved SWCNT exhibits some instability due to strain applied from the curvature. On the other hand, the 2D graphite layer is completely not strained. Nevertheless, the metallic behavior exhibited in both structures corroborates the experimental findings of Saito et al. [1], which indicates that the electronic conductivity of carbon nanotubes is dependent on the diameter and chiral angle since there is no difference in the C-C chemical bonding or any doping impurities. In this case, there will not be a significant difference

between rolling a graphite layer to create a (5,5) SWCNT and generating a curved (5,5) SWCNT.

The pronounced delimitations of the electronic conductivity of SWCNTs become more noticeable as the chirality configurations are of higher order. For instance, the gap present in nanotube (10,0) as shown in Fig. 5.15 is more prominent when compared SWCNT (7,0) in Fig. 5.13. In addition, the metallic characteristics are more prominent in SWCNTs (15, 15) and (30,0) displayed in Fig. 5.16. Generally, metallic energy bands are unstable due to Peierls distortion [1]. The Peierls distortion refers to the distortion of a regular one-dimensional structure with a partially occupied band to give bond alternation. Nevertheless, the Peierls gap is suppressed by increased carbon nanotube diameter, which causes the structure to quickly converge to zero energy gap as in graphite (Fig. 5.12(b)). These effects are clearly demonstrated through the DOS determined for SWCNTs (15,15) and (30,0) in Fig. 5.16.

The observed behavior of impure SWCNTs (5,0) and (5,5) in Fig. 5.9 due to attached carboxyl groups affect mostly the properties of nanotube (5,0) since both structures exhibit metallic behavior. The doping caused by the carboxyl groups clearly has an effect in the conductivity of both systems. Both structures portray metallic behavior which are reinforced by the addition of the carboxyl groups. The band structure results determined in the previous section were not conclusive; however, the DOS results clearly display the crossing of 1*D* energy bands at degenerate points in the structure. As pointed by Dresselhaus et al. [51], the isolated SWCNTs with no interstices behave differently from SWCNTs with interstices since it affects the stability due to absorbed dopants.

In conclusion, the band structure and DOS provide adequate information regarding the conductivity of the SWCNT structures as well as more complex geometric configurations. The results are not considering temperature changes; therefore, a temperature of 0 K is assumed. Nevertheless, this parameter may potentially enable changes in the conductivity of the systems. Moreover, important remarks can be deduced from these virtual experiments. First, stability of the structure are key to assure convergence of the calculations since curvature incites metallic behavior. Second, the chirality and diameter of the carbon nanotube is strongly correlated with the electronic conductivity of the structure.

SWCNT	Metallic	Semiconductor
(5,0)		\checkmark
(5,5)	\checkmark	
(7,0)		\checkmark
(7,7)	\checkmark	
(8,0)		\checkmark
(8,8)	\checkmark	
(9,0)	\checkmark	
(9,9)	\checkmark	
(10, 0)		\checkmark
(10, 10)	\checkmark	
(15, 15)	\checkmark	
(30, 0)	\checkmark	

Table 5.1: Tabulated scheme of the SWCNTs simulated using $Gaussian03^{TM}$.

DOS		
(5, 0)	(5,5)	
curved (5,5)	graphite	
(7,0)	(7,7)	
(9,0)	(9, 9)	
(10, 0)	(10, 10)	
(15, 15)	(30, 0)	

Table 5.2: Carbon nanotube cases for which DOS are generated using output from $Gaussian 03^{TM}$.

Finally, carbon nanotube doping- in particular carboxyl groups- increases conductivity in the structures. Therefore, these preliminary calculations regarding the electrical properties of carbon nanotubes demonstrate the need to simulate more complex configurations considering other parameters to establish a pattern of response regarding the electrical properties of these systems.



Figure 5.1: SWCNT models developed in Gaussian 03^{TM} . All straight nanotubes (a)-(h) are assumed to to have infinite length.



Figure 5.2: Configurations generated to determine band structure and density of states using Gaussian 03^{TM} for (a) SWCNT (5,0) triangular lattice, (b) curved (5,5) SWCNT, (c) SWNCT (5,0) with attached carboxyl group, and (d) SWCNT (5,5) with attached carboxyl groups.



Figure 5.3: Total energy per atom for all the different types of SWCNTs and SWCNT configurations.



Figure 5.4: Band structure of metallic SWCNT (5,5). The virtual and occupied bands are in contact with each other at the Fermi level.



Figure 5.5: Band structure of metallic SWCNTs (a) (9,0) and (b) (9,9). The virtual and occupied bands are in contact with each other at the Fermi level.



Figure 5.6: Band structure of metallic SWCNT (30,0). The virtual and occupied bands come in contact at the Fermi level.



Figure 5.7: Band structure of semiconductor (5,0) SWCNTs (triangular lattice). There exists a very minimal gap between the virtual and occupied bands at the Fermi level.



Figure 5.8: Band structure of semiconductors SWCNTs (a) (7,0) and (b) (10,0). A prominent gap between the virtual and occupied bands exist at the Fermi level.



Figure 5.9: Band structure determined from $Gaussian03^{TM}$ output for SWCNTs (a) semiconductor (5,0) and (b) metallic (5,5) with attached carboxyl groups.



Figure 5.10: DOS generated for semiconducting SWCNTs (a) (5,0) using GaussSumTM and (b) triangular lattice (5,0) using MATLABTM. The solid line represents the Fermi level.



Figure 5.11: DOS generated for metallic (a) SWCNTs (5,5) and (b) triangular lattice (5,5) using $GaussSum^{TM}$. The solid line represents the Fermi energy level.



Figure 5.12: DOS generated for (a) metallic SWCNT (5,5) with curvature and (b) graphite using GaussSumTM. The solid line represents the Fermi level.



Figure 5.13: DOS generated for SWCNTs (a) semiconductor (7,0) using MATLABTM and (b) metallic (7,7) using GaussSumTM. The solid line represents the Fermi level.



Figure 5.14: DOS generated for metallic SWCNTs (a) (9,0) using MATLABTM and (b) (9,9) GaussSumTM. The solid line represents the Fermi level.



Figure 5.15: DOS generated for SWCNTs (a) metallic (10,0) using MATLABTM and (b) semiconductor (10,10) using GaussSumTM. The solid line refers to the Fermi level.



Figure 5.16: DOS generated for metallic SWCNTs (a) (15,15) using GaussSumTM and (b) (30,0) using MATLABTM.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

The work accomplished in this research provides an overall analysis of the characteristics observed when the carbon nanotube structure is treated as a mechanical problem. Many challenges were met during this work due to the complexity of the model as well as the variability of the geometric and material parameters. One of the main obstacles in analyzing these structures was the lack of consistency regarding the properties of carbon nanotubes, particularly the elastic modulus, Poisson's ratio, moment of inertia, and C-Cbond length. For this reason, an adequate approach was selected from different criteria models. Ultimately, the approach by Chen and Cao [8], which models the C-C bond as beam elements, was employed and simulated through finite element methods.

When developing the space-frame finite element model, the main challenge relied on physically reproducing the nanotube at a nanoscale level in a finite element package. A major concern for this calculation approach was the error accumulation when configuring a nanoscale model using a finite element code. Nevertheless, the motivation to create the finite element model was to have a better understanding on the mechanical aspects of SWCNTs and their behavior under certain loading types and boundary conditions. The results obtained through the space-frame models revealed different and distinctive stress distributions presented in the carbon nanotube structures. When comparing the response of SWCNTs (5,5), (7,7), (10,0) and (12,0) under tension, as shown in Figs. 4.10–4.15 and Figs. A.1–A.6, armchair carbon nanotubes displayed the higher stress values. However, for the simulation runs performed in the same carbon nanotube, the stress calculations were very similar to each other when different parameters were applied. The intention of these simulations was to compare the element stress distribution responses of the same carbon nanotube applying different parameter sets, not to compare carbon nanotubes with different chiralities.

Important conclusive remarks can also be gathered from the application of different loading conditions to the space-frame model. The stress distribution of the carbon nanotubes could not be compared between the cases generated due to tension, bending, and torsion. The stress responses of these load types produced different deflection patterns in carbon nanotube structures. For instance, the element stress distribution of SWCNT (5,5) in Figs. 4.10 and 4.25 reiterate the importance of manipulating and controlling the nanotube's orientation. This may be accomplished by better understanding of the loading conditions in the system.

In addition, the models in the space-frame structure resembled that of a beam, except for the case when t = 1.47 Å [12], where the beam becomes a solid disk of constant thickness. The decision to assume this constant thickness in the simulation cases relied on modeling the structures within a wide range of input geometric values. As a result, the stress distribution obtained from this last model showed consistently lower stress values for all loading cases. This is very important since an inverse proportionality was observed between the thickness of the C-C bonds and the element stress distribution of the system.

The element strain distribution for all loading types was plotted for the space-frame model in ANSYSTM. Small strain value responses were identified for the cases of SWCNTs (5,5), (7,7), and (10,0). The deformations were plotted in Figs. 4.31(a)-(c) which showed small strain values ranging from $10^{-8}-10^{-12}$.

Meanwhile, the multilinear continuum system focused on modeling the elastic-plastic capabilities of the carbon nanotube structure. The input of the stress-strain values given by Ogata et al. [13] were for the entire carbon nanotube structure; therefore, the most adequate model was a continuous hollow cylinder. The space-frame model cannot assume these input parameters since the parameters specified are for the properties of C-C bonds. For the space-frame finite element model, values of stress, strain and effective elastic modulus needed to be specified, which physically differs from the multilinear continuum model. Moreover, a major obstacle in applying the multilinear case was observed during the meshing of the structure since meshing would cause collapse and severe structural deformation. Although it was possible to model and closely observe the response of SWCNTs to different loading conditions, there is a need for consistent mechanical parameters which will allow better approximations for models of higher complexity.

Finally, the electrical contribution of this research work focused on carrying out virtual experiments through molecular dynamic simulations to study the different electronic properties pertaining to infinitely straight, strained, impure and triangular configuration schemes of SWCNTs. The subsequent results demonstrated the dependency of carbon nanotubes to chirality, diameter, and doping as displayed in Figs. 5.10–5.16. The characteristic DOS for the doping nanotubes validated the importance of high purity structures, while the triangular configurations corroborated the property differences between isolated SWCNTs and SWCNT bundles.

In conclusion, the main objectives of the current research were accomplished. Many challenges in the configuration of the structure regarding the modeling as well as assumptions had to be overcome. Nevertheless, the results gathered through these analyses satisfied a study of great depth to better understand the properties and, in turn, future applicabilities of SWCNTs in science and technology.

6.2 Future work

There is still a need to develop a better understanding regarding the mechanical and electrical properties of carbon nanotubes. In order to interpret the complexity of these systems from a structural analysis perspective, the following models are proposed:

- A pre-stress finite element model can be applied to the space-frame scheme so that the interatomic forces between carbon atoms due to the π and σ orbitals of the atoms are considered. In this way, more detailed behavior regarding the delocalized electrons of the atoms would be quantified.
- A detailed stability analysis regarding the *C*-*C* bonds can be implemented to optimally model more stable carbon nanotube structures. The study may focus on optimization of the bond length and the application of these findings to the carbon structure.

- Molecular dynamic models can be compared with different functionalizations. In the current research only two models were considered, namely SWCNT (5,0) and (5,5) with carboxyl groups. Although these models provided information regarding impurities in the carbon structure, other groups should also be considered such as metals, amino acids, and fullerenes.
- Temperature variability can be introduced into the finite element and molecular dynamic models. It has been shown that temperature affects the electronic conductivity of semiconductor carbon nanotubes. As temperature effects are not considered in the current research, gradual changes in the structure to this parameter need to be addressed.
- Car-Parrinello molecular dynamic simulations should be conducted to determine the mechanical properties (elastic modulus) and conductivity characteristics of SWCNTs. The Car-Parinello approach is ideal for large unit cell systems such as nanotubes.

By including these considerations, an understanding of the C-C bond characteristics as well as optimal proposed SWCNT models can be developed for better applicability and optimal structure control.

Appendix A

Additional Results

A.1 Results for SWCNTs (10,0) and (12,0) undergoing tensile load

Additional results for the space-frame models are displayed in Figs. A.1–A.6. The maximum element stress distribution is determined under tension.

A.2 Maximum element stress outputs for SWCNTs (5,5)-(12,0)

The following tabulated data lists the maximum element stress outputs obtained for the case of tensile loading assuming a space-frame structure. The tensile load as well as the location of stress peaks are specified (see Tables A.1–A.4).

$\mathbf{SWCNT} \ (5,5)$			
Author	$\sigma_{\rm max}^{axial} imes 10^7 ({\rm kg}/{\rm \AAs^2})$	Tensile load	Element peak No.
Chen and Cao	3.9	F_4	174,290
Yakobson et al.	1.7	F_4	174,290
Pantano et al.	1.2	F_4	174,290
Kudin et al.	0.74	F_4	174,290
Tserpes et al.	0.12	F_4	174,290

Table A.1: Maximum tensile element stress, peak location and load type specified for the space-frame structure (5,5) determined in ANSYSTM.



Figure A.1: Maximum axial stress response as a function of element and tensile load for SWCNT (10,0). The maximum stress output is plotted for (a) t=0.50 Å and (b) t=0.66 Å.

SWCNT (7,7)			
Author	$\sigma_{\rm max}^{axial} imes 10^7 ({\rm kg}/{\rm \AAs^2})$	Tensile load	Element peak No.
Chen and Cao	3.7	F_5	254-278,384
Yakobson et al.	1.6	F_5	254 - 278, 384
Pantano et al.	1.1	F_5	254-278,384
Kudin et al.	0.70	F_5	254-278,384
Tserpes et al.	0.17	F_5	254-278,384

Table A.2: Maximum tensile element stress, peak location and load type specified for the space-frame structure (7,7) determined in ANSYSTM.



Figure A.2: Maximum axial stress response as a function of element and tensile load for SWCNT (10,0). The maximum stress output is plotted for t=0.75 Å.

SWCNT (10,0)			
Author	$\sigma_{\rm max}^{axial} \times 10^7 ({\rm kg}/{\rm \AAs^2})$	Tensile load	Element peak No.
Chen and Cao	2.3	F_5	363 - 380, 578
Yakobson et al.	1.1	F_5	363 - 380, 578
Pantano et al.	0.70	F_5	363 - 380, 578
Kudin et al.	0.42	F_5	363 - 380, 578
Tserpes et al.	0.098	F_5	363 - 380, 578

Table A.3: Maximum tensile element stress, peak location and load type specified for the space-frame structure (10,0) determined in ANSYSTM.

SWCNT (12,0)			
Author	$\sigma_{\rm max}^{axial} imes 10^7 ({\rm kg}/{\rm \AAs^2})$	Tensile load	Element peak N°.
Chen and Cao	2.3	F_5	628-630, 640-665
Yakobson et al.	1.1	F_5	628-630, 640-665
Pantano et al.	0.69	F_5	628-630, 640-665
Kudin et al.	0.42	F_5	628-630, 640-665
Tserpes et al.	0.097	F_5	628-630,640-665

Table A.4: Maximum tensile element stress, peak location and load type specified for the space-frame structure (12,0) determined in ANSYSTM.



Figure A.3: Maximum axial stress response as a function of element and tensile load for SWCNT (10,0). The maximum stress output is plotted for (a) t= 0.89 Å and (b) t=1.47 Å.


Figure A.4: Maximum axial stress response as a function of element and tensile load for SWCNT (12,0). The maximum stress output is plotted for (a) t=0.50 Å and (b) t=0.66 Å.



Figure A.5: Maximum axial stress response as a function of element and tensile load for SWCNT (12,0). The maximum stress output is plotted for t = 0.75 Å.

A.3 Multilinear Model Graphic-User Interface Results in ANSYSTM

Maximum stress $ANSYS^{TM}$ output results for SWCNTs (8,0)–(10,0). For these cases, a multilinear model is assumed to generate a nodal solution for the carbon nanotube continuum model (see Figs. A.7–A.16).



Figure A.6: Maximum axial stress response as a function of element and tensile load for SWCNT (12,0). The maximum stress output is plotted for (a) t=0.89 Å and (b) t=1.47 Å.



Figure A.7: SWCNT (8,0) maximum nodal stress distribution considering thickness parameters (a) t = 0.50 Å and (b) t = 0.66 Å determined in ANSYSTM.



Figure A.8: SWCNT (8,0) maximum nodal stress distribution considering thickness parameters (a) t = 0.75 Å and (b) t = 0.89 Å determined in ANSYSTM.



Figure A.9: SWCNT (8,0) maximum nodal stress distribution considering thickness paramete t= 1.47 Å determined in $ANSYS^{TM}$.



Figure A.10: SWCNT (8,8) maximum nodal stress distribution considering thickness parameters (a) t = 0.50 Å and (b) t = 0.66 Å determined in ANSYSTM.



Figure A.11: SWCNT (8,8) maximum nodal stress distribution considering thickness parameter t = 0.89 Å determined in ANSYSTM.



Figure A.12: SWCNT (9,0) maximum nodal stress distribution considering thickness parameters (a) t = 0.50 Å and (b) t = 0.66 Å determined in ANSYSTM.



Figure A.13: SWCNT (9,0) maximum nodal stress distribution considering thickness parameters (a) t = 0.75 Å and (b) t = 0.89 Å determined in ANSYSTM.



Figure A.14: SWCNT (10,0) maximum nodal stress distribution considering thickness parameters (a) t = 0.50 Å and (b) t = 0.66 Å determined in ANSYSTM.



Figure A.15: SWCNT (10,0) maximum nodal stress distribution considering thickness parameters (a) t = 0.75 Å and (b) t = 0.89 Å determined in ANSYSTM.



Figure A.16: SWCNT (10,0) maximum nodal stress distribution considering thickness parameter t= 1.47 Å.

Appendix B

Sample ANSYS Code to Obtain Maximum Axial Stresses for Space-Frame Model

B.1 ANSYSTM code sample to determine maximum axial stresses for a SWCNT

/BATCH,LIST

*DEL,ALL

/PREP7

/COM, Structural

/filename, cnt55_cc1

!This code is to calculate output for SWCNT (5,5) with t = 0.50 Å

!Mechanical Properties

ET,1,beam4

mp, prxy, 1, 0.190

 $_{\rm mp,dens,1,2.68e-27}$

keyopt,1,2,0

keyopt,1,6,1

keyopt,1,7,0

keyopt, 1, 9, 0

keyopt,1,10,0

R,1,0.3421194,0.0093142,0.0093142,0.660,0.6600,0,

RMORE, ,0.0186284, , , , , ,

*DIM,Emod,ARRAY,10,1

*VREAD, Emod(1,1), mod, txt, ., 10, 1, 1, 0

(E11.5)

*CFOPEN,Emod_cc2,txt

*VWRITE,Emod(1,1)

(6E14.6)

*CFCLOSE

*DIM,force,ARRAY,10,1

*VREAD,force,morse_force,txt,,,10,1,1,0

(E11.5)

*CFOPEN,force cc2,txt

*VWRITE,force(1,1)

(6E14.6)

*CFCLOSE

elem=290

type,1

real,1

mat,1

!keypoint coordinates specified here for SWCNT (5,5)

k , kp_number, x - axis, y - axis, z - axis

!lines declared are specified here for SWCNT (5,5)

l , kp_number_1, kp_number_2

 ${\tt LESIZE, ALL, ,, 1}$

LMESH,ALL

 $*{\rm DIM, elem_num, ARRAY, elem}$

*DO,i,1,elem !i refers to no. elements

elem_num(i)=i

*ENDDO

*DIM,axial_elstrain,ARRAY,elem

*DIM,bend_yelstrain,ARRAY,elem

*DIM,bend_zelstrain,ARRAY,elem

 $*{\rm DIM,max_stress,ARRAY,elem}$

*DIM,min_stress,ARRAY,elem

 $*{\rm DIM,x_force,ARRAY,elem}$

*DIM,y_force,ARRAY,elem

 $DIM,z_force, ARRAY, elem$

 $*DIM,mom_x,ARRAY,elem$

 $*DIM, mom_y, ARRAY, elem$

*DIM,mom_z,ARRAY,elem

 $*DO,E_{col,1,1}$

*DO,E_row,1,10 !item is the no. Emod

/PREP7

 $mp,ex,1,Emod(E_row,E_col)$

/SOLU

!*

ANTYPE,0

FLST, 2, 10, 1, ORDE, 10

FITEM,2,1

FITEM, 2, -2

FITEM,2,5

FITEM,2,-6

FITEM,2,9

FITEM, 2, -10

FITEM,2,13

FITEM,2,-14

FITEM, 2, 17

FITEM,2,-18

!*

/GO

D,P51X, ,0, , , ,ALL, , , , ,

FLST,2,10,1,ORDE,10

FITEM,2,183

FITEM,2,-184

FITEM, 2, 187

FITEM, 2, -188

FITEM, 2, 191

FITEM,2,-192

FITEM,2,195

FITEM,2,-196

FITEM,2,199

FITEM,2,-200

/GO

F,P51X,FZ,force(E_row)

/STATUS,SOLU

SOLVE

FINISH

EPLOT

/POST1

/PNUM,ELEM,0

/REPLOT

!set up etable

ETABLE, epeldir, LEPEL, 1

ETABLE, epelbyb, LEPEL, 3

ETABLE,epelbzb,LEPEL, 5

ETABLE, smax, NMISC, 1

ETABLE, smin, NMISC, 2

ETABLE,mforx,SMISC,1

 ${\it ETABLE, mfory, SMISC, 2}$

ETABLE,mforz,SMISC,3

ETABLE,mmomx,SMISC,4

ETABLE, mmomy, SMISC, 5

ETABLE,mmomz,SMISC,6

ESEL,ALL

*VGET,axial_elstrain,ELEM,,ETAB,epeldir

*VGET,bend yelstrain,ELEM,ETAB,epelbyb

*VGET,bend_zelstrain,ELEM,,ETAB,epelbzb

 $*VGET, max_stress, ELEM,, ETAB, smax$

*VGET,min_stress,ELEM,,ETAB,smin

*VGET,x_force,ELEM,,ETAB,mforx

*VGET,y_force,ELEM,,ETAB,mfory

*VGET,z_force,ELEM,,ETAB,mforz

*VGET,mom_x,ELEM,,ETAB,mmomx

*VGET,mom_y,ELEM,,ETAB,mmomy

*VGET,mom_z,ELEM,,ETAB,mmomz

 $CFOPEN, cnt55_p1_\%E_row\%_\%E_col\%, dat$

*VWRITE,elem_num(1),axial_elstrain(1),bend_yelstrain(1),

 $bend_zelstrain(1), max_stress(1), min_stress(1)$

(F4.0,3X,E12.5,3X,E12.5,3X,E12.5,3X,E12.5,3X,E12.5)

*CFCLOSE

*CFOPEN,cnt55_p2_%E_row%_%E_col%,dat

 $VWRITE, elem_num(1), x_force(1), y_force(1), z_force(1),$

 $mom_x(1), mom_y(1), mom_z(1)$

(F4.0,3X,E12.5,3X,E12.5,3X,E12.5,3X,

E12.5,3X,E12.5,3X,E12.5)

*CFCLOSE

FINISH

*ENDDO

*ENDDO

Appendix C

Sample ANSYS Code to Obtain Deflections for the Multilinear Model

C.1 ANSYSTM Code for the deflection output of SWCNTs through the multilinear model

/BATCH,LIST

*DEL,ALL

/PREP7

/COM, Structural

/PREP7

! The sample code refers to SWCNT (9,0) for t = 0.50 Å

!*

ET, 1, SOLID45

!*

KEYOPT, 1, 1, 0

KEYOPT,1,2,1

KEYOPT, 1, 4, 0

KEYOPT,1,5,0

KEYOPT,1,6,0

!*

R,1, ,

!*

MPTEMP,,,,,,

MPTEMP,1,0

MPDATA, EX, 1,, 77.9894 !youngs modulus

MPDATA, PRXY, 1, 0.19 !poissons ratio

MPTEMP,,,,,,

MPTEMP,1,0

 ${\tt MPDATA, DENS, 1, 2.68e-27 \ ! density}$

TB, MELA,1,1,11,

TBPT	"	0.00000	,	0.00000
TBPT	"	0.10678	,	8.32771
TBPT	"	0.12115	,	8.99277
TBPT	"	0.13450	,	9.62892
TBPT	"	0.14836	,	10.06270
TBPT	"	0.16170	,	10.43860
TBPT	"	0.17557	,	10.69880
TBPT	"	0.19199	,	10.95900
TBPT	"	0.21561	,	10.90120
TBPT	"	0.22998	,	10.66990
TBPT	"	0.24435	,	10.23610

CYL4,0,0,3.5230,,4.0230, ,41.970 !cylinder coords, ri, ro, length

/VIEW, 1, 1, 1, 1

/ANG,1

/REP,FAST

AESIZE, ALL, 3, !length of the volume sweep

CM,_Y,VOLU

VSEL, , , , 1

CM,_Y1,VOLU

CHKMSH,'VOLU'

CMSEL, S, Y

!*

VSWEEP,_Y1

!*

CMDELE,_Y

CMDELE,_Y1

CMDELE,_Y2

/SOLU

NLGEOM, ON !NONLINEAR GEOMETRY ON

NSUBST,100,1000,1 ! LOAD STEPS

OUTRES, ALL, ALL !OUTPUT DATA FOR ALL LOAD STEPS

AUTOTS, ON ! AUTO TIME SEARCH ON

LNSRCH,ON !LINE SEARCH ON

NEQIT,1000 !100 ITERACTION MAXIMUM

ANTYPE, STATIC !STATIC ANALYSIS

Appendix D

Sample Gaussian 03^{TM} Input File

D.1 Sample Gaussian 03^{TM} input file for SWCNT (7,0) 1440 k-points

	$%$ chk=C:*.chk									
	%mem=276MW									
	%nproc=1									
$\# p lsda/3-21g^*/auto pbc=nkpoints=1440 scf=fermi iop(5/103=2)$										
	0	1								
	С	-0.71498400	0.00000000	-2.75934100						
	С	-2.13598400	0.00000000	-2.75934100						
	С	1.42100000	1.19723300	-2.48608000						
	С	0.00000000	1.19723300	-2.48608000						
	С	-0.71498400	2.15733900	-1.72042100						
	С	-2.13598400	2.15733900	-1.72042100						
	С	1.42100000	2.69015800	-0.61401100						
	С	0.00000000	2.69015800	-0.61401100						
	С	-0.71498400	2.69015800	0.61401100						
	С	-2.13598400	2.69015800	0.61401100						
	С	1.42100000	2.15733900	1.72042100						
	С	-0.00000000	2.15733900	1.72042100						
	С	-0.71498400	1.19723300	2.48608000						
	С	-2.13598400	1.19723300	2.48608000						
	С	1.42100000	0.00000000	2.75934100						
	С	-0.00000000	0.00000000	2.75934100						

\mathbf{C}	-0.71498400	-1.19723300	2.48608000
С	-2.13598400	-1.19723300	2.48608000
С	1.42100000	-2.15733900	1.72042100
С	-0.00000000	-2.15733900	1.72042100
С	-0.71498400	-2.69015800	0.61401100
С	-2.13598400	-2.69015800	0.61401100
С	1.42100000	-2.69015800	-0.61401100
С	0.00000000	-2.69015800	-0.61401100
С	-0.71498400	-2.15733900	-1.72042100
С	-2.13598400	-2.15733900	-1.72042100
С	1.42100000	-1.19723300	-2.48608000
С	0.00000000	-1.19723300	-2.48608000
Tv	4.23000000	0.00000000	0.00000000

References

- R. Saito, G. Dresselhaus, and M.S. Dresselhaus. *Physical Properties of Carbon Nan*otubes. Imperial College Press, London, UK, 1999.
- [2] http://www.emsl.pnl.gov/.
- [3] M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos. Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. *Reviews of Modern Physics*, 64:1045–1097, 1992.
- [4] http://britneyspears.ac/physics/dos/dos.htm.
- [5] C. Kittel. Energy bands. In *Introduction to Solid State Physics*, chapter 7, pages 157–180. John Wiley and Sons, Inc., New York, NY, 1986.
- [6] http://hyperphysics.phy-astr.gsu.edu/hbase/solids/fermi.html.
- [7] ANSYSTMUniversity Advanced v 9.2. Ansys release 9.0 help documentation, 2000.
- [8] X. Chen and G. Cao. A structural mechanics study of single-walled carbon nanotubes generalized from atomistic simulation. *Nanotechnology*, 17:1004–1015, 2006.
- [9] B.I. Yakobson, C.J. Brabec, and J. Bernholc. Nanomechanics of carbon tubes: Instabilities beyond linear respnse. *Phys. Rev. Letter*, 76:2511–2514, 1996.
- [10] K.N. Kudin, G.E. Scuseria, and B.I. Yakobson. C, F, BN, and C nanoshell elasticity from ab initio computations. *Phys. Rev. B*, 64(23):235406, 2001.
- [11] A. Pantano, D.M. Parks, and M.C. Boyce. Mechanics of deformation of single and multi-walled carbon nanotubes. J. Mech. Phys. Solids, 52:789–821, 2004.
- [12] K.I. Tserpes and P. Papanikos. Finite element modeling of single-walled carbon nanotubes. *Composites Part B*, 36:468–477, 2005.
- [13] Shigenobu Ogata and Yoji Shibutani. Ideal tensile strength and band gap of singlewalled carbon nanotubes. *Phys. Rev. B*, 68(16):165409, Oct 2003.
- [14] L.V. Radushkevich and V.M. Lukyanovich. O strukture ugleroda, obrazujucegosja pri termiceskom razlozenii okisi ugleroda na zeleznom kontakte. Zurn Fisic Chim, 26:88– 95, 1952.
- [15] M. Monthioux and V.L. Kuznetsov. Who should be given the credit for the discovery of carbon nanotubes? *Carbon*, 44:1621–1623, 2006.
- [16] S. Iijima and T. Ichihashi. Single-shell carbon nanotubes of 1-nm diameter. Nature, 363:603–605, 1993.

- [17] S. Iijima. Helical microtubules of graphitic carbon. Nature, 354:56–58, 1991.
- [18] http://en.wikipedia.org/wiki/Main_page.
- [19] J. Han. Structures and properties of carbon nanotubes. In M. Meyyappan, editor, *Carbon Nanotubes: Science and Applications*, chapter 1, pages 1–24. CRC Press LLC, New York, NY, 2005.
- [20] A.P. Moravsky, E.M. Wexler, and R.O. Loutfy. Growth of carbon nanotubes by arc discharge and laser ablation. In M. Meyyappan, editor, *Carbon Nanotubes: Science* and Applications, chapter 3, pages 65–94. CRC Press LLC, New York, NY, 2005.
- [21] M. Cinke, J. Li, and et. al. Pore structure of raw and purified hipco single-walled carbon nanotubes. *Chemical Physics Letters*, 365:69–74, 2002.
- [22] P. Laborde-Lahoz, W. Maser, and et. al. Mechanical characterization of carbon nanotube composite materials. *Mechanics of Advanced Materials*, 12:13–19, 2005.
- [23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople. Gaussian 03, Revision C.02. Gaussian, Inc., Wallingford, CT, 2004.
- [24] C.W.S. To. Bending and shear moduli of single-walled carbon nanotubes. *Finite Elements in Analysis and Design*, 42:404–413, 2004.
- [25] X. Sun and W. Zhao. Prediction of stiffness and strength of single-walled carbon nanotubes by molecular-mechanics based finite element approach. *Material Science* and Engineering A, 390:366–371, 2005.
- [26] M. Meo and M. Rossi. Prediction of young's modulus of single wall carbon nanotubes by molecular mechanics based finite element modeling. *Composites Science and Technology*, 66:1597–1605, 2006.
- [27] T. Belytschko, S.P. Xiao, G.C. Schatz, and R.S. Ruoff. Atomistic simulations of nanotube fracture. *Physical Review B*, 65:2354301–2354308, 2002.
- [28] T. Hertel, R.E. Walkup, and P. Avouris. Deformation of carbon nanotubes by surface van der waals forces. *Physical Review B*, 54:13870–13873, 1998.
- [29] A. Sears and R.C. Batra. Macroscopic properties of carbon nanotubes from molecularmechanics simulations. *Physical Review B*, 69:2354061–23540610, 2004.

- [30] J.R. Xiao, B.A. Gamma, and J.W. Gillespie Jr. An analytical molecular structural mechanics model for the mechanical properties of carbon nanotubes. *International Journal of Solids and Structures*, 42:3075–3092, 2005.
- [31] G. Cao and X. Chen. The effects of chirality and boundary conditions on the mechanical properties of single-walled carbon nanotubes. *International Journal of Solids and Structures*, article in press, 2007.
- [32] P. Liu, Y.W. Zhang, H.P Lee, and C. Lu. Atomistic simulations of uniaxial tensile behaviors of single-walled carbon nanotubes. *Molecular simulation*, 30:543–547, 2004.
- [33] D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.J. Stuart, B. Ni, and S.B. Sinnott. A second-generation reactive empirical bond order rebo potential energy expression for hydrocarbons. *J. Phys. Condens. Matter*, 14:783–802, 2002.
- [34] P.M. Agrawal, B.S. Sudalayandi, L.M. Raff, and R. Komanduri. A comparison of different methods of young's modulus determination for single-wall carbon nanotubes swcnt using molecular dynamics md simulations. *Computational Materials Science*, 38:271–281, 2006.
- [35] K.M. Liew, C.H. Wong, and M.J. Tan. Tensile and compressive properties of carbon nanotube bundles. Acta Materiala, 54:225–231, 2006.
- [36] C. F. Cornwell and L.T. Wille. Elastic properties of single-walled carbon nanotubes in compression. *Solid state communications*, 101:555–558, 1997.
- [37] G. Zhou, W. Duan, and B. Gu. First-principles study on morphology and mechanical properties of single-walled carbon nanotube. *Chemical Physics Letters*, 333:344–349, 2001.
- [38] ABAQUS 2004. Abaqus 6.4 user's manual.
- [39] D. Srivatasa, M. Menon, and K. Cho. Nanoplasticity of single-wall carbon nanotubes under uniaxial compression. *Physical Review Letters*, 83:2973–2976, 1999.
- [40] M. Griebel and J. Hamaeckers. Molecular dynamics simulations of the elastic moduli of polymer-carbon nanotube composites. *Computer methods in applied mechanics and engineering*, 193:1773–1788, 2004.
- [41] E.H. Dill. Formulation of the finite element method for linear elasticity. In *The Finite Element Method for the Mechanics of Solids*, pages 31–39. Rutgers, The State University, Piscataway, NJ, 2005.
- [42] A.L. Kalamkarov, A.V. Georgiades, S.K. Rokkam, V.P. Veedu, and M.N. Ghasemi-Nejhad. Analytical and numerical techniques to predict carbon nanotubes properties. *International Journal of Solid and Structures*, 2006:6832–6854, 2006.
- [43] T. Natsuki and M. Endo. Stress simulation of carbon nanotubes in tension and compression. *Carbon*, 42:2147–2151, 2004.
- [44] C. Li and T.W. Chou. A structural mechanics approach for the analysis of carbon nanotubes. International Journal of Solids and Structures, 40:2487–2499, 2003.

- [45] X.L. Gao and K. Li. Finite deformation continuum model for single-walled carbon nanotubes. International Journal of Solids and Structures, 40:7329–7337, 2003.
- [46] P. Giannozzi. Density functional theory for electronic structure calculations, 2002.
- [47] A.D. Boese and J.M.L. Martin. The role of the basis set: Assessing density functional theory. *Journal of Chemical Physics*, 119:3005–3014, 2003.
- [48] P.R. Briddon and R. Jones. Lda calculations using a basis of gaussian orbitals. *Phys. stat. sol.*, 217:131–171, 2000.
- [49] http://www.netlib.org/linalg/html_templates/node20.html.
- [50] P. Zhang, Y. Huang, P.H. Geubelle, P.A. Klein, and K.C. Hwang. The elastic modulus of single-wall carbon nanotubes: a continuum analysis incorporating interatomic potentials. *International Journal Solids Structure*, 39:3893–3906, 2002.
- [51] M.S. Dresselhaus and P.C. Eklund. Phonons in carbon nanotubes. Advances in Physics, 49:705–814, 2000.
- [52] H.E. Troiani, M.M. Yoshida, G.A. Camacho-Bragado, and M.A.L. Marques et al. Direct observation of the mechanical properties of single-walled carbon nanotubes and their junctions at the atomic level. *Nano Letters*, 3:751–755, 2003.
- [53] D.A. Buzatu, A.S. Biris, A.R. Biris, D.M. Lupu, J.A. Darsey, and M.K. Mazumber. Electronic properties of single-wall carbon nanotubes and their dependence on synthetic methods. *IEEE Transactions on Industry Applications*, 40:1215–1219, 2004.
- [54] MATLAB. The mathworks inc. http://www.mathworks.com., Natick, MA, 2007.
- [55] N.M. O'Boyle. GaussSum 2.0, 2006. http://www.gausssum.sf.net.
- [56] L.V. Van Hove. The occurrence of singularities in the elastic frequency distribution of a crystal. *Physical Review*, 89:1189–1193, 1953.

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