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Investigating Mechanical and Physical Properties of Nanostructures

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ABSTRACT

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In the first part of the dissertation, mechanical properties of bundles of carbon nanotubes are investigated. Earlier experiments showed that these tubes are tightly packed in the bundles, proving that they are strongly interacting. Furthermore, extensive applications of bundles of CNTs in microelectronics such as electrical interconnect have been reported which makes determining their mechanical properties very important. Having used beams with partial interlayer resistance and Euler-Bernoulli beams, it was found that the stiffness of the system of tubes is more than the summation of the tubes individual stiffness. In the second part, the growth of single end cap carbon nanotubes is investigated using Molecular dynamics and Monte Carlo simulations. Simulations show that adding dimers to cap lead to the tube growth with preserving the hexagonal structure. Results from both methods were consistent providing a proof that 5-7 dislocations cause the structure to anneal and remove defects. Furthermore, a rotation theory for growth of chiral tubes was introduced. In the third part, edge evolution of finite graphene structures is investigated. Graphene edges could be an arrangement of Armchair (AC) or Zigzag (ZZ). It has been always a
challenging problem to find which edge (AC or ZZ) is dominant during Graphene evaporation. Having investigated the problem through different geometries and edge types, it was found that irrespective of initial geometry and shape, all structures tend to reach a common equilibrium introducing AC edge as a dominant edge. In the last part, we study novel boron structures and their mechanical and electronic properties, using *ab initio* calculations. The α-sheet has been proven to be the most stable structure energetically out of the two dimensional boron sheets. The properties of achiral (AC and ZZ) tubes obtained from α-sheets were reported earlier. In the same line, the properties of chiral nanotubes obtained from α-sheet is investigated. The computations confirm their high stability and mechanical stiffness parameters within 50% of CNTs. Relaxation results reveals the curvature-induced buckling of certain atoms off the original plane. Finally, the electronic structure of the chiral tubes were found to be consistent with the earlier work results which confirmed that for small tubes (diameter <1.7nm) the tubes are expected to be metallic, while semi-conducting for larger tubes.
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Chapter 1

Introduction

1.1 Carbon Nanotube

It was in 1991 that Ijima [1] synthesized the first carbon nanotubes. The tubes were composed of several concentric tubes like shells with 3.4 Å separations. The structure was named multiwall carbon nanotubes (MWCNTs). These tubes were only a few nanometers wide but in various lengths ranging from hundred nanometers to several centimeters. Not long after discovery of carbon nanotubes, single-wall carbon nanotube (SWCNT) was synthesized by arc-discharge methods. SWCNT have a small diameter (in the order of 1 nm). They usually have closed ends (caps) but they may also have open ends. The unique molecular formation of nanotubes causes spectacular macroscopic properties as high tensile strength and ductility, conductivity and semi-conductivity. The strong sigma bonding (sp$^2$ bonding which is similar to graphene), makes nanotubes the strongest material in the world for stretch experiment [2]. A single wall CNT could be described as rolled a cylindrical graphene sheet.
In the following the structural parameters of the carbon nanotubes are introduced which will be used frequently in the thesis. Considering the fact that nanotube could be wrapped from hexagonal lattice, one could determine the geometrical properties of all nanotubes from hexagonal graphene lattice. Fig. 1.2 depicts a unit cell of (4,2) nanotube [4]; the tube could be made by wrapping the unit cell cut. The chiral vector \( c \) goes around the circumference of the made tube. Diameter and chiral angle control the macroscopic properties of the tube. Accepting \( a_1, a_2 \) as the basic unit vectors of the hexagonal lattice, one could write:

\[
c_h = n_1 a_1 + n_2 a_2 \text{ where } (n_1, n_2), \text{ both positive integers, are the chiral indices of a tube or in other terms, chirality.}
\]
Figure 1.2 Graphene sheet honey-comb lattice with lattice vectors $a_1$ and $a_2$. The Chiral vector $c_h$ represents how the unit-cell sheet is wrapped to form a nanotube ((4, 2) here). The angle $\theta$ between $c_h$ and $a_1$ is the chiral angle. Figure from [4]

The translational vector of the nanotube is given by: $T = t_1a_1 + t_2a_2$, where

$$t_1 = \frac{n_1 + 2n_2}{d_R}, \quad t_2 = -\frac{2n_1 + n_2}{d_R}$$

and $d_R$ is the greatest common divisor of $(n_1 + 2n_2)$ and $(2n_1 + n_2)$. The number of carbon atoms per unit cell of the nanotube is given by:

$$N_c = \frac{4(n_1^2 + n_2^2 + n_1n_2)}{d_R} \quad (1.1)$$

For special case where $n_1 = n_2 = n$, the tube is called armchair, and when $n_2 = 0$, the tube is called zigzag nanotube (Fig. 1.3). The chiral angle ranges from $\theta = 0$ for zigzag to $\theta = 30^\circ$ for armchair nanotubes.
Although bucky family [5, 6] (CNT and fullerenes) have a regular (periodic for tubes) atomic structure, it should be noted that sometimes the regular pattern of atomic arrangement could be interrupted in the form of defects. The defects could highly influence the properties of the bucky family. There are various types of defects such as chemical defects (chemical functional groups for ex. Oxygen atom absorbed on the grapheme layer), linear defects (ex. edge dislocation in graphene in the form of 5-7 pair) or point defect (ex. one or two extra or missing atoms; single/di-vacancy).

1.2 Simulation Methods

It has been many years that molecular modeling and simulation has been used to theoretically estimate the physical, chemical and mechanical properties of nanostructures. The assistance of computer numerical for large numerical calculations has played a significant role for modeling nanostructures and has enabled scientists to simulate larger and larger nanostructures every day. Generally, molecular modeling
studies include three steps: first an appropriate model is chosen to estimate the interaction between atoms in the nanostructure. The model calculates the energy of the atoms and molecules for different arrangements as well as estimating the correspondence of energy to each arrangement. The second step is the calculation process which could be in the form of Monte Carlo simulation, molecular dynamics or structure optimization. And the third step is to analyze the results and estimate the desired properties.

### 1.2.1 Bond Order Potential

Bond order potentials are a division of analytical (empirical) potentials widely used in molecular dynamics and statics simulations. One could bring the Tersoff potential [32], the Brenner potential [33], the Finnis-Sinclair potentials and the second-moment tight-binding potentials as examples. Comparing to conventional molecular mechanics force fields, bond order potentials have the advantage of describing several different bonding states of an atom, and hence being able to describe chemical reactions correctly to some extent. Although the potentials were developed independently, the strength of a chemical bond depends on the bonding environment, including the number of bonds, angles and bond length. Basically, it is from Linus Pauling bond order:

\[ V_{ij}(r_{ij}) = V_{\text{repulsive}}(r_{ij}) + b_{ij}V_{\text{attractive}}(r_{ij}) \]  

\( \text{(1.2)} \)
The potential is written as a pair potential depending on the distance between two atoms $r_{ij}$, while the strength of this bond is modified by the environment of the atom $i$ via the $b_{ijk}$ term. In other terms, the energy can be written in the form:

$$V_i(r_{ij}) = V_{\text{pair}}(r_{ij}) - D \sqrt{\rho_i}$$

(1.3)

where $\rho_i$ is the electron density at the location of atom $i$. These two forms are proved to be equivalent.

1.2.2 Monte Carlo Simulation

Monte Carlo algorithm [7] could be especially useful in studying systems with a large number of coupled degrees of freedom such as disordered materials, fluids and cellular structures. Considering a system, Monte Carlo simulation produces new configurations using random changes. It applies Markov chain to determine new states for the system and then based on stochastic nature of the system, decides whether the system should be accepted or not considering the energy or other parameters. Each change or random walk in the system could be considered as a move. The moves have to obey the basic balance condition to satisfy equilibrium condition. The approach is easy to constraint and perform, much less time consuming than many other approaches which has been used in diverse areas; from simulating physical and mathematical systems, the related topics could be named as molecular simulation, computational material sciences, chemical processes. Monte Carlo algorithm is also very useful for systems which cannot be explained dynamically such as Ising model.
1.2.3 Molecular Dynamics Simulation

Basically, molecular dynamics (MD) [8] is a computer simulation where atoms and molecules could interact over a period of time using physics approximations. MD has been widely used in materials science. MD provides scientist a significant tool to observe the motion of individual atoms which is one cannot observe in the actual experiment. As Richard Feynman said, "If we were to name the most powerful assumption of all, which leads one on and on in an attempt to understand life, it is that all things are made of atoms, and that everything that living things do can be understood in terms of the jiggling and wiggling of atoms."

Considering Newton’s second law, the successive configurations of the desired system could be produced. Newton’s law of motion basically determines the positions and velocities of the system which is solved considering the ordinary different equation of motion:

\[
F = ma. \quad \frac{d^2 x_i}{dt^2} = \frac{F_{x_i}}{m_i}
\]

(1.4)

which describes the motion for any particle with mass \( m_i \) for any coordinate \( x_i \) while the force \( F_{x_i} \) is the force component on the particle. In chemistry and biophysics, the interaction between the particles is described by a "force field" (classical MD), a quantum chemical model, or a mix of two; while in physics; usually the interactions are described by the name of the theory or approximation and called the potential energy or the "potential".
1.2.4 Density Functional Theory (DFT)

Density functional theory is a quantum mechanical theory that has become very popular in computational physics and chemistry. While traditional methods particularly Hartree-Fock theory [9] is based on the complicated many-electron wave function, DFT replaces the many-body electronic wave function with the electron density as the basic quantity. The many-body wave function has direct relation to $3N$ ($N$ is the number of electrons) while density is only a function of three variables and is a simpler quantity to deal with. DFT has gained popularity since 1970s in many problems especially in solid state physics which gives reasonably accurate results comparing to experimental data.
1.2.5 Tight Bonding Approximation

Generally the system Hamiltonian $H$ is approximated by the Hamiltonian of an isolated atom centered at each lattice point in tight-binding approximation. It is assumed that the atomic orbitals (eigenfunctions of the single atom Hamiltonian) are very small if located further than lattice constant. Also assuming a linear solution as a combination of atomic orbitals for the time-independent single electron Schrödinger equation [10], this approximation for the wave function was used to calculate Bloch energy. It should be noted that the calculation was done based on the assumption that the $m^{th}$ atomic energy level is important for the $m^{th}$ energy band.
Chapter 2

Determining the stiffness of bundles of carbon nanotubes

2.1 Introduction

In 1994, Ge and Sattler [11] observed assemblies of carbon nanotubes in the form of bundles. The bundles were reasonably long (up to 200 nm and widths between 15 and 50 nm) containing well aligned nanotubes over the length. The tubes were tightly packed in the bundles, proving that they were strongly interacting. From their experiment, they suggested that the bundles were produced rather simultaneously with the tubes in the growth process, not by moving single tubes at the substrate. The samples were prepared by carbon vapor deposition on a HOPG (highly oriented pyrolytic graphite) substrate in UHV (ultrahigh vacuum). They were composed of concentric tubules with 2-4 nm in diameter. They also reported a tendency for the tubes to form bundles considering that the inter-tube interaction was weaker than the intra-tube interaction.

Later, many authors as Zhu et al [12] reported extensive applications of bundles of CNTs in microelectronics as electrical interconnect. They applied the transfer technology to assemble the fine-pitch CNT bundles on the copper substrate which was promising for fabrication of field emitters, electrical interconnects, thermal management structures in microelectronics packaging.
We present in this paper results from modeling of bundles of carbon nanotubes (CNT) as layered beams with incomplete interaction between layers. We also make a comparison with the homogeneous Timoshenko beam, by considering the shear deformation contribution coming from the interlayer media. This approach can lead to a simple method for calculating the deformation of bundles of CNT and its effective bending stiffness. In modeling bundles of single wall carbon nanotubes (SWCNT) under bending according to the theory of composite beams with partial interaction, the links between SWCNT are supposed to have a linear behavior between transferred shear force and relative displacement.

The theory of composite beams with partial interaction was developed in the 1950s, in the field of Civil Engineering, by many authors such as Newmark, Siess and Viest [13]. The theory applies to composite layered beams with deformable link between layers, such that each layer can slip over each other. The theory of composite beams with partial interaction is based in the Euler-Bernoulli theory of bending of beams, accounting for the relative displacement between each two layers. The theory presented by the authors and reviewed by Girhammar and Gopu (1993) [14] was applied for many kinds of composite beams with two dissimilar members or symmetric sections with three members. The principle of the theory is the equilibrium of infinitesimal part of the section, equilibrium of infinitesimal part of each layer and compatibility of displacements between layers. In a similar way, with basis on the
same principles, Ha (1993) [15] modeled sandwich beams, generally defined as beams composed of two outermost layers and a core.

The Timoshenko theory of bending [16] applies to beams where the shear deformation of the material is such that non-negligible displacements take place, in beams with large ratio between beam cross section’s height and length. Timoshenko beams also have been applied for sandwich beams, considering the contribution for shear deformation just from core.
2.2 Modeling of layered systems under bending

Consider a layered system composed by a bundle of $N$ carbon nanotubes subjected to a vertical load defined by a function $q(x)$ (Fig. 2.1).

Equilibrium of forces and moments leads to:

$$M(x) = M_1(x) + N_1(x)a_1 + M_2(x) + N_2(x)a_2 + \ldots + M_N(x) + N_N(x)a_N$$  \hspace{1cm} (2.1)
\[ 0 = N_1(x) + N_2(x) + \ldots + N_N(x) \quad (2.2) \]
\[ 0 = V_1(x) + V_2(x) + \ldots + V_N(x) \quad (2.3) \]

Where, the equilibrium of each part leads to:
\[ dN_i = -V_s \, dx \quad (2.4) \]

The behavior of links to shear is given by:
\[ V_s = K_s \Delta u \quad (2.5) \]

**Figure 2.2** Equilibrium and Kinematics of layered systems

From bending theory:

\[
\begin{align*}
EI_1 \frac{d^2v}{dx^2} &= M_1 \\
EI_2 \frac{d^2v}{dx^2} &= M_2 \\
& \quad \vdots \\
EI_N \frac{d^2v}{dx^2} &= M_N
\end{align*}
\quad (2.6)
\]

So that:
\[ EI_o \frac{d^2 v}{dx^2} = M_o \]  

(2.7)

or: \[ EI_o \frac{d^2 v}{dx^2} = (M - \sum_{j=1}^{N} N_j a_j) \]  

(2.8)

after two times of derivation we will have:

\[ EI_o \frac{d^4 v}{dx^4} = (q - \sum_{j=1}^{N} \frac{d^2 N_j}{dx^2} a_j) \]  

(2.9)

Compatibility of displacements between each layer and their neighbors lead to:

\[ \Delta u_{i+1} = u_i - u_{i+1} + \frac{dy}{dx} d_{i,i+1} \]  

(2.10)

or: \[ \frac{d}{dx} \Delta u_{i,i+1} = \varepsilon_i - \varepsilon_{i+1} + \frac{d^2 v}{dx^2} d_{i,i+1} \]  

(2.11)

From theory of compressed members from Strength of Materials:

\[ \varepsilon_i = \frac{N_i}{EA_i} \]  

(2.12)

Thus, with equations above, we can write:

\[ \frac{d^2 N}{dx^2} = K \left( -\frac{N_{i-1}}{EA_{i-1}} + \frac{2N_i}{EA_i} - \frac{N_{i+1}}{EA_{i+1}} \right) + K \frac{d^2 v}{dx^2} (d_{i+1} - d_{i-1}) \]  

(2.13)

\[ \frac{d^2 v}{dx^2} = \frac{1}{EI_o} \left[ M - \sum_{j=1}^{N} N_j a_j \right] \]  

(2.14)

\[ 0 = \Sigma^{*} + N_{i-1} + N_i + N_{i+1} \]  

(2.15)

Or equivalently:

\[
\begin{bmatrix}
-N_{i-1} = \Sigma^{*} + N_i + N_{i+1} \\
-N_{i+1} = \Sigma^{*} + N_i + N_{i-1}
\end{bmatrix}
\]  

(2.16)
Then we will have 1.13 as:

$$\frac{d^2 N_i}{dx^2} = K \left( \frac{\sum N_{i,j-1}^* + N_i}{EA_{i-1}} + \frac{2N_i}{EA_i} + \frac{\sum N_{i+1,j}^* + N_i}{EA_{i+1}} \right) = 0 \quad (2.17a)$$

$$\frac{d^2 N_i}{dx^2} - \alpha_i^2 N_i + \frac{\sum N_{i,j-1}^*}{EA_{i-1}} + \frac{\sum N_{i+1,j}^*}{EA_{i+1}} = 0 \quad (2.17b)$$

where:

$$\alpha_i^2 = K \left( \frac{1}{EA_{i-1}} + \frac{2}{EA_i} + \frac{1}{EA_{i+1}} \right) \quad (2.18)$$

Then we will have:

$$EI_o \frac{d^2 \psi}{dx^2} = M - (\Sigma^{**} + N_{i-1}a_{i-1} + N_i a_i + N_{i+1}a_{i+1}) \quad (2.19)$$

$$N_i a_i = M - (\Sigma^{**} + N_{i-1}a_{i-1} + N_{i+1}a_{i+1}) - EI_o \frac{d^2 \psi}{dx^2} \quad (2.20)$$

$$\frac{d^2 N_i}{dx^2} = q - \frac{d^2}{dx^2} (\Sigma^{**} + N_{i-1}a_{i-1} + N_{i+1}a_{i+1}) - EI_o \frac{d^4 \psi}{dx^4} \quad (2.21)$$

Thus:

$$\frac{d^2 N_i}{dx^2} = -\alpha_i^2 N_i - \frac{\sum N_{i+1}^*}{EA_{i+1}} a_i - \frac{\sum N_{i-1}^*}{EA_{i-1}} a_i = 0$$

(1.21a)

$$\left( q - \frac{d^2}{dx^2} (\Sigma^{**} + N_{i-1}a_{i-1} + N_{i+1}a_{i+1}) - EI_o \frac{d^4 \psi}{dx^4} \right) - \left( \alpha_i^2 [M - (\Sigma^{**} + N_{i-1}a_{i-1} + N_{i+1}a_{i+1}) - EI_o \frac{d^2 \psi}{dx^2}] \right) = \frac{(\sum^{**} + N_{i+1})}{EA_{i+1}} a_i + \frac{(\sum^{**} + N_{i-1})}{EA_{i-1}} a_i \quad (2.22)$$
\[
q - EI_o \frac{d^4 v}{dx^4} - (\Sigma \alpha_i^2 / N)EI_o \frac{d^2 v}{dx^2} - (\Sigma \alpha_i^2 / N)M - (\Sigma \alpha_i^2 / N)(\Sigma N_k a_k - N_i a_i)
\]

\[-\Sigma \frac{d^2}{dx^2}(\Sigma N_k a_k - N_i a_i) = \frac{1}{EA}(\Sigma (\Sigma^* + N_{i+1})a_i + \Sigma (\Sigma^* + N_{i-1})a_i)
\]

(2.23)

In other words: \( EI_\infty = EI_0 + EA \sum a_i^2 \)  

(2.24)

From the equations above, we can obtain a general equation in terms of vertical displacement:

\[
v'' - \alpha^2 v'' = \alpha^2 \frac{M(x)}{EI_\infty} - \frac{q(x)}{EI_o}
\]

(2.25)

From calculus, the solution of this equation is given by:

\[
v(x) = a_1 \sinh(\alpha x) + a_2 \cosh(\alpha x) + a_3 x + a_4 + v_p(x)
\]

(2.26)

where \( v_p(x) \) is the particular solution depending on moment, \( M(x) \). If \( M(x) \) is a polynomial function of degree \( m \) namely \( P_m \), then the particular solution is \( x^2 \cdot P_m \), since two of the four roots of the characteristic equation are zero. The unknown coefficients of \( P_m \) are determined by the method of undetermined coefficients from calculus. The constants \( a_1, a_2, a_3, a_4 \) can be determined by the boundary conditions for \( v(x) \) and its derivatives.

For the simplest cases of two and three layers systems, the solution for vertical displacement can be found in literature for several loading cases. In the following the most common is presented:
Simply supported beam with uniform load

\[ v(x) = \frac{q}{24EI_o} \left( x^4 - 2x^3L + xL^3 \right) + \frac{q}{\alpha^4EI_o} \left( \frac{EI_o}{EI_o} - 1 \right) \times \]

\[ \left[ - \tanh \left( \frac{\alpha L}{2} \right) \sinh \alpha x + \cosh \alpha x - \frac{1}{2} \alpha^2 x^2 + \frac{1}{2} \alpha^2 xL - 1 \right] \]

\[ v_{\text{max}} = v(L/2) = \frac{5q_oL^4}{384EI_o} + \frac{q_o}{\alpha^4EI_o} \left( \frac{EI_o}{EI_o} - 1 \right) \left( \frac{1}{\cosh(\alpha L/2)} + \frac{1}{8} \alpha^2 L^2 - 1 \right) \]  \hspace{1cm} (2.27)

Other cases such as simply supported beam with concentrated load at mid span, simply supported beam with concentrated load at distance \( a \) from support, cantilever with end concentrated load and cantilever with uniform load will have similar procedure.

### 2.3 Effective Bending Stiffness

The effective bending stiffness, or effective stiffness, for the system can be defined in terms of the classical bending stiffness, so that the effective stiffness is the system's stiffness as if it was considered as a homogeneous beam, that is:

\[ EI_{\text{eff}} v''(x) = q(x) \]  \hspace{1cm} (2.28)

Here, we define bending stiffness as the product of Young modulus \([2]\) and second moment of inertia, both well defined for a homogeneous beam.

By taking the simple case of uniform distributed load as example, we can define the effective stiffness as:

\[ EI_{\text{eff}} = \frac{5L^4}{384} \left( \frac{\Delta v}{\Delta q} \right)^{-1} \]  \hspace{1cm} (2.29)

with:
\[
\frac{\Delta v}{\Delta q} = \frac{1}{24EI_o} \left( x^4 - 2x^3L + xL^3 \right) + \frac{1}{\alpha^4EI_o} \left( \frac{EI_o}{EL_o} - 1 \right) \times \\
\left[ - \tanh \left( \frac{\alpha L}{2} \right) \sinh \alpha x + \cosh \alpha x - \frac{1}{2} \alpha^2 x^2 + \frac{1}{2} \alpha^2 xL - 1 \right]
\] (2.30)

From equation above, the effective stiffness depends on the abscissa \( x \). taking the abscissa where \( v(x) \) has a maximum, we can write:

\[
\frac{\Delta v}{\Delta q} = \frac{5L^4}{384EI_o} + \frac{1}{\alpha^4EI_o} \left( \frac{EI_o}{EL_o} - 1 \right) \left[ \frac{1}{8} \alpha^2 L^2 - 1 \left( \cosh(\alpha L/2) + \frac{1}{8} \alpha^2 L^2 - 1 \right) \right]
\] (2.31)

So the effective stiffness for a system under uniform distributed load is given by:

\[
EI_{eff} = \frac{5L^4}{384} \left[ \frac{5L^4}{384EI_o} + \frac{1}{\alpha^4EI_o} \left( \frac{EI_o}{EL_o} - 1 \right) \left[ \frac{1}{8} \alpha^2 L^2 - 1 \left( \cosh(\alpha L/2) + \frac{1}{8} \alpha^2 L^2 - 1 \right) \right] \right]
\] (2.32)

For any loading case, the solution for deflection is composed by two parts: the first comes from classical theory, and the second comes from shear between layers:

\[ v(x) = v^{EB}(x) + v^{Shear}(x) \] (2.33)

Therefore:

\[
EI_{eff} = EIC^{EB} \left[ C^{EB} + C^{Shear} \right]
\] (2.34)

The coefficients (dependent on abscissa) \( C^{EB} \) and \( C^{Shear} \) depend on loading case. However, it has been noticed that the ratio between \( C^{EB} \) and \( C^{Shear} \) is constant for any loading case for same support conditions. That suggests that a general expression for the effective stiffness can be proposed, depending only on the shear stiffness and other geometrical parameters. We have found that for simply supported beam, the effective stiffness may be given by:
\[ E_{I_{\text{eff}}} = EI \frac{1}{1 - \frac{48}{40 - 5\alpha^2 L^2} \left( \frac{EI - EI_o}{EI_o} \right)} = EI \frac{1}{1 + \frac{k^{\text{Shear}}}{k^{EB}} \frac{EI - EI_o}{EI_o}} \] (2.35)

Where \( k^{EB} = \frac{5}{384} \) and \( k^{\text{Shear}} = \frac{1}{\alpha^4 L^4} \left( \frac{1}{\cosh(\alpha L/2)} + \frac{1}{8} \alpha^2 L^2 - 1 \right) \) (2.36)

Figure 2.3 shear stiffness vs. \( \alpha \), \( K^{\text{Shear}} \approx 0.013 \) is equivalent to \( K^{\text{Shear}} = \frac{5L^4}{384} \)

One may note the limits of \( k^{\text{Shear}} \): full composite action (infinite slip stiffness, \( K \to \infty, k^{sh} \to 0 \)) and no composite action (zero slip stiffness, \( K \to 0, k^{sh} \to k^{EB} \)) represent the upper and lower bounds for the partial composite actions.

Plotting \( K \) vs Alpha (Fig. 2.3) complies with the derived result. It also shows that by increasing alpha shear stiffness approaches zero.
2.4 Extending method for bundles of $n$ layers of CNT

If we consider bundles with $n$ layers of CNT (Fig.4), we can consider an innermost level and other layers ($(n-1)/2$ levels for odd $n$ and $n/2$ for even $n$) surrounding the innermost level.

For the beginning, we consider the same distance "$a$" between levels, the same number of CNTs in each level, and the same links density between levels. This way, for the system of three-level systems, we had:

$$EI_{eff} = EI_o + \Phi(EI - EI_o)$$  \hspace{1cm} (2.37)
Where $\Phi = \frac{1 - e}{1 + \frac{(E_I - E_{I_0})}{E_{I_0}}} e$ and $e = \frac{k_{Shear}}{k_{EB}}$

Applying the formula for a system with a central layer plus one pair of layers, up and down:

$$E_I^{(1)}_{eff} = 2E_I + 2\Phi_{(1)}E_{A_i}y_{(1)}^2$$  \hspace{1cm} (2.38)

Applying the formula for increasing number of pair of layers, up and down:

$$E_I^{(N)}_{eff} = E_I^{(N-1)}_{eff} + 2E_I + 2\Phi_{(N)}E_{A_i}y_{(N)}^2$$  \hspace{1cm} (2.39)

$$E_I^{(N)}_{eff} = E_I + 2E_{A_i}(\Phi_{(1)}y_{(1)}^2 + \Phi_{(2)}y_{(2)}^2 + \cdots + \Phi_{(N)}y_{(N)}^2)$$  \hspace{1cm} (2.40)

$N = (n - 1)/2$ Where $n$ is the total number of layers in a symmetrical system ($n$ odd number), $(EA)_1$ is the individual axial stiffness of each level, $(EI)_1$ is the individual bending stiffness of each level (with respect to its own axis), $a_1$ is the distance between each level, and $K$ is the shear stiffness of the bridges between each level.

In other words, we can consider a symmetrical system with $N$ layers as a successive superposition of systems of three layers. The system is taken as a core plus two outermost layers. The core is taken as a new system of three layers (see Fig. 2.4).

For each pair $i$ of outermost layers considered the effective stiffness of the system composed by the inner core and the pair of layers is given by:

$$(E_{I_{eff}})_i = (E_{I_0})_i + 2\Phi E_{A_i}r_i^2 = 2E_I + (E_{I_{eff}})_{i-1} + 2\Phi E_{A_i}r_i^2$$  \hspace{1cm} (2.41)
Considering $N$ the total number of layers and $n$ the number of pairs of layers (above and below) the inner core. If the system has even number of layers, then $N=2n$. If the system has odd number of layers, then $N=2n+1$ (see figures 1 and 2).

Note that the parameter $\Phi$ may be considered as a "correction" factor considering the slip between outer layers and the inner layers. The final formula is dependent only on $K$, $L$, $EA_1$, $EI_1$ and $c$ (distance between the axis of two neighbor layers).

2.5 Comparison with homogeneous theory of Timoshenko beam

For a cantilever beam, Kis et al. (2004) [17] found that the effective Young modulus could be written as:

$$\frac{1}{Y_b} = \frac{1}{Y} + \frac{10}{3} \frac{D^2}{L^2} \frac{1}{G}$$

(2.42)

where $Y$ is the Young modulus, $D$ is the diameter of the bundle considered as a homogeneous circular cross section beam, $L$ is the length of the bundle, and $G$ is the shear modulus.

For a simply supported beam, we can write that the effective bending stiffness of a homogeneous beam can be given as:

$$\frac{1}{EI_{eff}} = \frac{1}{EI} + \frac{32}{3} \frac{1}{L^2} \frac{1}{GA}$$

(2.43)

where $EI$ denotes the bending stiffness and $A$ denotes the effective area cross section.

If we consider a layered system as homogeneous, considering that contribution for bending stiffness comes from layers and that contribution for shear stiffness comes
from interlayer fictitious continuous medium, then we can apply the theory from Timoshenko beam with the proper values for GA and the shear coefficient.

Nowzartash and Mohareb (2005) [18] made a formulation for sandwich beams using variational approach and the kinematics according to Timoshenko beam. The authors considered uniform distribution for shear stresses in the core. Maheri and Adams (1998) [19] applied the Timoshenko theory to the analysis of vibration of sandwich beams and presented a wide discussion about the shear correction factor.

Essentially, the bundles of CNT may be considered as sandwich beams with alternate layers with bending stiffness and shear stiffness, where bending stiffness comes from the CNT and the shear stiffness comes from bridges between CNT.

![Graph](image)

**Figure 2.5** effective stiffness vs. link shear stiffness for bundle of CNT with the following parameters: 3 number of layers, 5e-9 (m) radius, 1.25e-9 (m) layers separation, 1e-7 (m) bridge length, 1.5e11 (N/m²) link shear stiffness
2.6 Shear stiffness between layers

The shear stiffness between layers may be defined as the relationship between the interlayer shear force per unit length \( T \) and the relative displacement between layers \( \Delta \) (see Fig. 2.6).

Consistent values from \( K \) may be obtained starting from data from literature for "shear modulus" for bridges. Suppose that the bridges can be considered as a planar media (with a fictitious width \( b \)) with a shear modulus \( G \). Then, knowing that \( \tau = T/b \) and \( \gamma = \Delta/c \), then we can write that \( T = \tau b = K \Delta x = K \gamma \Delta y \). Since for a continuous media \( \tau = G \gamma \), comparing this equation with \( \tau b = K \gamma \Delta y \), we can write \( G = K \Delta y / b \), or \( G = K \Delta y^2 / (b \Delta y) \), or \( G \Delta = K \Delta y^2 \).

From the result above, \( G \Delta \) can be defined for the interlayer media without necessity of defining the media thickness.

Sammalkorpi et al (2005) [20] found that for a bundle of seven NT, one central and six NTs equally spaced around the central one, the shear modulus for links was given by \( G = a_G n_{bonds} \), where \( a_G = 14.5 \text{N/m} \) and \( n_{bonds} \) is the linear inter-tube bond density. Xia et al (2007) [21] found that the shear modulus of links formed by \( sp^3 \) bonds in MWCNT
was $G=f.880$ GPa, where $f$ is the density of bonds. Kis et al (2004) [17] investigated the possible configurations for bridges between CNT in ropes and estimated a shear modulus of about 200GPa for a density of 0.8nm$^{-1}$ for some kinds of bridges. The distance between CNT in ropes according to these authors is 0.34nm. Kis et al. also presented a figure with results of tests of equivalent Young modulus of twelve bundles of CNT considered as a bar with Young modulus $Y$ and Shear modulus $G$, as a function of the diameter of the bundle. Considering in all kinds of simulation a link length of 0.34nm (that is, $\Delta y=0.34$nm), and the above physical meaning for shear stiffness ($T=K\Delta x$, where $T$ is the shear force per unit length), we can find that $K$ for a row of bridges linking two NT lengthwise, can be computed according to density of bridges, and some values are shown in Table 1.

<table>
<thead>
<tr>
<th>Density of bridges</th>
<th>Shear modulus (GPa)</th>
<th>Corresponding Shear stiffness (N/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shear modulus from Kis et al (2004)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f=1%$</td>
<td>8.8</td>
<td>1674.0</td>
</tr>
<tr>
<td>$f=3%$</td>
<td>26.4</td>
<td>5022.2</td>
</tr>
<tr>
<td>$f=6%$</td>
<td>52.8</td>
<td>10044.4</td>
</tr>
<tr>
<td><em><em>Shear modulus from Sammalkorpi et al (2007</em>)</em>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_{bonds}=0.01\text{Å}^{-1}$</td>
<td>0.145</td>
<td>27.6</td>
</tr>
<tr>
<td>$n_{bonds}=0.02\text{Å}^{-1}$</td>
<td>0.290</td>
<td>55.2</td>
</tr>
<tr>
<td>$n_{bonds}=0.03\text{Å}^{-1}$</td>
<td>0.435</td>
<td>82.3</td>
</tr>
<tr>
<td>$n_{bonds}=0.04\text{Å}^{-1}$</td>
<td>0.580</td>
<td>110.3</td>
</tr>
</tbody>
</table>

**Table 2.1** Values of shear stiffness computed from values of shear modulus from literature.
We emphasize that according to the formulation presented above the shear transfer is expressed in terms of force per unit length, in such a way that the shear force balances the increment in length of normal stresses in the cross section of each CNT.

2.7 Example problems and discussion

We first consider a bundle of three levels of CNT as shown in Fig. 2.7. Considering all CNTs with diameter \( d = 10 nm \), we have: \((EA)_i = 2.26e-5N\), \((EI)_i = 1.131e-21Nm^2\). With a links density of 10% links per unit length, and a distance between CNTs equal to 1.25nm, we have:

![Figure 2.7 Three levels of CNT with bridges](image)

From results of simulations of experiments of shear between the walls of a double-walled MWCNT as described in the article, these authors got the following result:

The shear modulus \( G \) of the bridges is given by \( G = f \times 880 GPa \), where \( f \) is the density of bonds between walls of double-walled MWCNT.
For some arbitrarily chosen values of $f$, say 1%, 3% and 6%, we have:

- $f = 1\%$: $G = 0.01 \times 880 = 8.8$ GPa
- $f = 3\%$: $G = 0.03 \times 880 = 26.4$ GPa
- $f = 6\%$: $G = 0.06 \times 880 = 52.8$ GPa

**Figure 2.8** Double-walled MWCNT with bridges (in blue) between walls. The inner tube is displaced towards left and the outer tube is fixed. The arrows indicate shear stress over the bridges. Suppose that the bridges are distributed in the whole cylindrical interface.

Our problem is how to transform these values of $G$ (shear modulus) into values of $K$ (shear stiffness). From definitions of $K$ and $G$ we had:

$K = \frac{T}{\Delta x}, \quad G = \frac{\tau}{\gamma}$ where:

- $T =$ shear force per unit length of interface between two surfaces (these surfaces may be two CNT, two walls, two sheets of graphite, etc)
- $\tau =$ shear stress
- $\Delta x =$ shear displacement between surfaces (distance CE or DF)
- $\gamma = \Delta x/\Delta y =$ shear strain
Δy = "c" = distance between surfaces (distance AC or BD)

In the other hand, T = τ.b, where b is the width of the interface between surfaces. Also, Δx = γ.Δy, thus K = (τ.b)/(γ.Δy) = (τ/γ).(b/Δy) = G.b/Δy

but, "b" in the case of double-walled MWCNT is equal to π.d, where d is the diameter of the tube. That is K = G. πd/Δy

Thus, in order to find the values of K starting from the values of G from the simulations, we should know the values of the middle surface diameters of the tubes used in the authors’ simulation. As we don’t know these values, we can assume a range of diameters (2 to 30 nm) and find a range of values of possible values of K:

\[
\begin{align*}
\text{f = 1\%:} & \quad G=0.01 \times 880 = 8.8 \text{ GPa} \\
K &= 8.8 \times \pi \times 2 \times 10^{-9} / 0.34 \times 10^{-9} = 1.63 \times 10^{11} \\
K &= 8.8 \times \pi \times 30 \times 10^{-9} / 0.34 \times 10^{-9} = 24.4 \times 10^{11}
\end{align*}
\]

\[
\begin{align*}
\text{f = 3\%:} & \quad G=0.03 \times 880 = 26.4 \text{ GPa} \\
K &= 26.4 \times \pi \times 2 \times 10^{-9} / 0.34 \times 10^{-9} = 4.88 \times 10^{11} \\
K &= 26.4 \times \pi \times 30 \times 10^{-9} / 0.34 \times 10^{-9} = 73.2 \times 10^{11}
\end{align*}
\]

\[
\begin{align*}
\text{f = 6\%:} & \quad G=0.06 \times 880 = 52.8 \text{ GPa} \\
K &= 52.8 \times \pi \times 2 \times 10^{-9} / 0.34 \times 10^{-9} = 9.76 \times 10^{11} \\
K &= 52.8 \times \pi \times 30 \times 10^{-9} / 0.34 \times 10^{-9} = 146 \times 10^{11}
\end{align*}
\]

Shear modulus from Xia and Guduru (assuming tubes diameter ranging from 2nm to 30nm in the simulations)
<table>
<thead>
<tr>
<th>Density of bridges</th>
<th>Shear modulus (GPa)</th>
<th>Corresponding Shear stiffness (N/m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f=1%$</td>
<td>$G=f^*880=8.8$GPa</td>
<td>1.63 to $24.4 \times 10^{11}$</td>
</tr>
<tr>
<td>$f=3%$</td>
<td>26.4</td>
<td>4.88 to $73.2 \times 10^{11}$</td>
</tr>
<tr>
<td>$f=6%$</td>
<td>52.8</td>
<td>9.76 to $146 \times 10^{11}$</td>
</tr>
</tbody>
</table>
Chapter 3

Theory of single end cap nanotube growth

3.1 Introduction

Forming various graphitic structures makes carbon a special element. Graphene [22], carbon nanotubes (CNT) [23] and carbon cages especially buckminster fullerene $C_{60}$ [24], could be regarded as significant representatives; signifying the importance of understanding the growth and defect of these structures in atomistic level.

There has been wide range of works regarding CNT growth; Bernholc et al [25] developed a theory of growth for various CNTs using molecular dynamics. They investigated the role of tip-tip interaction on stabilizing open-ended tube growth and found heptagon-pentagon defect pairs as nucleation centers for the formation of dislocation.

Q. L. Zhang et al [26] have presented an evidence for the formation of $C_{60}$ fullerene. They also proposed one possible model of a growing soot particle without interlayer bonding between spheroidal shells in which under fast growth conditions each new shell could begin to form before the current shell finished. McKay and Kroto [27] developed the topic and discussed carbon nucleation scheme in quasi-icosahedral spiral shell carbon particles while fullerene cap rotation was proposed by Endo & Kroto [28,29] four years later.

Tubes growth has been believed to originate from the addition of atoms to the tube facets [30] and then closed by growth; however, the new theoretical work propose the
idea that growth could happen for single end cap tubes as well. The mechanism of
growth for single end cap CNT is investigated considering no metal presence
(assuming that carbon dimers are ingested from vapor).

3.2 Method

3.2.1 Molecular dynamics

We searched models considering stability of local structures formed during the growth
procedure; hence, we examined the structures forming after each carbon dimer
ingestion procedure and their respective dynamics.

First, (5,5) armchair carbon nanotube half closed (one end cap, the other end open)
with 100 carbon atoms was considered; considering (5,5) cap as the half C_{60} soccer
ball [31], ingesting new carbon dimers deform the cap with the formation of new
defects (non-hexagon polygons ex. 4-5-7-8). Total energy calculation was done using
many-body potential of the Tersoff form [32] using parameters from Brenner [33].
Dimers were added to the cap forming various possible structures occurring during
growth. The structures were relaxed using conjugate gradient method, as well as
measuring and comparing their energies.

In molecular dynamics method, canonical (N,V,T const.) ensemble averages were
generated with the Nose-Poincare thermostat [34]. It was reported before that there are
different ways for insertion of carbon into a segment of fullerene [25, 28], essentially
the reverse of O’Brien et al [35] We used the same idea (Figs. 3.1) together with
considering pentagons as the active locations contributing in Stone-Wales (STW) transformation [36]. Excessive cap defects (polygons beside 6 pentagons needed to form a cap proposed by Euler theory) were expected to anneal by bond rotations especially STW transformation; annihilation of two adjacent 5-7 pairs into four hexagons or annihilation of a heptagon having two neighboring pentagons with a hexagon in between to three hexagons and one pentagon (5-6-5-7 to 6-5-6-6) all energy favorable to initial structure.

We have used Trocadero non-orthogonal tight-binding code, atoms were heated to 3000K target temperature, with 0.5fs time step and hundred thousand time steps (50ps) for the whole process, recording the coordinates every 2 step, velocities were scaled to reach equilibrium every 10 time step. Many parallel simulations were done in each dimer addition step and random speeds (using random seed) were assigned for each simulation. All but few simulations led to partial tube evaporation or disassembly but few simulations led to bond rotations specially STW annealing (Figs 3.1.c-e) the structure. Only one or two dimers were added at a time as adding 3 or more dimers were causing the tube to open letting carbon atoms fly away. This was expected as with three or more dimers at a time, the small tube was vulnerable to large deformation making an unstable high energy structure that grow at one step in MD simulation.
Dimers were added step by step to observe the growth (Figs. 3.1). Adding the new dimers was consistent with the theory proposed by Bernholc et al [25] considering pentagon active locations for annihilation; the new structures needed either STW transformation or double 5-6 rotation. In other terms, random addition places could not
anneal through MD. The resulting structures from MD were not in neat shape (Figs 3.2) as coming from high

For (5,5) tube 10 dimers were added to increase the growth of the tube by one armchair unit cell (20 Carbon atoms). All dimers were added to the cap and the relaxed structures were gone through MD simulations. Few results showed that when dimers were added to the wall, 5-7s didn’t disappear and were gliding down the tube axis ruining the hexagonal tube wall. After adding 10 dimers a cap similar to original cap (half C_{60}) was obtained that could be transformed to original cap with two bond rotations. The tube grew that was almost %42 of its diameter,

The following figure shows the growth from the original (5,0) nanotube to the grown structure (after adding 10 dimers)

Figures 3.2 a) original (5,5) CNT \( d = 6.6\,\AA, \ L = 11.19\,\AA \), b) relaxed tube after adding 10 dimers to the cap and MD simulation \( L = 14.02\,\AA \), c) respective caps before (upper) and after (lower) adding dimers

3.2.2 Monte Carlo

We had to assume unrealistic large deposition rate for large scale tube growth considering classical MD simulation time restriction (nanosecond) comparing to much
longer experimental growth time (millisecond); hence, we built in a modified Monte-Carlo method that was performing bond rotation at temperature 0K. There have been methods for bond switching kinetic Monte-Carlo methods by Maiti et al [37] before. The new method turned out to be much faster than classical MD calculation. The growth for the same (5,5) tube was done with the help of Monte Carlo algorithm. Total energy calculation was done using many-body potential of the Tersoff form [32] using parameters from Brenner [33]. Dimers were added to the cap forming various possible structures occurring during growth. The structures were relaxed using conjugate gradient method, as well as measuring and comparing their energies.

The code had some restrictions imposed on rotation procedure; for example, the atoms or bonds contributed in one rotation were not allowed to rotate the next step. The basic idea for the code was to look for defects locations (ex. 5 and 7) and use graph theory to rotate all possible bonds; then using Tersoff-Brenner potential, testing if every bond rotation would lead to more energy favorable structure or not. One example that turned out to happen frequently was the STW transformation [36]. The bond rotations were recorded step by step as well as their corresponding energies. Every step could be regarded as a frame to make a movie for each Monte Carlo process with attention to their energy range that had to be in decreasing order.

The (5,5) tube was grown from 100 carbon atoms to 120 that is one unit cell growth for (5,5) tube that was increasing the length of nanotube by $2.44\,\text{Å} \approx 0.37d$ (d denotes the tube diameter). Different dimer places were tried but only the dimers
that were added to the cap were contributing to grow the tube; the dimers that were added to the tube wall formed a 5-7 that was gliding down the tube and disordered the hexagonal tube. The same exact half C60 cap was obtained after several Monte-Carlo simulations; however, results were obtained faster comparing to MD.

![Diagrams](image)

**Figures 3.3** a) original (5,5) CNT, \( d = 6.6 \text{Å}, L = 11.19 \text{Å} \), b) relaxed tube after adding 10 dimers to the cap and MC simulation \( L = 13.63 \text{Å} \), c) same cap for both before and after adding dimers

### 3.3 Chiral nanotube growth

The same Monte Carlo code was used for (12,1) half closed chiral nanotube, it was investigated how adding dimers affects the growth. There are thousands of possible theoretical caps for most of chiral nanotubes [38]. As there is no unique cap for chiral tubes, a low energy rather smooth and flat cap was chosen as the initial structure that had 213 carbon atoms. Dimers were added to the cap the same way mentioned before, having relaxed the structure, it could anneal through Monte Carlo simulation getting ready for new dimers. Since, the tube was larger in diameter comparing to (5,5), more dimers (3-4) could be added at a time making the growth faster.
Another technique that was used for (12,1) was to fix the lower half of the tube that turned out to be an efficient way for reducing calculation time in the code. Furthermore, preventing 5-7s to glide down the tube, as well as avoiding wrong bond rotations at the lower end ruining the hexagonal wall that was common in some simulations.

Forty four dimers were added to the tube to help it grow led to growth of 10Å in length that was almost 76% of the tube diameter, 9.93Å.

**3.3.1 Cap Rotation**

The cap formation was changing after each new dimer addition; however, it was interesting to observe the initial cap appeared few times in rotated form with respect to
initial orientation. It was like one could cut the cap and insert new dimers to the chiral tube wall, then rotate the cap and put it back to the tube wall making the same structure with the growth. This was consistent to a basic idea proposed previously by Endo & Kroto for spiral graphite sheets and asymmetric fullerene ends cap [28]. Their cap was connected to a helical cylindrical array of hexagonally linked carbon atoms. Ijima found before an important property of the cylindrical walls of the nanofibers that they are arrayed in a helical screw relative outlook [39]. They introduced the Schlegel diagram (Fig. 3.4) for the smallest “asymmetric (ex. non-C_{60} type) isolated pentagon fullerene end caps”. Adding hexagons to the configuration results a cylindrical tube with atoms arrayed in a helix. Inserting dimers to the wall lead to a cap which is indistinguishable beside rotation. If new atoms/dimers are ingested at the cap, after disposing the configuration, the new atoms/dimers could knit the tube and lead to tube growth. Then one could consider the cap to move in a screw transformation. Our result could be considered a generalized scheme for any chiral tube \((m,n)\). It may be beneficial to note chiral fullerene-76 has been extracted by Ettl et al [40] possess the same diagram.

Figure 3.5 Schlegel diagram
For measuring cap rotation, we built the border of wall and cap with dimers. In Fig. 3.6, considering $a_1, a_2$ as the base vectors of the honeycomb, from vector $C_h$ starting point, we chose the atoms adjacent/closest to $C_h$ vector and moved forward to reach the end of the vector. Considering second path the same way above first, we have built up a chain of zigzag ring through the chiral vector of the tube. $N_s$ is the number of atoms in each spiral path that is obtained by dividing chiral.

\[
d_c = \frac{C_h}{\cos(\theta)} = \frac{2a(n^2 + m^2 + mn)}{2n + m} \tag{3.1}
\]

\[
N_s = \frac{d_c}{a} = \frac{2(n^2 + m^2 + mn)}{2n + m} \tag{3.2}
\]

Since each zigzag spiral through the chiral vector contains two time of this $N_s$ (Fig. 3.6, blue dots), the rotation angle $\Delta \phi$ dependency to number of dimers added $N_d$ will be:

\[
\Delta \phi = \frac{2\pi N_d}{N_s} = \frac{\pi N_d (2n+m)}{m(n^2 + m^2 + mn)} \tag{3.3}
\]

![Diagram](image.png)

**Figure 3.6** edge for (4,2) nanotube, the number of blue dots denote $N_s$ as the spiral semi-ring
For (12,1) tube we will have:

\[ C_h = (12,1) \]
\[ T = (14,-25) \]
\[ d_i = \frac{L}{\pi} = \frac{a\sqrt{n^2 + m^2 + mn}}{\pi} = 9.93\text{Å} \quad (2.4) \]
\[ T = \frac{\sqrt{3}L}{d_R} = 17.20\text{Å} \]

\[ \Delta \theta_{(12,1)} = \frac{\pi N_d}{6.28} \quad (2.5) \]

Expected rotation value from 29 dimers to 44 dimers (as they had the same cap form) from derived formula was 430° ~ 69° but the (Fig. 3.7) but measured value was 65° with the error of 1.1%

### 3.4 Discussion

Molecular Dynamics and modified Monte Carlo method were used to simulate tube growth. Dimers were added step by step to (5,5) and (12,1) tubes were used to simulate the growth with the help of tight binding calculation. Results from MC & MD
were matching for (5,5) tube showing the tube unit cell growth by one unit cell. Furthermore, it was observed that 5-7 could glide through the cap and cause the structure to anneal and remove the defects for example by stone-wales transformation. It is beneficial to note MC method was found to be an efficient way and generally faster comparing to MD especially for larger tubes with larger number of atoms. New relation was introduced for the possible mechanism of chiral tube growth that was a linear dependence of rotation angle to the number of dimers added. It was observed that the cap could be cut off, new dimers added to the tube wall then rotating and raising the cap could be put back to the tube. Future development and experiments is needed to verify the rotation idea.
Chapter 4

Investigating edge evolution in graphene evaporation

4.1 Introduction

Graphene edges could be an arrangement of Armchair (AC) or Zigzag (ZZ). It has been always an interesting problem to find which edge (AC or ZZ) is dominant during Graphene evaporation [41, 42]. Having investigated the problem using Monte Carlo algorithm for different geometries and edge types, we found that irrespective of initial geometry and shape, all structures tend to reach a common equilibrium introducing AC edge as dominant.

4.2 Method

Having used modified Monte Carlo code, total energy calculation was done using many-body potential of the Tersoff form [32] using parameters from Brenner [33]. Evaporation process was done for Graphene structures with various geometries. Removing dimers from the edge of the structures was done by choosing the least energy cost for different possibilities. Few examples are included in the following for regular (ex. polygons) and amorphous (ex. islands) geometries.

Many common features were observed during the sublimation process. It was found energetically favorable to remove atoms sitting on sharp corners (in other words
intersection of ZZ and AC edges) [43]. Having done energy calculation for simple edge types (fig.1), the energy cost ordinance was found as:

\[
\begin{align*}
\text{Corner Trimer} &< \text{ZZ-AC Dimer} < \text{AC Dimer} < \text{ZZ Trimer} \\
7.2\text{ev} &< 8.2\text{cv} < 9.0\text{ev} < 11.0\text{ev}
\end{align*}
\]

The corner trimers that were appearing at intersection of ZZ and AC edges were found to be the most energy favorable mechanism for evaporation consistent with earlier belief of cutting sharp edges. Another form that appeared on AC and ZZ intersection was denoted as ZZ-AC dimer that was the second most energy favorable removal mechanism.

Comparing dimer removal from AC and ZZ edges, the energy cost for AC dimer removal was significantly lower than ZZ dimer as removing ZZ dimers was found to be the least energy favorable mechanism. One could note the formation of excessive dangling bonds and hanging monomer carbons after ZZ dimer removal that would not happen for AC dimer removal could have caused this big energy difference (3.3 eV).

Furthermore, it was found that energy cost for AC/ZZ dimers removal sitting on the same edge is the same (Fig.4.1), again making the corner atoms (trimers/dimers) the sources for evaporation propagation. Also, the energy difference for removing dimers from dents was found to be in the order of 10-50mev.

We have defined a ratio for AC atoms contribution on structure's edge as \(n/(n+m)\) with respect to all atoms of the edge; where \(m\) denotes atoms assigned as AC and \(n\) for that of ZZ. Decision whether AC or ZZ was based on the bond order patterns of the neighboring atoms. Having done statistical analysis of evaporation process for
different geometries, it was found that AC edge appearance was prominently dominant over ZZ. The mean average value was found to be 0.7 with small variation (0.02) for different geometries. Noting \( r = 0 \) for pure ZZ and \( r = 1 \) for pure AC, the ratio was independent of initial ratio for edge types for different shapes. As shown in result section, the curve reaches equilibrium and the average value rapidly (roughly after evaporating perimeter of the geometry) for all cases.

![Energy cost through the edge for an arbitrary simple Graphene.](image)

**Figure 4.1** Energy cost through the edge for an arbitrary simple Graphene. ZZ, AC, corner dimers and trimers are denoted by green, blue, orange and red squares respectively. Three plots for the corresponding edges were calculated with classical potential. Energy drop at the corners are quite significant.

Different edge types were considered (Fig. 4.2) to investigate the effect of dimer removal on the edges. The preliminary evaluations were found to build the basis of the
structure evaporation process. These edges evolutions were used as a building block to get an analytical solution of finding the average ratio later (under progress).

Figure 4.2 different edge evaporations; a) trimer from ZZ edge, b) dimer from AC edge, c) trimer from AC-ZZ edge, d) dimer from AC-ZZ edge

<table>
<thead>
<tr>
<th>Edge Type</th>
<th>En (eV)</th>
<th>Edge Type</th>
<th>En (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimer ZZ-AC 90 deg</td>
<td>7.20</td>
<td>ZZ-AC 90</td>
<td>7.20</td>
</tr>
<tr>
<td>Trimer ZZ-AC 30 deg</td>
<td>7.90</td>
<td>ZZ-AC 30</td>
<td>7.90</td>
</tr>
<tr>
<td>Trimer ZZ 60 deg</td>
<td>7.90</td>
<td>ZZ-ZZ 60</td>
<td>7.90</td>
</tr>
<tr>
<td>Dimer AC 60 deg</td>
<td>8.10</td>
<td>AC-AC 60</td>
<td>8.10</td>
</tr>
<tr>
<td>Dimer ZZ 120 deg</td>
<td>8.10</td>
<td>ZZ-ZZ 120</td>
<td>8.10</td>
</tr>
<tr>
<td>Dimer ZZ-AC 90 deg</td>
<td>8.20</td>
<td>ZZ-AC 90</td>
<td>8.20</td>
</tr>
<tr>
<td>Dimer ZZ-AC 150 deg</td>
<td>8.60</td>
<td>ZZ-AC 150</td>
<td>8.60</td>
</tr>
<tr>
<td>Trimer AC 120 deg</td>
<td>8.90</td>
<td>AC-AC 120</td>
<td>8.90</td>
</tr>
<tr>
<td>Dimer Pure AC</td>
<td>9.10</td>
<td>Pure AC</td>
<td>9.10</td>
</tr>
<tr>
<td>Trimer Pure ZZ</td>
<td>11.00</td>
<td>Pure ZZ</td>
<td>11.00</td>
</tr>
</tbody>
</table>
Table 4.1 sorting edge types and their corresponding energies and equivalents

4.3 Results

4.3.1 Evaporation of regular structures

A few regular geometries with different edge types were considered (ex. in Fig.4.3). One example included here was a hexagon Graphene with 600 carbon atoms. Two types were considered, one with all ZZ edges and the other one all AC edges. It was interesting for both processes; their evaporations were quite similar in evolution that after reaching the average value for AC ratio and after equilibrium. First, sharp corners (intersections of AC & ZZ edge) were removed introducing more AC edges. This process could be viewed as smoothing the shape. The medial structures were similar to a large Coronene looking structure; final structure was just like Coronene albeit without saturating Hydrogens. The medial structures were tending to be similar to Wulff construction [44] The same process was observed for other regular geometries.

Figure 4.3 a) pure ZZ, b) pure AC evaporation evolution
4.3.2 Evaporation of Amorphous Structures

In order to get a wider picture, the evaporation was done for amorphous structures (ex. Island Fig. 4.5). Basically, the same process was observed for islands; however, due to bigger sharp portions, it generally took longer for islands to reach equilibrium (expected average AC ratio value of 0.7). After evaporation of the sharp portions, quasi-regular structures were observed in the proceeding.

Figure 4.5 Arbitrary island-like structure evaporation with 500 atoms; right figure, AC ratio curve vs. dimer evaporation steps.
Many other examples were done for regular and irregular shapes and similar evaporation was observed. It is beneficial to note the same behavior for similar structure, as experimented recently in [45]. Extensive analysis is being done to verify the evaporation of holes inside Graphene structures as was experimented in [46].

**Kinetic model for Graphene evaporation**

A simplified kinetic model is considered to represent graphene evaporation. We assume the relevant steps in the evaporation mechanism are

\[
\begin{align*}
2.5 \text{AC} + 1.5 \text{ZZ} & \rightarrow 2 \text{ZZ} + 1.5 \text{AC} \\
\text{Rate:} \quad r_1 &= k_1 R_{AC} (1 - R_{AC}) \\
1.5 \text{AC} + 1.5 \text{ZZ} & \rightarrow 2.5 \text{AC} \\
\text{Rate:} \quad r_2 &= k_2 R_{AC} (1 - R_{AC}) \\
3 \text{AC} & \rightarrow 1 \text{AC} + 2 \text{ZZ} \\
\text{Rate:} \quad r_3 &= k_3 R_{AC} \\
\text{ZZ} & \rightarrow 3 \text{AC} \\
\text{Rate:} \quad r_4 &= k_4 (1 - R_{AC})
\end{align*}
\]

In this notation, \( R_{AC} = \text{AC}/(\text{AC} + \text{ZZ}) \) is the fraction of AC bonds in the boundary, and correspondingly \( 1 - R_{AC} = \text{ZZ}/(\text{AC} + \text{ZZ}) \) is the fraction of ZZ bonds.

Considering the stoichiometry in the processes (1) – (4), the rate of change of the fraction of AC bonds is given by

\[
\frac{dR_{AC}}{dt} = -r_1 + r_2 - r_3 + 3r_4 = (k_2 - k_1 - k_3 - 3k_4)R_{AC} + (k_1 - k_2)R_{AC}^2 + 3k_4
\]

It is convenient to define the auxiliary parameters:

\[
\alpha = k_1 - k_2, \quad \beta = k_2 - k_1 - k_3 - 3k_4, \quad \gamma = 3k_4
\]

and to factorize the right-hand side of Eq. (5) in terms of the roots

\[
R^*_i = \frac{-\beta}{2\alpha} \pm \frac{1}{2\alpha} \sqrt{\beta^2 - 4\alpha\gamma}
\]
\[
\frac{dR_{AC}}{dt} = \alpha \left( R_{AC} - R_+^* \right) \left( R_{AC} - R_-^* \right) \quad (4.8)
\]

It is clear from the differential Eq. (8) that the steady-state solution is given either by

\[ R_{AC} = R_+^* , \text{ or by } R_{AC} = R_-^*. \]

Assuming the initial condition \( R_{AC}(0) = R_0 \), the differential Eq. (8) can be exactly solved by separation of variables, to obtain

\[
R_{AC}(t) = \frac{R_+^* - R_-^* \frac{R_0 - R_-^*}{R_0 - R_-^*} \exp(\alpha \left[ R_+^* - R_-^* \right] t)}{1 - \frac{R_0 - R_-^*}{R_0 - R_-^*} \exp(\alpha \left[ R_+^* - R_-^* \right] t)}
\]

(4.9)

By simple inspection, we notice that the steady-state solution of Eq. (9) will be:

\[
\lim_{t \to \infty} R_{AC}(t) = \begin{cases} 
R_+^*, & \text{if } \alpha \left( R_+^* - R_-^* \right) > 0 \\
R_-^*, & \text{if } \alpha \left( R_+^* - R_-^* \right) < 0
\end{cases}
\]

(4.10)
4.3.3 Evaporation of circle

Considering different geometries of graphene, more regular shapes were considered ranged from different polygons, the evolution of a few polygons during evaporation and the AC ratio. An especial figure was a circle which could be considered an infinite side polygon. Due to constraints for cutting the circle from a hexagonal lattice, a big enough cut was approximated as a rounded circle.

During circle evaporation, it was seen that the circle was changing to a hexagon shape which was the same expected evolution as the prior calculations. Artificial examples are seen in the following figures.

![Figure 4.6 Circle evaporation process; \#C denotes the number of carbon atoms for each structure and r denotes the AC ratio.](Image)

\#C: 1925  \ r = 0.56  
\#C: 1841  \ r = 0.67  
\#C: 1724  \ r = 0.78  
\#C: 1691  \ r = 0.79  
\#C: 1566  \ r = 0.74  
\#C: 1417  \ r = 0.75
And the AC ratio during the circle evaporation was as following with average value of 0.74.

Figure 4.7 AC ratio vs. number of evaporated dimers for circle

Another challenge was to find the AC ratio of the circle irrespective of the evaporation which will follow in the following section.
4.4 Evaluation of AC Ratio for a Regular Polygon

Fig. 4.8 shows a typical regular polygon (P) drawn on the hexagonal (graphene) lattice.

![Figure 4.8 a regular polygon (black) and the underlying lattice (red)]

Note that in general, P does not need to fit lattice points (the black P does not follow the lattice). However, for large P slight modification of angles and length is possible, such that P fits the underlying lattice (see the red P) and does not deviate from initial polygon (black P). Results below are derived for polygons which are large enough, such that discrete nature of angles and sides is not important.

Considering an arbitrary polygon with k sides, each of length L, the first edge of a polygon is at angle $\theta_1$ (initial angle shown in Fig. 4.8) with x axis. Consider first edge of A polygon shown in Fig. 4.9, the $i^{th}$ edge of the polygon is at angle $\theta_i + 360 \times (i - 1) / k$, where $i = 1...k$. 
The edge of the polygon is indicated by a red line with letters z and a, indicating zigzag and armchair atoms (the atom type was labeled based on two edge neighbor atoms’ bond order following AC and ZZ edge construction; based on this method, atoms with the bond order 2-2-3, 3-2-2, 2-3-3, 3-3-2 for 3 successive edge atoms are labeled as AC and 2-3-2, 3-2-3 as ZZ, where the second number is the desired atom’s bond order and the first and third number corresponding to the two neighboring atoms). Overall there are (n-m) ZZ atoms and 2m AC atoms and AC ratio (the ratio of AC atoms over all atoms) is given by $r = \frac{2m}{n+m}$. From geometry:

\[
m = \frac{L\sin(\theta_i)}{\sin(60)} \quad n + m = \frac{L\sin(60 + \theta_i)}{\sin(60)} \quad r = \frac{2m}{m + n} = \frac{2\sin(\theta_i)}{\sin(60 + \theta_i)} \quad (4.11)
\]

Above derivation is valid for $\theta_i \leq 30^\circ$ due to 6 fold symmetry of hexagonal lattice (Fig. 4.9). If the angle $\theta_i$ is larger then $30^\circ$ but less then $60^\circ$ degrees, (ex. $40^\circ$), the expression above is valid only if angle is mapped with the following mapping:
If 0 ≥ 30°, then 0 = 30 – mod(0, 30) where 0 is the reduced angle.

Generally the following mapping is correct for any angle:
Assuming γ = mod(θ, 60); if (γ > 30), then 0 = 30 – mod(γ, 30); else 0 = γ

Graphically this mapping is illustrated on Fig. 4.10.

Figure 4.10 θ vs. θ, period of 60 degree

Therefore, for k sided polygon, with edge of length L the AC ratio of the entire structure can be written as:

\[
 r = \frac{2(m_1 + m_2 + ... + m_k)}{(n_1 + m_1 + n_2 + m_2 + ... + n_k + m_k)} = \frac{2(\sin(\tilde{\theta}_1) + \sin(\tilde{\theta}_2) + ... + \sin(\tilde{\theta}_k))}{\sin(60 + \tilde{\theta}_1) + ... + \sin(60 + \tilde{\theta}_k)}
\]

If we consider two simple cases of pure AC and ZZ hexagon for a regular hexagon we will have:

Let k=6, and θ_i = 0°. This corresponds to zigzag edge hexagon. Having

\[
\theta_i = \{0,60,120,180,240,300\} \rightarrow \tilde{\theta}_i = \{0,0,0,0,0\} \rightarrow r = 0 \text{ (pure ZZ edge)}
\]

And for k=6, and θ_i = 30°, we have

\[
\theta_i = \{30,90,150,210,270,330\} \rightarrow \tilde{\theta}_i = \{30,30,30,30,30,30\} \rightarrow r = 1 \text{ (pure AC edge)}
\]
Plotting $r = r(n, \theta_i)$ for a few polygons; Fig. 4.11 and 4.13 below show the plot of AC ratio as a function of $\theta_i$ for a few parameters $n$. Larger $n$ correspond to more circular regions.

![Graph showing AC ratio for 3-10 sided polygons](image)

**Figure 4.11** AC ratio for 3-10 sided polygons

The hexagon case was spectacular covering all the range of the ratio during the rotation:
Figure 4.12 hexagon rotation

And for higher angles Fig. 4.13 shows a convergence when $n$ is increasing.

Figure 4.13 AC ratio for polygons where number of sides is a multiple of 6

4.5 Conclusion

It appears (see Fig. 4.11) from above calculations that the AC ratio of 0.7 best fits hexagonal or $n=12$ polygons rotated relative to $x$ axis by about 20 degrees.
Furthermore, from global results figure one could notice the convergence of the ratio to 0.53... This number corresponds to the circle geometry having infinite number of sides in which the evaporation was investigated before. The value could be calculated even without numerical computation.

Considering the ratio from the beginning as \( r = \frac{2m}{m+n} = \frac{2\sin(\theta)}{\sin(60+\theta)} \)

One could calculate get the value by calculating the mean value for 0 to 60 degrees (the hexagonal lattice has six-fold symmetry).

\[
\int_{\theta=0}^{\pi/6} \frac{2\sin(\theta)}{\sin(60+\theta)} \, d\theta = \frac{\pi}{6} = 0.5359 = 2\tan(15^\circ)
\] (4.13)

Considering Fig. 4.9 for any angle at indices \((m,n)\) there are \((m-n)\) ZZ atoms and \((2n)\) AC atoms. Using the law of sines we will have:

\[
\text{for } \forall \theta : \frac{AC}{ZZ} = \frac{2\sin(\theta)}{\sqrt{3}\sin(30-\theta)}
\] (4.14)

For random \(0^\circ < \theta < 30^\circ : \frac{AC}{ZZ} = \frac{2\sin(\theta)}{\sqrt{3}\sin(30-\theta)} \) (4.15)

since \(\sin(\theta) = \sin(30-\theta) : \frac{AC}{ZZ} = \frac{2}{\sqrt{3}} \rightarrow \frac{AC}{ZZ+AC} = \frac{2}{2+\sqrt{3}} = 0.5359... = 2\tan(15^\circ)\)

One could conclude the AC ratio is more than half (the ratio corresponding to same distribution of AC and ZZ over the edge) which was not primitive to anticipate.
Chapter 5
Ab Initio prediction of Geometry & Stability of Chiral \( \alpha \)-Boron Nanotubes

5.1 Introduction

Recently boron clusters (including tubes) [47, 48] have attracted attention of researchers. Especially since Pfefferle et al [49] synthesized the first boron nanotubes growing on Si template support (Fig. 5.1). Besides this experiment, there has been two theoretical observations recently, that has increased attention to boron synthesis. The first observation was that one particular pattern, namely \( \alpha \)-sheet, has the best electron bands occupancy and lowest total energy among the possible two-dimensional patterns of boron atoms [50, 51].

Figure 5.1 SEM and STEM images of boron nanotubes growing on a Si template support. [49]
Another observation was that boron could form stable hollow spheres similar to carbon fullerenes, such as $B_{65}$, $B_{92}$, $B_{110}$ and especially boron buckyball $B_{80}$ [52].

Below, one could note the study of Ismaeil-Beigi and Tang [50] suggesting that $\alpha$-sheet (in which considering any 3 principal directions in boron sheet, every other hexagon lacks a central boron atom) is the most stable comparing to other possible boron sheets. Fig. 5.2 suggests that $\alpha$-sheet provides best occupancy of the bands by electron and lowest total energy. Also considering the binding energy vs. hexagon hole density, maximum binding energy occurs for $\alpha$-sheet.

![Figure 5.2 Projections are onto in-plane (sum of s, pₓ, and pᵧ, solid red) and out-of-plane orbitals (pₜ, blue). Thick vertical black lines show the Fermi energy. [50]](image-url)
Fig 5.3 from left to right: boron α-sheet, (6,6) armchair and (12,0) zigzag boron α-tube. Boron α-tubes could be made by wrapping boron sheets as in Fig 5.3. Both hollow spheres and born-α sheets could be regarded as precursors for synthesis of boron nanostructures. As Sadrzadeh et al [53] showed in Fig 5.4, boron α-sheet could be cut and folded to a boron fullerene sphere B₈₀ and more than that extending to a bigger cage as B₁₂₀. Similar process could be done for unwrapping the cage to sheet.

Figure 5.4 (a) formation of B₈₀ from boron α-sheet (b) extension to longer cage B₁₂₀ (c) also to nanotubes by adding additional rings. d) Tube can be unfolded into α-sheet.

The considered precursors have more importance in theoretical point of view and future experiments should verify the synthesis of the theoretical models. Also the electronic structure of α-tubes formed from the metallic sheet is expected to be metallic that is different than the metallicity nature of carbon nanotubes which has
both metallic and semiconducting characteristics. The metallic characteristic for boron α-tubes could play a big role in future electronics. Using \textit{ab initio} calculation, I have investigated the mechanical and electronic behavior of these tubes. While the tubes are found to be stable, buckling of specific boron atoms separating from in-plane positions was observed which could come from cylindrical curvature; this could have a major role on the electronic properties; the tubes with diameters smaller than 1.7 nm were found to be semiconducting while the bigger tubes were found to be metallic.

5.2. Method

VASP (Vienna \textit{ab initio} simulation package) was used for structural optimization of the nanotubes using wave method with a plane wave basis set using periodic boundary conditions (PBC) and conjugate gradient with GGA (generalized gradient approximation) of PBE [54] for the energy of exchange correlation [55, 56]. Equivalent set of k-points were used to sample 1-D Brillouin zones of tubes. When the absolute value of the force on each ion was less than 0.001 eV/Å, the structure was considered as fully relaxed. Enough spacing (not less than 12 Å) was chosen between periodic images of the tubes to avoid any interactions.

5.3 Structural properties

Recently Sadrzadeh et al [53] also reported the same binding energy for the α-sheet ($E_b=5.99\text{eV}$) and bond length ($b=1.67\text{Å}$) close to the values of Tang et al [50]. New
indexing was needed for α-sheets similar to conventional CNT indexing. As shown in Fig. 5.4 accepting \( b_1, b_2 \) as the basic vectors for α-sheet (while \( a_1, a_2 \) correspond to conventional basic vectors for honeycomb lattice) the tube parameters are derived as:

\[
\begin{align*}
  b_1 &= 2a_1 - a_2 \\
  b_2 &= a_1 + a_2 \\
  C_h &= na_1 + ma_2 = (n - m)b_1 / 3 + (n + 2m)b_2 / 3 \\
  &\Rightarrow n - m = 3k \\
  N_B &= \frac{16(m^2 + n^2 + mn)}{3d} = 4N_{C(m,n)}
\end{align*}
\]

(5.1) (5.2)

Figure 5.5 Boron α-sheet, basic vectors

It is interesting to note that the number of boron atoms in a unit cell is four times than that of honeycomb carbon unit cell. Three chiral tubes (4,1), (5,2) and (6,3) were considered for verifying the properties for chiral tubes (the number of atoms in chiral unit cells for larger tubes were not affordable for computations with desired accuracy considering current allowable Rice clusters memories and number of processors for one job script). Sadrzadeh et al considered various armchair and zigzag tubes. They found that relaxation to be diameter dependent and mostly occur around the filled hexagons.
5.4 Mechanical properties

Having relaxed the chiral boron α-tubes for different PBC lengths, the relaxed lengths of the tubes were estimated and the mechanical in-plane stiffness $C$, the flexural rigidity $D$ and Poisson’s ratio $\nu$, were calculated from the curve obtained from energies at different points.

![Figure 5.6 (6,3) boron α-tube energy vs. axial strain](image)

The hexagonal symmetry of 2D lattice of α-sheet was assumed as isotropic and the atomistic structure was considered as a continuum shell model [57]. Having computed the energy per atom $E$ vs. the axial strain $\varepsilon$ in uniaxial stretch (the elastic energy curve) the in-plane stiffness was calculated using the following relation:

$$C = \frac{1}{a} \frac{\partial^2 E}{\partial \varepsilon^2}, \text{ where } a \text{ is the area per atom in the } \alpha\text{-sheet}$$

(5.3)
Also considering the tube shrinkage while stretched, the Poisson’s ratio $\nu$ relates the axial strain and radial strain as:

$$\nu = -\frac{\varepsilon_x}{\varepsilon_r},$$

the minus sign is for shrinkage due to stretch. \hfill (5.4)

**Figure 5.7** Poisson’s ratio $\nu$ for (6,3) boron $\alpha$-tube, $\varepsilon_r, \varepsilon_x$ correspond to radial and axial strain respectively

The energy per atom versus strain curve was fitted to a parabola and using $\frac{E}{N} = \frac{1}{2}Ce^2$

The obtained results for the chiral tubes were found to be less than achiral (zigzag and armchair) tubes which were found to be %60 of CNTs, $C = 210$ N/m [53] where similar result was found for Poisson’s ratio $\sim 0.2$.

Furthermore, flexural rigidity $D$ was calculated using the following relation similar to [53].

$$E_b = \frac{2D}{d^2} + \text{const}$$, where $E_b$ is the binding energy per atom \hfill (5.5)
Figure 5.8 binding energy $E_b$, vs. $1/d^2$ where $d$ represents tube diameter results [53]

Relaxed tubes are included in Fig. 5.9. The chiral tube (4,1) was not considered in the results as a severe twist was observed from all relaxation results which was believed to originate from the very small nature of tube diameter which brings the suspect of not being stable enough to form under normal conditions. Having measured periodic bond length values in three directions, 0.6-5.4% elongation was observed comparing to boron $\alpha$-sheet bond length (1.67Å). Table 5.1 includes the results for the axial and circumferential bond lengths and dihedral angle of buckled atoms.

Figure 5.9 relaxed tubes and their corresponding cross sections
Axial Bond  Axial Bond  Circumferential  Dihedral Angle of  
Nanotube Length 1 (Å) Length 2 (Å) Bond Length 3 (Å) Buckled Atoms

(5,2)  1.69,1.71  1.68,1.71,1.75  1.68,1.70,1.76  16-17°
(6,3)  1.69,1.72  1.69,1.70,1.74  1.69,1.70,1.73  17-18°

Table 5.1 axial and circumferential bond lengths and dihedral angle of buckled atoms

It was found that resistance to mechanical deformation of boron tube is within 50% of that of CNTs. Knowing the in-plane stiffness and flexural rigidity characterize the elastic mechanical behavior of the boron tubes. Table 5.2 includes the mechanical properties of several chiral and achiral tubes in the order of their increasing diameter.

<table>
<thead>
<tr>
<th>Nanotube</th>
<th>Diameter (Å)</th>
<th>C(N/m)</th>
<th>v</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5,2)</td>
<td>5.90</td>
<td>189.0</td>
<td>0.30</td>
</tr>
<tr>
<td>(6,3)</td>
<td>7.44</td>
<td>189.6</td>
<td>0.16</td>
</tr>
<tr>
<td>(5,5)</td>
<td>8.13</td>
<td>209.4</td>
<td>0.18</td>
</tr>
<tr>
<td>(9,0)</td>
<td>8.63</td>
<td>206.7</td>
<td>0.21</td>
</tr>
<tr>
<td>(6,6)</td>
<td>9.93</td>
<td>202.1</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 5.2 mechanical properties of several chiral and achiral tubes in the order of diameter

Also a new method was used for finding the tube shrinkage. Assuming that the initial axis line of the tubes do not rotate during the stretch, all the boron atoms could lie into
a circle of radius $R$ with probable small deviation from the center. Then the problem boils down to finding a circle with unknown center $(x_0, y_0)$ and radius $R$ (Fig. 5.10). Having $N$ boron atoms gives $N$ circle equations; hence, having $N$ equations with 3 unknown parameters, the problem was solved using Guass-Newton method assisting nonlinear least-square method *Lsqnonlin* in MATLAB. A function was implemented using the derived parameters and inputs of boron atoms coordinates to calculate the solve the problem. Assuming tubes are aligned in axial direction (arbitrarily Z-direction), the equations for $N$ boron atoms will be:

Figure 5.10 average circle of atoms, $C_{avg}$ represents $(x_0, y_0)$ and $r_{avg} = R = R_0$

\[
\begin{align*}
(x_1 - x_0)^2 + (y_1 - y_0) &= R_1^2 \\
(x_2 - x_0)^2 + (y_2 - y_0) &= R_2^2 \\
... \\
... \\
(x_n - x_0)^2 + (y_n - y_0) &= R_n^2
\end{align*}
\] (5.6)

Least square method minimization:
\[ S(x_0, y_0, R_0) = \sum_{i=1}^{n} \left[ R_0^2 - (x_i - x_0)^2 + (y_i - y_0)^2 \right]^2 \]
\[ \frac{\partial S}{\partial x_0} = 0, \frac{\partial S}{\partial y_0} = 0 \quad \text{and} \quad \frac{\partial S}{\partial R_0} = 0 \] 

(5.7)

Then the input parameters for MATLAB will be:

\[ R_0^2 = \frac{1}{n} \sum_{i=1}^{n} [(x_i - x_0)^2 + (y_i - y_0)^2] \]
\[ x_0 = \frac{\sum_{i=1}^{n} x_i \Phi_i}{\sum_{i=1}^{n} \Phi_i}, \quad y_0 = \frac{\sum_{i=1}^{n} y_i \Phi_i}{\sum_{i=1}^{n} \Phi_i} \]
\[ \Phi_i = R_0^2 - (x_i - x_0)^2 + (y_i - y_0)^2 \] 

(5.8)

Table 5.3 shows the results for (5,2) and (6,3) tubes. A small deviation from zero is observed in the results which is consistent with earlier assumption.

<table>
<thead>
<tr>
<th>Nanotube</th>
<th>(x_0)</th>
<th>(y_0)</th>
<th>(R_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5,2)</td>
<td>3x10^{-4}</td>
<td>1x10^{-4}</td>
<td>2.948</td>
</tr>
<tr>
<td>(6,3)</td>
<td>3.2x10^{-3}</td>
<td>8x10^{-4}</td>
<td>3.721</td>
</tr>
</tbody>
</table>

Table 5.3 Lsqnonlin results for results for (5,2) and (6,3) tubes; all values are in Å.
5.5 Electronic structure

Although the $\alpha$-sheet is metallic, Sadrzadeh et al [53] found earlier that zigzag and armchair nanotubes with smaller diameters are semiconducting. The gap in armchair nanotubes is in the range of 0.6eV. Considering the band structure of unrelaxed armchair tube, one could investigate the unexpected gap opening. While unrelaxed tubes show a metallic structure, the same relaxed tubes turned out to be semiconductor. They reported the buckled boron atoms because the charge density of the VBM and the effect of rehybridization induced by the buckling.

![Figure 5.11 electronic structures for (5,2) (left) and (6,3) suggest metallic structures](image)

In agreement with achiral tubes, that is for diameters bellow 1.7nm are semiconductor while above are metallic. The metallicity of the larger diameter boron tubes together with their low effective mass and fair conductivity make boron $\alpha$ tubes a good nanoscale conductor and a potential wide range of use in electronic devices.

It was found that mechanical stiffness of Chiral $\alpha$ Boron Nanotubes is slightly less than achiral tubes and within range 50% of carbon nanotubes. Consistent with earlier reports smaller diameter tubes were found to be semiconductor and larger tube to be metallic. $\alpha$-Boron tubes are expected to play important role in future electronic devices which brings attention to the importance of their synthesis.
References