Atomistic Simulation of NanoElectro Mechanical Systems Based on Carbon Nanotubes

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Atomistic Simulation of Nano-Electro-Mechanical Systems Based on Carbon Nanotubes

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Abstract

Carbon nanotubes (CNTs) possess unique electrical and mechanical properties and are of great interest for both basic and applied research. One active research field is that of nano-electro-mechanical systems (NEMS) based on CNTs. With respect to conventional NEMS, CNTs are extremely light, have very high Young’s Moduli (∼5TPa), contain a small amount of structural defects, and it is anticipated that they will oscillate at high frequencies. Hence, assuming all other properties being equal, carbon nanotube resonators are expected to reach the ultimate mass, stress and pressure sensitivities.

Since, the natural frequency is sensitive to the applied external load, one of the principles of sensing is based on the natural frequency shift of a carbon nanotube resonator under an external perturbation. Hence, in order to design and optimize CNT NEMS one has to understand vibrational behavior of these systems.

This thesis presents numerical studies of vibrational behavior of single walled carbon nanotubes (SWCNTs). Carefully equilibrated molecular dynamics simulations of doubly clamped armchair SWCNTs including a precise analysis of the four lowest modes of vibrations are presented. We provide clear evidence for the failure of simple analytic models such as Euler-Bernoulli to accurately extract resonance frequencies as the ratio, (R/L), between the tube radius (R) and the length (L) varies. Our
results are in excellent agreement with the Timoshenko beam model, which includes the effect of both rotary inertia and of shearing deformation. Invoking the Euler-Bernoulli model implies that the bending rigidity is constant. We showed that if $\lambda_n$ is the wavelength of the $n$th mode, for larger values of $R/\lambda_n$ this is most definitely not true. Yakobson’s paradox, relates to a scatter of between 1 and 5 TPa in the Young’s modulus from atomistic simulations. In this thesis we shed light on this by giving an upper cutoff estimate for the effective SWCNT thickness, and show that in the Timoshenko model, there are two different sources for the nanotube thickness.

In an attempt to determine whether the nanotube type affects vibration we report on the vibrational behavior of four different types of SWCNTs: armchair, zigzag and two different chiral ones, which were fully clamped at both ends. Comparison between the vibrational behavior of these four types of nanotubes gave the result that the SWCNT structure does not affect the vibrational frequencies under these conditions.

We also presents a study of the effect of boundary conditions on the vibrational behavior of carbon nanotubes. Fully doubly clamped nanotubes of all three types exhibit the same vibrational modes, and their vibrations in the directions perpendicular to the nanotube axis are degenerate. We studied SWCNTs with boundary conditions which imitate the partly clamped experimental conditions. Our results demonstrate that armchair, zigzag and chiral nanotubes indeed vibrate differently. The symmetry between the two perpendicular directions is broken, and SWCNT type does influence the vibrational modes. A final study of proof of concept for varying atomic mass shows that the vibrating doubly clamped nanotube can sense zeptogram masses.
List of Symbols

\( \vec{C}_h \) : chiral vector that connects two carbon atoms of the graphene sheet

\( \vec{a}_1, \vec{a}_1 \) : unit vectors along two directions in the hexagonal graphene sheet

\( n, m \) : integer numbers which denote the number of unit vectors

\( L \) : nanotube length

\( D \) : diameter of the nanotube

\( A_{xy} \) : area of cross section of the nanotube

\( U \) : total binding energy

\( r_{ij} \) : distance between carbon atoms \( i \) and \( j \)

\( V_R(r_{ij}) \) : pair repulsive interaction term

\( V_A(r_{ij}) \) : pair attractive interaction term

\( B_{ij} \) : a term representing the bond between atom \( i \) and its local environment

\( K_B \) : Boltzmann factor

\( T \) : temperature
List of Symbols

c_n : constants coefficients of the Predictor-Corrector algorithm
\mathcal{T} : instantaneous temperature
T_O : reference temperature
\zeta_T : temperature relaxation time
c_n : constants coefficients of the Predictor-Corrector algorithm
I : moment of inertia
\rho : density
A_m : cross sectional area of nanotube
\omega : angular frequency
f : vibrational frequency
E : Young’s modulus
T_0 : Tension
\eta : symmetry breaking parameter for relative frequency
Chapter 1

Introduction to carbon nanotubes

Carbon nanotubes (CNT) are thin long tubes made from rolled up graphene (single sheets of graphite). They are truly nanometer size in diameter and can be grown in lengths ranging from a few nanometers to hundreds of microns. Experiments have been conducted in several areas such as the electrical actuation and detection of the guitar-string-like oscillation modes of doubly clamped nanotube oscillators [1]. With respect to conventional NEMS (Nanoelectromechanical Systems), CNTs are extremely light, and have a high Young’s Modulus (∼5TPa). They have enormous potential for a variety of applications, many still to be explored. For a typical CNT of 100nm length and 1nm in diameter the total mass is four orders of magnitude smaller than conventional NEMS, hence, assuming all other properties being equal, CNT resonators are expected to reach the ultimate mass sensitivity required for detecting small molecules.

While the wonderful world of the nanoscale can be probed in experiment, it can be observed completely in simulation. Experiments at the nanoscale and especially at an atomistic scale are much harder to carry out than experiments at longer length
scales. Simulations at the atomistic or nanoscale are much easier to do than simula-
tions at larger length scales.

Since carbon nanotubes were discovered in 1991 [3], they have received extensive
attention from various branches of science, [4], [5] and [6]. They can be produced
by an array of techniques, such as arc discharge, laser ablation, and chemical vapor
deposition. Depending on the synthesis conditions, nanotubes can be single-walled or
multi-walled. A single-walled carbon nanotube is a cylinder of graphene with a single
layer of carbon atoms, and its diameter is of the order of 1 nm. Multi-walled carbon
nanotubes are cylinders of graphene with multiple layers of carbon atoms along the
tube thickness, and their diameters are much larger. The length of carbon nanotubes
can be as large as 104-105 times the diameter [5]. Both experimental and theoreti-
cal studies showed that carbon nanotubes have exceptional mechanical and electronic
properties such as high stiffness-to-weight and strength-to-weight ratios and enormous
electrical and thermal conductivities [4] and [7]. Due to their remarkable mechanical,
physical and chemical properties, carbon nanotubes may be used as structural ele-
ments in nanoscale devices or potential reinforcements in nanocomposite materials [8]
and [9].

In recent years, a lot of research has been devoted to the application of carbon
nanotubes as chemical and mechanical sensors [10], [11], [12], [6]. The basic principle
of sensing is based on the natural (resonant) frequency shift of a carbon nanotube
resonator when it is subjected to a axial strain resulting from external axial loading.
It is found that the natural frequency is sensitive to the applied axial load. In conse-
quence, the effect of axial load on the nature of transverse vibrations of carbon tubes
is of practical interest.

Theoretical modeling of mechanical response of carbon nanotubes has been carried
out [5] and [7] [4]. These modeling approaches generally include both atomistic and continuum mechanics modeling. Many elastic continuum models have been applied to the investigation of the vibrational behavior of carbon nanotubes [13], [14], [15] and [16]. Sohlberg et al. [17] theoretically analyzed the vibration of carbon nanotubes by simply regarding nanotubes as solid slender rods.

In this thesis we will discuss the experimental, theoretical and computational background in Chapter 2. Chapter 3 will be devoted to numerical methods and models and in Chapter 4 we will introduce our simulation procedure. The remaining chapters will describe our results and conclusions.
Chapter 2

Background

2.1 Structure of carbon nanotubes

CNTs are tubular forms of carbon that can be envisaged as graphene sheets (two-dimensional graphite planes) rolled into cylindrical form. They have diameters in the range of a few nanometers and their lengths are up to several micrometers. Each nanotube is made up of a hexagonal network of covalently bonded carbon atoms. CNTs are of two types: single-walled and multi-walled. A single-walled carbon nanotube (SWNT) consists of a single graphene sheet rolled up into a cylindrical shape (see Fig. 2.1), whereas a multi-walled carbon nanotube (MWNT) comprises several concentric graphene cylinders.

A SWNT is formed by wrapping up a regular hexagonal lattice. The rolling up of the honeycomb lattice is characterized by the wrapping (chiral) vector $\vec{C}_h$ that connects two carbon atoms of the graphene sheet which coincide after folding and is defined as:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 , \quad (2.1)$$
2.1. STRUCTURE OF CARBON NANOTUBES

Figure 2.1: Side views of various nanotubes: a) Armchair (7,7), b) Zigzag (11,0), c) Chiral (8,5). Figures were generated by Tali Mutat with the visualization program, AViz [19], [76].

where \( n \) and \( m \) are integers (\( 0 \leq |m| \leq |n| \)) which denote the number of unit vectors \( \vec{a}_1, \vec{a}_2 \) along two directions in the hexagonal lattice of graphene as shown in Fig. 2.2. A nanotube constructed in this way is called an \((n,m)\) nanotube. SWNTs are classified as armchair tubes for \( n = m \) (Fig. 2.1a) and zigzag tubes for \( m = 0 \) (Fig. 2.1b), according to the pattern of the chain of carbon atoms along the direction of the vector \( \vec{C}_h \) in the graphite plane. For any other values of \( n \) and \( m \) the tubes are called chiral tubes since in those cases the chains of atoms spiral around the tube axis instead of closing around the circumference (Fig. 2.1c).

The electronic properties of nanotubes depend on their structure. For example, it is known that \((n,m)\) nanotubes are metallic if \((2n + m)\) is a multiple of 3 and that other nanotube structures are semiconducting. The geometry of nanotube \((n,m)\) also affect its radius. Recently, Lee et.al [18] demonstrated that the radius of carbon nanotubes should be calculated carefully with specific corrections and not as described
Figure 2.2: The structure of a CNT is based on a two-dimensional graphene sheet. The chiral vector is defined on the hexagonal lattice as $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$, where $\vec{a}_1$ and $\vec{a}_2$ are unit vectors, $n$ and $m$ are integers, and $T$ denotes the tube axis. Picture taken from [21].

previously by Dresselhaus et.al [5].

2.2 Synthesis of CNTs

Many techniques of synthesis have been developed to produce CNTs in the laboratory. One of the most common chemical methods is called chemical vapor deposition (CVD) which is ideal for growing large quantities of tubes. It generally involves a reaction in a hot environment (temperatures above 600°C) between a carbon-containing gas (such as acetylene, ethylene, ethanol, etc.) and a metal catalyst particle (usually cobalt, nickel or iron). The metal particle catalyzes the decomposition of the carbon-containing gases, and the carbon dissolves in the catalyst particle. Once the catalyst particle is supersaturated with carbon, it extrudes out the excess carbon in the form
of a tube. See the atomic resolution image of a CNT in Fig. 2.3. This technique is successfully implemented in Yuavl Yaish’s laboratory.

Figure 2.3: Atomic scale image of a CNT with a diameter of 1.3nm, taken by a scanning tunnelling microscope (STM). Individual carbon atoms can be seen as the reddish or yellow blobs in this image, with dark hexagonal holes between the atoms. Picture taken from [22].

2.3 Experimental background for NEMS

Various Nano-Electro-Mechanical Systems (NEMS) are under study currently in order to realize ultra-sensitive mass resonators, and to achieve the ultimate single atom detection limit. The detection scheme for mass sensing with a mechanical resonator is achieved by monitoring the resonance frequency of one of the modes. First four vibrational modes are presented in Fig.2.4 and denoted by $n = 1, 2, 3$ and $4$, respectively.

The dependence of the normal mode frequency on the effective mass $m$ allows for sensitive detection of additional mass being adsorbed on the surfaces of the resonator. Ekinci et al [26] showed that the sensitivity of such mass sensors depends on the effective mass, quality factor, resonance frequency and measurement averaging time. Typical NEMS are usually nanomechanical bridges or cantilevers made out of silicon, silicon nitride etc [27] [28] like in Fig.2.5. The change in mass is detected by
Figure 2.4: First 4 vibrational modes. L denotes length of the nanotube.

monitoring the frequency shift as molecules are adsorbed onto the resonators.

Figure 2.5: NEMS: cantilevers of cluminium nitride [27] and beams of silicon nitride [28]

The highest measurable mass sensitivity is in the range of zeptograms $\sim 10^{-21}$ gr (30 xenon atoms or individual 4 kDa molecule) is achieved by 133-190MHz SiC beams with a quality factor (Q) of $\sim 5000$ and $M \sim 10^{-17} - 10^{-14}$ gr [29]. For example, the mass of a single DNA molecule $\sim 1600$ base pairs ($1.6 \cdot 10^{-21}$ kg) was measured,
by a silicon nitride cantilever [27]. The sensitivity required for detecting a single small molecule (∼5 atoms) is about $10^{-23}$ gr, 4 orders of magnitude smaller than the world record. There are technical limitations to manufacturing lighter nanomechanical beams with conventional photo or e-beam lithography techniques, and degradation is expected in the quality factor as the surface-to-volume ratio increases. NEMS based on CNTs promise a broad range of applications, from ultra-sensitive mass spectrometers that can be used to detect hazardous molecules, through biological applications at the level of a single DNA base-pair, to the study of fundamental questions such as the interaction of a single pair of molecules. NEMS based on Single Walled Carbon nanotubes (SWCNTs) have a potential to develop ultra sensitive mass and force sensors.

The starting point of this research was the work of Vera Sazonovva, Yuval Yaish et al [1] who studied a suspended NT, clamped at both ends (Fig.2.6). In this method a high frequency signal applied to a gate electrode electrostatically excites the mechanical vibration of a suspended NT. It was observed that the suspended SWCNT behaved as a tunable electromechanical oscillator, with resonance frequencies ranging between a few to 200 MHz, quality factors ranging between 50 to 200. Chiu et al [30] reported recently that they succeeded in measuring mass of the single Xe atom ($8.5 \cdot 10^{-23}$ gr) by SWCNT device with operational frequency about 300MHz, the effective mass was reported to be $10^{-23}$ gr and the $Q \sim 1000$. Very exiting news are that Hüttel et al recently reported about SWCNT NEMS which operate with resonance frequencies up to 350MHz with $Q \sim 150000$ [31].
2.4 Yakobson’s paradox

The unique physical properties of CNTs such as high tensile strength, low weight, high thermal and electrical conductivity have made them a primary focus of nanotechnology research. Each carbon atom of the single (graphene) sheet of graphite which forms a planar honeycomb lattice, is connected via a strong chemical bond to three neighboring atoms. Because of these strong bonds, CNTs are expected to be the ultimate high-strength fibers. SWNTs are stiffer than steel, and are very resistant to damage from physical forces.

SWCNTs are a very elastic material, which promises the high vibrational frequencies, that are important for sensing application. Their elasticity is defined by Young’s modulus. But estimates for the Young’s modulus of carbon nanotubes are scattered in the literature range between 1-6 TPa [4,23–25]. This scattering is known as Yakobson’s paradox [32]. Huang et al [33] assert that such a range is a result of the
scattering of the estimates for the thicknesses of the nanotube. They obtained an ana-
lytical expression for the tube thickness, and therefore the elastic moduli, and showed
their dependance on the type of loading e.g., uniaxial tension, uniaxial stretching as
well as on the nanotube radius $R$ and chirality when $R < 1nm$. They also demon-
strated that the graphene thickness is also inter atomic potential dependent, however
they did not address the issue of modeling the frequency dependence of nanotube
vibrations on radius and length. This study is based on a continuum model, but as
the specimen size diminishes, the discrete structure of the material can no longer be
homogenized into a continuum. It is easy to see that the nanotube thickness will
also vary as a function of its vibrational modes $(n)$ near the places where it is more
sharply bent or extended. The entire picture may be more complex. Since knowledge
of the frequency dependence on length, radius and loading is essential to progress
towards deeper understanding and technological applications, molecular dynamics
(MD) simulations of SWCNTs and a precise analysis of their vibrations are presented
in Chapter 5 and following chapters.

2.5 Previous simulations

Atomistic Simulations are helpful to understand the underlying physics of such NEMS.
The study of the vibrational behavior of carbon nanotubes is new field which is un-
dergoing rapid development. Due to the fact that the investigation mechanism of
nanotube vibration (which is essential for further design and optimization of CNTs
NEMS) by experimental techniques is difficult, computer simulations and especially
atomistic simulations are a very powerful tool.
Extensive research has been made concerning the vibrational modes of single walled CNTs (SWCNTs). They have been studied with molecular dynamics (MD) simulations [34, 35], continuum mechanics models [16, 36–38], structural mechanics approaches [24] and molecular mechanics [39]. However attention was mainly primary to multi and double walled carbon nanotubes [16,37,38]. For example, [6] et al compares the vibrational frequencies of single and double wall carbon nanotubes and report that fundamental frequencies of double walled carbon nanotubes are about 10% lower than those of single walled carbon nanotubes with the same length and outer diameter. Sohlberg et al [38] theoretically studied the vibration of carbon nanotubes by simply assuming nanotubes to be solid slender rods, Yoon et al [16] investigated the intertube vibration of multi walled carbon nanotubes by a multiple-elastic beam model. In most atomistic studies a single type of nanotube was studied.

Wang et al [36] studied wave propagation in carbon nanotubes (CNTs) with two nonlocal continuum mechanics models: elastic Euler-Bernoulli [40] and Timoshenko [41] beam models. Wavelength and diameter-dependent results were explicitly derived from nonlocal continuum models. This work not only reveals the significance of the small-scale effect on CNT mechanical response, but also points out the limitation of the applicability and feasibility of local continuum models in analysis of CNT mechanical behaviors.

Cao et al studied the thermal vibration of (5,5) Single Walled Carbon Nanotube by Molecular Dynamics (see detailed explanation in 3.1) using consistent valence force field (CVFF) [42] potential. In this work the contributions of various vibration modes in radial, axial and lateral direction to the overall thermal dynamics of the SWCNT were studied. A simple continuum beam model [40] was used to predict the vibration frequencies, and simulation based on the finite element method (FEM) is
compared with Molecular Dynamics (MD). The authors concluded that the lateral vibration frequencies are robust along the axis of the nanotube and remain essentially unchanged at all temperatures (100 - 800K). They claim that with varying temperature (T), there is no new vibration mode or frequency activated; instead, only the overall vibration amplitude increases [34].

Relevant studies to the vibrational behavior of different nanotube types are simulations which study mechanical properties of different structures of CNTs. The main method for calculation of mechanical properties (Young’s modulus) is monitoring of the dynamics of carbon nanotubes, i.e. their vibrational frequencies but the interpretation of the dynamics in terms of the Young’s modulus can be problematic. For example, Lu et al. [43] found that for single and multiwall nanotubes the elastic moduli are shown to be insensitive to structural details such as the helicity, the radius, and the number of walls using an empirical force-constant model (EFCM). Ustinel et al. [44] based on [43], but without the distinction of distinct nanotube structure studied vibrational behavior of such a devices with slack which was caused by hanging the nanotube over the gap during NEMS fabrication.

Gupta et al [39] studied radial, axial and torsional vibrational modes of armchair and zigzag SWCNTs with molecular mechanics technique with open ends boundary conditions. They reported a different vibrational behavior of zigzag and armchair nanotubes and conclude that vibrational modes of the continuum structures deviate noticeably from those of the molecular mechanics method, and this deviation increases with an increase in the vibrational mode.
2.6 Biological application of nanosensors based on CNTs

2.6.1 Introduction

There has been growing interest in CNTs for biological applications [45–48] especially in medical technology [49] and sensors [50, 51] which can be broadly classified into two categories: chemical sensors [52] and biosensors [53–55]. The application of CNTs have been explored for the development of ultrasensitive nano-bio sensors [47], electroanalytical nanotube devices [48] and electromechanical actuators for artificial muscles [56]. The development of nano-bio sensors [57] and nanoscale bioreactor systems based on CNTs has been driven by the experimental evidence that biological entities such as proteins, enzymes, bacteria can be immobilized either in the hollow cavity or adsorbed onto the surface of carbon nanotubes [45, 46]. Significant success has been achieved in the use of CNTs as superior biosensor materials in the light of successful fabrication of various electroanalytical nanotube devices. These devices, prepared as SWCNT transistors, have shown promising sensitivities required for such applications as antigen recognition [58], enzyme-catalyzed reactions [59], and DNA hybridizations [60].

Resonance based sensors offer the deeper potential of achieving the high-fidelity requirement of many sensing applications. The key issue of mass detection is in quantifying the change in the resonant frequency due to the added mass. This is a young and rapidly developing field, but there is a lack of basic research in this field, especially basic atomistic study, which allows us to model such a systems as close as it possible to the real atomistic behavior. However there are some nonatomistic
2.6. BIOLOGICAL APPLICATION OF NANSENSORS BASED ON CNTS

works [61–63] in this field.

2.6.2 Previous studies and motivation

For example, Chowdhury et al [61] examined the potential of single-walled carbon nanotubes (SWCNTs) as mass sensors using a continuum mechanics based approach based on Euler–Bernoulli (EB) beam theory [40] and Finite Element Analysis (FEA). The carbon nanotube resonators were assumed to be either in bridged or in cantilevered configurations with attached mass as depicted in Fig. 2.7(a) and (b) respectively. The length of the CNTs was 8 nm and the length of the biological attached mass varied between 0.5 - 3.5 nm see Fig. 2.7(c) for the FEA model. It was observed that the proposed sensor-equations work reasonably well when the length of the bacteria is more than 1 nm for both cantilevered and bridged configurations. The numerical results indicate that the mass sensitivity of carbon nanotube-based nanobalances can reach up to $10^{-24}$ kg.

Joshi et al [62] presented the FEA simulation of the mechanical responses of individual carbon nanotubes treated as thin shells with thickness based on the previous work of Chowdhury et al [61]. The resonant frequencies of the cantilevered and the bridged SWCNT have been investigated. This analysis explores the resonant frequency shift of SWCNTs caused by the changes in the size of CNT in terms of length as well as the masses. They showed sensitivity of the SWCNTs to different masses and different lengths. As Chowdhury et al this results indicate that the mass sensitivity can reach $10^{-24}$ kg and the mass sensitivity increases when smaller size nanotube resonators are used in mass sensors as predicted by Euler–Bernoulli beam theory.
The work of Aydogdu et al [63] is the most detailed until now. They studied axial vibration behavior of single-walled carbon nanotube-based mass sensors using nonlocal elasticity theory. Carbon nanotubes with different lengths, attached mass and position on the CNT, boundary conditions (cantilevered or bridged) were considered in the formulations. The effects of positioning, length of the carbon nanotubes and attached mass are investigated in detail for each considered problem. It has been shown that for the cantilevered CNTs the frequency decreased with increasing of the mass distance from point of CNT clamping, however for the bridged CNTs the frequency change is symmetric with respect to midpoint of the SWCNT where the minimum frequency is obtained. They reported a sensitivity of nanotube-based mass sensors in the zeptogram range.
Chapter 3

Numerical methods

In this chapter we describe the computational algorithms, analytic models and techniques for analyzing the simulation of results.

3.1 Molecular dynamics simulation

Molecular dynamics (MD) is a technique where the time evolution of a set of interacting atoms is followed by integrating their equations of motion. Equations of motion based on Newton’s law are employed to calculate the positions and velocities of all the molecules as a function of time. The atoms interact via forces derived from a potential, that can be either a classical one, or calculated by solving Schrödinger’s equation at each time step. Statistical mechanics provides the theoretical basis for extracting properties from such MD simulations such as energy, pressure and temperature as well as dynamic and transport properties of a classical many body system. In this way, MD provides insight into structure and dynamics at a molecular scale.

In MD simulations, a sample is prepared in the following way: a model system
consisting of N particles of mass \( m \) is selected and Newton’s equations of motion for this system are solved until the system reaches equilibrium, where the properties of the system no longer change with time. After such an equilibration, the actual measurement can be performed.

Molecular dynamics simulation consists of the numerical, step-by-step, solution of the classical equations of motion, which for a simple atomic system may be written

\[
\ddot{\mathbf{r}}_i(t) = m_i^{-1} \mathbf{F}_i(t). \tag{3.1}
\]

For this purpose we need to be able to calculate the forces \( \mathbf{f}_i \) acting on the atoms, and these are usually derived from a potential energy \( U(r^N) \), where \( r^N = (r_1; r_2, \ldots, r_N) \) represents the complete set of 3N atomic coordinates. In the next section (3.1.2) we focus on this function \( U(r^N) \), restricting ourselves to an atomic description for simplicity.

Different boundary conditions of the simulated structure can be applied:

- free boundary conditions in all directions - all atoms of the structure can freely move in x, z and y directions;

- frozen edges - atoms at the edges of the structure does not move and their positions are not updated;

- periodic boundary conditions - simulation box is defined and a particle which goes out from the simulation box by one side is reintroduced in the box by the opposite side.
3.1. Molecular dynamics: program steps

In this section a number of important features of MD simulation are presented. The MD program is constructed as follows:

- Specification of parameters that describe the conditions of the run such as temperature, number of molecules, dimensions of the system, time steps, number of MD cycles, type of potentials etc.;

- Initialization of positions and velocities (section);

- Computation of the forces that act on all molecules.

- Integration of Newton’s equations of motion based on the acceleration of each atom in the system. This step and the previous one are repeated in the central loop until the system has been run for its specified length of time;

- Computation and printing the averages of measured quantities as the central loop ends.

To start the simulation, initial positions and velocities should be assigned to all particles in the system. The particles should be positioned in accordance with the simulation structure, and not at positions where an appreciable overlap of the atomic or molecular cores could occur. The initial velocities are assigned random directions and a fixed magnitude based on the Maxwell-Boltzmann distribution. The temperature is defined by the average kinetic energy of the system according to the kinetic theory of gases. The temperature can be estimated by averaging over the velocities of all of the atoms in the system:

$$\langle v^2_\alpha \rangle = k_B T/m$$  \hspace{1cm} (3.2)
It is assumed that once an initial set of velocities has been generated the Maxwell-Boltzmann distribution will be maintained throughout the simulation. The relation in Eq. (3.2) can be used to define an instantaneous temperature at time \( t \), \( T(t) \):

\[
K_B T(t) \equiv \sum_{i=1}^{N} \frac{m v_{a,i}^2(t)}{N_f}.
\]  

(3.3)

All the velocities are shifted by the velocity center of mass, so that the total momentum is zero.

### 3.1.2 REBO potential

In this project, the reactive empirical bond order (REBO) potential, which is an empirical many-body classical potential is used. It was developed by Brenner [2] based on potentials first introduced and parametrized by Abell [64] and Tersoff [65] and it is empirically derived by fitting to data sets from experiments and to ab initio calculations. Therefore it does not treat electrons explicitly or include any explicit quantum effects. The REBO potential was originally developed for use in simulating the chemical vapor deposition of diamond [2], and has more recently been extended to provide more accurate treatment of the energetic, elastic, and vibrational properties of solid carbon and small hydrocarbons. In its various incarnations, this potential has been used to model many different materials and processes, including fullerenes, carbon nanotubes (CNT) and amorphous carbon.

Abell introduced a general expression for binding energy that is a sum of near neighbor pair interactions that are moderated by the local atomic environment. Tersoff derived an analytic potential-energy function based on the Abell expression that qualitatively describes bonding in silicon for a large number of solid state structures. The binding energy according to the Abell-Tersoff formalism is written as a sum over
3.1. MOLECULAR DYNAMICS SIMULATION

atomic sites $i$,

$$E_b = \frac{1}{2} \sum_i E_i,$$  \hspace{1cm} (3.4)

where $E_i$ is written as

$$E_i = \sum_{j(\neq i)} \left[ V_R(r_{ij}) - B_{ij}V_A(r_{ij}) \right].$$  \hspace{1cm} (3.5)

The sum in Eq. (3.5) is over nearest neighbors $j$ of atom $i$. $V_R(r)$ and $V_A(r)$ are pair additive repulsive and attractive interactions, determined by the atomic types of atoms $i$ and $j$, which depend only on the distance $r_{ij}$ between the two atoms. $B_{ij}$ is a manybody function representing a coupling between the bond between atoms $i$ and $j$ and the local environment of atom $i$. A variety of chemical effects that affect the strength of the covalent bonding interaction are all accounted for in this term. Coordination numbers, bond angles, and conjugation effects all contribute to the strength of a particular bonding interaction [66]. In his original proposal, Abell suggested that the first approximation of $B_{ij}$ can be given as a function of near the neighbors coordination number $Z$ in the form:

$$B_{ij} \propto Z^{-\delta},$$  \hspace{1cm} (3.6)

where the value of $\delta$ is determined by the system’s characteristics. This analysis yields a relation between bond length, binding energy and coordination of the local environment of each atom.

The Abell-Tersoff expression can realistically describe carbon-carbon single, double and triple bond lengths and energies in hydrocarbons, solid graphite and diamond. However, there are situations where calculating the binding energy using near-neighbor interactions combined with the sum over atomic sites (Eq. (3.4)) leads to nonphysical results. One situation is when conjugated and nonconjugated double
bonds are examined.

This potential for carbon has been fit to yield a bond strength appropriate for graphite and refer it as conjugated system where each bond in graphite has approximately one-third double-bond and two-third single-bond character. On the other hand in the molecule \((\text{CH}_3)_2\text{C} = \text{C}(\text{CH}_3)_2\) the two carbon atoms connected by the central bond have the same local environment as in graphite, but because the bond is not conjugated it has an almost entirely double-bond character. Hence the potential can not distinguish between the two situations unless nonlocal effects are included. Similar nonphysical behavior occurs when a carbon atom with three nearest neighbors is bonded to a carbon atom with four neighbors: the Abell-Tersoff formalism regards it as intermediate between a single and double bond. However, a double bond results from the overlap of unbounded \(2p\) orbitals. Since the atom with 4 neighbors does not have a free orbital, \(\pi\) overlap cannot occur and the bond is better described as a single bond plus a radical orbital.

In order to describe both situations, the potential was corrected and parametrized by Brenner to fit binding energy of carbon bonds with different local environments. This is done by rewriting Eqs. (3.4)-(3.6) in the form:

\[
E_b = \sum_i \sum_{j(i)} \left[ V_R(r_{ij}) - \bar{B}_{ij} V_A(r_{ij}) \right], \tag{3.7}
\]

where

\[
\bar{B}_{ij} = (B_{ij} + B_{ji}) / 2. \tag{3.8}
\]

The overbinding of radicals can now be fixed by adding corrections to Eq. (3.8) for bonds between pairs of atoms that have different local environments. As discussed below, nonlocal effects are also added to distinguish between conjugated and nonconjugated bonding. The bond strength depends on whether it is defined as part
of conjugated system and is realized in the manybody function. For example the carbon-carbon $B_{ij}$ term is larger between triply coordinated ($sp^2$) carbon atoms than between quadruply coordinated ($sp^3$) carbons (in CH$_4$). This weights the attractive term $V_A$ more heavily for $sp^2$ carbons, resulting in an increased strength for double bonds.

### 3.1.3 Integrating the equations of motion

Newton’s equations of motion can be integrated after all forces between the particles have been computed. The algorithms that we decided to use are Velocity Verlet (VV) and Predictor Corrector (PC) algorithms. Velocity Verlet looks like the Taylor expansion for the coordinates:

$$r(t + \Delta t) = r(t) + v(t) \Delta t + \frac{f(t)}{2m} \Delta t^2$$  \hspace{1cm} (3.9)

However, the update of the velocities is different from the Euler scheme:

$$v(t + \Delta t) = v(t) + \frac{f(t + \Delta t) + f(t)}{2m} \Delta t + O(\Delta t^2).$$  \hspace{1cm} (3.10)

Note that, in this algorithm, we can compute the new velocities only after we have computed the new positions and, from these, the new forces. We use the velocities to compute the kinetic energy and the temperature. Now that we have computed the new positions, we may discard the positions at time $t - \Delta t$. The current positions become the old positions and the new positions become the current positions. After each time step, we compute the current temperature, the current potential energy calculated in the force loop, and the total energy. Note that the total energy should be conserved.
In the PC algorithm estimation of the positions, velocities, etc., at a time \( t + \Delta t \) may be obtained by a Taylor expansion about time \( t \). For example, the Taylor expansion of the position of a particle is given by:

\[
\begin{align*}
  r(t + \Delta t) &= r(t) + \Delta t \frac{\partial r}{\partial t} + \frac{\Delta t^2}{2!} \frac{\partial^2 r}{\partial t^2} + \frac{\Delta t^3}{3!} \frac{\partial^3 r}{\partial t^3} + \cdots.
\end{align*}
\]  

(3.11)

The ideas behind the Predictor-Corrector algorithm can be summarized as follows:

- Use the positions and their first \( n \) derivatives (velocities, accelerations etc.,) at a time \( t \) to predict the position and its first \( n \) derivatives at the time \( t + \Delta t \), to a sufficient degree of accuracy;

- Compute the forces, and hence accelerations from the predicted positions;

- Correct the predicted positions, velocities, accelerations etc., using the new accelerations [53];

Using the notation:

\[
\begin{align*}
  v(t) &= \Delta t \frac{\partial r(t)}{\partial t}, \\
  a(t) &= \frac{\Delta t^2}{2!} \frac{\partial^2 r(t)}{\partial t^2}, \\
  b(t) &= \frac{\Delta t^3}{3!} \frac{\partial^3 r(t)}{\partial t^3}.
\end{align*}
\]  

(3.12)

The Taylor series predictor becomes:

\[
\begin{align*}
  r'(t + \Delta t) &= r(t) + v(t) + a(t) + b(t) \\
  v'(t + \Delta t) &= v(t) + 2a(t) + 3b(t) \\
  a'(t + \Delta t) &= a(t) + 3b(t) \\
  b'(t + \Delta t) &= b(t).
\end{align*}
\]  

(3.13)
The forces at $t + \Delta t$ can be calculated from the predicted positions $r^p$. These can be compared with the predicted accelerations from Eqs. (3.13), to estimate the size of the error in the prediction step:

$$\Delta a(t + \Delta t) = F(t + \Delta t) \frac{(\Delta t)^2}{2m} - a^p(t + \Delta t).$$  \hspace{7cm} (3.14)

This error, and the results of the predictor (Eq. 3.13) form the corrector step:

$$r^c(t + \Delta t) = r^p(t + \Delta t) + c_0 \Delta a(t + \Delta t)$$
$$v^c(t + \Delta t) = v^p(t + \Delta t) + c_1 \Delta a(t + \Delta t)$$
$$a^c(t + \Delta t) = a^p(t + \Delta t) + c_2 \Delta a(t + \Delta t)$$
$$b^c(t + \Delta t) = b^p(t + \Delta t) + c_3 \Delta a(t + \Delta t),$$  \hspace{7cm} (3.15)

where $c_n$ are constants coefficients yield an optimal stability and accuracy of the trajectories. The choice of coefficients depends upon the order of the differential equation being solved. In this study the third-order Predictor-Corrector algorithm is used (i.e., one that uses $r_0$ through $r_3$, where $r_0 = r$, $r_1 = v$, $r_2 = a$, $r_3 = b$), the values for $c_n$ are: $c_0 = 1/6$, $c_1 = 5/6$, $c_2 = 1$, $c_3 = 1/3$.

### 3.1.4 Thermostat algorithm

A modification of the Newtonian MD scheme in order to generate a thermodynamical ensemble at constant temperature is called a thermostat algorithm [67]. The use of a thermostat is motivated by aim of matching experimental conditions to study temperature dependent processes. In this project the Berendsen thermostat was tested, (it will be discussed in section 3.1.5). The use of a thermostat requires the definition of an instantaneous temperature $T$. This temperature will be compared to
the reference temperature $T_O$ of the heat bath to which the system is coupled,

$$T = \frac{2}{3Nk_B} \mathcal{K},$$

(3.16)

where

$$\mathcal{K} = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{r}_i^2.$$  

(3.17)

Since the instantaneous temperature is directly related to the atomic internal velocities (Eqs. 3.16 and 3.17), maintaining the temperature constant (on average) requires imposing some control on the rate of change of these velocities. For this reason, thermostat algorithms require a modification of Newton’s second law,

$$\ddot{r}_i(t) = m_i^{-1} F_i(t).$$

(3.18)

Most of the isothermal equations of motion are based on the Langevin equation,

$$\ddot{r}_i(t) = m_i^{-1} F_i(t) - \gamma_i(t) \dot{r}_i(t) + m_i^{-1} R_i(t),$$

(3.19)

where $R_i$ is a stochastic force and $\gamma_i$ a (positive) atomic friction coefficient. A simplified form of a thermostat can be obtained by using a single friction coefficient for all atoms and avoiding the stochastic force in Eq. (3.19)

$$\ddot{r}_i(t) = m_i^{-1} F_i(t) - \gamma(t) \dot{r}_i(t).$$

(3.20)

In this case, $\gamma$ is no longer limited to positive values. A positive value indicates that heat flows from the system to the heat bath whereas a negative value indicates heat flow in the opposite direction. Consider a system characterized by an average instantaneous temperature $\mathcal{T}$, in contact with a heat bath at a different temperature $T_0$. $\mathcal{T}$ is spatially-averaged over the entire system and time-averaged over an interval that is short compared to the experimental timescale, but long compared to the time...
separating atomic collisions. The difference between $\overline{T}$ and $T_0$ may result from a natural fluctuation of $\overline{T}$ within the system. From a macroscopic point of view, the rate of heat transfer from the heat bath to the system should be proportional to the temperature difference $T_0 - \overline{T}$ and to the thermal conductivity $\kappa$ of the system. Thus, the rate of change in the average instantaneous temperature can be written (at constant volume) as

$$\dot{T} = c_v^{-1} \overline{E}(t) = \dot{T}^{-1} [T_0 - \overline{T}(t)], \quad (3.21)$$

with the definition of the temperature relaxation time:

$$\zeta_T = \xi^{-1} V^{-1/3} c_v \kappa^{-1}, \quad (3.22)$$

where $c_v$ is the system isochoric heat capacity, $V$ the system volume, and $\xi$ is a dimensionless constant depending on the system shape and on the temperature inhomogeneity within the system.

### 3.1.5 Berendsen thermostat

The Berendsen thermostat is based on a first-order relaxation equation [68]. The idea behind this thermostat is to modify the Langevin equation of motion (Eq. (3.19)) in the sense of removing the local temperature coupling through stochastic collisions (random noise), while retaining the global coupling (principle of least local perturbation) [67]. This prescription is equivalent to assuming that Eq. (3.21) also applies to the instantaneous temperature $T$ i.e. that

$$\dot{T}(t) = \tau_B^{-1} [T_0 - T(t)], \quad (3.23)$$

where an appropriate value for $\tau_B$ would be the temperature relaxation time $\zeta_T$ mentioned in Eq. (3.22). Modifying Eq. (3.20) by scaling the atomic velocities after each
CHAPTER 3. NUMERICAL METHODS

iteration step, based on the stepwise integration of Newton’s second law (Eq. (3.18)) of the leap-frog integrator [69], this can be written

\[ \dot{r}_i \left( t + \frac{\Delta t}{2} \right) = \lambda(t; \Delta t) \dot{r}_i \left( t + \frac{\Delta t}{2} \right) \]

\[ = \lambda(t; \Delta t) \left[ \dot{r}_i \left( t - \frac{\Delta t}{2} \right) + m_i^{-1} F_i(t) \Delta t \right], \quad (3.24) \]

where \( \lambda(t; \Delta t) \) is a time- and timestep-dependent velocity scaling factor. Imposing the constraint \( \lambda(t; 0) = 1 \), recovers Eq. (3.20) in the limit of an infinitesimal timestep \( \Delta t \), with

\[ \gamma(t) = -\lim_{\Delta t \to 0} \frac{\lambda(t; \Delta t) - 1}{\Delta t} = -\frac{\partial \lambda(t; \Delta t)}{\partial (\Delta t)} \bigg|_{\Delta t=0}. \quad (3.25) \]

The quantity \( \lambda(t; \Delta t) \) in Eq. (3.24) is found by imposing

\[ T' \left( t + \frac{\Delta t}{2} \right) = T' \left( t - \frac{\Delta t}{2} \right) + \tau_B^{-1} \Delta t \left[ \frac{g}{3 N_{df}} T_0 - T \left( t - \frac{\Delta t}{2} \right) \right], \quad (3.26) \]

where \( N_{df} \) is the number degrees of freedom, and the choice \( g = N_{df} - 1 \) is the appropriate one for the algorithm to generate a canonical ensemble of configurations at temperature \( T_0 \) Using Eqs. (3.16) and (3.17), this leads to the condition

\[ \lambda^2(t; \Delta t) T' \left( t + \frac{\Delta t}{2} \right) = T' \left( t - \frac{\Delta t}{2} \right) + \tau_B^{-1} \Delta t \left[ \frac{g}{3 N_{df}} T_0 - T \left( t - \frac{\Delta t}{2} \right) \right]. \quad (3.27) \]

Solving for \( \lambda(t; \Delta t) \) gives

\[ \lambda(t; \Delta t) = \left\{ \frac{T \left( t - \frac{\Delta t}{2} \right)}{T' \left( t + \frac{\Delta t}{2} \right)} + \tau_B^{-1} \Delta t \left[ \frac{g}{N_{df}} T_0 - T \left( t - \frac{\Delta t}{2} \right) \right] \right\}^{1/2} \]

\[ \approx \left\{ 1 + \tau_B^{-1} \Delta t \left[ \frac{g}{N_{df}} \frac{T_0}{T(t)} - 1 \right] \right\}^{1/2}. \quad (3.28) \]

Thus, Eq. (3.25) gives

\[ \gamma(t) = \frac{1}{2} \tau_B^{-1} \left[ \frac{g}{N_{df}} \frac{T_0}{T(t)} - 1 \right]. \quad (3.29) \]
Inserting into Eq. (3.20) gives the equation of motion corresponding to the Berendsen thermostat,
\[ \ddot{r}_i(t) = m_i^{-1} F_i(t) - \frac{1}{2} \tau_B^{-1} \left[ \frac{g}{N_{df}} \frac{T_0}{T(t)} - 1 \right] \dot{r}_i(t). \] (3.30)

The Berendsen equation of motion is smooth and deterministic, but time irreversible. In practice, \( \tau_B \) functions as an empirical parameter and should be adjusted appropriately to determine the strength of the coupling. Large values of \( \tau_B \) (loose coupling) may cause a systematic energy (and thus temperature) drift due to numerical errors. On the other hand, a too small value (tight coupling) will cause unrealistically low temperature fluctuations.

### 3.2 Continuum model

The oscillation motion of NEMS based on CNTs is often described via continuum mechanics, where SWCNTs are modeled as continuous beam or shells with fixed wall thickness, \( h \), and fixed Young’s modulus, \( E \) \([41,70]\). Typically the ”tube length” /”tube radius” \((L/R)\) aspect ratio is very large, and the SWCNT may be regarded as a homogenous beam with the same section and elastic properties.

#### 3.2.1 Euler-Bernoulli beam theory

A continuous, homogeneous, isotropic, linear elastic beam whose properties do not vary along its length will obey Euler-Bernoulli beam equation
\[ EI \frac{\partial^4 u}{\partial y^4} - T_0 \frac{\partial^2 u}{\partial y^2} = -\rho A_m \frac{\partial^2 u}{\partial t^2} = \omega^2 \rho A_m u, \] (3.31)
where \( I = \pi Rh(4R^2 + h^2)/4 \) is the moment of inertia, \( u \) is the transverse beam displacement (in our case, in either \( x \) or \( z \) direction), \( T_0 \) is the residual tension,
density $\rho$, cross sectional area of $A_m = 2\pi Rh$, and angular frequency $\omega$. One can perform the following transformation $y = \xi L$ for dimensionless parameter $\xi$ and 3.31 becomes

$$\frac{\partial^4 u}{\partial \xi^4} - \frac{L^2}{L_0^2} \frac{\partial^2 u}{\partial \xi^2} = \frac{\partial^4 u}{\partial \xi^4} - \frac{1}{\rho^2} \frac{\partial^2 u}{\partial \xi^2} = \frac{\omega^2 \rho A_m L^4}{EI} u = \beta^4 u. \quad (3.32)$$

$L_0^2 = EI/T_0$, $p = L_0/L$, and $\beta^4 = \omega^2 \rho A_m L^4/EI$. 3.32 has analytical solution and with the appropriate boundary condition the resonance frequencies can be found. For $T_0 = 0$, and boundary condition of clamped beam at both ends solution for 3.32 for the first four modes yields $\beta^0_n = 4.73, 7.85, 10.99, 14.13$ respectively [70]. Having $\beta^0_n$ the resonance frequencies turn out to be

$$f_n = \frac{\beta^0_n}{2\pi} \sqrt{\frac{EI}{\rho A_m L^2}}. \quad (3.33)$$

3.33 predicts that the frequency depends linearly on tube radius and as $1/L^2$ on its length, assuming that $r, h, \rho$ and $E$ are constant.

### 3.2.2 Timoshenko beam theory

An extension of the EB beam model for larger $\mu$ is known as the Timoshenko beam model [71] which takes into account shear deformation and rotational inertia effects, making it suitable for describing the behavior of short beams, in the limit when the wavelength approaches the thickness of the beam. Figure 3.1 helps to understand difference in deformation as a results of vibration of the blue crossection. According to theory this crossection remains perpendicular to the nanotube axis, however according Timoshenko beam model the blue crossection is also rotated but does not remain perpendicular to the axis of the nanotube.

Physically, taking into account the added mechanisms of deformation effectively
3.2. CONTINUUM MODEL

Figure 3.1: (a) Nondeformed nanotube; nanotube deformation as a result of vibration according to (b) Euler-Bernoulli; (c) Timoshenko beam theories.

lowers the stiffness of the beam, and lowers the predicted resonance frequencies. The Timoshenko beam equation has the following form [71]:

\[
EI \frac{\partial^4 u}{\partial y^4} + \omega^2 \rho I \left(1 + \frac{E A_m}{A_e G k}\right) \frac{\partial^2 u}{\partial y^2} = \omega^2 \rho A_m \left(1 - \frac{\omega^2 \rho I}{A_e G k}\right) u, \tag{3.34}
\]

where \(G\) is the shear modulus, and \(k\) is the Timoshenko shear coefficient, which depends on the geometry. Normally \(k = 9/10\) for circular cross sections. The appearance of the cross section of the tube in Eq. 3.34 originates from two different sources: \(A_m\) derives from the force balance equation, whereas \(A_e\) is a cross section originating from the elastic stress-strain constitutive relation [71]. Therefore, \(A_m = 2\pi Rh_m\) and \(A_e = 2\pi Rh_e\). Since the total mass per unit length for each tube in the simulation, \(m = A_m \rho\), is known, one can replace \(\rho\) by \(m/A_m\), and has the freedom to chose \(h_m = 3.4\) Å. After replacing \(\rho\) by \(m/A_m\), and changing to the dimensionless
parameter $\xi = y/L$, Eq. 3.34 transforms into

$$
\frac{\partial^4 u}{\partial \xi^4} + \frac{\omega^2 m L^2}{A_m E} \left( 1 + \frac{E A_m}{A_e G k} \right) \frac{\partial^2 u}{\partial \xi^2} = \frac{\omega^2 m L^4}{E I} \left( 1 - \frac{\omega^2 m I}{A_m A_e G k} \right) u, \tag{3.35}
$$

which has the same form as Eq. 3.32 with the following assignments:

$$
\frac{1}{p^2} = \frac{\omega^2 m L^2 10^{-3}}{A_m E} \left( 1 + \frac{E A_m}{A_e G k} \right), \tag{3.36}
$$

$$
\beta^4 = \frac{\omega^2 m L^4 10^{-3}}{E I} \left( 1 - \frac{\omega^2 m I 10^{-3}}{A_m A_e G k} \right), \tag{3.37}
$$

where $\omega$ is in THz, $m$ in fg, $L, R, h_e, h_m$ are in nm, and $E$, and $G$ are in TPa.

One may observe that Eq. 3.35 has the same structure as Eq. 3.32 for $T_0 = -|T_0|$, which means that the beam is under compression, and as a result the resonance frequencies will be smaller than the $f_0^0$, given by Eq. 3.33. Before solving Eq. 3.35 let us first examine Eq. 3.32. This equation has an analytical solution for $T \neq 0$ as well, however the expression is quite cumbersome, but may be defined in the following relation, $\beta_n = F(T L^2 / E I) = F(p^2)$ where $T = -T_0 > 0$. For $q = 1/p \rightarrow 0 \ \beta_n \rightarrow \beta_n^0$, hence we can expand $F(p^2)$ for small $q$. Up to second order in $p$ one finds

$$
\beta_n \simeq \beta_n^0 - \frac{\alpha_n}{p^2} = \beta_n^0 - \alpha_n \frac{T L^2}{E I}, \tag{3.38}
$$

where $\alpha_n = 0.029, 0.024, 0.019, 0.015$ for modes number n=1-4 respectively. Eq. 3.38 demonstrates how the vibrational mode frequencies decrease as the beam is subjected to a compressive load, $T$. From a Taylor expansion one has $\beta_n - \beta_n^0 \sim \frac{\partial \beta_n}{\partial \omega} \delta \omega$, and together with Eqs. 3.36, 3.37, and 3.38 one obtains

$$
\delta \omega_n = \omega_n - \omega_n^0 = -\frac{\alpha_n}{p^2} \frac{\partial \beta_n}{\partial \omega} = -2 \alpha_n (\beta_n^0)^3 \omega_n^0 \frac{I}{L^2 A_m} 1 + \frac{E A_m}{A_e G k A_m} \frac{2 \omega_n^0 m I}{A_m A_e G k}, \tag{3.39}
$$

For $\sigma = R/L \ll 1$, $h_e = 0.66$ Å $h_m = 3.4$ Å and $G = E/2(1+\nu)$ as anticipated for a homogenous material, Eq. 3.39 becomes

$$
\delta \omega_n = -2 \alpha_n (\beta_n^0)^3 \omega_n^0 \frac{E I}{L^2 G k A_e} \simeq -\alpha_n (\beta_n^0)^3 \omega_n^0 \frac{R^2 E}{L^2 k G}. \tag{3.40}
$$
where the last approximation is justified when $h_e \ll R$, which is usually the case.

After substitution of all the relevant coefficients in Eq. 3.40 one finds

$$
\delta \omega_n = -C_n \omega_1^0 \left( \frac{\beta_0 R}{\beta_1^0 L} \right)^2 \frac{E}{kG},
$$

(3.41)

where $C_n = 3.07, 11.67, 25.32,$ and $44.20$ for modes number $n=1-4$ respectively.

### 3.3 Fourier techniques

In the analysis of our simulations, in order to decompose the overall vibration of the SWCNT onto a single harmonics we use the technique of Fourier Transform (FT) and in particular the Discrete Fourier Transform (DFT). Fourier analysis is a family of mathematical techniques, all based on decomposing signals into sinusoids. The discrete Fourier transform is the family member used with digitized signals provides the means of transforming a signal defined in the time domain into one defined in the frequency domain. When a function is evaluated by numerical procedures, it is always necessary to sample it in some fashion. This means that in order to fully evaluate a FT with digital operations, it is necessary that the time and frequency functions be sampled in some form or another. Thus the digital or Discrete Fourier Transform is the primary tool.

The Fourier transform is used to transform a continuous time signal into the frequency domain. It describes the continuous spectrum of a nonperiodic time signal. The Fourier transform $X(f)$ of a continuous time function $x(t)$ can be expressed as:

$$
X(f) = \int_{-\infty}^{\infty} x(t)e^{-i2\pi ft} \, dt
$$

(3.42)

The inverse transform is:

$$
x(t) = \int_{-\infty}^{\infty} X(f)e^{i2\pi ft} \, df
$$

(3.43)
The Discrete Fourier Transform (DFT) is used in the case where both the time and the frequency variables are discrete (which they are if digital computers are being used to perform the analysis). Let \( x(nT) \) represent the discrete time signal, and let \( X(mF) \) represent the discrete frequency transform function. The DFT is given by:

\[
X(mF) = \sum_{n} x(nT)e^{-i\frac{mn2\pi}{FT}} \tag{3.44}
\]

and the inverse discrete transform is:

\[
x(nT) = \frac{1}{N} \sum_{m} X(mF)e^{i\frac{mn2\pi}{FT}} \tag{3.45}
\]

In our project we used the Fast Fourier transform (FFT), that is simply a class of special algorithms which implement the discrete Fourier transform with considerable savings in computational time. It must be pointed out that the FFT is not a different transform from the DFT, but rather just a means of computing the DFT with a considerable reduction in the number of calculations required.

### 3.4 AViz

Our computational physics group developed the Atomistic Visualization package **AViz** [19]. This is very powerful visualization tool which helps to enhance 3D perception. It includes various options which let one to rotate the still sample, change relative sizes of atoms, create animations and movies, add and remove the bonds and borders of the sample, use color coding, slice the sample and much more. The Atomistic Visualization package **AViz** will be used in all stages of this work. It will allow us to follow the vibrations of the Single Walled Carbon Nanotubes at any time interval and by using different color.
AViz provides an interactive interface which visualizes datasets prepared in previous or simultaneous simulations. It uses the xyz data format (these being the spatial coordinates of the objects) with additional optional data columns for velocities and other aspects such as angle or direction for quadrupole or spin objects. Initiating the code brings up a visualization box and a dialog box. The dialog box enables selection of dataset, viewpoint, lighting, and other options to be discussed later on and buttons for mode (object type), style (depends on object), size and quality (rendering quality) selection.

3.5 Facilities

In this project we use the SUN/EMET 128 dual-core processor (2 processors per node), 2.2 GHz AMD Opteron LINUX cluster with a fast interconnect based on DDR Infiniband. It is funded by the Russell Berrie Nanotechnology Institute [72]. This cluster - NANCO has a distributed memory architecture. The memory is distributed between the nodes, but shared between 4 processors of one node (see Fig. 3.2). In order to use optimally such an useful and a complicated tool we designed a parallel code using Message Passing Interface (MPI). A detailed explanation of the program can be found at [74].
Figure 3.2: Nanco supercluster. A schematic representation of the memory. [73]
Chapter 4

Code and data preparation

4.1 Code modifications

In these simulations the original code of Brenner [75], which is written in Fortran77 was used. The following subroutines were added as part of the current project:

- **center mass** - this subroutine calculates the Centered Axis of the nanotube (center of mass of every period);

- **velocity verlet** - this is the subroutine of the Velocity Verlet integration algorithm;

- **save forces** - this subroutine saves forces of the previous step and is needed for the Velocity Verlet algorithm;

- **update neighbors** - this subroutine updates the neighbor list.

The code passed initial debugging and then the reliability of the code and the method chosen for the simulations and dependency of the results on the initial conditions was
tested. In order to carry out such an experiment we chose different initial velocities for every particle in the simulation in such a way, that the total initial temperature of the system (Eq. 3.3) will stay unchanged (see section 3.1). The test showed that the initial conditions did not affect the final results in either the time or frequency domain. The subroutine which was written by Tali Mutat [76] that generates the sequence of the xyz files was debugged and extended to obtain the sequence of the xyz files of special points along the nanotube (center of mass of special segments of the nanotube). The subroutine which was produced by Yaniv Gershon [77] that inserts the external force in one direction at every atom was also debugged, and was added to the calculations of the overall forces in the system. The careful analysis of the Fourier Transform and the sampling frequency then proceeded, and a Matlab code that transforms the time domain to the frequency domain was written, and is presented in Appendix B.

Basic parallelization of the code was done using Message Passing Interface (MPI). The details are presented in Appendix A. This parallelization is made in order to simplify usage of the serial code by synchronization of running jobs with different input parameters like temperature, time step, thermostat, but with similar overall run time.

4.2 Data preparation

We studied vibrational frequencies by applying a FFT on the time domain, i.e. we monitored the displacement as a function of time. Since resolution of the frequency peaks depends strongly on the overall time of the monitoring (see Chapter 3.3 for details) it was important to allow to nanotubes to vibrate as much as it possible.
However these type of calculations can be robust and time consuming and require significant computing power. In order to strike a balance between the run time and FFT peak resolution we needed to find the optimum run time. We decided to begin from very long runs \( \sim 4 \) nanoseconds or \( \sim 8500000 \) steps with \( \Delta t=0.5 \) fsec.

### 4.3 One example and validation details

To describe details of our procedure we now present one case in detail. Consider the armchair nanotube shown in Fig.4.1(a), which depicts a (7,7) SWCNT, with a single period (28 atoms here) drawn in Fig.4.1(c). The axis of the nanotube is in the Y direction, and we study vibrations in the Z direction. (Our validation process included confirming identical (within statistical error) results for vibrations in the X direction.) Different boundary conditions were explored, but for the purposes of recording vibrations the nanotubes were clamped at both ends, by freezing the first(last) 3 periods as shown in Fig. 4.1(b) (where only the left half of the tube is drawn).

In order to reduce the amount of data needed for the vibrational analysis we selected some special points where data was recorded. The centers of mass (spheres inside the nanotube in Fig.4.1(a)) for each period were identified, making up a line of points which we call the centered axis (CA). The center of mass (CM) of the entire nanotube (large sphere in Fig.4.1(a)) falls in the middle of this line.

We monitored the vibration of 98.38 Å armchair nanotube with a diameter of 9.4 Å and a chiral vector of (7,7). This nanotube has 40 periods and the center of mass (CM) of the entire tube is near \( Y = 20 \). We monitor the vibration of \( Y=10 \), the
Figure 4.1: (a) Single Walled Carbon Nanotube (green), with the CA made up of the centers of mass of each period of the nanotube as (red) spheres inside the nanotube, and a (blue) large atom to indicate its CM. The * marks one place where all the first 4 modes have finite amplitude (b) vibrating nanotube with clamped ends (only the left half of the tube was drawn) (c) one period of a (7,7) SWCNT. The images are generated with AViz [78] (d) FFT analysis of the first four thermal vibrational modes (n=1-4) in the Z direction at a point near the center of mass of the 30th period at 300K.
results are presented in Fig. 4.2 and demonstrate strange behavior. At the beginning the nanotube vibrates with an amplitude of about 1.3 Å, then the amplitude decreases and begins to increase till it reaches 3 Å and remains constant.

We could not explain physically this phenomenon hence we decided to test time step, ∆t, influence on the vibrational behavior of this CNT and detect more carefully the time where vibrational behavior of nanotubes begins to change. The nanotube vibration was calculated with ∆t = 0.1, 0.2, 0.25 and 0.5 fsec the results are depicted in Fig. 4.3. This Figure clearly shows that the results for all time steps are similar till 600 nanosec after which the discrepancy could be detected which increases with time. It is important to note that there is no similarity between any of ∆t. It can be explained by the fact that after about 600 nanosec the mathematical error from integration steps is collected and increases, which gives unreal MD results. In order to remain in a physically correct mode we decided to run our simulations no longer then 600 nanosec with ∆t = 0.5 fsec. Fig. 4.4 demonstrates vibration of Y = 10 in the Z direction in this time regime. Its Fourier Transform which gives
Figure 4.3: Basic MD calibration: $\Delta t$ numerical testing. Vibration of center of mass of one of the periods in the $Z$ direction as a function of time.
4.3. ONE EXAMPLE AND VALIDATION DETAILS

Figure 4.4: Vibration of 10th period on the Z direction as a function of time

frequencies of nanotube’s vibrational modes is shown in Fig.4.1(d). It can be seen that the peak resolution is good enough in this time regime. We applied a Fast Fourier Transform (FFT) analysis to the data at several points, (including one near the CM) to calculate the power as a function of frequency for each nanotube. Fig.4.1(d) depicts the frequency as a function of the power of the vibrational modes after the FFT for the shortest nanotube (98.38 Å) at the point indicated by * in Figs.4.1(a), and (b), about 1.42 Å from the CM of the 10th period. As expected, at this point the 2nd mode had the highest amplitude and the 4th had the lowest.

Two different thermodynamic ensembles, canonical (NVT) and microcanonical (NVE) and two different integration algorithms, predictor corrector (PC) and velocity verlet (VV) were tested (see Table4.1). No substantial difference in frequency values was found as a result of change in integration algorithm and we used PC integration
Table 4.1: Frequency values in THz of (7,7) armchair nanotube in different thermodynamic ensembles. Canonical ensembles preserves constant temperature of 300K: NVT-1 uses PC and NVT-2 uses VV algorithms.

<table>
<thead>
<tr>
<th>$n$</th>
<th>NVE</th>
<th>NVT-1</th>
<th>NVT-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2769</td>
<td>0.2767</td>
<td>0.2767</td>
</tr>
<tr>
<td>2</td>
<td>0.6669</td>
<td>0.6673</td>
<td>6.674</td>
</tr>
<tr>
<td>3</td>
<td>1.150</td>
<td>1.156</td>
<td>1.156</td>
</tr>
<tr>
<td>4</td>
<td>1.679</td>
<td>1.676</td>
<td>1.673</td>
</tr>
</tbody>
</table>

in our atomistic simulations. We wanted to study vibrational behavior at constant temperature and we present the canonical ensemble results below.

In order to keep temperature constant a Berendsen thermostat [68] was applied. To ensure stable nanotube structure and eliminate intrinsic tension, we collected data after a period of slow initial thermalization to 300K (periodic boundary conditions with no frozen edges) waiting until the length of the equilibrated nanotube remained constant up to insignificant fluctuations (see Fig 4.5). In order to obtain adequate statistics for all vibrational modes we let every nanotube vibrate 1000 times more than the period of its lowest frequency, using a MD timestep of 0.5 fsec.
Figure 4.5: Example of thermalization of CNT to a constant temperature.
Chapter 5

Mechanism of nanotube vibrations

In this chapter the mechanical vibration of single walled carbon nanotubes, and frequencies as a function of length and radius for armchair nanotube are described.

5.1 Model and details of the simulations

We initially investigated the effect of the length on the vibrational frequencies, building (7,7) SWCNTs with lengths (L) of 98.38, 147.57, 196.76, 245.95 and 295.14 Å with a diameter (= 2R) of 9.5 Å. Due to the fact that the 3 last/first periods are frozen the vibrating fragments of the nanotubes are 83.62, 132.81, 182.00, 231.19 and 280.38 Å long respectively. In Fig. 5.1 we show the frequencies of the first four modes as a function of the length of the nanotube (symbols +, ◦, *, and □ are for modes 1-4 respectively).

We also simulated the frequencies of the first four modes as a function of nanotube radius. We changed the aspect ratio to create different nanotubes of fixed 98.38
5.2 Comparison with a simple continuum model

Figs. 5.1, and 5.2 depict detailed comparisons between the simulated data and Eq. 3.33. Initially, a best fit for the first mode of Fig. 5.1 was derived, and very good agreement was obtained (dashed-dot red line in Fig. 5.1). It is worth mentioning that the mass
Figure 5.2: First 4 modes vibrational modes as a function of radius. Symbols +, ◦, *, and □ are for modes 1-4 respectively, and continuous lines are derived from Fig. 3.33.

per unit length was calculated directly by counting the number of carbon atoms per unit cell in these armchair tubes and then multiplying it by the number of unit cells in one meter, and not by using the approximate value given by the density \( \rho \). The bending rigidity, \( EI \), turns out to be \( EI = 6.7 \pm 0.6 \cdot 10^{-26} \text{Nm}^2 \), and from Eq. 3.33 one may obtain the anticipated higher vibrational modes for the different tube lengths. These results are plotted with continuous black lines in Fig. 5.1. Since \( EI \) depends on the tube radius, the bending rigidity for the second set of data presented in Fig. 5.2 was calculated using ratios between various moments of inertia. For that purpose a tube thickness, \( h \), of 0.66Å was assumed.

From both figures it is clear that for small \( \mu = R/\lambda_n \), where \( \lambda_n \) is the wavelength of the \( nth \) mode, the Euler-Bernoulli (EB) beam model predicts the natural frequencies as well as the higher vibrational modes of SWCNTs very well.
Moreover, for $h = 0.66\text{Å}$, and Poisson’s ratio $\nu = 0.4$, it gives a tension rigidity $Eh/(1 - \nu^2) = 236 \text{ GPa \cdot nm}$, which is in excellent agreement with the calculated tension rigidity from Huang et al [33]. However, as $\mu$ increases the deviations from the classical beam model become more and more significant and alternative models should be considered. One simplified model can allow for the Young’s modulus to be varied over the different lengths and tube radii as long as Eq. 3.33 is satisfied. The result of such an analysis is shown in Fig. 5.3, where the ratio of the calculated bending rigidity to $(EI)_0$ at small $\mu$ is plotted as function of $\mu$. The $\circ / +$ symbols are attributed to the f vs L / f vs R data. One can notice that most of the data is scattered along some imaginary line that starts around 1 and drops down to fifth of its initial value as $\mu$ increases. The significant drop starts around $\mu \simeq 0.05$ and by examining each point separately together with its corresponding location in Figures 2 or 3 one can observe that for points below $\mu \simeq 0.05$ the agreement with the EB model is very good, but above this value it becomes poorer, as $\mu$ increases. Although several theoretical studies predict radius dependance of the bending rigidity [24, 33, 79] the overall change is expected to be smaller than that presented in Fig. 5.3.

5.3 Extended model and discussion of results

One way to proceed further is to abandon the beam model of SWCNTs and adopt the shell model [4] in order to explain the simulated data. However, since in the limit of small $\mu$, the EB beam model coincides very well with the data, it would be beneficial to extend this model to larger $\mu$. An extension of the EB beam model for larger $\mu$ is known as the Timoshenko beam model [71](see Chapter 3.2.2).
Eq. 3.41 predicts the following: i) the shift of the resonance frequencies is negative and it scales as $\sigma = R/L$ as expected. ii) the shift increases for higher vibrational modes. iii) $\delta \omega_n/C_n/\omega_n^0 \propto (R/L)^2$ and the proportionality coefficient is $\frac{E}{kG}$. The simulated data agree very well with these predictions, and indeed linear dependence of $\delta \omega_n/C_n/\omega_n^0$ versus $(R/L)^2$ is found with coefficient $\frac{E}{kG} = 3.5 \pm 0.5$ for small $\sigma = R/L$. Assuming $k \simeq 0.9$, one gets $E/G \simeq 3.15 \pm 0.45$ which is in good agreement with $E/G = 2(1 + \nu) = 2.8$ for homogenous material. Knowing the ratio of $E/kG$ leaves us with two variables, $h_e$ and $E$. The following procedure was used in order to find the eigenvalues, $\omega_n$, of Eq. 3.35 that correspond best to the simulated data.

The solution for Eq. 3.32 with double clamped beam boundary conditions can be written as $\beta_n = \mathcal{F}(p)$ and is plotted for the first four modes in Fig. 5.4 (colored continuous lines). One can notice that for $p > 1$ $\beta_n \rightarrow \beta_n^0$, meaning that the residual
Figure 5.4: Fitting procedure. The four continuous colored lines represent the solutions of Eq. 3.32, i.e., $\beta_n = \mathcal{F}(p)$ for the first four vibrational modes. The blue dashed-dot line satisfies Eq. 5.1, i.e., $\beta = \mathcal{V}(p)$. The solutions for Eq. 3.35 are the intersection points between these lines (black +). The fitting procedure minimizes the absolute distance between these intersection points with the simulated data (green ◦).

tension plays no major role. However, as $p$ decreases, $\beta_n$ decreases as well until $p \to p_{cr}(n)$ where beyond these points no solution for Eq. 3.32 exists. For example for the first mode $p_{cr}(n = 1) = 1/(2\pi) \approx 0.16$, where after substituting the definition of $p$ one receives $|T_{cr}| = 4\pi^2 \frac{EI}{L^2}$ which is the Euler Bernoulli instability criteria for buckling. Next, we eliminate $\omega$ from Eqs. 3.36, and 3.37 and find

$$
\beta_n = \left( \frac{A_m G A_e (L^2 p^2 (A_m E + A_e G) - EI)}{I p^4 (A_m E + A_e G)} \right)^{1/4} = \mathcal{V}(p).
$$

Solutions to Eq. 3.35 are found from the intersection points of $\beta = \mathcal{V}(p) = \mathcal{F}(p)$. Fig. 5.4 depicts four intersection points (black +) for the first four modes with Eq. 5.1 (blue dashed-dot line) for $E = 5.5TPa$ and $h_e = 0.47 \text{ Å}$. The fitting procedure modifies only $E$ and $h_e$ in order to minimize the distance in the $\beta - p$
plane between the eigenvalues of Eq. 3.35 (black +) and the simulated frequencies (green ◦). The minimization is performed using all the simulated data points with two fitting parameters \(E\), and \(h_e\), and the results are depicted in Figs. 5.5, and 5.6. The continuous lines are based on the theoretical model, and the discrete points are the simulated data. The Young’s modulus is calculated to be \(E = 3.83\, TPa\), and the tube thickness is \(h_e = 0.67\, \text{Å}\). These values match those found in Huang et al [33]. For the data of \(f\) versus \(L\) the agreement between experiment and theory is excellent. This is expected since for this data set, the maximum value of \(\mu = R/\lambda_n = 0.11\) which is smaller than the maximum, \(\mu = 0.22\), of the other set. However, in the case of the second set of data, \(f\) versus \(R\), the model matches the simulated data quite well, and the ”roll off” of the resonance frequencies for larger radii are well observed.

Three fundamental questions arise with regard to these findings: i) Why do the resonance frequencies almost saturate for big radii? ii) Can we extract \(E\) and \(h_e\) uniquely? iii) In light of several studies that predict that the tension rigidity, \((E \cdot h_e)/(1 - \nu^2)\) depends on radii, how do the above results change if one allows for the tension rigidity to be varied slightly?

Let us start with the first question. By examining Eq. 3.36 and substituting \(\omega_n^0\) one finds

\[
\frac{1}{p^2} \simeq (\beta_n^0)^4 \left( \frac{R}{L} \right)^2 \frac{E}{2Gk}.
\]

Hence, as the radius increases and/or the vibrational modes under consideration become larger, \(p\) becomes smaller, the effective compression is stronger, and as a result the beam approaches its critical buckling singularity points. Thus, the beam become softer and the anticipated resonance frequencies are reduced in comparison with \(f_n^0\). Since a SWCNT can be considered in the framework of the shell model, local as well as global buckling are predicted [4]. These local buckling instabilities can affect the
Figure 5.5: Main panel: First 4 vibrational modes as a function of length. Symbols +, o, *, and □ are for modes 1-4 respectively, continuous lines are derived from Eq. 3.35 with $E = 3.5kG = 3.83TPa$ and $h_e = 0.67\text{Å}$, and dashed-dot lines are solutions for the same Eq. with the same bending and shear rigidities but with $0.4 \leq h_e \leq 0.6\text{Å}$. Inset: Possible solutions for Eq. 3.35 are marked by o in the $E - h_e$ plane and the continuous line corresponds to $E \cdot h_e = 246\text{GPa} \cdot \text{nm}$. 
Figure 5.6: Main panel: First 4 vibrational modes as a function of radius. Symbols +, ○, *, and □ are for modes 1-4 respectively, continuous lines are derived from Eq. 3.35 with $E = 3.5kG = 3.83TPa$ and $h_e = 0.67\text{Å}$, and dashed-dot lines are solutions for the same Eq. with the same bending and shear rigidities but with $0.4 \leq h_e \leq 0.6\text{Å}$. 
circular cross section \([9]\), and hence modify the bending and shear rigidities. If one allows for the effective tube thickness \((h_e)\) to be modified slightly with radius but keeps the same Young’s and shear moduli as were found before (Figs. 5.5, and 5.6) excellent agreement between the model and simulated data is also obtained for the \(f\) versus \(R\) data (dashed-dot lines in Figs. 5.5, and 5.6). The overall modification of the tube thickness was small (between 0.6 Å for the small radius to 0.4 Å for the thickest tube), however, its influence on the fitted data is significant, mainly for the high \(\mu\) points.

We have also been concerned about the issue of the origin of the radius dependence of the shell thickness. Of course this is of quantum mechanical origin, and members of our group have considered this in the context of both nanotubes and other carbon allotropes. In a recent paper \([80]\) an ab initio study (with VASP \([?]\)) of electronic density of sp\(_2\) and sp\(_3\) bonds is compared with classical potential studies of sp\(_2\)/sp\(_3\) diamond samples. The Brenner potential is indeed classical but is parameterized well enough to give correct results for atomic locations when is compared with the VASP results. To get the actual electronic density widths one would need to rely on ab initio calculations.

Figs. 5.5-5.6 show good agreement between experiment and theory for \(E = 3.83TPa\) and \(h_e = 0.67\) Å. Are these values are unique, or may one find other values with similar matching? As was discussed by many experimentalists and theoreticians in this field, and known as Yakobson’s paradox, the combination of \(Y = Eh_e\) is the quantity is usually measured and studied. Despite the big scattering in the values of \(E\) and \(h_e\) that were published in the literature, and may be dependent on loading as well \([33]\), the distribution of \(Y\) is quite sharp and it is centered around \(246 GPa \cdot nm\). From the Timoshenko beam model, one can observe from Eqs. 3.35, 3.36, and 3.37 that
\( \frac{1}{p^2} \propto \frac{\omega^2}{h_eE} \) and \( \beta^4 \propto \frac{\omega^2}{h_eE}(1 - a \frac{\omega^2}{G}) \). Thus, for \( a \frac{\omega^2}{G} \ll 1 \), the same paradox will appear for this model. However, as \( \mu \) and \( \omega \) increase this term becomes larger and therefore partially resolves Yakobson’s paradox. Specifically, the possible solutions for \( E \) and \( h_e \) according to the presented model in the \( E - h_e \) plane are depicted in the inset of Fig. 5.5. They indeed fulfill the condition of \( E \cdot h_e = Const = 246 \, GPa \cdot nm \) (continuous line) but \( h_e = 3.4 \, \text{Å} \) is beyond this range.

### 5.4 Section summary

Summarizing this section the simulation agrees well with Euler-Bernoulli continuum beam model for small \( \mu = R/\lambda \) ratios. However, for bigger \( \mu \) the data deviates significantly from the predicted model, and an alternative model (known as the Timoshenko model), that takes into account the effects of rotary inertia and shearing deformation was adopted. The new model agrees well with the simulated data, and the reduction of the eigenvalues of the vibrational modes was attributed to softening of the tube by compression close to global or local buckling instabilities. The results of this study may be relevant also for the design of high frequency NEMS based on SWCNTs. In contradiction to common belief that as the tube become shorter, or thicker, the resonance frequencies increase, the simulation and the model emphasis the significance of the dimensionless parameter \( \mu \) and show that for \( \mu > 0.05 \) the resonance frequencies are much lower than expected.
Chapter 6

Chirality effect

6.1 Introduction

Nanotubes have three main geometrical classifications as described in detail in Chapter 2.1 - armchair, zigzag and chiral, due to the different wrapping vector \((n, m)\) values of the underlying graphene sheets. Experiments and some theories show differences in electronic properties between the different types and subtypes [81]. Several older studies [43, 44] claim that there is no difference in the mechanical properties of the different classifications, without providing extensive data. On the other hand, one Molecular Mechanics study [39] clearly shows that for nanotubes that are not doubly clamped, radial breathing modes differ for different structures and the atomistic study of Huang et al. [33] proposes that chirality may be relevant in calculations of Young’s modulus. Many numerical studies of vibrations [16, 17, 24, 34-37, 82-85] are either based on continuum models or if atomistic, consider only a single type of tube. In a continuum analytic model it is hard to differentiate between the different atomistic structures. A recent study [18] provides accurate parameters for all types
of nanotubes, and shows that the simple expression [81] for the radius as a function of \( n \) and \( m \) is more complex [86] thereby further emphasizing the need to use atomistic models. We are unaware of a comprehensive study that considers the effect of structure on multiple lateral modes of doubly clamped SWCNTs and in view of the above-described contradictions this issue requires clarification.

We report below on the vibrational behavior of four different types of SWCNTs: armchair, (denoted by A), zigzag, (Z) and two different chiral ones (C1 and C2). We use the approach that we carefully validated for the armchair case in Chapter 5.1. We generate high quality data with MD simulations on carefully equilibrated clamped tubes (using the Brenner [2] potential) for the thermal vibrations decomposed into different modes. We obtain the dependence of the four lowest modes on length for each of these four nanotubes. Details about the computational procedure and its validation from the Timoshenko beam model can be found in Chapter 5.2 and 5.3.
6.2 Model and details of simulations

SWCNTs are periodic and consist of a specific number of repetitive unit cells. The number of unit cells for a given length varies widely between the types. For example, a (7,7) armchair nanotube (A) with $L = 66.41\,\text{Å}$ consists of 27 periods with 28 atoms in every unit cell, a (12,0) zigzag nanotube (Z) with $L = 68.16\,\text{Å}$ consists of 16 periods with 48 atoms in each unit cell, a (8,6) chiral nanotube (C1) with a $L = 103.65\,\text{Å}$ consists of 4 periods with 296 atoms in every unit cell and a (9,5) chiral nanotube (C2) with $L = 157.05\,\text{Å}$ consists of only 3 periods with 604 atoms in every unit cell (see Fig. 6.1 and Tables 6.1-6.2 for more details). In Fig. 6.1 we show one unit cell for an armchair, zigzag and one of the chiral nanotubes. The axis of the nanotube is in the $y$ direction, and we study vibrations in the $z$ direction. (Our validation process included confirming identical (within statistical error) results for vibrations in the $x$ direction for each case). The frequencies of the vibrational modes depend on both $L$ and $R$, see [87] and Chapter 5.2 - 5.3 for details of the correct dependence for the armchair case.

In order to compare frequencies between different nanotube types we need to match the radius and length of the different nanotube types as closely as possible. To obtain almost identical lengths of vibrating segment ($L_v$) for the four nanotube types we studied (A, Z and the two different chiral ones C1 and C2) we clamped (froze) their ends differently for each type. Each vibrating segment was built up from an integer numbers of unit cells, to avoid any possible boundary conditions effects on the vibrational frequencies. The first(last) three periods were frozen for the As, the first(last) two periods for the Zs and one first(last) period for the chiral nanotubes. To achieve identical radii we selected suitable chiral vectors that were as close as
Figure 6.2: FFT analysis of the first four thermal vibrational modes (n=1-4) in the $z$ direction at a point near the center of mass at 300K for the (8,6) chiral nanotube (C1). The inset is a zoom into the 4th vibrational mode.

possible to those of the A and Z tubes. The radii of the nanotubes of types A, Z, C1 and C2 are 4.75Å, 4.70Å, 4.76Å and 4.81Å respectively and details of the total length and of the length of the vibrating segments for all cases are given in Tables 6.1-6.2.

It has been shown that nanotube distortions can influence their band structure [88–92] in a different way for different chiralities. The distortions investigated were of the order of several nanometers, whereas the movements for our lateral deformations are only about $\sim 10^{-1}$Å, hence, causing insignificant modification of the nanotube’s band structure. In order to maintain a constant temperature a Berendsen thermostat [68] was applied. To ensure stable nanotube structure and eliminate intrinsic tension, we collected data after a period of slow initial thermalization to
6.2. MODEL AND DETAILS OF SIMULATIONS

<table>
<thead>
<tr>
<th></th>
<th>(7,7) Zigzag nanotubes</th>
<th>(12,0) Armchair nanotubes</th>
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</tr>
<tr>
<td>295.14</td>
<td>280.38</td>
<td>120</td>
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</table>

Table 6.1: Data sets of length and vibrating length of our A (armchair (7,7)) and Z (zigzag (12,0)) nanotubes.

300K (periodic boundary conditions with no frozen edges) waiting until the length of the equilibrated nanotube remained constant up to insignificant fluctuations. Since a large number of SWCNTs with different chiralities and lengths were studied, the amount of data needed for the vibrational analysis was reduced by selecting some special points where data was recorded (see [87] for details). In order to obtain adequate statistics for all vibrational modes we let every nanotube vibrate 1000 times more than the period of its lowest frequency, using a MD time step of 0.5 fsec. We then applied a fast fourier transform (FFT) analysis to the data from the selected points, (including one near the center of mass) to calculate the power density as a function of frequency for each of the 24 nanotubes. For example Fig. 6.2 depicts vibrational modes after the FFT analysis for the shortest (8,6) chiral nanotube. Its power density versus frequency is presented for the first four thermal vibrational modes (n=1-4) in the z direction at 300K, and the inset zooms into the 4th vibrational mode with much lower oscillation amplitude.
### Chapter 6. Chirality Effect

<table>
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</tr>
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<td>5</td>
</tr>
<tr>
<td>314.1</td>
<td>261.75</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 6.2: Data sets of length and vibrating length for our chiral (8,6) and (9,5) nanotubes.

Figure 6.3: Frequencies of the first 4 vibrational modes as a function of length. The symbols and lines are given in the legend, where the continuous lines represent the interpolation result and symbols represent the experimental data. This graph contains raw data only.
Figure 6.4: Relative frequency changes relative to the frequencies of the zigzag nanotubes of the first 4 vibrational modes of the other tubes as a function of $L_v$. Blue, green and black colors refer to the A, C1 and C2 nanotubes respectively. The symbols +, ◦, □, and △ depict 1$^{st}$, 2$^{nd}$, 3$^{rd}$ and 4$^{th}$ modes respectively. The inset depicts relative frequency dependency of the 4$^{th}$ mode only.
6.3 Results

In Fig. 6.3 we show the frequencies of the first four modes as a function of the length of the nanotubes, with the types given in the legend. The graph includes raw data and interpolated lines which will be explained below. We observe no substantial differences in the vibrational behavior of the three nanotube types, or between the two chiral nanotubes. In order to further confirm this observation we studied the changes in relative frequencies ($\frac{\delta f}{f}$). For this purpose identical lengths of four chiral vector nanotubes are needed at each point. To achieve this we implemented a procedure that interpolates between any two adjacent points with the following length dependence: $f = aL + bL^2$ (see continuous lines in Fig. 6.3). Relative frequency changes are calculated using this interpolated data. Fig. 6.4 depicts the frequency changes of A, C1 and C2 nanotubes relative to those of zigzag nanotubes for the first four vibrational modes according to Eq. 6.1,

$$\frac{\delta f}{f} = \frac{(f - f_{\text{nanotube}})}{f_{\text{nanotube}}}$$

where $f_{\text{nanotube}}$ is the frequency of the nanotube type we compare with (in the case of Fig. 6.4 $f_{\text{nanotube}}$ is $f_Z$). The inset shows the same changes for the 4th vibrational mode only. Since $\frac{\delta f}{f}$ is close to zero, it can be concluded from the figure that no substantial difference between the nanotubes could be detected.

We carried out the same procedure relative to the frequencies of the A nanotubes. The graphs are qualitatively similar and present the results in Fig. 6.5. Again, no substantial difference between the four nanotube types was detected.
Figure 6.5: Relative frequency $\delta f$ changes relative to the frequencies of the armchair nanotubes of the first 4 vibrational modes as a function of length. Red, green and black color referring to the B, C1 and C2 nanotubes respectively. The symbols $+$, $\circ$, $\Box$, and $\triangle$ depict $1^{st}$, $2^{nd}$, $3^{rd}$ and $4^{th}$ modes respectively. The inset depicts the relative frequency dependency of the $4^{th}$ mode only.
6.4 Conclusions

These results show that the vibrational behavior of doubly clamped SWCNTs does not depend on the type or chirality (in other words on the types and subtypes) of the nanotube (armchair, zigzag or chiral). Moreover, change of the chiral vector of one of the nanotube types (as long as the radius does not change by more than ±0.5Å (in our case 4.76Å and 4.81Å are the radii of the C1 and C2 chiral nanotubes respectively) does not affect the vibrational frequencies. This is useful for the design of ultrahigh NEMS sensors because it shows that one can select the nanotube without making allowance for the chirality. These results are based on extreme care both with equilibration and with the matching or interpolation of radii and lengths. We have shown that the frequencies of the lateral modes of doubly clamped SWCNTS depend only on the nanotube length and radius and not on the nanotube type.
Chapter 7

Affect of boundary conditions

7.1 Introduction

For high quality CNTs the growth is performed at the ends of the fabrication process [92]. In these situations the nanotube is suspended between two electrodes, with its lower part attracted to the electrodes by Van der Waals forces [1]. In such a geometry (see Figure 7.1, [93]) the ends of the vibrating nanotube are partially supported on their lower surfaces. Thus when modeling this system in order to study its vibrations one would study a nanotube that is neither doubly clamped at both ends, nor has completely free ends. One observes from Fig.7.1, which was done in the laboratory of Yuval Yaish that the suspended atoms can be displaced by the AFM tip, but those on the electrode do not move so freely. A partly clamped nanotube would therefore provide the situation closest to the experimental one.

There is also a question of which criterion to use to best characterize the vibrational behavior. In our previous studies where we reported about vibrating SWCNTs which are frozen at both ends, (see details in [87,94] and Chapter 5, 6), we selected
direct measurement of the first four vibrational modes as the tool for vibrational characterization. This was achieved by directly monitoring the displacement during vibration. Such characterization avoids routes such as deducing Young’s modulus from a single or partial set of modes and then applying a specific analytical model. As we showed in [87] and Chapter 5 at least one model, viz. that of Euler-Bernoulli does not even describe nanotube vibrations correctly.

Studies with various external parameters and methods have been made see details in Chapter 2.5. The effect of clamping on the vibrational frequencies has not been systematically investigated, since each study used a single type of BC. Continuum studies use models with doubly clamped ends where the first and second derivatives of position are zero. Many previous atomistic studies investigated nanotubes where the ends of the nanotubes can move freely, although we studied doubly clamped tubes.
Both extremes differ from the real situation as introduced above. Study of the clamping effect is also important because in experiment it is one of the possible origins of dissipation mechanisms and low $Q$.

In this chapter the effect of changing BCs to partially clamped is presented in order to approach experiment as closely as possible. We modeled the vibrational behavior of three different types of SWCNTs: armchair, (denoted by A), zigzag, (ZZ) and chiral (C) under half doubly clamped (HDC) conditions as depicted in Fig.7.2(b) and compare their vibrations to those of the same nanotubes under fully doubly clamped (FDC) conditions (Fig.7.2(a)). We found that the BCs do affect the vibrational modes. Once the full clamping is released, the structure (zigzag, armchair, chiral) does indeed affect the nature of the vibrations. Moreover the HDC conditions lift the double degeneracy of the vibrations in the directions perpendicular to the nanotube axis. The nature of this symmetry breaking depends on the nanotube chirality. We conclude with a reconciliation of previous studies showing that it is indeed the nature of the boundary conditions which influence whether structure affects vibrational frequencies.

Using the approach that we carefully validated in [87, 94], we have generated high quality data with MD simulations on carefully equilibrated clamped tubes (using the Brenner [2] potential) for the thermal vibrations decomposed into different modes. We obtain the dependence of the four lowest modes on length for each of these three nanotubes. Details about the computational procedure can be found in [87] and Chapter 5, and details of the precautions made in order to compare the different types are in [94] and Chapter 6.
7.2 Model and details of simulations

In order to compare frequencies between different nanotube types we need to match the radius and length of the different nanotube types as closely as possible, as explained in [94]. To achieve this for the three nanotube types (A, ZZ and C) we clamped (froze) their ends differently for each type. The first(last) three periods were frozen for the A nanotubes, the first(last) two periods for the Z nanotubes and a half of first(last) period for the chiral nanotubes. Figure 7.3 demonstrates HDC conditions with frozen atoms in light grey (yellow online) (a) three periods of an A; (b) two periods of a Z and (c) half a period of a C nanotube. The dark (blue online) atoms are free to move.

To achieve close-to identical radii we selected suitable chiral vectors that were as close as possible to those of the A and Z tubes. We showed previously that small (less that 0.5 Å) variations in radius do not affect the frequencies [87,94]. The radii
### 7.2. MODEL AND DETAILS OF SIMULATIONS

<table>
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<th>$L_v$ (Å)</th>
<th>No. of periods</th>
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<td>295.14</td>
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<td>120</td>
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<td>$(12,0)$ Zigzag</td>
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<td>315.67</td>
<td>297.10</td>
<td>17</td>
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</tbody>
</table>

Table 7.1: Data sets of length and vibrating length for (7,7) armchair, (12,0) zigzag and chiral (9,6).

of the nanotubes of types ZZ, A, C are 4.70Å, 4.75Å, and 5.10Å respectively (less that 0.5Å) and we give details of the total length and of the length of the vibrating segments ($L_v$) for all cases in Table 7.1.
Figure 7.3: One edge of our nanotubes with frozen atoms shown as light grey (yellow online) on (a) Armchair (A), (b) Zigzag (ZZ), (c) Chiral (C) nanotubes. The Y axis points into the page. The atoms adjoining this end are all dark (blue online) until at the other end there is a second boundary region identical to this one as in Figure 7.2.
7.3 Results

We compared the first four vibrational modes of nanotubes with both types of boundary conditions (FDC and HDC) and of different lengths, as listed in Table 7.1. The frequencies as a function of vibrational length are depicted in Figures 7.4-7.6 for each of the A, ZZ and C nanotubes respectively. In each case we compare the degenerate X-Z results of the FDC case with the different X-Z results for the HDC case. There are two clear observations here:

- HDC nanotubes vibrate with lower frequencies in the Z and X directions than FDC nanotubes (see Figs. 7.4-7.6);

- as a result of the change in boundary conditions the degeneracy of frequencies in the X and Z directions that was observed for FDC conditions was lifted.

In order to systematically investigate the differences in vibrational behavior between the three nanotube types under the HDC boundary conditions we plotted the vibrational frequencies as a function of the nanotube length for A, ZZ and C nanotubes in the X (see Fig. 7.7) and in the Z directions (see Fig. 7.8) in separate plots. Figures 7.7-7.8 show some differences between the three nanotube types, but it is hard to determine a specific pattern.

Alternatively, one can study the dependence of the symmetry breaking parameter \( \eta = (f_x - f_z)/\bar{f} \) on the nanotube type, where \( \bar{f} \) is the average frequency of \( f_x \) and \( f_z \). The symmetry breaking parameter is plotted in Figures 7.9-7.12 for the first, second, third and fourth modes respectively, of the different CNT types. The graphs show clear differences in the vibrational behavior of nanotubes of the A, ZZ and C types. Differences between frequencies in the X and Z directions can be summarized as follows:
Figure 7.4: First 4 modes of the vibration as a function of length of (7,7) armchair nanotubes: black lines depicts vibration of FDC nanotubes in the X and Z direction; blue is for HDC nanotube vibration in the Z direction; green is for HDC in the X direction.
7.3. RESULTS

Figure 7.5: First 4 modes of the vibration as a function of length of (12,0) zigzag nanotubes: black lines depicts vibration of FDC nanotubes in the X and Z direction; blue is for HDC nanotube vibration in the Z direction; green is for HDC in the X direction.
Figure 7.6: First 4 modes of the vibration as a function of length of (9,6) nanotubes: black lines depicts vibration of FDC nanotubes in the X and Z direction; blue is for HDC nanotube vibration in the Z direction; green is for HDC in the X direction.
Figure 7.7: Vibrational modes as a function of length in the X direction of armchair, zigzag and chiral nanotubes. The symbols and lines are given in the legend.
Figure 7.8: Vibrational modes as a function of length of armchair, zigzag and chiral nanotubes in the Z direction. The symbols and lines are given in the legend.
Figure 7.9: $\eta$ of 1st vibrational mode as a function of length of armchair, zigzag and chiral nanotubes. The symbols and lines are given in the legend.

1. $\eta$ values of A, ZZ and C are different for all investigated modes for the nanotubes that are shorter than 20 nm;

2. $\eta$ of short nanotubes is negative for the 3rd and 4th modes;

3. only chiral nanotubes have negative $\eta$ values already for the 2nd vibrational mode;

4. the $\eta$ values of chiral nanotubes are much larger than those of armchair and zigzag nanotubes.
Figure 7.10: \( \eta \) of 2\textsuperscript{nd} vibrational mode as a function of length of armchair, zigzag and chiral nanotubes. The symbols and lines are given in the legend.
Figure 7.11: $\eta$ of 3rd vibrational mode as a function of length of armchair, zigzag and chiral nanotubes. The symbols and lines are given in the legend.
Figure 7.12: $\eta$ of 4th vibrational mode as a function of length of armchair, zigzag and chiral nanotubes. The symbols and lines are given in the legend.
7.4 Discussion and conclusions

The above results demonstrate that boundary conditions are extremely important in the field of SWCNT NEMS design and optimization. Firstly, we see from Fig. 7.4-7.6 that the vibrational frequencies of FDC CNTs are higher than those of HDC. This result can be understood on the base of the actual length of the vibrating segment. For HDC CNT the actual vibrating length is a little bit larger and hence the vibrational modes are lower. Secondly we observe that a change from FDC to HDC conditions breaks the symmetry of carbon nanotubes which splits the degeneracy of vibration in the X and Z directions. It can be seen from this picture that a different number of atoms are frozen in different geometries according to the nanotube symmetry allowing vibrations of C-C bonds in different directions. The symmetry is broken differently for armchair, zigzag and chiral nanotubes, and this is expressed in different vibrational behavior of three nanotube types. This could not be observed under symmetric doubly clamped boundary conditions. These observations are consistent with [94] and [39] where in the former case the full double clamping led to identical behavior, and in the latter incomplete clamping led to different behavior for different chiralities.

From the experimental AFM image in Figure 7.1 it is clear that HDC is closer to the laboratory situation. Since only in MD or MM such HDC conditions are likely, this confirms the need for direct atomistic simulation to understand CNT NEMS.
Chapter 8

Atomistic study of nanosensors based on CNTs

8.1 Model and details of simulations

We carried out atomistic simulations of a vibrating nanotube suitable for use in such a sensors based on (12,0) 110.76 Å zigzag carbon nanotube, which consist of 24 periods. We proceed the same thermalization procedure as explained in Chapter 4.2. Two first/last periods were frozen in order to remain with bridged boundary conditions, this remained 91.96 Å vibrating length.
8.2 Results and discussion

We first calculated the frequencies of first four modes of the natural nanotube. In order to simulate attached mass we decided to change some carbon atoms to its isotope $C_{13}$, changing mass of segments of SWCNT and calculate vibrational frequencies of nanotube with some periods replaced with $C_{13}$ the results are presented in Table 8.1. The isotope $C_{13}$ in only 1, 2, 3 or 4 periods does not affect on the frequencies, however the replacement of all atoms of the nanotube will give noticeable effect as can be seen from the Table 8.1.

The weight of single $C_{12}$ is 12 amu and this of $C_{13}$ is 13 amu which is equivalent to $1.9926466 \cdot 10^{-23}$ gr and $2.1587005 \cdot 10^{-23}$ gr respectively. Changing the whole vibrational segment (20 periods) to isotope $C_{13}$ will give us resolution of $1.5941174 \cdot 10^{-21}$ gr see Table 8.2. This zaptogram sensitively is in agreement with the reported by [61–63]. We plan to further research issues such as what minimal number of atoms need to be changed to different masses in order to achieve a differential response.
Table 8.2: Mass resolution in grams due to replacement of $C_{12}$ with $C_{13}$.

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<tr>
<td>24</td>
<td>1152</td>
<td>$1.9129409 \cdot 10^{-21}$</td>
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</table>

8.3 Conclusions

Current results are only the beginning of a detailed investigation of the mechanism of action of resonant sensors based on SWCNTs. In future we plan not only to change isotopes to heavier than $C_{13}$ but study the vibrational behavior of nanotubes with mismatches, i.e. with defects (without atoms in specific points of nanotube). We also plan to attach different molecules to the nanotube’s surface and study vibrational changes and sensing limitations of such devices.
Chapter 9

Summary and future plans

In the present research we applied numerical techniques and analytical solutions in order to understand the principle of action of SWCNT NEMS in depth. For this purpose we needed to answer three basic questions:

- What is the mechanism of vibration of single walled carbon nanotube?
- Is there any difference in the vibrational behavior between nanotube types?
- How do boundary conditions affect the vibrations of carbon nanotubes?

In Chapter 5 we answerer the first question by comparing our numerical results to two continuum models: the Euler-Bernoulli beam model and the Timoshenko beam model. According our results, the vibration of short, thick tubes could not be described by the EB continuum model, because it does not take in to account shearing deformation and rotatory inertia, but it can be applied when dealing with fundamental frequencies and long, thick nanotubes. However, in order to achieve high sensitivity of a NEMS one needs to miniaturize its dimensions. In the field of SWCNT NEMS it can be achieved by taking shorter nanotubes. The vibration of short tubes can be
described by the Timoshenko beam model, which is in excellent agreement with our numerical results.

One of the critical points on the way to understand the mechanism of nanotube vibration is to determine carefully Young’s modulus, whose estimates are scattered in the literature due to the scattering of estimates of nanotube thickness, this scattering is known as Yakobson’s paradox. In Chapter 5 we partially resolve this problem by estimating a low cut-off for the Young’s modulus.

The second question is answered in Chapter 6. According to our results there is no difference between the vibrational behavior of armchair, zigzag and chiral nanotubes under fully doubly clamped conditions. However if we change the boundary conditions to partially doubly clamped the symmetry is broken differently for different nanotube types and their vibrational frequencies vary about 15%. Moreover the degeneracy in X and Z vibration, which was observed for the fully doubly clamped case, is split giving different frequencies in these two directions.

The main conclusions from this research are

• A geometrical limit for EB like beam and Timoshenko like beam was proposed;

• The Yakobson’s paradox was partially resolved;

• The structure of SWCNTs does not affect on its vibrational behavior under fully doubly clamped conditions;

• The boundary conditions are extremely important in the field of SWCNT NEMS design and optimization

In Chapter 8 we presented a simulation of NEMS based on SWCNT based on our previous calculations and studies. This is very light and elementary demonstration of
one of the possible applications of such a NEMS. In future more careful and systematic work has to be presented in order to study limits of such a devices and optimize their operation.

The results of this study are relevant and important for the design of high frequency NEMS based on SWCNTs, however many more simulations could still be done in order to study and optimize SWCNT NEMS. For example, sometimes during NEMS production the nanotube is twisted, tensioned or oppositely has a slack over the gap. This enters tension or stretching into the system which would vibrate differently. One of the questions which can be answered numerically: How does the tension or torsion can affect nanotube vibrational frequencies?

The direct simulation of application of such a devices which has began in this research should be extended. For example, study of the vibrational behavior of nanotubes with mismatches, i.e. with defects (without atoms in specific points of nanotube) could be conducted. Different molecules could be attached to different points on a nanotube’s surface and the vibrational changes and sensing limitations of such devices be investigated.
Appendix A

Code

The attached CD contains the source code of the programs used in the present project. In this appendix an explanation of the files and codes is given. The details of the compilation and execution were provided by Dr. L. Van Dommelen at http://www.eng.fsu.edu/~dommelen/research/nano/brenner/. The code is a fortran MD code with Brenner potential. Initial nanotube coordinates were built with code in the above link.

A.1 Common blocks

The program uses common blocks for most variables which are loaded into each subroutine through common_files.inc:

- common_ch.inc: hydrocarbon potential common blocks
- common_lj_new.inc: Lennard-Jones common blocks
- common_tb.inc: tight binding
• `common_md.inc`: general

• `common_leon.inc`: added by Dr. L. Van Dommelen

• `common_yaniv.inc`: added by Polina

A.2 I/O units

The following Fortran I/O units are in use by the code:

• 1: `xmol.d` (to be post converted to `xmol.xyz`)

• 9: `output.d`

• 11: `coord.d`

• 13: `input.d`

• 14-18: REBO potential splines

• 23: for `bombard.f`

• 41: (used in the periodic box straining modification)

• 50: `overwrite.d`

• 51: `load.d`

• 53: `fort.53 debug file`

• 55: `max_ke.d`

• 85: `pair_energy.d` `eigenvectors.d`
• 86: eigen_energies.d

• 87: dos.d

• 88: ldos.d

• Was moved pair_energy.d to I/O unit 84.

Files are opened in open.inc, closed in close.inc.

### A.3 Subroutines

Here is a list of subroutines and what they do:

- **Bcuint**
  - Bicubic: interpolation of CLM; also returns derivatives.

- Berendsen: thermostat: KFLAG=1 damping; KFLAG=other(=5): rescale velocity.

- Bombard: Adds a single atom from file bombard.d.

- Caguts: Finds forces on atoms from pair potentials.

- Ccorr: Call the corrector.

- Cpred: Calls Pred (if there are nonrigid molecules) and increments time.

- Damage: Checks whether the number of carbons less than 1.8 apart changes, indicating damage.

- Gleq: Langevin (friction and random force).
A.3. SUBROUTINES


- Ljcont: Seems to give net Lennard-Jones potential exerted by a semi-infinite continuum with a normal in the 'ndir' direction, at a location 'surf'.

- Model: Calls Caguts (if not tight binding).

- Mtable: Creates tables of the potentials VA and VR from the Brenner potential.

- Param: C and H potentials.

- Pibond: Finds bonding forces involving C and H atoms.

- Pred: Nordsieck scheme prediction of zn+1 from zn only.

- Radic: Tricubic interpolation of CLMN.

- Rannum: Random number generator. Its argument is unused.

- Read_data: Reads input.d and coord.d.

- Set_md: Initialize time and such, also sets ENPR.

- Setgle: Set langevin parameters.

- Setin: Initialize kt, xmass, noa, sig, eps, pi, bolz, avo, epsi, econv.

- Setpc: Set Nordsieck parameters (except F22=1).

- Setpp: Calls param and mtable.

- Setran: Initializes RNG, called once at the start.

- Setrn: Random number initialization. Only called once, inside setran.
• Thermos: Chooses thermostat routine.

• Tor: Torsional interaction TLMN tricubic interpolation.

• Write_data1: Writes to output.d.

• Write_data2: Writes to unit 9, output.d, the step number, average energy per atom, some kinetic energy; writes to unit 6 (the screen) total potential energy. Modified by me to write more output to the screen less frequently.

• Write_data3: Overwrites 11, coord.d, .

• Xmol: Writes to 1, xmol.d data to be converted later to .xyz files.

• Zero: Zero velocities.

• vscale: Seems to be some attempt to select the scalings that give minimum potential energy.

A.4 MPI

This section presents the changes, which were done in the source code in order to run on parallel. The parallelized code is given in the attached CD. The parallel code is also based on the Brenner potential code to simulate the forces that connect the carbon atoms in the nanotube.

A.5 Added and Modified Subroutines

In the directory tube_md the following files were added in order to allow to the output files *.dat and *.xyz to be pointed to the proper directory:
A.5. ADDED AND MODIFIED SUBROUTINES

- `xmol.f` - was previously in the serial code mapping *.xyz and *.dat output files to the directory `tube_mdexe2/dat1`
- `xmol2.f` - mapping *.xyz and *.dat output files to the directory `tube_mdexe2/dat2`
- `xmol3.f` - mapping *.xyz and *.dat output files to the directory `tube_mdexe2/dat3`
- `xmol4.f` - mapping *.xyz and *.dat output files to the directory `tube_mdexe2/dat4`

In the directory `tube_mdexe2` the following files and directories were added:

- Directory `dat1` - input and output files for the calculations in the temperature of 300K.
- Directory `dat2` - input and output files for the calculations in the temperature of 400K.
- Directory `dat3` - input and output files for the calculations in the temperature of 500K.
- Directory `dat4` - input and output files for the calculations in the temperature of 600K.
- `pi3.f` - main for the mpi code

The following 4 files were modified from the previous main.f of the serial code and invoke subroutines from `tube_md` and `tube_md`:

- `mymain.f` - subroutine of the main MD code that reads input files from and writes output files to the dat1.
- `mymain2.f` - subroutine of the main MD code that reads input files from and writes output files to the dat2.
• mymain3.f - subroutine of the main MD code that reads input files from and writes output files to the dat3.

• mymain4.f - subroutine of the main MD code that reads input files from and writes output files to the dat4.

The following 4 files were modified from the previous open.inc of the serial code:

• open.inc - allow to open files from dat1.

• open2.inc - allow to open files from dat2.

• open3.inc - allow to open files from dat3.

• open4.inc - allow to open files from dat4.

• mpi_data_project.tar - back up of the input files from dat1, dat2, dat3 and dat4.

• mpiv.sh - compilation of the parallel code (see bellow the explanation of the compilation).

• md.mpi.run - executable of the parallel code (see bellow the explanation of the compilation).

• mpi_scrip.sh - the script for the queuing system (see bellow the explanation).

A.6 Installation and running

The algorithm is realized in FORTRAN77 in the operating system Linux If you wish to compile and run the programs on your personal parallel computer you need a Linux operating system. In order to run the program, follow these steps:
A.7. RUNNING INSTRUCTIONS USING QUEUING SYSTEM ON Nanco

- Download the tar file parallel.tar and save it on your home directory.

- To unzip those files, type in the command line:

  > tar -xf parallel.tar

- Check that you get two directories, tube_mdexe2 and tube_md. In the tube_mdexe2 you can find all kind of the data files that the program needs. In tube_md you find files containing subdirectories that are needed for calculation.

- To run the program from your home directory without recompiling it (without any changes in the code), change directory to tube_mdexe2 and activate the exe file md.mpi.run by typing in the command line:

  > mpirun_ssh -np number of processes(4 in our case) node(number of the node) node(number of the node) node(number of the node) node(number of the node) ./md.mpi.run

  for example:

  > mpirun_ssh -np 4 node5 node5 node5 node5 ./md.mpi.run

A.7 Running instructions using QUEUING system on Nanco

In the directory tube_mdexe2 you can find a script mpi_scrip.sh in order to run it under your user, first follow the instructions and comments in the script, then change the path (enter your user instead of pine).

In the command line type:
> mpisub number of processes (4 in our case) mpi_script.sh

In order to check the status of your job type:

> qstat

To see some outputs (for example output that goes to the screen) check the file:

mpi_script.sh your job ID
Appendix B

Fourier Transform Matlab Code

Current appendix presents Matlab code of Fourier Transform, this code is also given in the attached CD. The function test reads from the following output files:

- coord.d
- input.d
- xmol.d
- xmol_cm.d
- output.d

Note, that all files have to be in one directory.

```matlab
function test
clear all
close all
clc
drct=input('Insert the path of the requested job: ');
```
%cd(‘..’);
copyfile(‘./*.m’,drct);
cd(drct);
N=input(‘The number nanotube periods: ’);
param = ’input.d’;
fid1 = fopen(char(param));
param2 = textscan(fid1 , ’%f %f %f
 %f
 %f
 ’);
%LSTEP = param2{1}
LSTEP=input(‘The total number of MD steps: ’);
xmol= param2{2}
%ts = 1.0e-15*nxmol
t=input(‘The time step of this simulation in fsec: ’);
t = t*10^-15*nxmol;
%nxmol=input(‘The number of steps after them to call xmol
(to write xyz to xmol_cm_period.d): ’);
name=input(‘The desired name for this job: ’);
[fz,mz,fx,mx,fy,tot_energy,pot_energy,temp,mean_temp]=
... sig_procs(N,ts,name,LSTEP,nxmol);
cd(’~/freq_q_anal/Matlab_functions’);

function
[fz,mz,fx,mx,my,tot_energy,pot_energy,temp,mean_temp]
... =sig_procs(N,ts,name,LSTEP,nxmol)
close all
clc

[X,Y,Z,T]=getXYZT(N, ts, LSTEP, nxmol);

[pot_energy,tot_energy,temp,mean_temp]=energy;

N=N+1 % Set just to N if N is even

mkdir grafiki;

zstd_mat = [];

name2 = regexprep(name, '_', ' ');

for i=1:3
    n=((N+1)/4)*i;

    figure('Name',[Figure ' num2str(i) ':' name2],
           'NumberTitle','off')

    zmean = mean(Z(:, n));

    n=n

    zstd = std(Z(:, n))

    rms = (sqrt(mean(Z(:, n).^2)));

    zstd_mat = [zstd_mat ; i zstd];

    ZZ = Z(:, n)- zmean;

    [fz(i,:),mz(i,:)]=fut(ZZ,ts,
                          [name2 ':FFT of Z(t), Y =' num2str(n)]);

    saveas(gcf,['grafiki/' name ' 
                  _FFT_of_Zt_Y_' num2str(n) '.fig']);

    figure('Name',[Figure ' num2str(i+9) ':' name],
            'NumberTitle','off')

    plot(T(:,n), ZZ);

    set(gca,'FontSize',20);
% fontsize of the numbers of axis
xlabel ('time (sec)', 'Fontname', 'times', 'Fontweight', 'bold', 'Fontsize', 24);
ylabel('z(A)', 'Fontname', 'times', 'Fontweight', 'bold', 'Fontsize', 24);
title([name2 ':Time domain of Z at Y=' num2str(n)], 'Fontname', 'times', 'Fontweight', 'bold', 'Fontsize', 24);
grid on;
saveas(gcf, ['grafiki/' name '_Zt_Y_' num2str(n) '.fig']);
end
for i=4:6
    n=((N+1)/4)*(i-3);
    figure('Name', ['Figure ' num2str(i) ':' name2], 'NumberTitle', 'off')
xmean = mean(X(:, n));
XX = X(:, n) - zmean;
[fx((i-3,:),:), mx((i-3,:),:)] = fut(XX, ts, [name2 ':FFT of X(t), Y=' num2str(n)]);
saveas(gcf, ['grafiki/' name '_FFT_of_Xt_Y_' num2str(n) '.fig']);
figure('Name', ['Figure ' num2str(i+9) ':' name2], 'NumberTitle', 'off')
plot(T(:,n), XX);
set(gca,'FontSize',20); % fontsize of the numbers of axis
xlabel ('time (sec)', 'Fontname', 'times', 'Fontweight', 'bold', 'FontSize', 24);
ylabel('z(A)', 'Fontname', 'times', 'Fontweight', 'bold', 'FontSize', 24);
title ([name2 ':Time domain of X at Y=' num2str(n)], 'Fontname', 'times', 'Fontweight', 'bold', 'FontSize', 24);
grid on;
saveas(gcf,['grafiki/' name '_Xt_Y_' num2str(n) '.fig']);
end
for i=7:9
n=((N+1)/4)*(i-6);
figure('Name', ['Figure ' num2str(i) ':Simulation Plot Window-' name], 'NumberTitle', 'off')
ymean = mean(Y(:, n));
YY = Y(:, n) - ymean;
[fy((i-6),:),my((i-6),:)] = fut(YY, ts, [name2 ':FFT of Y(t), Y=' num2str(n)]);
saveas(gcf,['grafiki/' name '_FFT_of_Yt_Y_' num2str(n) '.fig']);
end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%make vector of the same size in order to plot them

time=T(:,1);
[k,j]=size(time);
[k2,j2]=size(temp);

if k<k2
    tot_energy = tot_energy(1:k);
    pot_energy = pot_energy(1:k);
    temp = temp(1:k);
else
    time=time(1:k);
end

i=20;
figure('Name',['Figure ' num2str(i) ':-' name2],
'NumberTitle','off')
plot(time , tot_energy,'b');
hold on
plot(time , pot_energy,'red');
set(gca,'FontSize',20); % fontsize of the numbers of axis
% set (get('XLabel'), 'FontSize',24);
xlabel ('time (sec)','Fontname','times',
'Fontweight','bold','FontSize',24);
ylabel('Total Energy','Fontname','times',
'Fontweight','bold','FontSize',24);
title ([name2 ':Energy'] ,'Fontname','times',
'Fontweight','bold','FontSize',24);
legend('Total Energy', 'Potential Energy',1);
grid on;
saveas(gcf,['grafiki/' name 'Total_energy.fig']);

\[ i=21; \]
figure('Name',['Figure ' num2str(i) ':=-' name],
'NumberTitle','off')
plot(time, temp,'b');
set(gca,'FontSize',20);  \% fontsize of the numbers of axis
\% set (get('XLabel'), 'FontSize',24);
xlabel ('time (sec)','Fontname','times','Fontweight','bold','FontSize', 24);
ylabel('Temperature','Fontname','times','Fontweight','bold','FontSize', 24);
title ([name2 ':Temperature '], 'Fontname','times','Fontweight','bold','FontSize',24);
legend([The mean tempereture is ' num2str(mean_temp) 'K'], 1);
grid on;
saveas(gcf,['grafiki/' name 'Temperature.fig']);

\[ \text{figure(gcf)} \]
save([name 'workspace.mat']);

function [X,Y,Z,T]=getXYZT(N,ts,LSTEP,nxmol)

tmp1 = 'xmol_cm_period.d';
\% X = []; Y=[]; Z=[]; T=[];
fid1 = fopen(char(tmp1));

number_of_points=LSTEP/nxmol;

%number_of_points=417600;
T = zeros(number_of_points, N);
X = zeros(number_of_points, N);
Y = zeros(number_of_points, N);
Z = zeros(number_of_points, N);
for n=1:number_of_points
    t = n*ts*ones(1,N);
%
%read from 4th line
    fgetl(fid1);
    fgetl(fid1);
    fgetl(fid1);
    fgetl(fid1);
    fgetl(fid1);

%tmp = textscan(fid1 , '%f %f %f %f %f
',N);
tmp = textscan(fid1 , '%f %f %f %f
',N);
    x = tmp{1 , 2}';
    y = tmp{1 , 3}';
    z = tmp{1 , 4}';
    X(n,:) = x;
    Y(n,:) = y;
    Z(n,:) = z;
    T(n,:) = t;
    if (mod(n,1000)==0)
fprintf(1,'%d\n',n);
end
end

% fclose(fid1);
% Uncomment it if you want to
cut first 1E6 steps
% X=X(50000:end,:);
% Z=Z(50000:end,:);
% Y=Y(50000:end,:);
% T=T(50000:end,:);
fprintf(1,'Done\n');
beep

beep
References


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שלונ אורככ של הננוזינונים קרוב ל-8 nm. ממידת אלא אנך מספייקם בכיי להרגיש מסהה. הכלה, אבל שוני של ארבך טביעה מחותוריה של הננוזינונים מניב שוני של תדריה התנגדה. באופף הרışı ושוני של כל אספורי הננוזינונים גורםلطוחה של התדריה הכל האופנים. לכל האופנים מנך של מדרים של תולה של ánל והת.Transactionalו. נתונים אפגי של גזרות של פטנוזיםპער עליה בקנאה את אודו התראות.
R/λ
data model can be written to the form $\frac{R}{\lambda} = \frac{v}{c}$, where $v$ is the speed of light and $c$ is the speed of sound.

The modes $R/L$ and $R/L$ are obtained by taking the limit as $\lambda \to 0$ and $\lambda \to \infty$, respectively. For a given mode, the frequency is determined by the electron-electron interaction and the electron-spin resonance.

For $n = 0$, the modes are given by $R/L = \frac{v}{c}$. For $n = 1$, the modes are given by $R/L = \frac{v}{c}$. For $n = 2$, the modes are given by $R/L = \frac{v}{c}$. For $n = 3$, the modes are given by $R/L = \frac{v}{c}$.

For $n = 4$, the modes are given by $R/L = \frac{v}{c}$.

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מולקולות קונטיקל אפיפיל אטומיים בודדים,ẵריך ללבך את מינון התנדדות של ננוצינוריות פחמני
העבוצה הנוכחית מציגת לימוד מעמיק יסוד של המינון הזה. העבוצה היא יסיסני לוגיה על
แชלה בשאלות בסיסיות:

• מה הוא מינון התנדדות של SWCNT

• האס המבנה של ננו פיזי הגופים משמשים על אופי התנדדות?

• מה היא התשובה של תנייה השפתי על אופי התנדדות?

ההתווה המגיעה שלHomeAsUpEnabled נומר נוגה אנליטי המבוסס על תיאורית הרצף של אופי התנדדות של
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• האם מבנה הפסים באופן זמני את אופי התנדדות של

• מה הוא התשובה של תנייה השפתי על אופי התנדדות?

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• האס המבנה של ננו פיזי הגופים משמשים על אופי התנדדות?

• מה היא התשובה של תנייה השפתי על אופי התנדדות?

בתוחלת הנוגה הלוגית על השאלת הרואשים "איה סימוליציה ממקלחת של המינה
במשל כעמא הקבוצה בשני קווים, העבורה הוא תכונה של ארבעת אופי התנדדות
הנמוכים בוגר של SWCNT. עקבה אחרא שנתי של אופי התנדדות כמקלחת של ארבע רזרס של
ננוצינורית.

וביצועהῶה היא עמא מספקת הוכחה חותכת לכל שמתסכל המנהליים של ראויילברגי, שיאו
ולוקה בשפתם משוער גורם, ano מתאר בעוזר מידי הקא המינה התנדדות של
TNCWS ריכוז לתוך הקבוצה דיאגונלי הנוגה עולות בקהדה את עם הממוד של טימוסקוק לקור, 
ביות אורות-דיס. התוחלת אליהם הגיעה עלולת בקהדה את עם הממוד של טימוסקוק לקור, 
אש לכל את השפעת התנועה הסטודה משוער גורם. הרואים שיבחס לאורד הגל (\lambda) של האופק
Cassar the mass, $m$, and the frequency, $f$, of the resonator, $k$.

Applying this formula to the mass sensitivity, $\Delta m=m \Delta f = \frac{2m}{Q}$.

Cassar, $Q$ can be defined as the quality factor ($Q$) of the resonator, which is $\frac{\Delta f}{m}$.

We also define $Q$ as the ratio of the energy stored to the power dissipated over one cycle.

In conventional systems, $Q$ is limited by technology, while in NEMS, $Q$ is practically unlimited due to the use of nanotechnology.

For example, SWCNTs can serve as high-quality resonators, with $Q$ values of up to $10^{23}$ and $300$ MHz.

Cassar also notes that $Q$ can be optimized for various applications, such as mass sensing or temperature sensing.

In summary, the use of nanotechnology in NEMS has opened up new possibilities for high-frequency and high-sensitivity applications.
 GTKLCHR

תקציר

גניזוריות מקיצים (SWCNT) וחיי מרומד מינויםiphy עם תכונות שמשלות ומכניות מיוחדות:

כמו למסל:

• אלסטיות גבהתם מדויקות של כ- 5 TPa
• חללים המשולש כשל מתכת (למשל Cu)
• ק檄 חוטים משולש נבדה במקף
• חלק מתנה צבבי,אחרות כפלים לחצן ממקף
• ע zupeł

scss לכל התכונות של הORAGE את תכונות וחיי מרומד כה ששמוחות להחזק רבע של יישומים.

 öldürה רכיב במערכות ניאלקטרוסוכננותית (NEMS) וחביות הביציים ב”עון קידריה, (cantilever) וקויידות (bridges) שמייצרות ביטה של NEMS ליטוינית המגון תמורות במים סיליקון, סיליקון ניטריד, סיליקון קרביד והאלומיניום ניטריד.

מספר ישימוס של عدة רוב של מסות ק.clear בתוכנה מואר, לח נוכחות (לughters ניון

AFM מ”ב. למסף א鑽 של או נושת משלי חנקון הפועל של התכניות של מכוסס על העובדה שבד

התרדית תליי באה באה הבא:

\[ f = \sqrt{\frac{k}{m}} \]
סימולציה אטומיסטית של מערכות ננו-אלקטרומכניות
מבליטות על בסיס ננוגנרטוריות

חיבורי על מחקר
לשם מילוי חלקים של דרישה לשילוב תואר דוקטור לפילוסופיה

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🙃

פניה פאני