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

Polina Pine
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Nano-Electro Mechanical Systems
Based on Carbon Nanotubes

RESEARCH PROPOSAL

For the Degree of Doctor of Philosophy

Polina Pine

RUSSELL BERRIE NANOTECHNOLOGY INSTITUTE, TECHNION - IIT
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This research proposal was supervised by Dr. Joan Adler and Dr. Yuval Yaish in the Russell Berrie Nanotechnology Institute.

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Chapter 1

Introduction

Nanoelectromechanical systems (NEMS) are electromechanical systems with nanometer dimensions operated in their resonant modes and are of interest to both technical and scientific areas. In this size regime extremely high resonant frequencies and small active masses can be achieved; the quality factors of resonance (Q) of NEMS being in the range of $10^3 - 10^5$. These attributes collectively make NEMS suitable for a multitude of technological applications such as ultrafast sensors, actuators and signal processing components. However there still exist fundamental and technological challenges to NEMS optimization. One way to achieve such optimization is to use Single Walled Carbon Nanotubes (SWCNTs) oscillators instead of conventional silicon or silicon nitride resonators.

Single Walled Carbon Nanotubes 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. With respect to conventional NEMS, carbon nanotubes are extremely light, and have very
high Young’s Modulus (1TPa). They have enormous potential for a variety of applications (field-effect transistors, hydrogen storage, mass, force sensing and more), and probably more still to be explored. Due to their remarkable mechanical, physical and chemical properties, carbon nanotubes may be used as structural elements in nanoscale devices or as potential reinforcements in nanocomposite materials [1, 2]. For a typical CNT of 100nm length and 1nm 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.

In recent years, experiments have been conducted in areas such as electrical actuation and detection of the guitar-string-like oscillation modes of doubly clamped nanotube oscillators [3]. Extensive research has been devoted to the application of carbon nanotubes as chemical and mechanical sensors [4] - [7]. It was found that the natural frequency is sensitive to the applied axial load, so one of the principles of sensing based on the natural frequency shift of a carbon nanotube resonator as a results of the applied force. In consequence, the effect of axial load on the property of transverse vibration of carbon tubes is of practical interest.

Experiments at the nanoscale are extremely difficult therefore theoretical studies are of great interest. An elastic continuum model has been applied to the investigation of the vibrational behavior of carbon nanotubes [8] - [12]. Technological breakthroughs in computational facilities gives us a powerful research tool. With the aim of modeling nanotube NEMS we have commenced a vibrational analysis of the single walled carbon nanotube. We have carried out atomistic simulations of nanotubes using the Brenner-Tersoff potential [13] in order to help in understanding and obtaining insight into the experimental results [3], and now present our first preliminary study
of Single Walled Carbon Nanotube oscillators.
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 lengths of 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. 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:

\[
\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 ,
\]

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 honeycomb lattice of graphene as shown in Fig.
2.1. STRUCTURE OF CARBON NANOTUBES

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 greatly 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. 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.)
Figure 2.2: The structure of a CNT is based on a two-dimensional graphene sheet. The chiral vector is defined on the honeycomb 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. [17].

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 is shown in Fig. 2.3.

### 2.2 Physical Properties of Carbon Nanotubes

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.
2.2. PHYSICAL PROPERTIES OF CARBON NANOTUBES

Figure 2.3: Atomic scale image of a CNT with a diameter of 1.3nm, taken by a scanning tunneling microscope (STM). Individual carbon atoms can be seen as the reddish or yellow blobs in this image, with dark hexagonal holes between the atoms. [18].

Each carbon atom of a 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. For example: pressing on an Atomic Force Microscope (AFM) tip made out of carbon nanotube will cause it to bend, but without damage to the tip. When the force is removed, the tip returns to its original state. This property makes CNTs very useful as probe tips for very high-resolution scanning probe microscopy.

Quantifying these effects has been rather difficult, and an exact numerical value has not been agreed upon. Using an atomic force microscope (AFM), the unanchored ends of a freestanding nanotube can be pushed out of their equilibrium position and the force required to push the nanotube can be measured. The current Young’s modulus value for SWNTs is about 1 TeraPascal, but this value has been disputed, and value as high as 1.8 TPa or even more have been reported. The differences probably arise from different experimental measurement techniques. Theoretically that Young’s modulus is found to depend on the size and chirality of the SWNTs, ranging
from 1.22 TPa to 1.26 TPa, with a value of 1.09 TPa for a generic nanotube. Others have noted that the measurements of the moduli of MWNTs using AFM techniques do not strongly depend on the diameter. Instead, they argue that the modulus of the MWNTs correlates with the amount of disorder in the nanotube walls. Not surprisingly, when MWNTs break, the outermost layers break first. [19] New research from the University of Pennsylvania indicates that CNTs may be the best heat-conducting material man has ever known. Ultra-small SWNTs have even been shown to exhibit superconductivity below 20K. Preliminary experiments and simulation studies on the thermal properties of CNTs show very high thermal conductivity. It is expected, therefore, that nanotube reinforcements in polymeric materials may also significantly improve the thermal properties of the composites [19].

2.3 Industrial Applications

The unique and remarkable chemical, physical, and mechanical properties of CNTs make them desirable for many industrial applications. They open an incredible range of applications in materials science, electronics, chemical processing, energy management, biomedical and many other fields [19].

2.4 Experimental Background of 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 molecule detection limit. The detection scheme for mass sensing with a mechanical resonator is achieved by monitoring the resonance frequency of one of the modes. 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 [20] recently 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. [21, 22] like in Fig. 2.4. The change in mass is detected by monitoring the frequency shift as molecules are adsorbed onto the resonators. The highest

![Cantilevers and Beams](image)

Figure 2.4: NEMS: cantilevers of aluminium nitride [21] and beams of silicon nitride [22]

measurable mass sensitivity $\sim 0.4 \cdot 10^{-18}$ kg is achieved by 10MHz silicon beam (of length 4 $\mu$m) with a quality factor ($Q$) of $\sim 2500$. Recently, the mass of a single DNA molecule $\sim (0.23 \cdot 10^{-18}$ kg) was measured, by a silicon nitride cantilever [21]. The sensitivity required for detecting a single small molecule ($\sim$10 atoms) is about $10^{-21}$ kg, 3 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 NTs 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 SWCNTs have a potential to develop ultra sensitive mass and force sensors, Sazonova et al. [3] studied a suspended NT, clamped at both ends (Fig. 2.5), where 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, and quality factors ranging between 50 to 200.

Figure 2.5: A doubly clamped Carbon Nanotube oscillator, device and geometry. [3]

2.5 Previous Computer Simulations

Cao et al. studied the thermal vibration of (5,5) Single Walled Carbon Nanotube by Molecular Dynamics (see detailed explanation in 3.1) using the consistent valence force field (CVFF) [23] potential. In this study the contributions of various vibration modes in radial, axial and lateral directions to the overall thermal dynamics of the SWCNT were studied. A simple continuum beam model was used to predict the vibration frequencies, and simulations based on the finite element method (FEM) were
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 claimed that with varying T, there is no new vibration mode or frequency activated; instead, only the overall vibration amplitude increases [24].

The current research began independently with the project of Yaniv Gershon who used Tali Mutat’s nanotube code to simulate the (7,7) 98.38Å Single Walled Carbon Nanotube (SWCNT) with radius of 4.75Å under external forces, when the edges of the nanotube were frozen and did not move (see Fig. 2.6). In this project Yaniv worked primarily on the visualization of the dynamics of SWCNT under an external force which follows from the gate voltage applied to the experimental system and its relaxation. The atomistic simulations were done using the REBO potential which was developed by Brenner et al. [13] and the equations of motion were solved using the Predictor Corrector algorithm.

Figure 2.6: Nanotube under external force in the direction opposite to the positive Z axis. The edges of the nanotube are frozen and do not move. The picture is generated by the visualization program AViz [15]
Chapter 3

Numerical Methods

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. To simulate this process classically, 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. 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.
The Newton’s equations for a simple atomic system may be written as

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

(3.1)

To solve this we need 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 (3.3) we focus on this function \( U(r^N) \), restricting ourselves to an atomic description for simplicity.

### 3.2 Molecular Dynamics: Program Steps

In this section a number of important features of MD simulations 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.

- 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.

- Computing and recording 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:

$$\langle v^2 \rangle = K_B T/m$$ \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 $t$, $T(t)$:

$$K_B T(t) \equiv \sum_{i=1}^{N} \frac{mv^2_{i}(t)}{N_f}.$$ \hspace{1cm} (3.3)

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

### 3.3 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 [13] based on potentials first introduced and parameterized by Abell [25] and Tersoff [26] 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 [13], 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 atomic sites $i$,

$$E_b = \frac{1}{2} \sum_i E_i,$$

(3.4)

where $E_i$ is written as

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

(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 many-body 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 [27]. In his original proposal, Abell suggested that the first approximation of $B_{ij}$ can be given as a function of the near
neighbors coordination number $Z$ in the form:

$$B_{ij} \propto Z^{-\delta},$$

(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 $\text{(CH}_3\text{)}_2\text{C} = \text{C(}\text{CH}_3\text{)}_2$ 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:

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

(3.7)

where

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

(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 non-conjugated 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.

### 3.4 Integrating the Equations of Motion

Newton’s equations of motion can be integrated after all forces between the particles have been computed. The algorithm that we decided to use is the Velocity Verlet algorithm. It looks like the Taylor expansion for the coordinates:

\[ r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 \]  

(3.9)

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

\[ v(t + \Delta t) = v(t) + \frac{f(t + \Delta t) + f(t)}{2m}\Delta t + \mathcal{O}(\Delta t^3). \]  

(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.

### 3.5 Thermostat Algorithm

A modification of the Newtonian MD scheme in order to generate a thermodynamical ensemble at constant temperature is called a thermostat algorithm [28]. 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 3.5.1). 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,

\[
T = \frac{2}{3NK_B} \mathcal{K}, \quad (3.11)
\]

where

\[
\mathcal{K} = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{r}_i^2. \quad (3.12)
\]

Since the instantaneous temperature is directly related to the atomic internal velocities (Eqs. 3.11 and 3.12), 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,

\[ \hat{\mathbf{r}}_i(t) = m_i^{-1} \mathbf{F}_i(t). \]  \hspace{1cm} (3.13)

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

\[ \hat{\mathbf{r}}_i(t) = m_i^{-1} \mathbf{F}_i(t) - \gamma_i(t) \hat{\mathbf{r}}_i(t) + m_i^{-1} \mathbf{R}_i(t), \]  \hspace{1cm} (3.14)

where \( \mathbf{R}_i \) 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. (3.14)

\[ \hat{\mathbf{r}}_i(t) = m_i^{-1} \mathbf{F}_i(t) - \gamma(t) \hat{\mathbf{r}}_i(t). \]  \hspace{1cm} (3.15)

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 \( \bar{T} \), in contact with a heat bath at a different temperature \( T_0 \). \( \bar{T} \) is 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 \( \bar{T} \) and \( T_0 \) may result from a natural fluctuation of \( \bar{T} \) 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 \( T_0 - \bar{T} \) 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

\[ \bar{T} = c_v^{-1} \dot{E}(t) = \zeta_T^{-1} [T_0 - \bar{T}(t)], \]  \hspace{1cm} (3.16)

with the definition of the temperature relaxation time:

\[ \zeta_T = \xi^{-1} V^{-1/3} c_v \kappa^{-1}, \]  \hspace{1cm} (3.17)
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.

### 3.5.1 Berendsen thermostat

The Berendsen thermostat is based on a first-order relaxation equation [29]. The idea behind this thermostat is to modify the Langevin equation of motion (Eq. (3.14)) in the sense of removing the local temperature coupling through stochastic collisions (random noise), while retaining the global coupling (principle of least local perturbation) [28]. This prescription is equivalent to assuming that Eq. (3.16) also applies to the instantaneous temperature $\tilde{T}$ i.e. that

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

where an appropriate value for $\tau_B$ would be the temperature relaxation time $\zeta_T$ mentioned in Eq. (3.17). Modifying Eq. (3.15) by scaling the atomic velocities after each iteration step, based on the stepwise integration of Newton’s second law (Eq. (3.1)) of the leap-frog integrator [30], this can be written

$$
\mathbf{r}_i \left( t + \frac{\Delta t}{2} \right) = \lambda(t; \Delta t) \mathbf{r}_i' \left( t + \frac{\Delta t}{2} \right) = \lambda(t; \Delta t) \left[ \mathbf{r}_i \left( t - \frac{\Delta t}{2} \right) + m_i^{-1} \mathbf{F}_i(t) \Delta t \right],
$$

where $\lambda(t; \Delta t)$ is a time- and timestep-dependent velocity scaling factor. Imposing the constraint $\lambda(t; 0) = 1$, recovers Eq. (3.15) in the limit of an infinitesimal timestep $\Delta t$, with

$$
\gamma(t) = - \lim_{\Delta t \to 0} \frac{\lambda(t; \Delta t) - 1}{\Delta t} = - \frac{\partial \lambda(t; \Delta t)}{\partial \Delta t} \bigg|_{\Delta t = 0}.
$$
The quantity \( \lambda(t; \Delta t) \) in Eq. (3.19) is found by imposing

\[
\mathcal{T} \left( t + \frac{\Delta t}{2} \right) = \mathcal{T} \left( t - \frac{\Delta t}{2} \right) + \tau_B^{-1} \Delta t \frac{g}{3N_{df}} \left[ T_0 - \mathcal{T} \left( t - \frac{\Delta t}{2} \right) \right],
\]  

(3.21)

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. (3.11) and (3.12), this leads to the condition

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

(3.22)

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

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

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

(3.23)

Thus, Eq. (3.20) gives

\[
\gamma(t) = \frac{1}{2} \tau_B^{-1} \left[ \frac{g}{N_{df}} \frac{T_0}{\mathcal{T}(t)} - 1 \right].
\]  

(3.24)

Inserting into Eq. (3.15) gives the equation of motion corresponding to the Berendsen thermostat,

\[
\ddot{\mathbf{r}}_i(t) = m_i^{-1} \mathbf{F}_i(t) - \frac{1}{2} \tau_B^{-1} \left[ \frac{g}{N_{df}} \frac{T_0}{\mathcal{T}(t)} - 1 \right] \dot{\mathbf{r}}_i(t).
\]  

(3.25)

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.
3.6 Continuum Model

The vibrational frequencies of our nanotube can also be modeled via continuum analysis. As a complementary approach to MD, the SWCNTs may be conveniently modeled as continuous cylindrical shells with fixed wall thickness, \( t \), and a fixed Young’s modulus, \( E \). Since the length/width aspect ratio is very large, the SWCNT may be regarded as a beam with the same section and elastic property. Analytical results for the modes and natural frequencies of vibration of such a beam are readily available. Let us consider a beam, oriented in the \( y \) direction (as shown in Fig. 3.1) and denote its deformation in the \( n \)th mode as \( z_n(y) \). The length prior to deformation is \( L \), its cross section area is \( A=2\pi rt \) (where \( r \) is the undeformed radius), \( \rho \) is the density and \( I=\pi rt(4r^2 + t^2)/4 \) the moment of inertia. The equation describing transverse, or flexural motion of such a continuous, homogeneous, isotropic, linear elastic beam whose properties do not vary along its length may be expressed as:

\[
EI \frac{\partial^4 z(y,t)}{\partial z^4} + \rho A \frac{\partial^2 z(y,t)}{\partial t^2} = 0 \quad (3.26)
\]
The profiles of the several lowest lateral vibration modes for a doubly clamped beam are:

\[
z_n(y) = D_n [(\sin(k_n L) - \sinh(k_n L)) (\cos(k_n y) - \cosh(k_n y)) - \\
(\cos(k_n L) - \cosh(k_n L)) (\sin(k_n y) - \sinh(k_n y))],
\]

(3.27)

where \(D_n\) is the vibration amplitude of the \(n\)th mode \((n=1,2,3,...)\) and \(k_n\) is the \(n\)th eigenvalue. For the first four modes trigonometry gives \(k_1 L = 4.730\), \(k_2 L = 7.853\), \(k_3 L = 10.996\) and \(k_4 L = 14.14\). The characteristic frequencies of the modes of the lateral vibration are:

\[
f_n = (EI/\rho A)^{1/2}(k_n L)^2/(2\pi L^2).
\]

(3.28)

### 3.7 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:

$$X(f) = \int_{-\infty}^{\infty} x(t)e^{-i2\pi ft} dt \quad (3.29)$$

The inverse transform is:

$$x(t) = \int_{-\infty}^{\infty} X(f)e^{i2\pi ft} df \quad (3.30)$$

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:

$$X(mF) = \sum_{n} x(nT)e^{-inm2\pi FT} \quad (3.31)$$

and the inverse discrete transform is:

$$x(nT) = \frac{1}{N} \sum_{m} X(mF)e^{inm2\pi FT} \quad (3.32)$$

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.

### 3.8 AViz

Our computational physics group developed the Atomistic Visualization package AViz [15]. 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 colors check the boundary conditions.

3.9 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 [31]. 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 useful and complicated tool we designed a parallel code using Message Passing Interface (MPI). A detailed explanation of the programme can be found at [33].
Chapter 4

Goal of the research

The primary goal of the proposed research is to take advantage of recent technological breakthroughs in the fields of nanomechanics and nano- and molecular-electronics and to study nano-electro-mechanical resonators based on Carbon Nanotubes (NTs) [3]. We plan to develop a theoretical understanding of dissipation processes and nonlinear dynamics in these resonators which will help the experimentalists to utilize them as ultra-sensitive mass and force sensors.

One of the most important parameters characterizing a resonator is its quality factor, $Q$ (the ratio of the energy stored in the resonator to the energy lost per cycle due to damping). Maximizing $Q$ is important for many applications. For instance the mass sensitivity. If measurement noise is dominated by thermomechanical fluctuations, the mass sensitivity is given by

$$
\delta M \sim 2M \left( \frac{k_B T}{E_0} \right)^{1/2} \left( \frac{\pi \tau}{2Q \omega_0} \right)^{1/2},
$$

(4.1)

where $k_B T$ is the thermal energy, $E_0$ is the energy stored in the resonator, $\tau$ the measurement averaging time, $\omega_0$ is the frequency of vibration and $Q$ is the quality factor. From Eq. 4.1 we can conclude that the sensitivity of a mass-resonator depends
on the effective mass, temperature and frequency of vibration. In other words it
depends also on the mode of vibration and quality factor (Q).

In the NEMS community, $Q$s in the range of 10,000 - 100,000 are typical, however
as the devices are miniaturized, their respective $Q$s decrease. This linear scaling of
the $Q$s with the surface-to-volume ratio has been attributed to losses associated with
dissipation at surfaces, giving promise for high quality factors from well-terminated
structures such as carbon nanotubes. Previous measurements on larger MWNTs and
ropes of SWNTs yielded $Q$s in the range between 150 to 2,500 at room temperature.
Therefore the aim of our project is to study the nature of such results, and to study
the mechanisms of energy loss in the SWCNT resonators. Specifically, we intend
to study the dependence of the resonator quality factor on the frequency and mode
shape, and to design NEMS based on carbon nanotubes for optimal operation.

Currently, conventional NEMS have the advantage of higher quality factors, higher
demonstrated resonance frequencies (1GHz), better frequency stability, and easier on-
chip integration. NTs possess extremely-small masses and therefore hold the potential
of becoming the ultimate mass sensors once their remaining properties have been
optimized.
Chapter 5

Preliminary Results

We have begun atomistic simulations to generate data for the SWCNT oscillators to find and tune the frequencies of different vibrational modes. We started with a small model of a 98.38Å armchair nanotube with a diameter of 9.4Å and a chiral vector of (7,7) clamped at both ends.

Our first numerical experiments are monitoring thermal vibrations of such a NT at 300K. We let the nanotube vibrate during 626 psec with a time step of 0.5 fsec. The center of mass (red dots in Figure 5.2) for each period of the nanotube (28 atoms in each period, see Fig. 5.1) was calculated. We call this line of points the Centered Axis (CA). We analyzed the vibrations of the CA near the center of mass of the nanotube with clamped ends (3 periods at each end do not move). The tube axis is in the Y direction, X and Z are perpendicular (see Figure 5.2). This nanotube has 40 periods and the center of mass (CM) of the entire tube is near Y = 20 (20th period).

In order to see the first 4 frequencies (including $n = 2$ and $n = 4$) we monitored the amplitude near the CM of the nanotube as a function of the time of the vibration
5.1 Code Modifications

In these simulations the original code of Brenner was used, where the code is written in Fortran77. The subroutine which generates the xyz files was added by Tali Mutat, and 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 was tested. A test of dependency of the results on the initial conditions was carried out, choosing 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 that generates the sequence of the xyz files was debugged and extended to get the sequence of the xyz files of the CA. The subroutine which was produced by Yaniv Gershon 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. Careful analysis of the Fourier Transform and the sampling frequency was done, and a Matlab code that transforms the time domain to the frequency domain was written.
5.2 Vibrational Analysis

First, we wanted to test the reliability of the method of Fourier Transform in the mode's frequency decomposition. We let the nanotube vibrate 10 times longer than the period \( T \) of the lowest mode \( (n = 1) \). The vibration of the CM of the nanotube in Z direction is presented in the upper image of Fig. 5.3. It can be seen from Fig. 5.3 (lower image) that the frequencies of the first modes can be distinguished with good resolution. It is important to note that due to the symmetry of the armchair nanotube \((7,7)\) that we decided to use, we get the same frequencies for the vibration of the nanotube in the X direction, (see Fig. 5.4). It can be seen from Fig. 5.3 that the amplitude of the first mode \( (n = 1) \) has a high value, however the amplitude of the second mode \( (n = 2) \) is lower than that of the third mode \( (n = 3) \). This is obvious because, since the center of mass of the 20th period of the nanotube is near the Center of Mass of the Nanotube (the distance being about 1.42Å from the CM), and the CM does not move in the second and fourth modes, its amplitude is low. See Fig. 5.5 for a cartoon of the modes of vibration.

In order to further check our results we followed the vibration of the nanotube at another point on the Centered Axis of the nanotube. The frequency domain of the vibrations of the 7th period of the nanotube \((Y = 7)\) is presented in Figure 5.6. The frequencies presented in the picture are the same as for the vibration of the 20th point on the Centered Axis (see Fig. 5.3). There is a difference in the amplitude, since this point is moving substantially also in the \( 2^{nd} \) and \( 4^{th} \) modes. The amplitudes in these modes should be higher than those of the 20th period and the amplitude of the \( 1^{st} \) mode should be lower than that of the 20th period, as it is clearly seen in Fig. 5.6.
Figure 5.3: Analysis of the thermal vibrations of the CM in the Z direction at 300K: upper image - time domain; lower image - frequency domain (FFT of the upper image). For \( n=1 \), \( f=0.269 \) THz; \( n=2 \), \( f=0.659 \) THz; \( n=3 \), \( f=1.130 \) THz, and for \( n=4 \), \( f=1.660 \) THz.
Figure 5.4: Analysis of the thermal vibrations of the CM in the X direction at 300K: upper image - time domain; lower image - frequency domain (FFT of the upper image). For $n=1$, $f=0.269$ THz; $n=2$, $f=0.659$ THz; $n=3$, $f=1.130$ THz, and for $n=4$, $f=1.660$ THz.
CHAPTER 5. PRELIMINARY RESULTS

Figure 5.5: Vibration and standing waves: the fundamental and the first 4 overtones \((n=1,\ldots,4)\).

Figure 5.6: Frequency domain of the thermal vibrations of the center of mass of the 7th period of the (7,7) SWCNT in the Z direction at 300K. For \(n=1\), \(f=0.269\) THz; \(n=2\), \(f=0.659\) THz; \(n=3\), \(f=1.130\) THz; and for \(n=4\), \(f=1.660\) THz.
5.3 Comparison with Continuum Model

We compared our results to the frequencies which were calculated analytically from the continuum model (see section 3.6) as presented in table 5.1. Since we treat a 98.38Å nanotube, which is clamped in both ends (3 periods at each end), the length of the vibrating part of the nanotube is 98.38Å minus the length of the 6 periods which do not move and is equal to 83.62Å. In our calculations of the analytical model for a vibrating beam we checked 3 different versions:

- The cross section of the nanotube is assumed to be a cross section of a hollow cylinder with a wall thickness of 0.34 nm (like the thickness of the sheet of graphene). We calculated the frequencies of vibration for a nanotube of density $\rho_1 = 1.300 \text{g/cm}^3$ (as reported in the literature [17]) and $\rho_2 = 9.517 \text{g/cm}^3$ assuming that the mass of the SWCNT is distributed uniformly along the beam.

- The cross section of the nanotube is assumed to be a cross section of a hollow cylinder with a wall thickness of 0.08 nm [24]. The frequencies are calculated for the same densities as in the previous case.

- The cross section of the nanotube is assumed to be a circular cross section with no wall thickness. The frequencies are calculated for the same densities as in the previous cases.

All results are tabulated but in the discussion we consider only the first continuum model with the density $\rho_1 (1.300 \text{g/cm}^3)$, since that model takes into account the most physical parameters. In this case the frequency values for all modes are in a good agreement with the simulated frequencies. The error of the simulated frequencies vs. the analytically calculated ones increases with $n$ (see Table 5.1). We still need
to investigate this effect in more detail. However, it is important to note, that in the analytical model the constant value of the Young’s modulus of 1 TPa was taken for all the modes, and this may not be correct for the simulations. There may be a nanosize effect that may be important when the ratio of the wave length to diameter becomes smaller, and the tube is locally compressed. This local compression is seen in animated visualizations of the nanotube.

5.4 Parallelization of the Code

In this project we have to transfer digital discrete signals from the time domain into the frequency domain. For this purpose we need to write out a constant number of output xyz files in a strongly defined time interval (which may be different from the molecular dynamics time step). This gives a huge amount of output data which needs to be arranged and stored in proper order for future processing. This need brought us to a parallelization of the initial code by using the Message Passing Interface (MPI). Such a procedure greatly simplifies the amount of book keeping needed, because files
from multiple nanotube parameter sets can be manipulated at once. The new pro-
gram is also designed to calculate dynamic behavior of carbon nanotubes for different
physical parameters simultaneously i.e. different temperatures. More details can be
found in [33].
Chapter 6

Research Plan

Our next step will be a test of different boundary conditions. For example, it is interesting to follow the frequency changes if, instead of the nanotube being clamped at both ends (3 periods in each end), only the atoms which are supposed to be connected to the surface will be frozen as is shown in Fig.6.1. In later stages in order to study the external energy loss mechanisms we will connect the nanotube to a silicon surface at its edge (see Fig. 2.5 or Fig. 6.2) by non-covalent bonds (perhaps the Van der Waals forces, we still need to investigate this in more details) and monitor the changes in energy, frequencies and the quality factor of the system. In this part of the research electronic effects between the nanotube and the surface play an important

Figure 6.1: Suspended Single Walled Carbon Nanotube, freezing only the white atoms, an optional boundary conditions. The image is generated by AViz [15].
role and need to be studied using ab initio models, where my previous experience with the electronic structure calculations could be very useful for this purpose.

Some other planned numerical experiments include studying the influence of the boundary conditions on Q by following changes in the angle between the nanotube and the silicon surface as is shown in Fig. 6.2.

In order to study mechanisms of dissipation in the system and processes which influence the quality factor we will carefully test different thermostats working in the canonical ensemble, where constant temperature conditions will be imposed (i.e., the number of molecules, the volume and the temperature will be kept constant).

In the experimental work the nanotube was suspended between two electrodes. A gate voltage was applied which caused an electrical force downward on the nanotube. Since the nanotube has an extremely high Young’s modulus $\sim 1$ TPa, as a result of the applied force it was deformed and the frequencies of the vibrational modes changed. One of the most important questions is how the frequencies were changed and what is the effect of such a change on the quality factor? In order to answer these questions we will study a tensioned nanotube by exposing the nanotube to external forces in the Z and Y directions as shown in Fig. 6.3 before analyzing the vibrational

Figure 6.2: Suspended SWCNT with different possible angles between the nanotube and the surface (yellow area).
properties of the SWCNT.

Once all these directions are explored we plan to simulate one of the potential applications of the Single Walled Carbon Nanotube NEMS by adsorbing a small molecule onto the nanotube exterior and by monitoring the resultant frequency shift to calculate the mass of the attached molecule.
References


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