A Study of Bending Deformations in Carbon Nanotubes
Using the Objective Molecular Dynamics Method

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Abstract

Bending of carbon nanotubes is a topic which has applications in several areas of nanotechnology, including nanotoxicology and NEMS. Atomistic simulations are necessary to understand in detail the fundamentals and the phenomena observed in experiments. Objective molecular dynamics allows the imposition of angular boundary conditions on atomistic systems. Coupled with the Tersoff potential, objective MD is used to systematically investigate reversible elastic bending in carbon nanotubes up to 4.2 nm in diameter. A contrasting behavior is revealed. Single-wall tubes buckle in a gradual way, with a clear intermediate regime before they fully buckle and significant hysteresis between bending and unbending cycles, in agreement with previous studies. Multi-walled tubes with closed cores, not commonly studied using direct atomistic methods, exhibit a hysteresis-free, rate- and size-independent direct transition to an unusual wavelike mode with a 1 nm characteristic length. This rippling mode has a nearly-linear bending response and causes a $\sim 35\%$ reduction in the stiffness of the thickest multi-walled tubes.
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Chapter 1

Introduction

The present thesis, on the subject of atomistically simulating bending in carbon nanotubes (CNTs) using objective molecular dynamics (MD), is divided into four main chapters and a conclusion. A summary of common terms used can be found in appendix A. All original figures containing atomic configurations were created using VMD[1].

• Chapter 2 first briefly describes the structure of CNTs and provides an overview of their properties. It then provides motivation for studying CNT bending using atomistic methods. First, an overview of the methods and results of several experimental studies on CNTs is given, along with an explanation of how a computational atomistic treatment can benefit the understanding of those studies. Next, the chapter describes two applications in which CNT bending is important – NEMS and respiratory nanotoxicology.

• Chapter 3 reviews current and past progress in studying CNT bending. First, the two main methods used to study CNTs in microscopic detail – atomistic studies and FEM – are described. Then, the current results of these studies are presented, categorized by whether they concern single-wall or multi-wall CNTs. The studies are compared and contrasted and systematic similarities are highlighted.

• Chapter 4 presents some of the theory behind the present study. Molecular dynamics (MD) in general is described, followed by a summary of traditional periodic molecular dynamics. It is then shown how periodic MD relates to objective MD, the method used here. The Tersoff interatomic potential is examined in detail,
specifically the reasoning behind the form of the potential. The energetics of bending a graphene sheet are examined due to their importance in relation to CNTs in general, and specifically buckling or rippling under bending. They are examined in terms of how they are treated with the Tersoff potential, as well as in terms of molecular orbitals, and the two cases are compared. The advantages and drawbacks of the Tersoff potential compared to other empirical interatomic potentials is examined.

• Chapter 5 describes the specific simulation protocol used, presents the results of the study, and provides discussion. The dependence of the critical curvature at which non-ideal behavior arises on the dimensions of the CNT is described. SWCNT results are compared with previous studies for confirmation of the validity of the current method. The distinct rippling mode in MWCNTs is analyzed, and interpreted as a phase transition. A convergent behavior appears in the reduction of the bending stiffness of MWCNTs by rippling.

• Chapter 6 summarizes the thesis and presents a possibility for future work. The importance of CNT bending to nanotoxicology, NEMS and understanding experiments is reviewed. The strengths, limitations, and results of current studies are summarized. A brief explanation of the advantages of the objective MD method and the reason for the choice of the Tersoff potential follow. The results of the simulations are then described in short. Finally, it is demonstrated how the data obtained in the present study may be used to develop a highly-efficient distinct-element method (DEM) treatment of MWCNTs.

Chapter 2

Carbon Nanotubes and Importance of CNT Bending

2.1 Introduction

Carbon nanotubes (CNTs) are remarkable nanostructures. The composition of a single-wall CNT (SWCNT) is usually described as a ribbon of graphene (a one-atom-thick layer of a graphite crystal) “rolled up” into a closed cylindrical tube (Fig. 2.1). CNTs also occur in the multi-walled variety (MWCNT), which is a set of concentric SWCNTs (Fig. 2.2). As in graphite, the individual layers interact with van der Waals (vdW) forces. Ever since their discovery [3], these fascinating quasi-one-dimensional structures have been a subject of intense interest. The investigations have uncovered extremely high mechanical strength and resilience (as the in-plane mechanical properties of graphene), electrical conductance that is tunable by mechanical deformations, and many other useful and interesting properties – mechanical and beyond.

2.2 Crystal Structure

The infinite crystal structure of a single SWCNT is defined by the chirality \((n, m)\). The values of \(n\) and \(m\) represent multipliers of the lattice vectors of plane graphene, \(\mathbf{a}\) and \(\mathbf{b}\). When a SWCNT crystal structure is constructed from a plane graphene crystal structure, the chiral vector \(C_h = n\mathbf{a} + m\mathbf{b}\) becomes the circumference of the
Figure 2.1: “Construction” of an SWCNT from a sheet of flat graphene. Naturally, physically rolling up a graphene layer and having it bind to itself is not possible – in practice CNTs are synthesized by a plethora of self-assembly methods, which are outside the scope of this work.

![Graphene Sheet to SWCNT](image)

Figure 2.2: Example MWCNT structure.

CNT (fig. 2.3): The angle $\chi$ this vector makes with the (1,0) direction is termed the chiral angle. Important to note is that while the $(n,0)$ – termed zigzag – and $(n,n)$ – termed armchair – CNTs have minimum translational lattice vectors which are always approximately 0.25 Å in length, chiral CNTs’ translational vectors are proportional to the radius of the CNT and inversely proportional to the greatest common factor of $2n + m$ and $2m + n$, and may therefore be very large[4].

2.3 Mechanical Characterization of CNTs

Naturally, bending is an important mode of mechanical deformation, and many experimental studies focus on the bending behavior of SWCNTs and MWCNTs. Different experimental methods have been used to study behavior of CNTs under bending. Iijima
and colleagues observed single-walled and thin-wall multiwalled CNTs bent during handling in a high resolution electron microscope (HREM) [5]. Falvo and colleagues bent MWCNTs to large angles directly using an atomic force microscope (AFM) tip and subsequently imaged them [6]. Noteworthy is the apparent reversibility of this bending, with no fracture occurring after repeated application of large bending strains – the bending is completely elastic. Both of these studies observed nonlinear buckling behavior in the CNTs (Fig. 2.4). Nanomechanical simulations are needed to understand in atomic detail the phenomena observed in experimental studies of bending behavior.

Figure 2.4: High-resolution TEM image of bent SWCNT as reported by Iijima et al. [5], showing characteristic kinking morphology. Reprinted with permission.
Elongation is another basic mode of deformation, and the Young’s modulus governing it is a fundamental constant needed to characterize the mechanical behavior of a material. However, the small size of CNTs makes it very difficult to directly apply axial strain. In the linear regime, the bending modulus of a beam \( YI \), where \( I \) is the cross-sectional moment of inertia, may be used to calculate the Young’s modulus \( Y \). Because of this, many experimental studies use bending behavior of CNTs to predict their Young’s modulus. \( I \) is usually taken as that of a hollow cylinder with wall thickness equal to equilibrium wall spacing, 3.4Å. It should be noted that, because SWCNTs are cylindrical shells of single-atom thickness, the definition of cross-sectional area, and therefore Young’s modulus, is somewhat arbitrary and lacks physical meaning. For comparison, the in-plane modulus of graphite is 1.06 TPa[7].

The first studies aiming to find the Young’s modulus from CNT bending behavior used transmission electron microscope (TEM) images of cantilevered CNTs undergoing thermally excited bending oscillations. The amplitude of the oscillations at a given temperature was used to calculate the Young’s modulus. Treacy and colleagues applied this technique to an array of tubes, with a resulting \( Y \) of 1.8±0.9 TPa[8]. The temperatures used ranged from room temperature to 1000 K – well within the solid phase of carbon. Following the method of Treacy et al., Krishnan and colleagues studied a number of SWCNTs and found their \( Y \) to be 1.25-0.35/+0.45 TPa[9]. The temperature was close to room temperature. When studying SWCNTs, longer tubes were found to kink under large bending deformations. These tubes could not be used for Young’s modulus determination. Poncharal and colleagues deflected thick MWCNTs electrostatically and used the magnitude of the deflection to deduce the Young’s modulus[10]. They found that as tubes got thicker, a dramatic drop in the measured value of \( Y \) occurred – from 1 TPa to 100 GPa. This drop was attributed to the emergence of a non-linear bending mode, which was confirmed by HREM images (Fig. 2.5). Note that this periodic wavelike rippling mode is distinct from the localized kinking observed in SWCNTs and thin-walled MWCNTs. Wong and colleagues also observed two distinct buckling modes when bending cantilevered MWCNTs with an AFM tip[11]. As a single MWCNT was bent, the force on the AFM tip (essentially the derivative of the strain energy) displayed a linear behavior with \( Y=1.28\pm0.59 \) TPa, followed by a sudden reduction in slope (Fig. 2.6). Micrographs suggested that the reduction in slope corresponds to the emergence of
a rippling mode. These deformations also showed no irreversible behavior. Bower and colleagues imaged bent and fractured CNTs found in a polymer-CNT matrix\cite{12}. Highly bent CNTs fractured, and thin CNTs formed localized buckles. However, moderately bent thick MWCNTs showed the same rippling behavior. By straightening some of the tubes by heating the polymer around them, it was once again shown that the rippling deformation is reversible. The wavelength of the rippling was also studied, and was found to depend on the product of the tube’s radius and its thickness. As before, it is clear that CNTs exhibit nonlinear behavior under bending, so learning the threshold at which CNT bending becomes nonlinear is important for understanding studies aiming to find the Young’s modulus of CNTs.

Figure 2.5: High-resolution TEM image of bent thick-walled MWCNT as reported by Poncharal et al.\cite{10}, showing characteristic periodic rippling pattern. Reprinted with permission.

2.4 Importance of CNTs for NEMS

CNTs have also been shown to change their electronic properties when subjected to mechanical deformations. An experimental study showed that severe local bending deformations applied to a metallic SWCNT significantly and reversibly lowered its conductance\cite{13}. Tight-binding atomic simulations verified this behavior. CNTs also show interesting electronic behavior when subjected to torsion. When the ideal cylindrical shape is preserved under torsion, CNTs exhibit a modulation of the band gap that is periodic with twist angle. A tight-binding study of has been done which considers the energetically favorable, non-ideal rippling modes of CNTs under torsion\cite{14}. It was
found that while MWCNTs follow the ideal behavior closely, SWCNTs deviate from this behavior and are less sensitive to torsional deformations. These remarkable electromechanical behaviors make CNTs an attractive component for nanoelectromechanical systems (NEMS). In fact, CNT-pedal devices – torsional pendulums with CNTs acting as springs – have been demonstrated. These have been either purely mechanical devices [15, 16, 17], or electro-mechanical devices where the resistance of the CNT was shown to vary with twist angle [18, 19, 20]. If CNTs are to be used in NEMS, it is necessary to characterize their mechanical response to fundamental deformations such as bending to facilitate device design.

2.5 CNT Toxicity Concerns

As a new material that is expected to find its way into many industrial and consumer products, the health risks of CNTs must be examined. In particular, CNTs are fibers
with a high aspect ratio that may be biopersistent. While CNTs are more reactive than a flat graphene layer due to curvature effects, they are still a fairly unreactive material, suggesting that they may persist for a long time in an environment such as the human lung. The shape properties of CNTs suggest that they may behave similarly to asbestos, which poses a serious health risk. Biopersistence raises an additional concern, as asbestos is especially toxic when it is a biopersistent type[21].

When typical nanoparticles are inhaled into the lung, they are engulfed by macrophages in a process termed phagocytosis and brought up the respiratory tract to be disposed of. This is mechanism effectively rids the lungs of most particles, rendering them relatively harmless. Particles that are too large to be phagocytized are generally too big to be deposited in the lung. However, this is not true for fibrous particles. If they are aligned properly, their small cross-section means that, despite their length, they may travel through the bronchial pathways. If they are long enough, phagocytes will not be able to engulf them completely, resulting in frustrated phagocytosis. Through various mechanisms such as granuloma formation (a body’s natural defense in case of frustrated phagocytosis) and trauma caused by loose fiber ends, an environment is created which favors the development of mesothelioma, cancer of the mesothelial lining, linked to asbestos exposure.

Some studies have confirmed that CNTs do, in fact, pose a health risk similar to asbestos. One study found that MWCNTs injected into the abdominal cavity of mice cause frustrated phagocytosis and granuloma formation[22]. Because the investigators found that long MWCNTs are more pathogenic than short ones, this study is strong

Figure 2.7: Micrographs showing frustrated phagocytosis of an asbestos fiber (left) and MWCNT (right), as reported by Poland et al. [22]. Reprinted with permission.
evidence that the pathogenicity is caused by the fibrous nature of MWCNTs. Fig. 2.7 illustrates the striking resemblance between the mesothelium’s biological responses to asbestos fibers and MWCNTs. Another, longer, study actually observed high mortality in mice treated in a similar way, caused by mesothelioma[23]. While the full evolution of mesothelioma is a complex biochemical process, the first step – frustrated phagocytosis – is largely a mechanical phenomenon, intrinsically related to the mechanical properties of CNTs. For example, it is likely that CNTs with lower stiffness are more likely to fold over and form clumps as opposed to long fibers, reducing their health risk.
Chapter 3

State of the Art Modeling of CNTs

3.1 Introduction

With so many questions of importance pertaining to CNT bending standing to benefit from the understanding provided by computational studies, it is no surprise that many have already been carried out. As with many other computational problems, there is a spectrum of studies, ranging from *ab initio* quantum mechanical atomistic studies, to continuum models treated using finite element method (FEM) and even beyond, to a highly simplified but reasonably effective beam model. Central to this variety of studies is the trade-off between detail and computational efficiency.\[2\]

3.2 Atomistic Studies

The most computationally expensive studies are *ab initio* studies, which explicitly solve Schrödinger’s equation without making recourse to any previously evaluated, empirical quantities. Invoking the tight-binding (TB) approximation significantly reduces the computational expense, while still accounting for the electronic nature of binding in solids. Finally, atomistic studies which employ classical analytical potentials are the least computationally expensive. These potentials, such as the Tersoff potential used here \[91\], aim to simulate interatomic binding in solids by fitting a relatively simple
Figure 3.1: SWCNT bending simulation results as reported by Yakobson et al.\cite{24}. This type of buckling configuration and energetic behavior is ubiquitous in SWCNT bending simulations. Reprinted with permission.

analytical formula to the material properties, which is then used to calculate the forces on each atom based on the positions of its surrounding atoms. In atomistic studies, the inter-wall vdW interactions in MWCNTs are typically modeled using a standard Lennard-Jones potential. Atomistic studies have been extensively used to study the properties of CNTs, ranging from their elastic constants to complex fracture mechanisms\cite{32,33}.

Even though many advancements have been made, traditional atomistic simulations are still very prohibitive in the size of the system, and it is still prohibitive to simulate large-diameter MWCNTs of realistic lengths. This is especially true when one considers angular deformations such as bending. This is because atomistic simulations of elasticity of solids generally use periodic boundary conditions to achieve extreme reductions in the number of atoms that needs to be simulated, making explicit recourse to the translational symmetry of the crystal lattice. However, angular deformations destroy this symmetry, meaning a large simulation cell must be employed to study them – an entire bent section of a CNT. There is also the issue of how to apply bending – most investigators do this by keeping the end atoms of the CNT frozen during the simulation,
and rotating the ends to impose bending. This has the possibility of creating axial and shear strain in the CNT, and care must be taken to avoid it.

### 3.3 Continuum Studies

Because of these difficulties, many investigators use a continuum shell description of CNTs. SWCNTs and individual walls of MWCNTs are represented as elastic shells with properties fitted to that of graphene. MWCNT inter-wall interactions are treated with a continuum version of the Lennard-Jones potential, averaged over the shell surface. This model is then treated with FEM. Thus, the discrete atomistic model is converted to a continuum model, which is then again discretized into finite elements, with many less degrees of freedom than the original atomistic model. This method allows for realistically long sections of even very thick MWCNTs to be simulated. Note that, while care must still be taken to ensure that there are no spurious end effects during bending, the larger simulation cells mean that the ends are typically farther from the area of interest. This reduces the influence of imperfect boundary conditions, if they are present. Even further simplifications have been proposed, using two- or even one-dimensional models to simulate CNTs.
A new frontier that has emerged is the hybridization of atomistic and continuum studies. One type of such study is *concurrent*, that is, both methods are used in parallel to describe the system. The area where atomic detail is required is simulated atomistically, while some distance away from the area of interest, the atomistic treatment is coupled with an FEM mesh. This approach has already been successfully applied to several problems. When applied to CNT bending, a concurrent hybrid approach generally involves simulating the relatively straight end sections using FEM, and the highly deformed center section atomistically, alleviating some of the end effect issues.

Figure 3.3: SWCNT cross-section collapse under bending as reported by Kutana et al.\textsuperscript{[25]} Reprinted with permission.
present in normal atomistic simulations. Other studies are hierarchical, where a continuum method is used to treat the entire system and predict a configuration which is subsequently treated with a more accurate atomistic method.

3.4 Current Results of Bending Studies

3.4.1 SWCNTs

Despite the problems mentioned, SWCNTs under bending have been successfully simulated in atomistic studies numerous times. These studies show a remarkable qualitative
agreement between each other, FEM simulations, and experiments. Iijima and colleagues, one of the groups mentioned previously, performed atomistic simulations using the Tersoff-Brenner potential in order to compare the results to their experimental observations. They found that the SWCNT bends smoothly up to a certain angle, at which point it buckles and develops a deep kink. This is in agreement with the experimental observations of kinked SWCNTs. The strain energy of the nanotube is has a nearly quadratic dependence on bending angle, as an elastic beam, before the kink occurs. At the kink, there is a drop in energy, followed by a near-linear dependence of the strain energy on the angle. They also investigated the dependence of the critical curvature $\kappa_c$, the curvature at which the buckling occurs, on the radius, chirality, and length of the SWCNT. They found no length dependence, a strong $\propto 1/R^2$ dependence and a weak term containing radius and chirality.

A study by Yakobson and colleagues using the same potential found the same kinked configuration and the same energetic behavior (Fig. 3.1). This group also considered
the dependence of $\kappa_c$ on nanotube radius. The authors proposed a $\propto 1/R^2$ dependence based on the theory of buckling of shells. Further, they derived the coefficient using known material constants for the graphitic layer making up a SWCNT, arriving at a very close agreement with their simulation data. They did not study length dependence, and explicitly excluded chirality dependence from their analytical model, modeling the SWCNT as an isotropic elastic shell. In agreement with observations, bond breaking was not observed until very high bending angles by Iijima et al., and not at all by Yakobson et al. showing that nanotube buckling is a reversible, elastic behavior. None of the subsequent studies discussed discuss bond breaking, and, naturally, any continuum model explicitly excludes the possibility of bond breaking.

Another study focused on the energetic and morphological details of the cross-section collapse during kinking\textsuperscript{[25]}. This study uses the second-generation reactive empirical bond order (REBO) potential by Brenner, with a Lennard-Jones potential to model interactions between opposite sides of the kinked cross-section. They found a similar quadratic-to-linear transition of the strain energy as the other studies mentioned. However, for larger nanotubes, a second discontinuity arose in the energy-angle curve (Fig. 3.2). The first discontinuity corresponded to the beginning of cross-section collapse, while the second corresponds to its completion, when the two sides are at the VDW
Figure 3.7: Comparison of SWCNT bending energies of hybrid FEM/atomistic method with full atomistic results, as reported by Sun et al.\cite{27} Reprinted with permission.

equilibrium distance (Fig. 3.3). It was also found that larger tubes exhibit significant hysteresis in the energy curve between bending and unbending, and that the region of hysteresis corresponded to the angle range over which the gradual cross-section collapse was occurring (Fig. 3.4).

The agreement between atomistic simulations and elastic shell theory strongly suggests the possibility of simulating an SWCNT as an elastic shell discretized using FEM. Cao and Chen investigated this possibility by simulating various SWCNTs using both *ab initio* atomistic methods and FEM\cite{26} (Fig. 3.5). They found that both FEM and *ab initio* simulations suggest the same $\kappa_c \propto 1/R^2$ dependence as Yakobson et al., albeit with a lower coefficient for FEM and even lower for their atomistic simulation (Fig. 3.6). The dependence of $k_c$ on the simulated tube aspect ratio was also studied, with definite length-dependent behavior arising for certain lengths and tube diameters in disagreement with Iijima et al. Cao and Chen also found that chirality had no effect on $k_c$, once again contrary to the findings of Iijima and colleagues. It should be noted that, in this study, very long nanotubes were found to have several kinks in them when bent,
both atomistically and using FEM. However, it is known that highly deformed CNTs have many metastable states that are different in morphology, but are very close in energy. Because of this, as well as the possible spurious end effects induced by fixed end bending, it is unclear whether the multi-kink configurations are the absolute minimum energy states.

Because both FEM and atomistic studies have proven to be valid approaches to studying the bending of CNTs, several concurrent hybrid studies between the two methods have emerged. A study by Sun and Liew used an atomistic center section treated by the Brenner potential, while treating the ends with FEM. The ends overlap with the center, and when searching for the minimum energy configuration, the energy in the overlap regions is taken to be the average of the FEM and atomistic energies. When subjected to bending, this model provides results that are very consistent with the full atomistic treatment, both morphologically and energetically (Figs. 3.7 and 3.8). Im and colleagues carried out a similar study, focusing heavily on the details of the FEM implementation. Their results showed similar behavior and agreement to full atomistic studies.
3.4.2 MWCNTs

In contrast to SWCNTs, atomistic simulations of MWCNTs under bending are scarce due to the increased computational expense. Iijima et al. also conducted simulations of open-core, two-wall tubes for comparison with their observations of thin-walled MWCNTs[5]. They found that at small angles, these tubes buckle in a manner similar to SWCNTs, but at higher angles, develop a two-kink morphology reminiscent of their observations. However, once again, this may simply be a metastable state of the CNT.

Simulations of thick MWNCTs are almost completely the realm of FEM simulations. Pantano and colleagues performed bending simulations of sections of MWCNTs of various diameters[28]. The simulations were performed by keeping the ends of the CNT on
planes and increasing the angle between them. The rippling configuration emerged, and
the wavelength of the ripples was studied in detail (Fig. 3.9). The investigators found
that the wavelength increased as the tube was bent to increasingly higher angles. The
initial rippling wavelength agreed with the wavelength predicted by shell theory, while
the longer, final wavelength agreed with the experimental data by Bower et al. [12]. The
bending moment-curvature relationship obtained by Pantano and colleagues is shown
in Fig. 3.10. Note the bilinear behavior and similarity to the force-deflection relationship found by Wong et al. [11] (Fig. 2.6). In a hierarchical hybrid study, Pantano later
used configurations found by FEM as a basis for tight-binding studies to characterize
the electronic properties of CNTs under bending [35]. Arroyo and Belytschko used a
method similar to Pantano et al. to simulate a 34-walled CNT under bending [29]. They
uncovered a new distinctive, diamond-like rippling pattern [3.11]. This pattern, termed
the Yoshimura pattern, as well as a symmetric, sinusoidal pattern termed the Fourier

Figure 3.11: Rippling of 34-walled MWCNT as reported by Arroyo et al. [29], showing
unique Yoshimura pattern. Reprinted with permission.
pattern, are known in compressive buckling of thin shells. Later, in a work by Arroyo and Arias, the FEM loading was revisited and improved. It was noted that keeping the ends of the CNT planar may not be appropriate, and this work used a 3-point bending setup. The ends, in fact, were not planar in the final relaxed configurations. This finding highlights the ubiquitous issue of spurious end effects in all bending simulations. The Yoshimura pattern was uncovered once again, but it was noted that the CNTs displayed a Fourier-like pattern as well, for a small range of bending angles, before entering Yoshimura rippling. The investigators also found the bilinear energetic behavior similar to Pantano et al. Based on this, a one-dimensional phase-transforming beam model was proposed for MWCNTs, with promising agreement to experimental data. Another reduced-dimension treatment of MWCNT bending was carried out by Liu and colleagues. They characterized rippling of MWCNTs under bending using a two-dimensional model – a cross-section of a nanobeam that is a stack of graphene layers. They found that the ripple wavelength is proportional to the thickness of the nanobeam.

### 3.5 Conclusion

In conclusion, several trends arise from simulations of CNTs under bending. Both MWCNTs and SWCNTs initially bend as ideal cylindrical shells, followed by buckling. SWCNTs develop deep localized kinks, but MWCNTs exhibit distributed rippling. These results are in agreement with experimental observations. In addition, energetic behavior is uncovered by simulations. Both SWCNTs and MWCNTs exhibit harmonic behavior before buckling – they have quadratic energy curves and, therefore, linear
moment curves. After buckling, the behavior is contrasting between MWCNTs and SWCNTs. SWCNTs display a linear energy curve (constant moment), while MWCNTs display a quadratic energy curve (linear moment), albeit with a lower stiffness than before buckling.
Chapter 4

Theoretical Background

4.1 Objective Molecular Dynamics

Molecular dynamics simulations and static atomistic simulations model physical systems that are too complex for analytical methods. This is accomplished by explicitly describing the atoms in the system as point masses, with the potential energy of the system being determined by a potential energy function $\phi(x_1, x_2, ..., x_n)$, where $x_i$ is the position of atom $i$ and $n$ is the number of atoms in the system. If the simulation is dynamic, then each atom is treated with classical mechanics, where the force on atom $i$ of mass $m_i$ is

$$m_i \frac{\partial^2 x_i}{\partial t^2} = -\frac{\partial \phi}{\partial x_i}, \quad i = 1, ..., n. \tag{4.1}$$

This equation of motion can then be numerically integrated to obtain the time-dependent displacement $x_i(t)$ of each atom $i$.\[38\]

The potential $\phi$ can be a classical analytical formula, ranging from a very simple sum of two-body terms, such as the Lennard-Jones potential, which models vdW interactions, to many-body potentials for modeling metals and semiconductors, such as the Tersoff potential[31]. Invoking the Born-Oppenheimer approximation, which allows one to separate Schrödinger’s equation into ionic and electronic components, and further choosing to treat the ions classically due to their large mass relative to the electrons, $\phi$ may then be of an explicitly quantum nature. In this case, the electronic Schrödinger’s
equation may be solved with various degrees of accuracy, and the resulting charge density and electronic band structure may be used to determine the potential energy of the full system and, if needed, the forces on the ions.

4.1.1 Periodic Molecular Dynamics

In realistic systems, the number of atoms \( n \) is extremely large, approaching infinity when dealing with bulk properties of crystals. Even with the simplest classical potential, the amount of computation required to simulate every atom in a macroscopic system is extremely prohibitive. This includes CNTs – even though they are only large in one dimension, it is still undesirable to simulate every atom in a realistically-long CNT. Because of this, atomistic simulations almost always use periodic boundary conditions (PBC) to greatly reduce the number of atoms that needs to be simulated. The case for structures that are periodic in one dimension is presented here. Explicitly making recourse to the translational symmetry of the system, under PBC one only simulates the \( n_T \) atoms contained in one translational cell. The energy calculated is per one translational cell, and only the forces on the atoms inside the cell are computed. However, these calculations take into consideration “images” of the original translational cell, the original atomic coordinates translated along the translational vector \( \mathbf{T} \), so that the full set of atomic coordinates considered is

\[
\mathbf{x}_{i,\zeta} = \zeta \mathbf{T} + \mathbf{x}_i, \quad i = 1, ..., n_T,
\]

(4.2)

where \( \mathbf{x}_i \) are the atomic coordinates within the original translational cell, and \( \zeta \) is the index of the image. Typically, \( \zeta \) runs from \(-N\) to \(N\), where \( N \) is chosen to be large enough so that the interatomic potential does not “see” any “empty” atomic sites. The velocities \( \mathbf{v}_{i,\zeta} \) of the atoms in the images are set to be equal to the velocities \( \mathbf{v}_i \) of the atoms in the original cell:

\[
\mathbf{v}_{i,\zeta} = \mathbf{v}_i, \quad i = 1, ..., n_T.
\]

(4.3)

The explicit requirement for the atoms outside of the original translational cell to follow the motion of those within may seem like a contradiction when in reality they would be free to move. It can be shown, however, that if the initial position and velocity conditions possess translational periodicity and the interatomic potential \( \phi \) satisfies certain conditions, the time-dependent solution must also possess the same translational
Periodicity\textsuperscript{38}. Periodic MD is the most common way to perform atomistic simulations, and has been used numerous times to accurately calculate various properties of many systems, including carbon nanotubes\textsuperscript{33}. If the interatomic potential is quantum-mechanical, the translational periodicity is also employed to calculate the reciprocal lattice and determine the electronic band structure and its contribution to the system energy.

Often, it is desirable to use MD to study deformations in materials. Axial deformations (compression or tension) can be applied within the PBC framework by varying the translational vector $T$ around the value corresponding to minimum energy. However, angular deformations such as bending, the subject of this work, generally destroy translational periodicity. As mentioned before, for this reason, the bending of CNTs is generally studied using a cluster approximation, introducing unwanted effects from treating only a finite number of atoms. A large section of a CNT is simulated with the end atoms fixed and no periodicity simplification of any kind employed\textsuperscript{5, 24, 26, 25, 39}. Again reiterating from the last chapter, this approach is not only computationally expensive, but raises the question of how to properly fix the end atoms. If care is not taken, unwanted axial and shear loads may be placed on the section of CNT being simulated.

4.1.2 Objective Molecular Dynamics

A recently developed method called objective molecular dynamics greatly generalizes the PBC framework to include angular symmetries\textsuperscript{38}. This method has been used to successfully model both elastic\textsuperscript{32, 14} and plastic\textsuperscript{40} deformations in CNTs under torsion. Due to the inherent helical symmetries of nanotubes, even when studying undeformed or linearly deformed CNTs, it is advantageous to use this method over PBC even for armchair nanotubes with the shortest translational cells ($|T| = 2.5\,\text{Å}$), because with objective MD, any ideal CNT can be simulated with only two atoms\textsuperscript{32}. The method was also used to study axial and torsional deformations in MoS$_2$ nanotubes and show that these nanotubes have an intrinsic twist in their relaxed configuration\textsuperscript{41}. While using the method to study bending does not allow for such a vast reduction to two-atom cells, it allows one apply pure bending any translational cell of a CNT by an arbitrary angle while maintaining periodicity and not having to worry about end effects
Analogous to how eq. 4.2 is the specific one-dimensional case, suitable for studying axial deformations in CNTs, of the general three-dimensional PBC formulation, I present a simple specific case of the objective formulation, featuring only rotation in one dimension. The general objective MD case allows for translation and rotation in up to three dimensions. The position periodicity requirement is similar to eq. 4.2, except replacing the translation \( T \) with the matrix \( R \) for rotation around one of the coordinate axes, taken to be the \( z \)-axis in this study. The full set of atomic coordinates considered is then

\[
x_{i,\zeta} = R_{\zeta}x_i, \quad i = 1, ..., n_T.
\]

(4.4)

The velocity periodicity equation for the objective method is

\[
v_{i,\zeta} = R_{\zeta}v_i, \quad i = 1, ..., n_T.
\]

(4.5)

Note that unlike the PBC equation 4.3, here the symmetry operation actually modifies the velocity vectors, as they need to be rotated. The original cell \( \zeta = 0 \) is analogous to the same cell in eq. 4.2. Eqs. 4.2 and 4.3 are used to study the relaxed configuration and axial deformations, where eqs. 4.4 and 4.5 are used to study bending (Fig 4.1). One could think of the “infinite” structure being simulated in the objective case as a circle of the CNT and the cell being considered as an arc of that circle. For armchair CNTs (the only type systematically considered in this study), cells may be as short as 2 atoms. Keeping the cell this short prevents localized phenomena such as buckling from occurring, and serves as a model for comparison. Larger cells (supercells) allow buckling to occur.

It is very important to recognize the benefit of the boundary conditions arising in objective MD over cluster representations using fixed end atoms. In the latter, all of the coordinates of the end atoms are held frozen. To avoid axial stress in the CNT, investigators must take extra steps to move the end atoms and re-relax the configuration. When we describe a bent section of a CNT using the objective method, the only constraint is the single angle contained in the matrix \( R \). The atomic positions are free to move away or towards the rotation axis of \( R \). This means that the CNT will inherently relieve itself of axial stress with relaxation, ensuring that the bending applied is pure.
Figure 4.1: Examples of PBC and objective cells for a (5,5) CNT – simulation cell \((\zeta = 0)\) highlighted in red. The top images show PBC cells which can be used to study the stress-free configuration, as well as axial deformations. The bottom images show objective cells for a bending angle of \(10^0/\text{nm}\). Here, \(O\) represents the origin of the coordinate system and \(\theta\) is the rotation angle in the rotation matrix \(R\). The images on the left show the minimum translational cell, which is very computationally efficient and can be used to study the energetics of the linear elastic regimes. The images on the right show larger cells. These can be used to study local phenomena, such as fracture under tension or buckling under compression using PBC, or buckling under bending – the subject of this study – using objective MD.

This also means that the curvature of the CNT,

\[
\kappa = 1/\overline{\tau},
\]

where \(\overline{\tau}\) is the average distance of the atomic coordinates from the rotation axis of \(R\), is not directly imposed. The value of \(\overline{\tau}\) will vary as a result of the axial relaxation of the CNT. An example of this axial relaxation can be seen in fig. 4.2.

An important note must be made about the forces in dynamic simulations using the objective method. When using classical potentials in the Trocadero\(^{[2]}\) computational package used here, forces are formulated in terms of \(F_{i,j,\zeta}\), which is the “pair force”
Figure 4.2: Example of how a section of a CNT under bending using the objective method inherently releases axial strain. Here, elongation is released during a conjugate-gradient method energy minimization. Two configurations obtained at different points in the relaxation are superposed on each other. Transparent atoms represent the elongated, higher energy state. Solid atoms represent the lower energy, more relaxed state. Simulation cell is highlighted in red.

acting on atom $i$ within the original cell due to the image $\zeta$ of atom $j$. Note that this does not mean that $F_{i,j\zeta}$ is a two-body term – in all but the simplest potentials, it depends on the environment around the atoms being considered. From Newton’s third law,

$$ F_{i,j\zeta} = -F_{j\zeta,i}, \quad (4.7) $$

and these reactions must be accounted for. Even though we are not interested in the forces acting on atoms outside of the original cell, because of the periodicity of the system, the force $F_{j,i\zeta}$ is the “same” as the force $F_{j\zeta,i}$. For PBC, this quite literally means that

$$ F_{j,i\zeta} = F_{j\zeta,i} = -F_{i,j\zeta}, \quad (4.8) $$

so whenever $F_{i,j\zeta}$ is calculated and accumulated into $F_i$ (the total force on atom $i$), $-F_{i,j\zeta}$ is accumulated into $F_j$. However, for objective, this is not quite true – in the rotation of the simulation cell, the forces are rotated as well, similarly to the velocities. Thus, for the one-dimensional rotation case presented in eqs. 4.4 and 4.5,

$$ F_{j,i\zeta} = R^{-\zeta}F_{j\zeta,i}, \quad (4.9) $$

Thus, combining eq. 4.7 with eq. 4.9 when $F_{i,j\zeta}$ is calculated and accumulated into $F_i$, in objective, $-R^{-\zeta}F_{i,j\zeta}$ is accumulated into $F_j$.
4.2 Tersoff Potential

4.2.1 Form of the Potential and Parameters

The overall form of the potential is\cite{43}

$$\phi = \frac{1}{2} \sum_{i \neq j} V_{ij}, \quad V_{ij} = f_c(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})]. \quad (4.10)$$

The potential function $\phi$ is modeled as a sum of pair terms $V_{ij}$, where $ij$ runs over every pair of atoms in the system that are within the cutoff radius $S$ of the potential. $V_{ij}$ has a superficially simple form, with three two-body terms – $f_R(r_{ij})$ (the repulsive potential), $f_A(r_{ij})$ (the attractive potential) and $f_C(r_{ij})$ (the cutoff function). The many-body term $b_{ij}$ scales the attractive term and accounts for all the complexity of semiconductor bonding. The repulsive and attractive terms have the following form:

$$f_R(r_{ij}) = A \exp(-\lambda r_{ij}), \quad f_A(r_{ij}) = -B \exp(-\mu r_{ij}). \quad (4.11)$$

Here, $A$, $B$, $\lambda$ and $\mu$ are fitted parameters. The exponential forms are a “universal” way to describe general bonding behavior\cite{31, 44}, due to several reasons aside from their computational efficiency. Introduced by Abell\cite{45}, it is logical to describe bonding in such a way because atomic wavefunctions decay exponentially with radius. Also, \textit{ab initio} studies of simple molecules showed a nearly exponential dependence of $f_R$ and $f_A$ on $r_{ij}$\cite{45}. The cutoff function has the form

$$f_C(r_{ij}) = \begin{cases} 
1: & r_{ij} < R \\
\frac{1}{2} + \frac{1}{2} \cos[\pi(r_{ij} - R)/(S - R)]: & R < r_{ij} < S \\
0: & r_{ij} > S. 
\end{cases} \quad (4.12)$$

This form is chosen simply because it is a smooth way to go from full interaction ($f_C = 1$) to no interaction ($f_C = 0$). Here, $S$ is the total cutoff radius beyond which atom pairs do not interact. $R$ is the beginning of the cutoff transition. These are chosen so that in equilibrium configurations, only nearest-neighbors interact, and they interact fully ($f_C = 1$). Finally, the all-important many-body term takes the form

$$b_{ij} = (1 + \beta^n c_{bij}^n)^{-1/2n}, \quad (4.13)$$
where
\[ \zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{ijk}), \quad g(\theta_{ijk}) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta_{ijk})^2}. \]  (4.14)

This form is justified by qualitative arguments about the nature of bonding in semiconductors. First, it is important to understand the specific challenge posed by modeling semiconductors. Semiconductors are unique in that their equilibrium states possess intermediate coordination. Metals assume close-packed structures, while the elements at the upper right of the periodic table tend to – disregarding weak long-range forces – form diatomic molecules. This is, of course, excluding the inert gases which form no molecular bonds at all. Semiconductors, on the other hand, are in between these two extremes in the sense that while they form coherent bulk structures (as opposed to isolated diatomic molecules) these structures are not close-packed. Moreover, many semiconductors have several stable configurations with different coordinations. Silicon, with small changes in pressure, can assume a large number of different coordinations\cite{31}. More pertinent to this work is the example of carbon, which, at room temperature and pressure, has the two commonly known bulk forms of graphite and diamond, not to mention the plethora of stable nanostructures. The difficulty in modeling this behavior is clear. Particularly, any potential that includes only two-body terms that are “physically reasonable” will have a minimum energy configuration that is close-packed\cite{31}.

Abell\cite{45} argued that the bond order \( b \) (the strength of each bond) weakens as the coordination number \( z \) (the number of bonds to a particular atom) increases. The more bonds connect to a single atom, the weaker (lower binding energy) each bond is. Thus, there is a trade-off between having few strong bonds or having many weak bonds. The exact dependence of bond order on coordination determines the equilibrium coordination. If the dependence is strong, each extra bond will reduce bond order greatly and will reduce total binding energy. The extreme case of this is elements which form diatomic molecules – only one bond. If the dependence is weak, each extra bond will not affect the bond order significantly and will therefore increase total binding energy. The extreme case here is metals, which have the maximum number of bonds possible – close packing. Semiconductors are special because their \( b-z \) relationship strikes a “delicate balance” which means the equilibrium configuration has an intermediate number of bonds\cite{31}. 

The measure of bond order in the Tersoff potential is the term $b_{ij}$. It can be shown that, for a potential of the form in eq. 4.10 with components from eq. 4.11, the energy is independent of coordination number if $b \propto z^{1/2}$. In eq. 4.13, $\beta$ and $n$ are fitted parameters, while $\zeta_{ij}$ is a measure of “effective coordination”. For simplicity, one can assume $\zeta_{ij} = z - 1$ for now. The form of eq. 4.13 was chosen because, with the correct choice of $\beta$ and $n$, at low $z$, $b_{ij}$ has a less negative slope than $z^{1/2}$, while at higher $z$, $b_{ij}$ has a less negative slope than $z^{1/2}$ [31]. In other words, compared to the $b \propto z^{1/2}$ case which creates a constant total binding energy as a function of $z$, taking away a bond at low coordination does not increase bond strength as much, while adding a bond at high coordination decreases the bond strength more. This creates a minimum total binding energy at intermediate coordination.

The term $\zeta_{ij}$ is meant to represent the number of bonds connecting to atom $i$ besides the $ij$ bond, thus the earlier assumption that it is equal to $z - 1$. Because this is the only term modifying the strength of a bond based on the local environment, however, it clearly cannot be that simple. Without some kind of angular dependence, the shear modulus of diamond is zero and all structures with the same coordination and nearest-neighbor distance have the same energy (elements that can assume a diamond structure would also be able to assume a planar square structure at the same energy, for example) [31]. So, the present form of $\zeta_{ij}$ (eq. 4.14) counts all the atoms $k \neq i, j$ around $i$ that are inside the cutoff (scaled appropriately if they are between $R$ and $S$), scaled by the angular function $g(\theta_{ijk})$. In $g$, the parameter $h$ represents the cosine of the optimal bond angle of the particular species it is fitted to. When $\cos(\theta_{ijk}) = h$, $g$ does not modify the bond strength. Any deviations from the optimal bond angle lower the bond strength. Parameters $c$ and $d$ are fitted. In practice, $h$ is also fitted and does not generally correspond to the bond angle of any single configuration. There is even no reason it has to lie between -1 and 1 [31].

Due to the importance of the angular dependence, it is informative to discuss the way it works in more detail. Recall the form of the many-body term $b_{ij}$ and its component functions, eqns. 4.13 4.14. When $\cos(\theta_{ijk}) = h$, the second term in the denominator of the third term of $g$, $(h - \cos \theta_{ijk})^2$, is zero, making the third term and the second term
of $g$ cancel, leaving only unity:

$$g(\theta_{ijk}) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2} + (h - \cos \theta_{ijk})^2 = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2} = 1.$$  \hspace{1cm} (4.15)

In this case, the bond $ik$ (assuming it is within the cutoff) contributes exactly unity to the effective coordination $\zeta_{ij}$, corresponding precisely to the simple, non-angular definition of coordination. If, however, $\cos(\theta_{ijk}) \neq h$, $(h - \cos \theta_{ijk})^2$ obviously increases, regardless of the sign of the deviation due to the square. This increase in the denominator of the negative third term of $g$ decreases said negative term and therefore increases $g$ for that bond. Therefore, the bond $ik$ then contributes more than unity to the effective coordination $\zeta_{ij}$ - it “counts as slightly more than one bond”. Then, since $b_{ij}$ is a monotonically decreasing function of $\zeta_{ij}$ as specified in eq. (4.13), the bond order, and therefore binding energy, decreases as $\cos \theta_{ijk}$ deviates from $h$. The further the deviation, the lower the binding energy.

Earlier versions of the potential also included a bond-length term in $\zeta_{ij}$, based on the idea that long bonds are weaker and would not affect shorter bonds as much. In the first version of the potential, this dependence was relatively heavy (non-zero in the first order). Due to problems such as high phonon energies, in ref. this effect was reduced so that it only comes into play if the bond lengths differ significantly. Finally, in the version of the potential used here, the bond length term is completely eliminated. This is appropriate to the specific problem of reversibly deformed CNTs, as bonds are never stretched or compressed significantly, the three nearest neighbors of a given atom always fall within the cutoff $R$, and all other atoms always fall outside the total cutoff $S$.

The parameters used in the Tersoff interatomic potential in this study were fitted by Tersoff in ref. and are found in table. Tersoff’s goal in fitting these parameters was an accurate representation of the binding energies of different carbon polytypes, as well as accurate values for the geometrical lattice constant of diamond and its bulk modulus. An additional requirement was a minimum energy value for the vacancy in diamond. It is stated that the cutoff parameters $R$ and $S$ were not rigorously optimized, but this should not be a concern, because, as mentioned before, all atoms that should be considered fall within the $R$ and all others fall outside $S$. While the only criteria
explicitly fitted for graphite was its binding energy, agreement of the energies of various defects with tight-binding results was evaluated and found to be satisfactory for graphite[46]. Shear and normal in-plane moduli of graphite were also examined, shear being significantly too high and normal being reasonably close. Of these properties, only the normal modulus of graphite is of concern when studying elastic bending in defect-free carbon nanotubes. This, as well as the bending modulus of a single sheet of graphene – another important property – will be discussed in detail in the next subsection. Naturally, due to the short range of the potential, the interlayer forces in graphite, or interwall forces in MWCNTs have to be treated separately.

Table 4.1: Tersoff potential parameters used in the present study, taken from refs. [43, 46].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ (eV)</td>
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</tr>
<tr>
<td>$B$ (eV)</td>
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</tr>
<tr>
<td>$\lambda$ (Å$^{-1}$)</td>
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</tr>
<tr>
<td>$\mu$ (Å$^{-1}$)</td>
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<td>$\beta$</td>
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<tr>
<td>$n$</td>
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</tr>
<tr>
<td>$c$</td>
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</tr>
<tr>
<td>$d$</td>
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</tr>
<tr>
<td>$h$</td>
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</tr>
<tr>
<td>$R$ (Å)</td>
<td>1.8</td>
</tr>
<tr>
<td>$S$ (Å)</td>
<td>2.1</td>
</tr>
</tbody>
</table>

4.2.2 Validity of the Tersoff Potential for Studying CNTs

Naturally, being over 20 years old, many criticisms of the Tersoff potential have emerged, and alternate empirical potentials have been proposed to replace it. However, many of the criticisms are inapplicable to the problem being studied here, and the potentials proposed to correct these issues are actually worse in certain respects than the Tersoff potential. The two most important properties for this study, when speaking in terms of plane graphene, are the bending modulus $D$ and surface Young’s modulus $Y_s$, defined
\[ D = \frac{\partial^2 W}{\partial \kappa^2}, \quad Y_s = \frac{\partial^2 W}{\partial \epsilon^2}, \]  

(4.16)

where \( W \) is the energy density (taken per atom for \( D \) and per unit area for \( Y_s \)), \( \kappa \) is the curvature of the graphene sheet being bent, and \( \epsilon \) is linear strain. It is generally accepted that graphene is a mechanically isotropic material. The importance of these two parameters comes from the nature of the problem. The bending modulus is most important because CNTs take the form of a rolled sheet of graphene. Additionally, the shape is bound to change as bending occurs. When the tube is bent, it tends to ovalize, changing the curvature in different regions around the circumference. The Young’s modulus is very important, as locally, bending in a tube (or rod, for that matter) is a phenomenon of axial strain – compression on the inner side of the bend and tension on the outer side of the bend. Finally, both the localized buckling and distributed rippling found in nanotubes under bending arise from an interplay of the bending and linear stiffnesses of the material. In parallel with simple column buckling, the nanotube will assume a buckled or rippled configuration when the energy caused by staying in the ideal shape and heavily compressing the inner side of the bend becomes so high that it is energetically advantageous to relieve the local strain by assuming a rippled or buckled configuration. The compressive strain is relieved, and some local bending strain is introduced. \( Y_s \) is modeled quite accurately in the Tersoff potential, being 17% higher than the \textit{ab initio} value\[46, 47, 48\]. \( D \), however, is 25% lower than the corresponding \textit{ab initio} value \[38\ 47, 48\].

Soon after the development of the Tersoff potential, Brenner presented his first-generation potential, building on top of Tersoff’s work\[49\]. His work, however, was centered on modeling hydrocarbons in chemical vapor deposition (CVD) and other multi-species and/or reactive situations. Brenner himself mentions that the Tersoff potential produces accurate carbon-carbon bond lengths in graphite. This, combined with the relatively accurate elastic constants, speaks to the suitability of the Tersoff potential for studying elasticity in CNTs. The problems cited by Brenner are the inability to describe radical orbitals, as well as an inability of the expression to accurately describe both conjugated and non-conjugated double bonds. The inability of the Tersoff potential to accurately describe C-H bonds is also mentioned. We are describing an all-carbon, nearly pure \( sp^2 \) system (the deviations from this behavior play an important role in
bending and are discussed shortly). Thus, Brenner’s concerns about the drawbacks of the Tersoff potential are largely unapplicable. To deal with the issues he raised, Brenner introduced corrections to Tersoff’s potential. Mainly, these corrections dealt with keeping track of the number of carbons and hydrogens bonded to each atom in a pair being examined. Thus, it became a second-nearest neighbor potential, increasing computational complexity. More importantly, the elastic constants for graphene actually became worse, $Y_s$ and $D$ being 32% and 44% lower than \textit{ab initio} values, respectively\cite{47, 48}.

There is a physical reason for the low values or $D$ in the Tersoff potential and Brenner’s first-order potential. It is therefore important to examine the treatment of bending in plane graphene in the Tersoff potential and compare it to the quantum-mechanical picture of carbon bonding in graphene and how it is affected by bending. Figure 4.3 shows a schematic of bending as seen by a nearest-neighbor potential such as the Tersoff potential. Assuming no change in bond length, the only things that change are the angles $\theta_{ijk}$, where $i = 1$. Because the potential is nearest-neighbor, the reduced distance between atom pairs not including atom 1 does not have any effect. The parameter $h = -0.57 = \cos 125^0$ corresponds to a larger angle than the $\theta_{ijk} = 120^0$ equilibrium bond angle in planar graphene. Bending will further decrease $\theta_{ijk}$, moving it further away from the value corresponding to $h$ and lowering the binding energy (increasing the total energy of the system) in accordance to the angular dependence mechanism outlined in the previous subsection. This is the full extent of the provisions the Tersoff potential has to describe bending stiffness in graphene.

Figure 4.3: Diagram showing an atom and its nearest neighbors in flat graphene (left) and a bent section of graphene, such as a CNT (right). The axis of the CNT is parallel to the y-axis, and the center of the CNT is in the positive z direction from the atoms pictured.
The quantum-mechanical picture is as follows. In graphene, the carbon atoms’ 2s, 2px, and 2py atomic orbitals hybridize into sp2 molecular orbitals, which are in the plane of the graphene sheet and form σ bonds – primarily responsible for the in-plane stiffness of graphene. The 2pz atomic orbitals become π molecular orbitals, perpendicular to the plane of the graphene sheet. These orbitals, while not interacting as strongly as the sp2 orbitals, contribute to binding, and are “happy” in their equilibrium configuration and overlap (fig. 4.4, left). These orbitals do not play a strong role in in-plane elasticity, but are important when considering bending. Once the σ bonds are no longer in-plane with each other, this causes changes in the overall hybridization and geometry heavily involving π orbitals. The π orbitals, according to the π-orbital axis vector model (POAV) [50, 51], will form equal angles with the σ bonds, causing an inclination of the π orbitals relative to each other. On the concave side of the bent section of graphene (or the inside of the nanotube), the π orbitals will be brought closer together, while on the opposite side, they will be spread apart. The repulsion on the concave will redistribute the charge towards the opposite side. The entire orbital picture is now changed. The orbital formerly named π has rehybridized into the hπ orbital, now containing not only the 2pz atomic orbital, but also some 2s character. Accordingly, the sp2 molecular orbital now contains less of the 2s atomic orbital – in fact, the σ bonds would not be able to “bend” without this happening. The whole picture now deviates from the sp2 bonding scheme, becoming a mix between sp2 and sp3 bonding schemes [51]. Fig. 4.4, right, shows a schematic image of the change from the π orbitals to the hπ orbitals.

While an empirical potential based on the nearest-neighbor atomic picture shown in fig. 4.3 is capable of capturing the resistance of σ bonds to bending, it is utterly incapable of capturing the effects stemming from the misalignment and repulsion of π orbitals. Referring to the right side of fig. 4.4, it is clear that a term containing at least four atomic coordinates, such as a dihedral-angle term, must be included in the potential-energy expression. In ref. [46], Tersoff mentions this shortcoming of his potential, but states that he chose to omit the treatment of dihedral-angle effects due to the computational advantages of the short range of the potential. Because the Tersoff potential and the first-generation Brenner potential were invented before the discovery of nanotubes and widespread study of carbon nanostructures, it is possible they underestimated the importance of dihedral-angle effects. This omission of dihedral-angle
Figure 4.4: Diagram illustrating $\pi$ orbitals in planar graphene (left) and their change into $h_{\pi}$ orbitals when the sheet is bent, such as into a CNT (right). The axis of the CNT is through the page, and the center is towards the top of the image.

Effects explain the low value of the bending modulus of graphene in the Tersoff and first-generation Brenner potentials, relative to the respective Young’s moduli in those potentials. The bond-angle dependence, which has the same form in both potentials, is not only the sole contributor to bending stiffness, but is a major player in the Young’s modulus, since the stretching or compression of the lattice changes the bond angles. Therefore, to compensate for the lack of dihedral-angle forces, the bond-angle dependence would have to be unrealistically strong, making the Young’s modulus too high. It is also possible some of the problems Tersoff encountered in his early work due to an overly strong angular term[44] would be reintroduced.

Much later, Pettifor et al. revisited the issue, directly stating that the lack explicit treatment of the $\pi$ bond was a shortcoming of the Tersoff and first-generation Brenner potentials, and confirming that the bond-angle dependence in these potentials corresponded to the $\sigma$ bond[52]. Shortly after, Brenner introduced his second-generation potential[53]. Once again, the goal was to not only reproduce equilibrium or quasi-equilibrium states of pure carbon, but to accurately represent hydrocarbons also, as well as to be able to model reactions. An additional problem with the Tersoff and first-generation Brenner potential was stated, in that their potential energy was bounded
as the distance between atoms decreased, meaning they could not be used to model energetic atom collisions. Once again, this issue is not a concern in the present study. Most importantly though, the second-order potential included an explicit dihedral-angle term to describe the ever-important interaction of the \( \pi \) orbitals. This vastly improved the bending modulus \( D \) of graphene, to a value only 5% lower than the \( ab\ initio \) value. Unfortunately, however, the Young’s modulus \( Y_s \) was still greatly underestimated, being 30% lower than the \( ab\ initio \) value\[^{54, 47, 48}\]. Also, the extra terms naturally increase computational expense.

The values of the elastic constants \( Y_s \) and \( D \) are summarized in table \ref{tab:4.2} for the Tersoff, first-generation Brenner and second-generation Brenner potentials compiled from refs.\[^{54, 47, 38, 46}\], in comparison with \( ab\ initio \) values from \[^{48}\]. In summary, while the Tersoff potential clearly has drawbacks, its mixture of satisfactory descriptions of \( Y_s \) and \( D \) compared to the alternatives, as well as its computational efficiency, make it a good choice for studying elastic bending in CNTs. Because of its drawbacks, however, the results of this study will be qualitatively verified by simulating select systems with a tight-binding method.

Table 4.2: Comparison of bending modulus \( D \) and Young’s modulus \( Y_s \) for graphene as simulated by the Tersoff potential\[^{46, 43}\], Brenner’s first-generation\[^{49}\] and second-generation\[^{53}\] potentials, and \( ab\ initio \) results\[^{48}\]. Percent deviation are shown from \( ab\ initio \) values. Data gathered from refs.\[^{46, 38, 54, 47}\].

<table>
<thead>
<tr>
<th></th>
<th>( Y_s ) (J/m(^2))</th>
<th>% deviation of ( Y_s )</th>
<th>( D ) (eV ( \text{Å}^2/\text{atom} ))</th>
<th>% deviation of ( D )</th>
</tr>
</thead>
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<td>Ab initio</td>
<td>345</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tersoff</td>
<td>405</td>
<td>+17</td>
<td>2.9</td>
<td>-25</td>
</tr>
<tr>
<td>First-gen Brenner</td>
<td>236</td>
<td>-32</td>
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<td>-44</td>
</tr>
<tr>
<td>Second-gen Brenner</td>
<td>243</td>
<td>-30</td>
<td>3.7</td>
<td>-5</td>
</tr>
</tbody>
</table>
Chapter 5

Simulation Setup and Results

5.1 Introduction

To perform the bending simulations, the computational package Trocadero was used \[42\]. To model the covalent interactions in CNTs, the Tersoff potential was used as described in chapter \[43\]. For simulating MWCNTs, the inter-wall vdW interactions were described by a standard 6-12 Lennard-Jones(L-J) potential. The Lennard-Jones parameters were \(\sigma = 3.851\) Å and \(\epsilon = 4.0\) meV. CNT configurations were initially generated using CoNTub\[55\].

5.2 SWCNT Bending Simulations

First, the bending of SWCNTs was studied. While this subject has been extensively and successfully studied using cluster representations of SWCNTs \[5, 24, 26, 25, 39\], it is necessary to confirm that the method used here is valid for studying bending. While objective MD has many advantages which have already been mentioned, it is possible that it is not an entirely realistic way to simulate a section of a CNT undergoing bending due to the interaction between the simulation cell and its images. This is unlikely to be a significant issue, especially considering the short range of the Tersoff potential. Nevertheless it is instructive to see how the new methodology performs when applied to a familiar problem. The critical curvature \(\kappa_c\) at which the transition from linear elastic bending to localized buckling, as observed many times in experiment and simulation
Figure 5.1: Strain energy of (15,15) SWCNT as a function of bending angle. Black curves represent forward bending and red curves represent unbending. Top graph is without MD, showing significant hysteresis. Bottom graph is with MD, showing reduced hysteresis. The “steps” observed are an artifact of performing MD every n steps instead of every step in this preliminary simulation. Angles and energies are plotted per 1 nm of length.
(discussed in chapters 3 and 4), was the focus. Due to the consensus that chirality plays either no role or a weak role in the value of $\kappa_c$ [5, 24, 26], only armchair tubes were studied, as they have the smallest minimum translational cell. Thus the simulation cell may be any multiple of approx. 0.25 nm. Both the radius and the length dependence of $\kappa_c$ was examined. To study the radius dependence, 2.5 nm sections of SWCNTs with radii ranging from 0.35 nm (5,5) to 1.40 nm (25,25) were studied. To study the length dependence, sections of a (6,6) CNT with lengths varying from 2.0 nm to 16.2 nm were studied. The number of atoms simulated ranged from 160 to 1152.

To perform the bending simulations, approximate bent configurations of CNTs were created and then relaxed to find the minimum energy configuration using the conjugate gradient method. The bending angle $\theta$ was varied in small steps, at most 0.05 degrees per nm of tube length, with relaxation performed at each step. In preliminary simulations, this procedure was performed in both forward and reverse directions. In agreement with ref. 25, significant hysteresis was found between bending and unbending cycles (fig. 5.1 left). This is the first piece of evidence that the methodology is, in fact, valid and in agreement with previous studies. It was found that this hysteresis could be reduced, albeit not completely eliminated, by performing molecular dynamics before the structural relaxation (fig. 5.1 right). Performing MD at a moderate temperature helps perturb the system to overcome the energy barrier between its current metastable state and the minimum-energy configuration. However, performing MD at too high of a temperature was found to occasionally leave the system in a higher-energy metastable state. The procedure was to perform MD at 300 K for 500 timesteps of 2 fs each at every bending step. The results presented from here on apply to the forward bending cycle.

Fig. 5.2(b) shows three examples of the bending energetics of SWCNTs. Plotted are the strain energy $E$, as well as the bending moment $M = dE/d\theta$, as a function of bending angle. For all SWCNTs studied, three regimes of bending emerge. The morphologies corresponding to these regimes are illustrated in fig. 5.2(a) using the example of a (15,15) SWCNT. At low bending angles, the tube is in the realm of linear elasticity. The strain energy is approximately quadratic and the bending moment is therefore approximately linear. The morphology is smooth and this bending regime can, if one desires, be simulated using the minimum translational cell (fig. 5.2(a),
Figure 5.2: (a) Configurations of a (15,15) SWCNT with bending angle $\theta$ (top to bottom) of 4 deg, 4.5 deg, and 30 deg. The atoms located inside the minimum simulation cell required to represent each morphology are represented in red. (b) Strain energy (continuous line) and bending moment (dashed line) vs. $\theta$ for two SWCNTs. Bending moment is defined as $M = dE/d\theta$. Length of the simulation cell is 2.5 nm. The transient regime is shaded with gray. Reprinted from [2] with permission.
As the bending angle increases, the tube eventually develops a localized kink (fig. 5.2(a), middle). Naturally, a cell that is larger than the minimum translational cell is required to study bending from this point forward. The formation of this kink has a dramatic effect on the energetics. In agreement with refs. [24, 25], buckling coincides to a discontinuity in the bending moment where it drops dramatically. It is this discontinuity that is used to pinpoint the critical angle and, by extension, the critical curvature $\kappa_c$ at which buckling occurs. During the initial stage of kink formation, the bending moment decreases, but at the highest values of $\theta$, the bending moment stops decreasing and flattens out. This signals the final regime, corresponding to a deeply kinked morphology (fig. 5.2(a), bottom). This existence of an intermediate regime, followed by a final deeply kinked regime, is in agreement with [25], except a second discontinuity in bending moment was not observed here. It also appears that the angle range of the intermediate, kink-formation regime increases with the diameter of the
CNT. The agreement in morphology and energetics of the present study with previous studies is clear, showing that the present methodology is valid for studying bending in CNTs. It appears that the interaction between the simulation cell and its $\zeta = \pm 1$ images is secondary and introduces no significant inaccuracies. Further proving this is the ability of the method to describe localized buckling of the same nature in very long nanotubes, such as the (6,6) in fig. 5.3. Note the similarity to the buckling shown in fig. 2.4 as imaged by Iijima et al. [5]. For longer SWCNTs, it is increasingly difficult to find the lowest-energy, single-kink configuration. MD must be performed until this configuration is found, as the system easily gets trapped in multiple-kink, higher-energy metastable states.

Once the method by which the critical curvature $\kappa_c$ can be identified is clear, the dependence of $\kappa_c$ on nanotube radius $R$ and nanotube length $L$ can be studied. Fig. 5.4 (a) shows the dependence of $\kappa_c$ on radius for SWCNTs using a simulation cell that is 2.5 nm in length. The data falls very closely on the fitted curve

$$\kappa_c = a/4R^2.$$  \hspace{1cm} (5.1)
This is the same relationship found in refs. [24, 26], further showing the validity of the present methodology in simulating CNT bending. The term $a$ is expected to be dependent on the length of the simulation cell, representing the length of the section of CNT being bent. The length dependence, as found by simulating a large collection of (6,6) SWCNTs of different lengths, is shown in fig. 5.4 (b). The constant $a$ was found to have a relatively weak negative power law dependence on length,

$$a = 0.148L^{-233}.$$

5.3 MWCNT Bending Simulations

When MWCNTs are bent beyond the linear elastic regime, the non-ideal deformations start in the outer wall, propagating to the inner walls at higher angles. This is a natural consequence of eqn. 5.1 for SWCNTs. When isolated, the larger diameter outer walls become mechanically unstable at a lower curvatures. Thus the outer wall enters a non-ideal deformation mode first, then, when the deformation becomes severe enough, the inner walls follow, driven by the shape of the outer wall through inter-wall vdW forces.

The MWCNTs studied were all armchair-type as well, with each wall having a (5$n$,5$n$) form. This results in 3.4 Å spacing between consecutive walls and is a common type of MWCNT to simulate [28, 35, 29]. In preliminary simulations, some MWCNTs were studied where $n$ did not start at 1 – they were missing the (5,5) core and possibly some of the consecutive inner walls as well. In agreement with [5], we found that these thin-walled MWCNTs behaved similarly to SWCNTs, developing deep localized kinks once the linear elastic regime has passed.

Thick $n$-walled MWCNTs of the form (5,5)@...@(5$n$,5$n$), where values of $n$ from 2 to 6 were studied, showed a strikingly different behavior. Because, if isolated, the inner walls buckle at much higher angles than the outer walls, the inner walls provide support, restricting the outer wall from forming a deep kink as in SWCNT buckling. Instead, the compressive strain on the inner side of the MWCNT is released by the means of a wavelike rippling mode, shown in fig. 5.5 (a), left. At higher angles, the inner walls can finally no longer provide enough support, and the tube collapses into a localized kinking mode similar to SWCNTs and thin-walled MWCNTs (5.5 (a), right).
Figure 5.5: (a) Rippled and kinked configurations of (5,5)@(10,10)@(15,15) MWCNT at (left to right) 3.4 deg and 4.2 deg bending per nm. 4 nm simulation cell is highlighted in red. (b) Outer wall strain energy, using a 1 nm (gray, filled) and 4 nm (black, outlines) simulation cell around the rippling regime. Left arrow represents onset of rippling in both cells, right arrow represents onset of localized buckling in the 4 nm cell. (c) Total strain energy (circles) with fitted curves for each regime (continuous for smooth and dashed for rippled), inter-wall energy of outer wall pair (dotted line – measured from strain-free state). The sudden large increase in the slope of the inter-wall energy coincides with the onset of rippling. (d) Bending moment (circles) with fitted lines for each regime. The sudden decrease in the slope of the bending moment coincides with the onset of rippling. Angles, energies, and moments are plotted per 1 nm of length. Reprinted from [2] with permission.
Note that the rippling observed is different from the Yoshimura pattern reported in refs. [29, 37] with a 10 nm characteristic scale, found in very thick MWCNTs. The Yoshimura pattern is analogous to the buckling pattern of the same name found in thin cylindrical shells under compression [56]. Unlike the Yoshimura pattern, however, the ripples observed here are more similar to the Fourier buckling pattern, also found in thin cylindrical shells under compression [56]. There appears to be a possible relation to the rippling pattern found in 2D finite element simulations [30]. However, as discussed next, the ripple length here was found to be independent of the MWCNT radius, contrary to the findings in ref. [30].

To investigate the rippling morphology, a set of MWCNTs of different diameters and lengths was simulated. These preliminary studies included 2-wall MWCNTs ranging from 0.75 nm to 4 nm in length, 3-wall MWCNTs ranging from 1 nm to 6 nm in length, and 4-wall MWCNTs ranging from 2 nm to 4 nm in length. Remarkably, the minimum energy state at intermediate bending angles appeared to be wavelike rippling with a 1 nm wavelength for all of these systems, regardless of diameter (number of walls) or length. Some simulations showed rippling with wavelengths of 0.8 nm and 0.75 nm, but these were found to be higher-energy metastable states. No rippling with wavelengths higher than 1 nm was observed. An example of the length-invariance of the rippling mode is shown in fig. 5.5 (b). The strain energy per length of a 1 nm simulation cell (restricted to rippling) and a 4 nm simulation cell (allowed to kink) are identical in the rippling regime. Only the outer wall energy is plotted, as the inner wall energies are nearly equal even after the 4 nm cell buckles, making the comparison more difficult to see. Unlike SWCNTs, MWCNTs showed no significant hysteresis between bending and unbending cycles, even when no MD was performed (fig. 5.6). Thus, the simulation procedure used was identical to that used for SWCNTs, but no MD was performed.

As in SWCNTs, the critical curvature $\kappa_c$ at which the transition (in this case between ideal and rippled regimes) occurs was the primary variable of interest. However, because the ripples were found to be length-invariant, no length-dependence needed to be investigated. The primary interest was to identify the dependence of $\kappa_c$ on the number of nanotube walls $n$. For this, MWCNTs of the form $(5,5)@...@(5n,5n)$ with $n$ up to 6 were simulated using 1 nm simulation cells, so that the simulation cell contained one ripple. The objective method is very suitable for simulating the rippling mode due
Figure 5.6: Strain energy of (5,5)@(10,10)@(15,15) MWCNT as a function of bending angle. Black curves represent forward bending and red curves represent unbending. Top graph is without MD. Bottom graph is with MD. Neither graph shows significant hysteresis. Angles and energies are plotted per 1 nm of length.
to its periodicity. The onset of the rippling mode may be identified by the beginning of a sudden increase in the slope of the inter-wall vdW energy of the outer wall pair (fig. 5.5 (c)). The onset of rippling also corresponds to a sudden decrease in the slope of the bending moment $M$ (fig. 5.5 (d)). The dependence of $\kappa_c$ on the CNT radius $R$ (proportional to the number of walls) is shown in fig. 5.4 (a):

$$\kappa_c = 0.207/4R^2.$$

(5.2)

The relation is of the same form as the one for SWCNTs, and is also a very good fit to the data. Note that the coefficient is higher for MWCNTs than SWCNTs – MWCNTs are more resistant to non-ideal morphologies due to the support provided by the inner walls.

5.3.1 Analysis and Interpretation

The length-invariance of the wavelike rippling pattern suggests that the switch between the ideal smoothly bent morphology to the rippled morphology may be interpreted as a phase transition. At low temperatures and constant load, the condition for a phase transition to occur is the equality of enthalpy $H$ between the two phases. For an angular system, as in one in which the work is being done via a moment $M$, $H = E - M\theta$, where $E$ is the energy of the system and $\theta$ is the angular deformation. This happens when the energy curves of the two phases share a common tangent. Let $E_a(\theta)$, $M_a(\theta)$, and $H_a(\theta)$ be the potential energy, bending moment, and enthalpy functions of phase $a$ and $E_b(\theta)$, $M_b(\theta)$ and $H_b(\theta)$ be the those functions for phase $b$. Suppose that the curves share a common tangent between the points $E_a(\theta_1)$ and $E_b(\theta_2)$, with the slope

$$p = \left. \frac{dE_a}{d\theta} \right|_{\theta=\theta_1} = \left. \frac{dE_b}{d\theta} \right|_{\theta=\theta_2} = M_a(\theta_1) = M_b(\theta_2).$$

(5.3)

Then, for the common tangent line to touch both points, the following must hold true:

$$E_b(\theta_2) - E_a(\theta_1) = p(\theta_2 - \theta_1)$$

$$E_b(\theta_2) - M_b(\theta_2)\theta_2 = E_a(\theta_1) - M_a(\theta_1)\theta_1$$

$$H_b(\theta_2) = H_a(\theta_1).$$
Table 5.1: Characterization of the wavelike rippling mode in (5,5)@...@(5n,5n) MWCNTs. Here \( n \) is the number of walls, \( \kappa_c \) the critical curvature, and \( B \) the bending stiffness.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \kappa_c ) ((\text{nm}^{-1}))</th>
<th>( B_{\text{ideal}} ) ((\text{eV nm}))</th>
<th>( B_{\text{rippled}} ) ((\text{eV nm}))</th>
<th>( B_{\text{rippled}}/B_{\text{ideal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.105</td>
<td>2,101</td>
<td>317</td>
<td>0.15</td>
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<tr>
<td>3</td>
<td>0.046</td>
<td>11,984</td>
<td>4,719</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>0.027</td>
<td>33,247</td>
<td>19,197</td>
<td>0.58</td>
</tr>
<tr>
<td>5</td>
<td>0.017</td>
<td>76,357</td>
<td>48,884</td>
<td>0.64</td>
</tr>
<tr>
<td>6</td>
<td>0.012</td>
<td>149,770</td>
<td>97,869</td>
<td>0.65</td>
</tr>
</tbody>
</table>

The phase transition occurs between the angles \( \theta_1 \) and \( \theta_2 \), and the two phases coexist in this angle range. However, as shown in fig. 5.5 (c) and (d), for the case of MWCNT rippling, both the energy and the moment are continuous at the point when the transition occurs. The energy curves meet at a point and are tangent to each other at that point. In other words, \( \theta_1 = \theta_2 \). At this single critical angle \( \theta_c \), \( H_{\text{ideal}}(\theta_c) = H_{\text{rippled}}(\theta_c) \). This means there is no angle range in which the smoothly bent and rippled phases coexist, and thus the transition always occurs at a set curvature value. This interpretation is in agreement with the lack of hysteresis between bending and unbending in MWCNTs.

A notable feature of the bending of MWCNTs is that the tube retains significant stiffness after entering the rippling regime – the bending moment continues to increase with angle. Not only this, but the behavior remains linear elastic, as in, the energy is quadratic and the bending moment is linear, as can be seen from the fitted curves in fig. 5.5 (c) and (d). Thus, it is possible discuss the bending stiffness of the tube during the rippling regime. This is in contrast to SWCNTs, where the bending moment actually decreases with angle immediately after buckling, followed by a region that has virtually zero slope, making a linear elastic treatment inapplicable. This response in MWCNTs is similar to the response observed experimentally in ref. [11] with cantilevered thick MWCNTs(fig. 2.6).

It is useful to compare the bending stiffnesses of MWCNTs before and after rippling, \( B_{\text{ideal}} \) and \( B_{\text{rippled}} \), for tubes possessing different numbers of walls \( n \) (table 5.1). To
compute $B$, $M$ was first converted to units of eV/rad to make the angle unitless. Then, $M$ was expressed as a function of curvature $\kappa$ (eqn. 4.6). Then, the bending stiffness is $B = dM/d\kappa$, a constant for a linear elastic case. The ratio $B_{rippled}/B_{ideal}$ appears to converge to a value of 65% as $n$ increases.

5.3.2 Tight-Binding Confirmation

Because of the drawbacks of the Tersoff potential described in chapter 4, MWCNT rippling was confirmed using a set of tight-binding simulations. To describe the covalent intra-wall interactions, the density-functional-based tight-binding (DFTB) method was used. The quantum-mechanical method implicitly accounts for the repulsive part of the van der Waals interaction, while the attractive “6” term from the L-J potential remained explicitly, independent of the DFTB treatment. This combination of methods was developed and tested in ref. [57]. Because of the much higher computational expense of the tight-binding method compared to empirical potentials, the simulations run were restricted to a 2 nm long cell of a (5,5)@10,10@15,15 MWCNT (960 atoms), containing two wavelengths of rippling. A handful of specific bending angles were investigated to obtain a qualitative understanding of the deviations from the Tersoff simulations. The relaxed configurations obtained using the Tersoff potential were used as a starting point for conjugate-gradient structural relaxation using the DFTB potential. If rippling is a non-physical morphology, they would either dissipate or be replaced by a single deep kink.

The results indicate that the wavelike rippling observed in the classical simulations is, in fact, a valid mode of MWCNT deformation under bending. However, the Tersoff potential overestimated the ease with which rippling occurs. At bending angles of 4.5 deg/nm or less, the ripples dissipated and the configuration returned to the ideal, linear elastic type (fig. 5.7 left). However, at bending angles of 5.0 deg/nm and higher (up to 6.0 deg/nm were simulated), the ripples were greatly reduced in magnitude, but reached a stable configuration (fig. 5.7 right). The relaxation continued to reduce the axial strain present in the nanotube due to differences between potentials, but the ripples remained stable (fig. 4.2). Note that by 5.0 deg/nm, a 2 nm long cell of this particular MWCNT would be well into the localized kink regime if simulated using the Tersoff potential.
The fact that the Tersoff potential is too “soft” when describing the resistance of a MWCNT to rippling is a natural consequence of the inaccuracies in elastic moduli of graphene as described by this potential. In essence, by assuming a rippling configuration, the system trades some local compressive strain for local bending strain – instead of the inner wall being heavily compressed, it becomes rippled – locally bent. From \[4.2\] the Tersoff potential underestimates the bending modulus, and therefore the bending strain, of graphene, and overestimates the Young’s modulus and axial strain. Thus, trading the exaggerated compressive strain for the underestimated bending strain becomes energetically advantageous earlier. Also, the reduced bending modulus allows for increased bending, resulting in deeper ripples.
Chapter 6

Conclusion and Future Work

6.1 Conclusion

Twenty years after their discovery, CNTs continue to be a subject of intense experimental and theoretical research. As nanotechnology evolves and new applications for CNTs are proposed, new questions appear. How will CNTs behave when incorporated into NEMS? CNTs are biopersistent and have a large aspect ratio – do they pose a health risk similar to biopersistent asbestos fibers? The bending response of CNTs is important in answering both of these questions and more. Bending of CNTs is also directly studied in experiment, as well as used to indirectly measure their Young’s modulus. In experiments, a general trend emerges. All CNTs behave as linear beams under mild bending. Under severe bending, SWCNTs form localized kinks, while MWCNTs form distributed ripples. Microscopic simulations are needed to understand the response of CNTs to bending in atomistic detail in order to characterize behavior and explain the phenomena seen in experiments.

To this end, many methods have been used to study bending in CNTs. Because traditional atomistic methods rely on PBC to reduce the number of atoms simulated, and bending is incompatible with translational symmetry, alternative methods need to be used to simulate CNTs with reasonable computational efficiency. Small SWCNTs have been simulated using direct atomistic methods by treating a section of CNT with fixed ends as a cluster and rotating the fixed ends to impose bending. This method is computationally expensive because of the need to simulate an entire realistically-long CNT,
and is not applicable to MWCNTs due to the expense. To reduce the computational expense, both SWCNTs and MWCNTs have been simulated by treating the CNT walls as a continuum shell, then treating this shell with FEM. Finally, some studies combine atomistic and continuum method, either in parallel – simulating different parts of the CNT with the different methods – or sequentially – using FEM to predict configuration which is then treated atomistically. All of these methods suffer from the complication of end effects – care must be taken to avoid subjecting the CNT to unwanted axial or shear strains. Despite the drawbacks of these methods, they are generally successful and replicate the trend of buckling in SWCNTs and rippling in MWCNTs seen in experiments.

The present study uses a new method, termed objective MD, which allows for angular periodicity to be used in atomistic simulations. This makes it perfect for angular deformations such as bending. In addition to the reduction in simulation cell, objective MD eliminates spurious end effects and guarantees that the system being studied is subjected to pure bending. However, there is concern that the interaction between a simulation cell and its images may make the method inappropriate for studying localized phenomena. Here, the Tersoff interatomic potential is used to describe the covalent bonding within walls and the Lennard-Jones potential is used to describe the inter-wall vdw interactions. The Tersoff potential is based on basic arguments about the nature of binding in semiconductors and, despite its age, is in some ways superior to more modern empirical potentials. It is not without its drawbacks however, and the results of the study were confirmed using DFTB.

Despite concerns that interactions between the simulation cell and its images may cause spurious effects, objective molecular dynamics emerges as a powerful tool for studying bending response in SWCNTs using direct atomistic simulations. Simulations of SWCNTs showed agreement with previous work, notably in the inverse quadratic relationship between the critical buckling curvature $\kappa_c$ and the radius $R$ of the CNT. $\kappa_c$ also showed a weak negative power law dependence on the length of the CNT.

Applying the method to thick-walled MWCNTs, a wavelike rippling mode was discovered. This mode has a characteristic length of 1 nm, independent of the radius or length of the MWCNT. The $\kappa_c$ for entering the wavelike rippling also has an inverse quadratic relationship on $R$, but with a higher coefficient – thick-walled MWCNTs are
more resistant to non-ideal deformation modes than SWCNTs of the same diameter. The transition from ideal behavior to rippling may be interpreted as a phase transition. Also, the mechanical bending response after rippling remains linear elastic, with a stiffness that is a finite fraction of the original ideal bending stiffness. The stiffness reduction approaches a 35% value as the number of walls $n$ increases. This retention of stiffness has many implications. It is important for mesoscopic modeling of MWCNTs. It also suggests that MWCNTs may be more toxic than SWCNTs, as CNT toxicity is almost entirely dependent on the CNT remaining straight and stiff within the lung.

DFTB simulations confirm rippling under bending in MWCNTs, but show that the inaccuracies of the Tersoff potential have exaggerated the magnitude of the rippling, as well as lowered the value of $\kappa_c$.

### 6.2 Future Work

While objective MD provides a significant simplification, there are still many realistic problems that are out of reach of atomistic simulations or even FEM. CNTs can not only be extremely long, but may also form aggregates or ropes, increasing the computational expense even further. Highly simplified, accurate models are necessary. One possibility is employing Kirchhoff’s rod theory to model CNTs. Another method is presented next with preliminary results.

At low bending angles, CNTs act like elastic beams. We have used this fact to develop a distinct-element method (DEM) model for CNTs, using the software PFC3D by Itasca Consulting Group [58]. Several translational cells of a CNT are lumped into a distinct element “ball”. The balls are connected to simulate an elastic beam. Additionally, a relationship was derived that expresses the vdW interaction between two sections of CNT as a function of their center-to-center distance [59, 60]. Using this framework, we have successfully simulated a $(5,5)@\{(10,10)\}@(15,15)$ MWCNT, 500 nm in length, wrapped into a stable ring attached by vdW forces (fig. 6.1). This CNT contains 240,000 atoms, well beyond the capabilities of atomistic or FEM studies. Each ball lumps 240 carbon atoms. The model beam has the same radius as the CNT. $B_{\text{ideal}}$ found in this study from table 5.1 was used in conjunction with the radius to find the Young’s modulus for the beam. The curvature of the ring is less than 0.02 nm$^{-1}$, so it is
Figure 6.1: DEM simulation of a 500-nm long (5,5)@(10,10)@(15,15) MWCNT, showing the initial configuration (left) and the final configuration reached by sliding (right), held in the shape of a ring by vdW forces. Yellow represents the MWCNT, composed of DEM balls lumping 240 atoms each. Blue represents the vdW interaction radius. The bending stiffness for the model is the value found in the present study – $B_{\text{ideal}}$ from table 5.1. The curvature of the ring is $< 0.2 \text{ nm}^{-1}$, placing it well within the linear ideal regime of bending.

well within the linear ideal regime of bending. The shear modulus – much less important here because it plays no role in bending – was taken from a previous study\cite{32}. This first step demonstrates the ability of DEM to model CNTs in the linear ideal regime of bending. However, MWCNTs keep their linear behavior after rippling, albeit at a reduced bending stiffness (table 5.1). Because of this, we expect to be able to model MWCNT systems that are fully or partially rippled, appropriately adjusting the bending stiffness in different regions depending on local curvature.
References


Appendix A

Commonly Used Terms and Abbreviations

Note: Due to the large amount of notation used in [4.2], some of these symbols are reused in that particular section with different meanings.

- CNT – Carbon nanotube
- SWCNT – Single-walled carbon nanotube
- MWCNT – Multi-walled carbon nanotube
- MD – Molecular dynamics
- PBC – Periodic boundary conditions
- NEMS – Nano-electromechanical system
- FEM – Finite element method
- ζ – Objective image index
- R – CNT radius
- Y – Young’s modulus
- Y_s – Surface Young’s modulus of a 2D object, i.e. where 3D formulas containing Y involve a cross-sectional area, 2D formulas containing Y_s involve a width.
• \( D \) – Bending stiffness of graphene
• \( B \) – Bending stiffness of a CNT
• \( \text{vdW} \) – Van der Waals
• \( \phi \) – Interatomic potential function
• \( \text{DFTB} \) – Density-functional-based tight-binding
• \( \theta \) – Bending angle
• \( \kappa \) – Curvature
• \( E \) – Energy
• \( M \) – Bending moment
• \( H \) – Enthalpy