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NUMERICAL SIMULATION AND MODELING OF CARBON NANOTUBES

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2005

Numerical Simulation and Modeling of Carbon Nanotubes

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SUMMARY

The discovery of carbon nanotubes has triggered a significant amount of interest. Since then, much research has been done on these new forms of carbon because of its exceptional physical properties, which has been revealed in various theoretical and experimental studies. The focus of this thesis is on the mechanical and thermal properties of carbon nanotubes.

A detailed study of the mechanical and thermal properties of carbon nanotubes is described in this thesis by employing molecular dynamics simulation. In this research, a parallelized molecular dynamics computer program based on MPI library and FORTRAN 77 computer language is developed to assist in the simulation of the carbon nanotubes. Throughout the whole of this research, Brenner's "second-generation" empirical potential is used to describe the many-body short-range interatomic interactions, while the long-range non-bonded interactions is described using van der Waals forces characterized by Lennard-Jones (12,6) potential.

Buckling behaviour of single-walled and multi-walled carbon nanotubes is investigated. Results indicate that there exists an optimum diameter for single-walled carbon nanotubes at which the buckling load is at maximum value. The buckling load increases rapidly as the diameter of the single-walled carbon nanotube increases until the buckling load reaches a maximum value at a corresponding optimum diameter. The effect of the number of layers in a multi-walled carbon nanotube is also studied. When a multi-

SUMMARY

walled carbon nanotube buckles, the $C - C$ bonds change from sp^2 to sp^3 configuration resulting in an increase in strain energy.

The elastic and plastic deformation from single to four-walled carbon nanotubes under axial tension is also studied. The MD simulations show that the Stone–Wales defect leads to the plastic deformation. Fracture will first take place at the outermost layer of a multi-walled carbon nanotube, followed by the next inner layer and so forth until the whole multi-walled carbon nanotube breaks. The stress – strain relationship is obtained to describe the elastic and plastic behaviours of carbon nanotubes. The simulated results show that the mechanical properties are sensitive to the number of layers in the carbon nanotubes. Additionally, it is found that the effect of geometrical size on the mechanical properties of carbon nanotubes is insignificant.

Molecular dynamics simulations are also performed on carbon nanotube bundles subjected to axial load. The results demonstrate a significant improvement of the mechanical properties of non-twisted carbon nanotube bundles. On the contrary, twisted carbon nanotube bundles suffer degradation in their mechanical properties. This is mainly due to the geometry of the twisted carbon nanotube bundles as well as the strong intertube repulsive force present.

Another study involved the thermal stability of single-walled and multi-walled carbon nanotubes. The molecular dynamics simulation incorporating Berendsen thermostat is carried out. The results show that single-walled carbon nanotubes are thermally more stable than multi-walled carbon nanotubes. Carbon nanotubes with smaller diameters and shorter lengths are also able to withstand higher thermal loads.

LIST OF KEYWORDS

Carbon nanotubes; carbon nanotube bundles; twisted carbon nanotube bundles; single-wall carbon nanotubes, multi-wall carbon nanotubes; mechanical properties; thermal properties; Young's modulus; buckling load; failure load; critical strain; axial compression, axial tension; molecular dynamics; nanoscale simulations; analytical many-body potential function; second-generation REBO potential energy function; Lennard-Jones potential; Berendsen thermostat scheme.

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LIST OF SYMBOLS

(n, m)	Pair of integers that represent the lattice point which determines a possible structure of carbon nanotube
a_{c-c}	Nearest neighbour distance between two carbon atoms
a_0	Lattice constant
$\mathbf{a}_{1,2}$	Unit cell base vectors of a graphene sheet
b	Actual bond length between two atoms defining the bond
b_0	Equilibrium distance for the bond
b^{DH}	Torsional angle for $C - C$ bonds
$\bar{b}_{ij}$	Empirical bond order function between atoms i and j
$c_{n,k}$	Cubic spline coefficients
C_L	Circumferential length of carbon nanotube
$\mathbf{C}_h$	Chiral vector joining two equivalent points on a graphene sheet
d_{in}	Distance of interlayer separation in graphite and multi-walled carbon nanotube, or distance of intertube separation in carbon nanotube bundles
d_R	Greatest common divisor of n and m
d_t	Diameter of carbon nanotube
E	Energy of a particle
E_K	Kinetic energy

LIST OF SYMBOLS

E_{Ks}	Kinetic energy associated to the additional degree of freedom s in Nosé-Hoover thermostat
E^{LJ}	Lennard Jones (12,6) potential
E^{REBO}	Chemical binding energy
E_s	Strain energy of carbon nanotube
E_{tot}	Total potential energy due to short range chemical binding energy and long range van der Waals interactions
E_{vdw}	Energy due to van der Waals interactions
E_Y	Young's modulus
f^c	Switching function
F_{rep}	Repulsive force
F_{vdw}	van der Waals force
$\mathbf{F}_i$	Force of particle i
$\mathbf{F}_t$	Total force
h_t	Thickness of carbon nanotube
$\hbar$	Plank's constant divided by 2π
$\mathcal{H}$	Hamiltonian operator
I	Moment of inertia
k_b	Force constant for the bond
k_B	Boltzmann constant
k_θ	Force constant for the bond angle
l_t	Length of carbon nanotube
m	Mass of a single particle
n_p	Periodicity of angle due to rotation of bond

LIST OF SYMBOLS

N	Total number of atoms
N^C	Total number of carbon atoms
N_d	Number density of atoms
N_f	Number of degrees of freedom
N_H	Number of hexagons per unit cell in a carbon nanotube
P	Axial load
P_{cr}	Critical buckling load due to compressive force
P_{fl}	Critical failure load due to tensile force
p_s	Conjugate momentum of additional degree of freedom s in Nosé-Hoover thermostat
$\mathbf{p}_i$	Momentum of atom i
q_i	Partial charge on atom i
q_n	Quantum numbers
Q	Effective charge in screened Colomb potential
r_{cut}	Cutoff radius
r_{ij}	Scalar distance between the centres of atoms i and j
r_t	Radius of carbon nanotube
r_{verlet}	Verlet neighbour list cutoff radius
$\mathbf{r}_i$	Positional vector of particle i
$\ddot{\mathbf{r}}_i$	Acceleration of particle i
s	Additional degree of freedom in Nosé-Hoover thermostat
S	Cross-sectional area of carbon nanotube
t	Time
T	Temperature

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T_{bath}	Temperature of bath in Berendsen thermostat
T_L	Length of the translation vector $\mathbf{T}$
$\mathbf{T}$	Translation vector on a 1D carbon nanotube and is normal to vector $\mathbf{C}_h$
V_0	Equilibrium volume of carbon nanotube
V_n	Force constant for the rotation angle
V^A	Attractive energy
V^R	Repulsive energy
α_i	Constants used in Gear's predictor-corrector algorithm
ε	Strain
ε_{cr}	Critical strain
ξ	Well depth parameter
γ	Phase of the rotation angle
λ	Scaling factor in Berendsen thermostat
ω	Actual torsion angle
κ	Thermal conductivity
θ	The actual angle between the atoms defining the angle
θ_0	Equilibrium angle for the bond angle
θ_{ch}	Chiral angle which is defined as the angle between the vectors $\mathbf{C}_h$ and a ,
θ_{he}	Helical angle of twisted carbon nanotube bundle
θ_t	Twist angle in carbon nanotube bundle
ν	Mean rate in Andersen thermostat
ν_c	Interatomic collision frequency
ν_t	Poisson ratio of carbon nanotube
$\mathcal{U}$	Total potential energy

LIST OF SYMBOLS

$\mathcal{U}_b$	Potential energy due to bonded interactions
$\mathcal{U}_{nb}$	Potential energy due to non-bonded interactions
$\mathcal{U}_s$	Potential energy associated to the additional degree of freedom s in Nosé-Hoover thermostat
σ^e	Equilibrium distance between two atoms
σ	Stress
σ_{cr}	Critical stress
τ	Coupling parameter in Berendsen thermostat
Ψ	Wave function

TABLE OF ABBREVIATIONS

CNT	Carbon nanotube
MD	Molecular dynamics
MWCNT	Multi-walled carbon nanotube
REBO	Reactive empirical bond order
SWCNT	Single-walled carbon nanotube

PUBLICATIONS

The following publications are related to the present research:

1. Liew, K. M., Wong, C. H., He, X. Q., Tan, M. J., and Meguid, S. A., “*Nanomechanics of single and multiwalled carbon nanotubes*,” Physical Review B **69**, pp. 115429, 2004.
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CHAPTER 1

INTRODUCTION

In recent years, carbon nanotubes (CNTs) have attracted much attention because of their enormous potential and performance. CNTs are believed to possess many of the desirable mechanical properties of carbon fibres like high strength and good elastic properties. Moreover, CNTs also have other desirable properties such as their flexibility, extensibility, ability to withstand compression without fracture, and the ability to withstand cross-sectional and twisting distortions. They show excellent strength characteristics under extension and molecular dynamics (MD) simulations indicate that an elongation of several percent without fracture might be possible [1]. In addition to superb tensile properties, CNTs also show remarkable flexibility, and can be bent around small circles or about sharp bends without breaking [2]. Unlike carbon fibres that fracture easily under compression, CNTs form kink-like ridges under compression, and these kink-like ridges can relax elastically when the stress is released [3].

Due to the increasing popularity of CNTs and their excellent properties, it is important to understand the properties and behaviour of CNTs further. This thesis concentrates on

the mechanical and thermal properties of CNTs and the simulations are carried out with the use of MD methodology.

This chapter begins off with a brief discussion on the carbon atom and the three hybridisations and various structural forms it can assume. The history of fullerenes and CNTs are briefly discussed followed by the various structures and applications of the CNTs. The objectives of this research are detailed next. Finally the chapter concludes with the scope of this thesis.

1.1 Carbon

Carbon is the sixth element of the periodic table and is listed at the top of Group IV. Each carbon atom has six electrons which occupy $1s^2$, $2s^2$, and $2p^2$ atomic orbitals. Electrons are often described as being in orbitals around an atom. The state of an electron is described by the wave function Ψ .

An orbital, or more correctly a mathematical function, $4\pi r^2 \Psi^2$, describes the region in which an electron may be found in an atom. An orbital can hold up to two electrons.

The two most common orbitals are the s - and p -type orbitals which can be described by using quantum numbers q_n . The orbitals for the electrons in carbon, and their quantum numbers are given in Fig. 1.1. The nucleus of the carbon atom resides at the centre of the x -, y -, z -coordinate.

Fig. 1.1. Electrons of carbon atom in (a) $1s$, (b) $2s$, (c) $2p_z$, (d) $2p_x$, and (e) $2p_y$ orbitals.

In carbon, there are three possible hybridisations: sp , sp^2 , and sp^3 , while other Group IV elements such as silicon and germanium exhibit primarily sp^3 hybridisation. In sp hybridisation, a linear combination of the $2s$ orbital and one of the $2p$ orbitals of a carbon atom, for example $2p_z$, is formed. In sp^2 hybridisation, the $2s$ orbital and two $2p$ orbitals, for example $2p_x$ and $2p_y$, are hybridized. Carbon atoms with the sp^2 hybridisation configuration form a zigzag chain with an angle of 120° . In sp^3 hybridisation, the $2s$ orbital and all the three $2p$ orbitals are mixed together to form the hybridisation. Figure 1.2 depicts the schematic presentation of the three hybridisations.

Fig. 1.2. Schematic presentation of (a) sp , (b) sp^2 , and (c) sp^3 bonding hybridisation. The unshaded lobes represents strong bonds and the shaded lobes represents weak bonds.

1.2 Carbon materials

Carbon-based materials, clusters, and molecules are unique in many ways. One distinction relates to the many forms that carbon-based materials can assume. The reason why carbon assumes to many structural forms is that a carbon atom can form several distinct types of hybridisation configurations. The rest of the section briefly discusses the most important forms that have thus far been identified.

1.2.1 Graphite

The ideal crystal structure of graphite consists of layers in which the carbon atoms are arranged in an open honeycomb network, with consecutive layers of atoms on top of one another. Graphite has a sp^2 hybridisation configuration. The nearest neighbour distance between two carbon atoms a_{c-c} in a graphite is $1.421\text{\AA}$ and the lattice constant a_o is $2.462\text{\AA}$. The strong $C - C$ bond contributes to the high strength along the basal plane of graphite. However, the weak interplanar bonding of van der Waals forces makes graphite fragile normal to its plane. And hence graphite is generally considered as a soft material

due to its ability to slide along the planes. Nevertheless, graphite has a high in-plane Young's modulus E , of 1.02 TPa [4].

Graphite is a thermodynamically stable bulk phase of carbon up to very high temperatures under normal ranges of pressure. However, it is now well-known that this is not the case when there are only a finite number of carbon atoms. Preliminary experiments performed by Rohlfing *et al.* [5], which served as a precursor to the fullerene discovery [6], suggested that when the number of carbon atoms is less than a few hundreds, the structures formed correspond to the linear chains, rings, and closed shells. The latter is known as the fullerene with an even number of carbon atoms and nominal sp^2 bonding between adjacent atoms.

1.2.2 Graphite whiskers

A graphite whisker is a graphitic material formed by rolling a graphene sheet up into a scroll [7]. Graphite whiskers, which can be up to **30** mm long and 1 to 5 mm in diameter, exhibit great crystalline perfection, high electrical conductivity, and high elastic modulus. Since their discovery [7], graphite whiskers have provided the benchmark against which the performance of carbon fibres **is** compared. The growth of graphite whiskers has many similarities to the growth of carbon nanotubes.

1.2.3 Carbon fibres

Carbon fibres represent an important class of graphite-related materials. Despite the many precursors that can be used to synthesise carbon fibres, each having different cross-sectional morphologies. The preferred orientation of the graphene planes is parallel to the

fibre axis, thereby accounting for the high mechanical strength of carbon fibres [8]. Typical diameters for carbon fibres are about $10\mu\text{m}$, and their lengths can be very long. These fibres are often woven into bundles called tows and are then wound up as a continuous yarn on a spool. The remarkable high strength (approximately 6 GPa [8]) and high Young's modulus E , (approximately 800 GPa [8]) of carbon fibres make it one of the most sought after material for commercial purposes. Figure 1.3 shows a Scanning Electron Microscope (SEM) image of a carbon nanofibre synthesized by Mukhopadhyay *et al.* [9] using catalytic chemical vapor deposition technique.

Fig. 1.3. A SEM image of a carbon nanofibre synthesized by catalytic chemical vapor deposition [9].

1.2.4 Diamond

The diamond structure is probably the most thoroughly investigated of all crystallographic structures of carbon. An ideal diamond structure has the characteristic property that every carbon atom is surrounded by four other carbon atoms at the corners of a regular tetrahedron with a cube edge length of $a_c = 3.567 \text{ \AA}$, and this carbon atom is bonded to these neighbours by strong covalent sp^3 bonds. In the diamond structure, the nearest $C-C$ distance a_{c-c} is $1.544 \text{ \AA}$, nearly 10% larger than in graphite. Young's modulus E_Y of diamond is 0.11 TPa [10].

1.3 Discovery of fullerenes

The discovery of fullerenes provided exciting insights into how architectures built from pure carbon units can result in new symmetries and structures with remarkable physical properties. Fullerenes consist of all-carbon molecules with a closed cage structure formed by twelve five-member rings and any number of six-member rings as shown in Fig. 1.4. Speculation on the existence of fullerenes began when it was recognised that the bond angle of 120° between two sp^2 hybridised carbon atoms is equal to the 120° internal angles formed in hexagons. Therefore hexagons can easily be formed with bonds of the sp^2 carbon atom. Hexagons, together with pentagons which have internal angles of 108° , can then be assembled into polyhedral surfaces with each carbon having three nearest neighbours. Mathematically, it has been shown that twelve pentagons are required for a closed surface constructed of only five- and six-sided rings, with no restrictions on the number of hexagons.

The field of fullerenes began and was advanced by a series of discoveries. In 1985, a study at Rice University [6] was undertaken to examine the structure of small carbon clusters of 2 – 20 and 40 – 300 atoms. The experiment led to the significant discovery of an unusually stable and large even numbered molecule C_{60} . In 1990, a team led by Wolfgang Kratschmer at the Max Planck Institute for Nuclear Physics in Heidelberg, Germany, caught the chemical world off-guard when the team announced that bulk quantities of fullerenes can be produced with a single-step process by passing an electric current between two touching graphite electrodes surrounded by helium [11]. The heat produced vapourises the graphite, and fullerenes form as the gaseous carbon cools.

Fig. 1.4. A Fullerene structure.

In the early 1990s, Sumio Iijima, a microscopist at the NEC Corporation laboratories in Tsukuba, Japan, inspired by the fullerenes mass-production study by Kratschmer, tinkered with Kratschmer's experimental conditions. Instead of bringing the two electrodes together, Iijima kept them a short distance apart, so that sparks passed between them. To his surprise, he found hollow needles formed on the end of a graphite electrode. These hollow needles, just a few nanometres long and made of pure carbon, were CNTs [12].

1.4 Carbon nanotubes

What Iijima first observed were CNTs made up of a series of cylinders nestling one inside the other like Russian dolls – referred to as multi-walled carbon nanotubes (MWCNTs).

These MWCNTs range in length from a few angstroms to several micrometers, and in outer diameter from about 2.5 nm to 30 nm. Figure 1.5 shows the Transmission Electron Microscope (TEM) image of MWCNT. The TEM image shows individual layers making up the concentric tubes.

Fig. 1.5. Some of Iijima's first TEM images of MWCNTs [12].

In 1993, Iijima and Toshinari Ichihashi of NEC Corporation laboratories [13], and Donald Bethune and colleagues of the IBM Almaden Research Centre [14] in California independently reported the synthesis of single-walled carbon nanotubes (SWCNTs). An early image of a SWCNT sample is shown in Fig. 1.6. SWCNTs, which often bundle up via Van der Waals forces into larger assemblies of nanoropes, have very small diameters (typically 0.7 nm to 1.6 nm [13,14]), and are curled and looped rather than straight.

Fig. 1.6. Typical TEM image of SWCNTs [15].

Following their initial, ground-breaking work, Donald Bethune and his colleagues, in collaboration with workers from the California Institute of Technology and the Virginia Polytechnic Institute and State University, have carried out a series of studies on the production of SWCNTs using a variety of ‘catalysts’. In one such studies [16], they showed that the inclusion of sulphur to the cobalt in the anode, resulted in a much wider diameters ranging from 1 nm to 6 nm. It was subsequently shown that bismuth and lead could similarly promote the formation of large diameter nanotubes [15].

A year later in 1997, Journet and colleagues demonstrated that high yields of SWCNTs could be made possible with electric arc-discharge [17]. Although their method was similar to the original technique of Bethune and colleagues, the reactor had a slightly different geometry and the catalyst used was a nickel/yttrium mixture. The highest concentration of SWCNTs was found to form in a ‘collar’ around the cathodic deposit, with diameters around 1.4 nm. Overall, the yield of SWCNTs was estimated to be 70 – 90%.

However, in 1993, Subramoney of Du Pont in Willington, Delaware, together with researchers from SRI International, reported the production of CNTs in a rather different approach; instead of using iron group metal catalysts, they carried out electric arc-discharge using gadolinium-impregnated electrodes [18], and collected the soot which

consisted SWCNTs growing out of particles of gadolinium carbide. The SWCNTs were typically much shorter than those produced by the iron group metal catalysts, but had a similar range of diameters. Subsequent works by Saito and Zhou have shown that radial SWCNTs can be produced on a variety of other metals including lanthanum [19] and yttrium [20] respectively.

Other than producing SWCNTs with electric arc-discharge, SWCNTs can also be synthesised using a purely catalytic method [21]. For this method, the catalyst contained molybdenum particles supported on alumina and was placed inside a tube furnace through which carbon monoxide was passed at a temperature of 1200°C. The growth mechanism for the catalytically formed nanotubes involves the initial formation of a single layer cap, followed by the growth of this cap away from the catalytic particles, leaving a nanotube in its wake. The catalytically produced SWCNTs generally had small particles attached to one end. Also, the diameter of each SWCNTs appeared to be determined by that of the associated catalytic particle (approximately 1 – 5 nm). Finally, the catalytically formed SWCNTs were generally isolated rather than grouped into bundles as with the SWCNTs synthesized by electric arc-discharge method.

1.4.1 Purification

In many of the synthesis methods that have been reported, SWCNTs are invariably accompanied by large amounts of amorphous carbon, nanoparticles coated with carbon and other graphitic debris. As such, purification is needed to isolate the SWCNTs from other contaminants. Basically, purification techniques can be divided into mainly structure selective and size selective separations. The former technique will separate the

SWCNTs from the impurities, while the latter will produce a more uniform diameter d_t and size geometry of the SWCNTs.

Various methods have been proposed to purify SWCNTs. One such method, though inefficient, is the use of a cationic surfactant to suspend the nanotubes and accompanying material in solution, and then trapping of the CNTs on a membrane filter [22]. An improved method made use of ultrasonication [23], in which the impurities are separated from the SWCNTs by ultrasonic vibrations. Successful separation of the impurities is highly dependable on the surfactant, solvent and reagent used.

Another method involves a step-by-step process to remove the impurities [24,25]. First, the raw soot was refluxed in distilled water for 12 hours, before filtering and drying. This treatment removed some of the graphitic particles and amorphous carbon. After washing the SWCNTs with toluene, the soot was heated at 470 °C in air to oxidise more of the amorphous carbon and removes the carbon coatings from the nanoparticles. Lastly, the soot was treated with concentrated hydrochloric acid to dissolve the nanoparticles.

Ferromagnetic particles used for the catalytic growth of SWCNTs can be removed by the magnetic purification technique [26]. The SWCNT suspension is mixed with inorganic nanoparticles in an ultrasonic bath, which causes ferromagnetic particles to be mechanically removed from their graphitic shells. High purity SWCNT is then obtained after a chemical treatment.

SWCNTs have also been purified using size exclusion chromatography [27]. This method is used to separate small quantities of SWCNTs into fractions with small length and diameter distribution by running the SWCNTs over a column of porous material. The pore size will hence control the size distribution.

1.5 Structure of single-walled carbon nanotubes

An interesting and essential fact about the structure of a CNT is the orientation of the hexagon carbon ring in the honeycomb lattice relative to the CNT axis. The direction of the hexagon carbon ring in the honeycomb lattice can be taken almost arbitrarily, without any distortion of the hexagons except for the distortion due to the curvature of the CNT. This fact provides many possible structures for CNTs, even though the basic shape of the CNT wall is a cylinder. If we neglect the two ends of a CNT and focus on the large aspect ratio of the cylinder (i.e., length/diameter which can be as large as $10^4 - 10^5$), these CNTs can be considered as one-dimensional nanostructures.

A CNT is essentially a sheet of graphene (single layer of graphite) rolled into a cylinder with ends closed off by hemispherical caps of various shapes. These end caps have significant impact on the chemical and transport properties of CNTs. However, they are generally neglected in the studies of mechanical properties of CNTs. The reason is that CNTs have huge aspect ratios of length versus diameter, such that, unless detailed mechanical behaviour at the ends is concerned, they can be considered as open cylinders of graphene sheets.

It is possible to roll up graphene sheets into cylinders in different ways. Two of these are “non-helical” in the sense that the graphite lattices at the top and bottom of the CNT are parallel. These arrangements are termed “armchair” and “zig-zag”. The names of “armchair” and “zig-zag” arise from the shape of the cross-sectional ring at the edge of the CNTs (see Fig. 1.7). In Fig. 1.7, the cross-sectional rings at the edge of the CNT models are shown in dark blue. The cross-sectional rings in Fig. 1.7(a) and Fig. 1.7(b) resemble an “armchair” and a “zigzag” pattern respectively. In the armchair structure, two C – C bonds on opposite sides of each hexagon are perpendicular to the CNT axis;

whereas in the zig-zag arrangement, these bonds are parallel to the CNT axis. CNTs exhibiting armchair or zig-zag arrangement are typically known as achiral since their mirror image has an identical structure to the original one.

(a) (10,10) “armchair” CNT model

(b) (10,0) “zigzag” CNT model

Fig. 1.7. Models of a (a) (10,10) “armchair” CNT and, a (b) (10,0) “zigzag” CNT.

In all other arrangements, the C – C bonds lie at an angle to the CNT axis, introducing helicity to the structure, and are generally known as chiral since they exhibit a spiral symmetry whose mirror image cannot be superposed to the original one.

Theoretical calculations indicate that the electronic properties for a SWCNT will vary as a function of its diameter d_t and chirality θ_{ch} [28 – 30], and that the SWCNT may behave as a semiconductor or metallic conductor, giving rise to the possibility of novel applications in solid state chemistry and to the development of nano-scale electronic devices.

1.5.1 Chiral vector

The simplest form of specifying the structure of a SWCNT is in terms of the chiral vector $\mathbf{C}_h$ joining two equivalent points on the graphene sheet, labelled according to the notation of Dresselhaus *et al.* [10,31] as shown in Fig. 1.8. Each pair of integers (n,m) represents the lattice point which determines a possible CNT structure. Therefore, the chiral vector $\mathbf{C}_h$ can be expressed as

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m), \tag{1.1}$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit cell base vectors of the graphene sheet, and $n \geq m$. An armchair CNT corresponds to the case of $n = m$, while a zig-zag CNT corresponds to the case of $m=0$. All other (n, m) chiral vectors correspond to chiral CNTs.

Fig. 1.8. Graphene layer with atoms labeled using (n, m) in a hexagonal lattice.

The CNT diameter dt is given by C_L/π , in which C_L represents the circumferential length of the carbon nanotube and can be computed by

$$C_L = |\mathbf{C}_h| = a\sqrt{n^2 + nm + m^2}, \quad (1.2)$$

where

$$a = \sqrt{3}a_{c-c}, \quad (1.3)$$

and a_{c-c} denotes the nearest C–C distance which is 1.421 Å.

The chiral angle θ_{ch} is defined as the angle between the vectors $\mathbf{C}_h$ and $\mathbf{a}_1$, with values of θ_{ch} in the range $0 \leq |\theta_{ch}| \leq 30^\circ$, because of the hexagonal symmetry of the honeycomb lattice. The expression for the chiral angle θ_{ch} is

$$\theta_{ch} = \sin^{-1} \frac{\sqrt{3}m}{2\sqrt{n^2 + nm + m^2}}. \quad (1.4)$$

1.5.2 Translation vector

A unit cell of CNT is shown in Fig. 1.9 as a rectangle defined by the chiral vector $\mathbf{C}_h$ and translation vector $\mathbf{T}$. The translation vector $\mathbf{T}$ is the unit vector of a 1D CNT and is normal to the chiral vector $\mathbf{C}_h$. The vector $\mathbf{T}$ then extends from the origin O to the first lattice point B in the honeycomb lattice.

Hence, the translation vector $\mathbf{T}$ shown as $\overrightarrow{OB}$ in Fig 1.9 can be expressed in terms of the unit cell base vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ as

$$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 \equiv (t_1, t_2), \quad (1.5)$$

where t_1 and t_2 are integers and are expressed as

$$t_1 = \frac{2m+n}{d_R}, \quad t_2 = -\frac{2n+m}{d_R} \quad (1.6)$$

The value of d_R is defined using the greatest common divisor (gcd) of n and m . If $d = \gcd(n, m)$ then

$$d_R = \begin{cases} d & \text{if } (n-m) \text{ is not a multiple of } 3d \\ 3d & \text{if } (n-m) \text{ is a multiple of } 3d \end{cases} \quad (1.7)$$

In the case of Fig. 1.9, $\mathbf{C}_h = (6, 2)$, hence $d_R = d = 2$ and $\mathbf{T} = (5, -7)$. The length of the translation vector $\mathbf{T}$ is given by

$$T_L = |\mathbf{T}| = \frac{\sqrt{3}C_L}{d_R}, \quad (1.8)$$

where the circumferential length C_L of the CNT is given by Eqn. (1.2).

The unit cell of the 1D CNT is defined by the rectangle $OAB'B$ as shown in Fig. 1.9. The number of hexagons per unit cell N_H can be obtained as a function of n and m as

$$N_H = \frac{2(n^2 + nm + m^2)}{d_R} \quad (1.9)$$

And since each hexagon in a unit cell contains two carbon atoms, there are therefore $2N_H$ carbon atoms in each unit cell of a CNT.

Fig. 1.9. A unit cell of carbon nanotube as a rectangle defined by the chiral vector $\mathbf{C}_h$ and translation vector $\mathbf{T}$.

1.6 Structure of multi-walled carbon nanotubes

MWCNTs consist of several concentrically arranged SWCNTs within one another. Hence, the structures of MWCNTs are generally similar to the SWCNTs, with the difference that they contain two or more concentric layers. These layers are weakly bonded by van der Waals forces.

Since the distance separating graphite layers is $3.34 \text{ \AA}$, the concentric layers in a MWCNT could also be separated by the same distance. Then successive concentric layers

would differ in circumference by $2\pi \times 3.34 \approx 21 \text{ \AA}$. However, this is not possible for zig-zag MWCNTs because $21 \text{ \AA}$ is not a precise multiple of $24.6 \text{ \AA}$, i.e., the width of one hexagon. As such, the closest approximation of the interlayer distance between successive concentric layers for zig-zag MWCNTs is $3.52 \text{ \AA}$.

Fig. 1.10. Perspective view of a modelled $(5n,5n)$ MWCNT where $n = 3$ and $n = 2$ for the outer and inner layer respectively.

Armchair MWCNTs, however, will have an interlayer distance between successive concentric layers of $3.4 \text{ \AA}$. An example of armchair MWCNT is $(5n,5n)$ where $n = 1, 2, 3, 4, 5, 6$, etc. Figure 1.10 shows a modeled $(5n,5n)$ MWCNT with $n = 3$ for the outer layer and $n = 2$ for the inner layer.

1.7 Applications of carbon nanotubes

It is reasonable to assume that since they possess excellent properties, CNTs will find many commercial applications. Several experimental demonstrations have already pointed to the possible uses for CNTs. The remarkable electronic properties of CNTs qualify them for use as quantum wires and in heterojunction devices. The Delft group

[32] has built the first single-molecule field-effect transistor based on a single semiconductor SWCNT.

Preliminary results also showed that CNTs can be used in filler-based applications in polymer composites due to its high strength and elasticity. Some recent studies indicated that strong interfaces can be formed between epoxy resins and CNTs with interface strengths of few hundred megapascals reported [33]. The biggest advantage of CNTs in polymer composites is during the fabrication process, since they do not break down during processing as carbon fibres do so easily.

CNTs have been demonstrated to be used as nanoprobes, which could be used in a variety of applications such as high-resolution imaging, nanolithography, nanoelectrodes, drug delivery, sensors, and field emitters. There have been experimental demonstrations in which an individual MWCNT and SWCNT is attached to the end of an AFM or STM tip for imaging [34] and lithography [35]. The advantage of the CNT tip is its slenderness, providing the possibility to image features that are almost impossible to probe when using larger, blunter etched silicon or metal tips. Furthermore, due to the high elasticity of CNTs, the tips do not suffer from fracture on contact with the substrate as any impact will cause buckling in the CNT structure which is reversible in the elastic region.

The small dimensions of CNTs make them useful as field emitters. Field emission characteristics of CNT tips have been studied, and field emission has been shown from partially aligned CNT films [36,37]. Applications include flat panel displays [38], lamps [39], gas discharge tubes providing surge protection [40], and x-ray generators [41].

CNTs have also been considered for energy production and storage. For instance, the properties of catalytically grown CNTs have been found desirable for high-power

electrochemical capacitors [42]. Temperature programmed desorption spectroscopy has exhibited that hydrogen will condense inside SWCNTs under conditions that do not induce absorption in traditional porous carbon material [43]. It has been reported that CNTs' hydrogen uptake is high and can be compared to the best presently available material (metal hydrides). Hence high energy storage efficiency can be obtained if an optimum diameter of the CNT can be established for the best intake and release of hydrogen.

CNTs have also shown that they can be used as carbon nanothermometers [44] suitable for use in a wide variety of microenvironments. With the greatest liquid range of any metal and a low vapour pressure even at high temperature, liquid gallium inside a CNT varies linearly and reproducibly in the temperature range 50 – 500°C.

1.8 Objectives

The objectives of this research are the study of mechanical and thermal properties of CNTs through computational modeling. The objective can be divided into four main sections. The first section is to carry out a literature review on the current advances in CNTs and the work done by other researchers.

Secondly, the concepts of MD simulations and various analytical potential functions are studied. It is then followed by writing a MD simulations code in FORTRAN 77 to extract the properties of CNTs. The program should be modular so that future amendments and additions are easy.

Thirdly, the mechanical properties, in particular Young's modulus E_y , of CNTs are investigated. The elastic and plastic behaviour of CNTs are explored too. Additionally,

the behaviour of CNT bundles subjected to axial tensile and compressive load are also investigated.

Finally, the thermal properties of CNTs are studied. The investigation includes the response of various CNTs when subjected to different thermal loads to determine their thermal stability.

1.9 Scope

The introductory concepts of carbon atoms and the various forms of configuration they can assume are presented in Chapter 1. In addition, the various polymorphisms of carbon are also briefly discussed, along with a literature review of fullerenes prior to the introduction of carbon nanotubes and their structures. The applications of CNTs are also discussed. The objectives of this research and the organisation of this report are also detailed in Chapter 1.

Chapter 2 is devoted to the discussion of quantum mechanical calculations, molecular mechanics, and MD simulations. Chapter 2 also sees the introduction of analytical empirical potential function. Also, various finite difference methods are discussed together with techniques to reduce computation time.

Chapter 3 details the mechanical properties of CNTs of various forms. In particular, the buckling loads of CNTs are investigated. The buckling behaviour of carbon nanotubes is also studied.

Chapter 4 discusses the mechanical properties of CNT bundles of various sizes. The buckling behaviour of these CNT bundles is also analysed.

Chapter 5 concentrates on the thermal properties of carbon nanotubes. The effect of heat treatment on carbon nanotubes is determined. Various methods to implement constant-temperature MD simulations are also discussed.

The final chapter concludes this report by detailing the progress of this research work and goals that are set for future work.

CHAPTER 2

NANOSCALE SIMULATION METHODS

MD refers to the situation where the motion of atoms or molecules is treated in approximate finite difference equations of Newtonian mechanics. MD can be broadly divided into two categories: quantum mechanical calculations and molecular mechanics. Quantum mechanical calculations make use of Schrodinger's equation, within the Born-Oppenheimer approximation, to obtain the solution either using semi-empirical or *ab initio* method, with the latter being a more accurate method. Due to its slow computation time, empirical analytical potential functions provide the advantage of faster computation time using simplified mathematical expressions, which model interatomic forces arising from the quantum mechanical interaction of electrons and nuclei. Molecular mechanics, on the other hand, makes use of classical mechanics to determine the interactions within a system (atoms in a molecule) contributed by different processes. Even simple functions such as the Hooke's law, adequately describe these contributions.

This chapter briefly discusses the quantum mechanical calculations, molecular mechanics, while analytical potential functions is discussed in more detail. The basic concept of MD is also studied. Finite difference methods as well as techniques to reduce computation time are also discussed.

2.1 Quantum mechanical calculations for many-body systems

The ideal method for simulating many-body systems is of course to solve for the exact quantum mechanical state and its evolution through time as determined by Schrodinger's equation. Thus the many-body Schrodinger's equation reads

$$\left\{ \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_i} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) + V_i(\mathbf{r}_i, t) \right] + \sum_{i \neq k} V_{ik}(r_i, r_k) \right\} \Psi = i\hbar \frac{\partial \Psi}{\partial t}. \quad (2.1)$$

Equation (2.1) describes a system of N atoms. m_i is the mass of atom i moving through space given by a position vector $\mathbf{r}_i = x_i\mathbf{i} + y_i\mathbf{j} + z_i\mathbf{k}$ and time t under the influence of an external potential field $V_i(\mathbf{r}_i, t)$. $V_{ik}(r_i, r_k)$ represents the interaction potential between two atoms i and k . Ψ is the wave function and is dependent on the $3N$ coordinates of all atoms and time such that $\Psi = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, t) = \Psi(x_1, y_1, z_1, \dots, x_k, y_k, z_k, \dots, x_N, y_N, z_N, t)$. $\hbar$ represents the Planck's constant divided by 2π and i is the square root of -1 .

If the external potential field $V_i(\mathbf{r}_i, t)$ is time independent, then the wave function Ψ can be expressed as $\Psi(\mathbf{r}_i, t) = \psi(\mathbf{r}_i)T(t)$ where $\psi(\mathbf{r}_i)$ is the spatial part and $T(t)$ is the time part. This allows the time-dependent many-body Schrodinger's equation in Eqn. (2.1) to be computed in a time-independent form

$$\left\{ \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_i} \nabla^2 + V_i(\mathbf{r}_i) \right] + \sum_{i \neq k} V_{ik}(r_i, r_k) \right\} \psi(r_i) = E \psi(r_i), \quad (2.2)$$

where E is the energy of the atom and

$$\nabla^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}. \quad (2.3)$$

It is also usual to represent the left-hand side of Eqn. (2.2) with $\mathcal{H}\psi$, where $\mathcal{H}$ is the Hamiltonian operator

$$\mathcal{H} = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_i} \nabla^2 + V_i(\mathbf{r}_i) \right] + \sum_{i \neq k} V_{ik}(r_i, r_k), \quad (2.4)$$

and the many-body Schrodinger's equation is reduced to

$$\mathcal{H}\psi = E\psi. \quad (2.5)$$

Schrodinger's equation for molecular systems can only be solved approximately using either *ab initio* or semi-empirical methods. Semi-empirical methods use parameters that compensate for neglecting some of the time consuming mathematical terms in Schrodinger's equation, whereas *ab initio* methods include all such terms. The parameters used by semi-empirical methods can be derived from experimental measurements or by performing *ab initio* calculations on model systems.

In recent years, several accurate quantum MD schemes have computed the forces between atoms at each time step with quantum mechanical calculations within the Born-Oppenheimer approximation. One such scheme is the Car-Parrinello method [45] that

describes the electronic states and atomic forces using *ab initio* density functional method.

Ideally, one would like to make use of quantum mechanical calculations to study the many-body system as it provides accurate results. Unfortunately, problems arise when a large number of atoms are involved or long simulation times are computationally too expensive to be treated with quantum MD. For instance, although in semi-empirical schemes, some of the electrons are ignored, a large number of particles must still be considered and the calculations remain time-consuming.

2.2 Molecular mechanics

Many of the problems in molecular modelling are too large to be considered by quantum mechanics. In molecular mechanics (also known as force field methods), the electronic motions are ignored, and only the energy of the system as a function of the nuclear positions is calculated. As such, molecular mechanics is suitable for performing calculations with a large number of atoms.

In some cases, molecular mechanics can provide answers that are even as accurate as the highest-level quantum mechanical calculations, in a fraction of the computation time. However, molecular mechanics cannot provide properties that depend upon the electronic distribution in a molecule.

Molecular mechanics is based upon a simple model of the interactions within a system with contributions from processes such as the stretching of bonds, the opening and closing of angles, and the rotations about single bonds. Currently a wide variety of force field functions are available [46 – 49]. These force field functions are expected to work

well in the regimes of physical parameters in which they were constructed in the first place. However, these force fields are all empirical, that is, there is no 'correct' form for a force field.

The functional forms employed in molecular mechanics force fields are often a compromise between accuracy and computational efficiency. The most accurate functional form may be computationally inefficient, while a computationally efficient functional form may often be lacking in accuracy. In addition, no universal force field function works for all materials in all scenarios.

Despite all these, force field functions generally include two kinds of interactions that contribute to the total potential energy, $\mathcal{U}$, of the ensemble of atoms – non-bonded and bonded. The potential energy $\mathcal{U}_{nb}$ due to non-bonded interactions is expressed as

$$\mathcal{U}_{nb}(\mathbf{r}^N) = \sum_i \sum_j \frac{q_i q_j}{r_{ij}} + \sum_i \sum_j \xi_{ij} \left[\left(\frac{\sigma_{ij}^e}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}^e}{r_{ij}} \right)^6 \right], \quad (2.6)$$

where the first term is a Coulomb potential for electrostatic interactions and the second term is the Lennard-Jones pair-wise potential function [50,51] for van der Waals interactions. $\mathcal{U}_{nb}(\mathbf{r}^N)$ represents the potential energy due to non-bonded interactions, which is a function of positions ($\mathbf{r}$) of N atoms. ξ denotes the well depth parameter, σ^e is the collision diameter, q is the partial charge on atom i , and r_{ij} is the scalar distance between the centres of atoms i and j where

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|. \quad (2.7)$$

The potential energy $\mathcal{U}_b$ due to bonded interactions is expressed as

$$\mathcal{U}_b(\mathbf{r}^N) = \sum_{\text{bonds}} \frac{k_b}{2} (b_i - b_0)^2 + \sum_{\text{angles}} \frac{k_\theta}{2} (\theta_i - \theta_0)^2 + \sum_{\text{torsions}} \frac{V_n}{2} [1 + \cos(n_p \omega - \gamma)], \quad (2.8)$$

where $\mathcal{U}_b(\mathbf{r}^N)$ represents the potential energy due to bonded interactions, which is a function of positions ($\mathbf{r}$) of N atoms. The first term on the right-hand side of Eqn. (2.8) defines the bonding energy in a harmonic form where k_b is the force constant for the bond, b is the actual bond length between two atoms defining the bond, and b_0 is the equilibrium distance for the bond. The second term on the right defines the angle energy which imitates how the energy of a bond angle changes when it is distorted away from its equilibrium position, where k_θ is the force constant for the angle, θ is the actual angle between the atoms defining the angle, and θ_0 is the equilibrium angle. The third term describes how the energy of a molecule changes as it undergoes a rotation about one of its bonds, where n_p is the periodicity of the angle, γ is the phase of the angle, ω is the actual torsion angle, and V_n is the force constant.

2.3 Analytical many-body potential functions

Even though quantum mechanical calculations can be approximated with semi-empirical and *ab initio* methods, with the latter not subject to errors that can arise from assumed functional forms, clear disadvantages exist in suitability only for small number of atoms and long simulation times.

One solution to this problem is to use analytical potential energy functions (also known as empirical or classical potentials), which are simplified mathematical expressions that model interatomic forces arising from the quantum mechanical interaction of electrons and nuclei.

Probably, the earliest work using analytical potential energy functions in atomistic simulations was in 1936 when the hydrogen exchange reaction was modelled [52]. Subsequent works utilising analytical potential energy functions include simulations of condensed-phase phenomena such as ion-solid collisions [53] and liquid dynamics [54] using continuous interatomic forces. To be effective, the analytical potential energy expressions must be simple enough for fast calculations on large systems, flexible in accommodating a wide range of fitting data, and able to accurately reproduce an appropriate fitting database [55].

In this work, a second-generation reactive empirical bond order (REBO) potential energy expression [56], is used to model the potential energy in the studies of carbon nanotubes. This analytical potential function is described in detail below.

2.3.1 Second-generation REBO potential energy function

Carbon is unique among the elements that it forms unusually strong bonds in both sp^2 and sp^3 configurations. A successful empirical potential for carbon must hence accurately model structures in both of these bonding configurations as well as transition structures in between. The second-generation reactive empirical bond order (REBO) potential energy expression [56], hereafter simply known as Brenner REBO potential energy, is an improved version of an earlier work [57] that allows for bond breaking and forming with appropriate changes in atomic hybridisation. The Brenner REBO potential contains improved analytic functions and an extended database. These lead to a better description of bond energies, lengths, force constants, elastic properties, interstitial defect energies, and surface energies. The Brenner REBO potential energy has already been used to model a variety of applications in carbon nanotubes [58 – 65].

Following the intramolecular potential energy derived by Abell from chemical pseudopotential theory [66], the chemical binding energy can be expressed as a sum over nearest neighbours in the form

$$E_{ij}^{REBO} = V^R(r_{ij}) - \bar{b}_{ij} V^A(r_{ij}), \quad (2.9)$$

where $V^R(r)$ and $V^A(r)$ are repulsive and attractive pair terms and are expressed respectively as

$$V^R(r) = f^c(r) \left(1 + \frac{Q}{r} \right) A e^{-\alpha r}, \quad (2.10)$$

and

$$V^A(r) = f^c(r) \sum_{n=1,3} B_n e^{-\beta_n r}, \quad (2.11)$$

where r denotes the scalar distance between atoms, Q is the effective charge in the screened Coulomb potential, and the function $f^c(r)$ limits the range of the interactions, which assumes a value of one for nearest neighbours and zero for all other interatomic distances. The value of $f^c(r)$ is defined by a switching function of the form

$$f_{ij}^c(r) = \begin{cases} 1 & r < D_{ij}^{\min} \\ \left[1 + \cos \left(\frac{r - D_{ij}^{\min}}{D_{ij}^{\max} - D_{ij}^{\min}} \right) \right] / 2 & D_{ij}^{\min} < r < D_{ij}^{\max} \\ 0 & r > D_{ij}^{\max} \end{cases}, \quad (2.12)$$

where $D_{ij}^{\max} - D_{ij}^{\min}$ is the distance over which the function goes from one to zero. Parameter values for C – C pair terms for Eqn. (2.10) to Eqn. (2.12) are given in Table 2.1 below [56].

Table 2.1. Parameter values for C – C pair terms for Eqn. (2.10) to Eqn. (2.12) [56].

$B_1 = 12388.79197798 \text{ eV}$	$\beta_1 = 4.7204523127 \text{ \AA}^{-1}$	$Q = 0.3134602960833 \text{ \AA}$
$B_2 = 17.56740646509 \text{ eV}$	$\beta_2 = 1.4332132499 \text{ \AA}^{-1}$	$A = 10953.544162170 \text{ eV}$
$B_3 = 30.71493208065 \text{ eV}$	$\beta_3 = 1.3826912506 \text{ \AA}^{-1}$	$\alpha = 4.7465390606595 \text{ \AA}^{-1}$
$D_{\min} = 1.7$	$D_{\max} = 2.0$	

The empirical bond order function between atoms i and j in Eqn. (2.9) is given by

$$\bar{b}_{ij} = \frac{b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi}}{2} + b_{ij}^{\pi}, \quad (2.13)$$

where values for the functions $b_{ij}^{\sigma-\pi}$ and $b_{ji}^{\sigma-\pi}$ depend on the local coordination and bond angles for atoms i and j , respectively. The function b_{ji}^{π} can be further written as

$$b_{ij}^{\pi} = \pi_{ij}^{\text{RC}} + b_{ij}^{\text{DH}}. \quad (2.14)$$

The value of the first term π_{ij}^{RC} is dependent upon whether a bond between atoms i and j has radical character and is part of the conjugated system. The value of the second term b_{ij}^{DH} depends on the torsional angle for C – C bonds. It is worthwhile to note that for bonds that are not part of the conjugated system, and for planar double bonds, both terms are equal to zero. Following earlier effort [57], the function $b_{ij}^{\sigma-\pi}$ for CNTs in Eqn. (2.13) is given as

$$b_{ij}^{\sigma-\pi} = \left\{ 1 + \sum_{k(\neq i,j)} f_{ik}^c(r_{ik}) G_C[\cos(\theta_{ijk})] \right\}^{-1/2} \quad (2.15)$$

An identical expression is given for $b_{ji}^{\sigma-\pi}$ by swapping the i - and j -indices. In Eqn. (2.15), the angular function $G_C[\cos(\theta)]$ modulates the contribution that each nearest neighbour makes to the empirical bond order according to the cosine of the angle of the bonds between atoms i and k and atoms i and j . However, according to Brenner *et al.* [56], the values for $G_C[\cos(\theta)]$ determined for θ equal to 90° and 60° are too large for under-coordinated carbon atoms. In order to allow for both over-coordinated and under-coordinated atoms, a second spline function $\gamma_C[\cos(\theta)]$ was determined for angles less than 109.47° that was coupled to the original angular function $G_C[\cos(\theta)]$. Therefore the revised angular function between 109.47° and 0° for carbon atom i is given by

$$g_C = G_C[\cos(\theta_{ijk})] + Q(N_i^t) \{ \gamma_C[\cos(\theta_{ijk})] - G_C[\cos(\theta_{ijk})] \}, \quad (2.16)$$

where the function Q is defined by

$$Q(N_i^t) = \begin{cases} 1 & N_i^t \leq 3.2 \\ \{1 + \cos[2\pi(N_i^t - 3.2)]\}/2 & 3.2 < N_i^t \leq 3.7, \\ 0 & N_i^t > 3.7 \end{cases} \quad (2.17)$$

and since CNTs consist of pure carbon,

$$N_i^t = N_i^C, \quad (2.18)$$

$$N_i^C = \sum_{k(\neq i, j)}^{\text{carbon atoms}} f_{ik}^c(r_{ik}). \quad (2.19)$$

The term π_{ij}^{RC} in Eqn. (2.14) represents the influence of radical energies and π -bond conjugation on the bond energies. This is necessary because it accurately describes radical structures and it accounts for non-local conjugation effects such as those that govern the different properties of the $C-C$ bonds in graphite. This function is taken as a tricubic spline F :

$$\pi_{ij}^{RC} = F_{ij}(N_i^t, N_j^t, N_{ij}^{\text{conj}}), \quad (2.20)$$

which is a function of the number of neighbours atoms i and j have, as defined in Eqn. (2.18), and N_{ij}^{conj} , which determines if a bond is part of a conjugated system, is given by

$$N_{ij}^{\text{conj}} = 1 + \left[\sum_{k(\neq i, j)}^{\text{carbon}} f_{ik}^c(r_{ik}) F(X_{ik}) \right]^2 + \left[\sum_{l(\neq i, j)}^{\text{carbon}} f_{jl}^c(r_{jl}) F(X_{jl}) \right]^2, \quad (2.21)$$

where

$$F(X_{ik}) = \begin{cases} 1 & X_{ik} \leq 2 \\ [1 + \cos(X_{ik} - 2)]/2 & 2 < X_{ik} \leq 3, \\ 0 & X_{ik} > 3 \end{cases} \quad (2.22)$$

and

$$X_{ik} = N_k^t - f_{ik}^c(r_{ik}). \quad (2.23)$$

The term b_{ij}^{DH} in Eqn. (2.14) that describes the torsion angle for $C-C$ bonds is expressed as

$$b_{ij}^{\text{DH}} = T_{ij}(N_i^t, N_j^t, N_{ij}^{\text{conj}}) \left[\sum_{k(\neq i, j)} \sum_{l(\neq i, j)} (1 - \cos^2 \Theta_{ijkl}) f_{ik}^c(r_{ik}) f_{jl}^c(r_{jl}) \right], \quad (2.24)$$

where

$$\Theta_{ijkl} = \hat{\mathbf{e}}_{jik} \cdot \hat{\mathbf{e}}_{ijl}. \quad (2.25)$$

The function $T_{ij}(N_i^t, N_j^t, N_{ij}^{\text{conj}})$ is a tricubic spline, and $\hat{\mathbf{e}}_{jik}$ and $\hat{\mathbf{e}}_{ijl}$ are unit vectors in the direction of the cross products $\mathbf{R}_{ji} \times \mathbf{R}_{ik}$ and $\mathbf{R}_{ij} \times \mathbf{R}_{jl}$ respectively, where $\mathbf{R}$ are vectors connecting the subscripted atoms.

2.3.2 Lennard-Jones potential

Another important aspect in modelling CNT systems, which is missing in the Brenner REBO potential, is the non-bonding van der Waals interactions between atoms. In this work, the van der Waals potential in the form of Lennard-Jones (12,6) model is used:

$$E^{LJ} = 4\xi \left[\left(\frac{\sigma_{ij}^e}{r} \right)^{12} - \left(\frac{\sigma_{ij}^e}{r} \right)^6 \right], \quad (2.26)$$

where ξ denotes the well depth parameter and is 4.55 meV [67] and σ^e is equilibrium distance between two atoms.

Since the short-range interactions are characterized by the Brenner REBO potential, and the long-range non-bonding van der Waals interactions are characterized by the Lennard-Jones (12,6) potential, the combined expression for the total energy can be written as

$$E_{tot} = \sum_i \sum_{j>i} (E_{ij}^{REBO} + E_{vdw}). \quad (2.27)$$

As E_{vdw} is the contribution from the Lennard-Jones (12,6) potential and is only non-zero after the short-range Brenner REBO potential goes to zero, therefore E_{vdw} can be evaluated as [61]

$$E_{vdw} = \begin{cases} 0 & r_{ij} \leq r'_s \\ c_{3,k} (r_{ij} - r_k)^3 + c_{2,k} (r_{ij} - r_k)^2 & r'_s \leq r_{ij} \leq r'_m, \\ E^{LJ}(r_{ij}) & r'_m \leq r_{ij} \leq r'_b \end{cases} \quad (2.28)$$

where $c_{n,k}$ are cubic spline coefficients. In the case of CNT systems, $r'_s = D_{max} = 2.0$, since anything below 2.0 Å will be considered as short-range interaction as shown in Eqn. (2.12). r'_m and r'_b are 3.2 Å and 10.0 Å respectively.

A computer code based on FORTRAN 77 has been written that uses the Brenner REBO potential and the Lennard-Jones(12,6) model for van der Waals potential to model CNTs up to a few thousand atoms in size (please see Section 2.5 for description of the compute code). The Brenner REBO potential and the Lennard-Jones (12,6) model for van der Waals potential are then used in MD to compute the trajectories of atoms as discussed in Section 2.4.

2.4 Molecular dynamics

The essence of MD is to numerically solve the N-body problem of classical mechanics. MD simulations are in many respects similar to real experiments. When we perform an experiment, we prepare a sample of the material that we wish to study. We then connect this sample to a measuring instrument and measure the property of interest over a time period. If the measurements are subjected to statistical noise, then if more experiments are performed, the more accurate the measurements will be.

In MD simulation, successive configurations of the system are generated by integrating Newton's laws of motion. The result is a trajectory that specifies how the positions and velocities of the atoms in a molecule vary with time.

In the Newtonian interpretation of dynamics, the translational motion of a spherical particle i is caused by a force $\mathbf{F}_i$ exerted by some external agent. The trajectory and the applied force are embodied in Newton's second law

$$\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i, \quad (2.29)$$

where m_i is the mass of particle i which is independent of position, velocity and time.

The acceleration $\ddot{\mathbf{r}}_i$ of particle i is given by

$$\ddot{\mathbf{r}}_i = \frac{d^2 \mathbf{r}_i}{dt^2}. \quad (2.30)$$

Here $\mathbf{r}_i$ is a positional vector and t is time. If no external force acts on particle i , then Eqn. (2.30) reduces to

$$\ddot{\mathbf{r}}_i = \text{const.} \quad (2.31)$$

That is, a particle continues to move in a straight line at a constant velocity until a force acts on it, following Newton's first law. Newton's third law can also be obtained by considering an isolated system which contains atom 1 and 2. Since there is no external forces, the total force is zero

$$\mathbf{F}_t = 0. \quad (2.32)$$

Hence any force exerted by atom 1 on atom 2 must be balanced by a force exerted by atom 2 on 1

$$\mathbf{F}_t = \mathbf{F}_1 + \mathbf{F}_2 = 0. \quad (2.33)$$

And therefore,

$$\mathbf{F}_1 = -\mathbf{F}_2. \quad (2.34)$$

Although the forces and positions change with time, the functional form of Newton's second law is time independent. As a result, it is expected to have some function of positions and velocities whose value is constant in time; this function is called the Hamiltonian $\mathcal{H}$,

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = \text{const}, \quad (2.35)$$

where the momentum $\mathbf{p}_i$ of atom i is expressed in terms of velocity by

$$\mathbf{p}_i = m\dot{\mathbf{r}}_i. \quad (2.36)$$

In an isolated system, the total energy $\mathcal{E}$ is the addition of kinetic and potential energies of N atoms. If the total energy is identified as Hamiltonian, then $\mathcal{H}$ takes the form

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{2m} \sum_i \mathbf{p}_i^2 + \mathcal{U}(\mathbf{r}^N) = \mathcal{E}, \quad (2.37)$$

where $\mathcal{U}$ is the potential energy due to interatomic interactions. To obtain equations of motion, the total time derivative of Eqn. (2.37) yields a general result

$$\frac{d\mathcal{H}}{dt} = \sum_i \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \sum_i \frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i = 0, \quad (2.38)$$

after removing $\partial \mathcal{H} / \partial t$ from the equation since the Hamiltonian $\mathcal{H}$ has no explicit time dependence as in Eqn. (2.37). Taking the total time derivative of the isolated-system Hamiltonian in Eqn. (2.37) results in

$$\frac{d\mathcal{H}}{dt} = \frac{1}{m} \sum_i \mathbf{p}_i \cdot \dot{\mathbf{p}}_i + \sum_i \frac{\partial \mathcal{U}}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i = 0. \quad (2.39)$$

Comparing the first term on the right-hand side for both Eqn. (2.38) and (2.39), we obtain

$$\frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m} = \dot{\mathbf{r}}_i, \quad (2.40)$$

and comparing the second term on the right-hand side for both Eqn. (2.38) and (2.39),

$$\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = \frac{\partial \mathcal{U}}{\partial \mathbf{r}_i}. \quad (2.41)$$

Substituting Eqn. (2.40) into Eqn. (2.38) gives

$$\sum_i \left(\mathbf{p}_i + \frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \right) \cdot \dot{\mathbf{r}}_i = 0. \quad (2.42)$$

Since the velocities are all independent of one another, Eqn. (2.42) can be satisfied only if, for each atom i ,

$$\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -\dot{\mathbf{p}}_i. \quad (2.43)$$

Equations (2.40) and (2.43) are Hamilton's equations of motion. If we take the time derivative of Eqn. (2.36), it will yield

$$\dot{\mathbf{p}}_i = m\ddot{\mathbf{r}}_i, \quad (2.44)$$

and hence substituting Eqn. (2.44) into Eqn. (2.43) will result

$$\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -m\ddot{\mathbf{r}}_i. \quad (2.45)$$

Since $\partial \mathcal{H} / \partial \mathbf{r}_i = \partial \mathcal{U} / \partial \mathbf{r}_i$ according to Eqn. (2.41), then using Eqn. (2.45) to compare with Newton's first law in Eqn. (2.29) yields

$$\mathbf{F} = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} = -\frac{\partial \mathcal{U}}{\partial \mathbf{r}_i} \quad (2.46)$$

From the above, it can be seen that from the Newtonian view, motion is a response to an applied force, but from the Hamiltonian view, forces do not appear explicitly instead motion occurs in such a way to preserve the Hamiltonian function.

2.4.1 Integrating equations of motion

The Newtonian equations of motions, such as Eqn. (2.29) and Eqn. (2.30), in MD are approximated using finite-difference methods. The general idea is to determine the atomic positions, velocities, etc. at a later time $t + \Delta t$, to a sufficient degree of accuracy based on the positions, velocities, and other dynamic information at current time t . Of the vast number of finite-difference methods available, the Verlet's algorithm [68] and Gear's predictor-corrector algorithm [69] are most widely used in MD simulation. The Verlet's algorithm makes use of positions and velocities from previously calculated steps, while the Gear's predictor-corrector algorithm estimates positions and velocities for future

The following will discuss the two methods in further detail.

2.4.1.1 Verlet's algorithm

The Verlet's algorithm [68] is recognised as the simplest finite-difference method and has been widely used in MD. The algorithm is a combination of two Taylor series, first of which is the Taylor series for position, from time t to a later time $t + \Delta t$

$$r(t + \Delta t) = r(t) + \dot{r}(t)\Delta t + \frac{1}{2}\ddot{r}(t)\Delta t^2 + \frac{1}{3!}\mathbf{r}_i^{(iii)}(t)\Delta t^3 + O(\Delta t^4), \quad (2.47)$$

and the second Taylor series from time t backward to $t - \Delta t$

$$r(t - \Delta t) = r(t) - \dot{r}(t)\Delta t + \frac{1}{2}\ddot{r}(t)\Delta t^2 - \frac{1}{3!}\mathbf{r}_i^{(iii)}(t)\Delta t^3 + O(\Delta t^4). \quad (2.48)$$

Summing Eqn. (2.47) and Eqn. (2.48) and eliminating all odd-order terms leave

$$r(t + \Delta t) + r(t - \Delta t) = 2r(t) + \ddot{r}(t)\Delta t^2 + O(\Delta t^4), \quad (2.49)$$

or

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \ddot{r}(t)\Delta t^2 + O(\Delta t^4). \quad (2.50)$$

Equation (2.50) is the Verlet's algorithm for positions. And although it does not contain any third-order derivatives, it is a third-order equation since it has a local truncation error that varies as $(\Delta t)^4$. The third term on the right hand side of Eqn. (2.50) represents the acceleration and can be obtained from the interatomic forces and Newton's second law.

This method is time-reversible and has good energy conservation properties. Furthermore, it has low memory storage, as velocities $\dot{r}(t)$ are not explicitly involved. However, using the first-order central difference estimator, the velocities of the atoms can be estimated as

$$\dot{r}(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t} \quad (2.51)$$

After computing the new positions, the positions at $t - \Delta t$ are replaced by the current positions, while the new positions become the current positions. Hence, the Verlet's

algorithm is a two-step method, because it first estimates $r(t + \Delta t)$ from the current position $r(t)$ and the previous position $r(t - \Delta t)$. Therefore, initial positions $r(0)$ and velocities $\dot{r}(0)$ are not sufficient to begin a calculation.

The velocities $\dot{r}(t)$ do not explicitly appear in Eqn. (2.50). Hence, improvements to the Verlet's algorithm method, namely the Verlet-leapfrog [70] and velocity Verlet [71] algorithms which explicitly involve the velocity $\dot{r}(t)$ in the time evolution of the atomic coordinates has since been developed.

2.4.1.2 Gear's predictor-corrector algorithm

Another common finite-difference method used in MD is the Gear's predictor-corrector algorithm [69]. In this work, the Gear's fifth-order predictor-corrector algorithm is employed to evaluate the interatomic forces. The following describes the Gear's predictor-corrector algorithm in further detail.

Rahman [54] first introduced predictor-corrector algorithms that are often taken from a collection of methods devised by Gear [69] into MD. The basic idea behind the predictor-corrector algorithms is to use information about the position and its first n derivatives to arrive at a prediction for the position and its first n derivatives at time $t + \Delta t$, where the n number of derivatives, depending on the order of the predictor-corrector algorithm. The predicted forces and accelerations are then "corrected" to the match the observed accelerations.

A Gear's fifth order predictor-corrector algorithm consists of three main steps: prediction, evaluation, and correction. It starts by first predicting the atomic positions $\mathbf{r}_i$ at time $t + \Delta t$ using a fifth-order Taylor series based on positions and their derivatives at

time t . Therefore, the derivatives $\dot{\mathbf{r}}_i$, $\ddot{\mathbf{r}}_i$, $\mathbf{r}_i^{(iii)}$, $\mathbf{r}_i^{(iv)}$, and $\mathbf{r}_i^{(v)}$ are necessary for each step and are also predicted at time $t + \Delta t$ by using Taylor expansion at t :

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \dot{\mathbf{r}}_i(t)\Delta t + \frac{\ddot{\mathbf{r}}_i(t)(\Delta t)^2}{2!} + \frac{\mathbf{r}_i^{(iii)}(t)(\Delta t)^3}{3!} + \frac{\mathbf{r}_i^{(iv)}(t)(\Delta t)^4}{4!} + \frac{\mathbf{r}_i^{(v)}(t)(\Delta t)^5}{5!}, \quad (2.52)$$

$$\dot{\mathbf{r}}_i(t + \Delta t) = \dot{\mathbf{r}}_i(t) + \ddot{\mathbf{r}}_i(t)\Delta t + \frac{\mathbf{r}_i^{(iii)}(t)(\Delta t)^2}{2!} + \frac{\mathbf{r}_i^{(iv)}(t)(\Delta t)^3}{3!} + \frac{\mathbf{r}_i^{(v)}(t)(\Delta t)^4}{4!}, \quad (2.53)$$

$$\ddot{\mathbf{r}}_i(t + \Delta t) = \ddot{\mathbf{r}}_i(t) + \mathbf{r}_i^{(iii)}(t)\Delta t + \frac{\mathbf{r}_i^{(iv)}(t)(\Delta t)^2}{2!} + \frac{\mathbf{r}_i^{(v)}(t)(\Delta t)^3}{3!}, \quad (2.54)$$

$$\mathbf{r}_i^{(iii)}(t + \Delta t) = \mathbf{r}_i^{(iii)}(t) + \mathbf{r}_i^{(iv)}(t)\Delta t + \frac{\mathbf{r}_i^{(v)}(t)(\Delta t)^2}{2!}, \quad (2.55)$$

$$\mathbf{r}_i^{(iv)}(t + \Delta t) = \mathbf{r}_i^{(iv)}(t) + \mathbf{r}_i^{(v)}(t)\Delta t, \quad (2.56)$$

$$\mathbf{r}_i^{(v)}(t + \Delta t) = \mathbf{r}_i^{(v)}(t). \quad (2.57)$$

The next step involves computing the interatomic force $\mathbf{F}_i$ on each atom at time $t + \Delta t$, applying the predicted positions. For continuous potential energy functions $\mathcal{U}(\mathbf{r}_{ij})$ that act between atoms i and j , the force $\mathbf{F}_i$ is given by

$$\mathbf{F}_i = - \sum_{j \neq i} \frac{\partial \mathcal{U}(\mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} \hat{\mathbf{r}}_{ij}, \quad (2.58)$$

where $\hat{\mathbf{r}}_{ij}$ is the unit vector in the $\mathbf{r}_{ij}$ -direction.

The final step corrects the predicted positions and their derivatives using the difference between the predicted acceleration and the evaluated acceleration. With the

force $\mathbf{F}_i$ evaluated using Eqn. (2.58) and making use of Newton's second law in Eqn. (2.29), the evaluated acceleration can be computed. Hence,

$$\Delta \ddot{\mathbf{r}}_i = [\ddot{\mathbf{r}}_i(t + \Delta t) - \ddot{\mathbf{r}}_i^p(t + \Delta t)] . \quad (2.59)$$

This difference can then be used to correct all predicted positions and their derivatives, thus,

$$\mathbf{r}_i = \mathbf{r}_i^p + \alpha_0 \Delta \mathbf{R2} , \quad (2.60)$$

$$\dot{\mathbf{r}}_i \Delta t = \dot{\mathbf{r}}_i^p \Delta t + \alpha_1 \Delta \mathbf{R2} , \quad (2.61)$$

$$\ddot{\mathbf{r}}_i \frac{(\Delta t)^2}{2!} = \ddot{\mathbf{r}}_i^p \frac{(\Delta t)^2}{2!} + \alpha_2 \Delta \mathbf{R2} , \quad (2.62)$$

$$\mathbf{r}_i^{(iii)} \frac{(\Delta t)^3}{3!} = \mathbf{r}_i^{(iii)p} \frac{(\Delta t)^3}{3!} + \alpha_3 \Delta \mathbf{R2} , \quad (2.63)$$

$$\mathbf{r}_i^{(iv)} \frac{(\Delta t)^4}{4!} = \mathbf{r}_i^{(iv)p} \frac{(\Delta t)^4}{4!} + \alpha_4 \Delta \mathbf{R2} , \quad (2.64)$$

$$\mathbf{r}_i^{(v)} \frac{(\Delta t)^5}{5!} = \mathbf{r}_i^{(v)p} \frac{(\Delta t)^5}{5!} + \alpha_5 \Delta \mathbf{R2} , \quad (2.65)$$

where

$$\Delta \mathbf{R2} = \Delta \ddot{\mathbf{r}}_i \frac{(\Delta t)^2}{2!} . \quad (2.66)$$

The parameters α_i are constants that give numerical stability to the algorithm. The α_i depends on the order of the differential equations to be solved and on the order of the

Taylor series predictor. Values of α_i for third-, fourth-, and fifth-order predictors are given in Table 2.2 [72].

Although, the Gear's predictor-corrector algorithm is time-irreversible and is by far the most time-consuming calculation in MD simulation due to more calculations on the accelerations involved, it produces a more accurate integration.

Table 2.2. Values of α_i parameters in Gear's predictor-corrector algorithm [72].

α_i	Third-order	Fourth-order	Fifth-order
α_0	$\frac{1}{16}$	$\frac{19}{120}$	$\frac{3}{16}$
α_1	$\frac{5}{6}$	$\frac{3}{4}$	$\frac{251}{360}$
α_2	1	1	1
α_3	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{11}{18}$
α_4	–	$\frac{1}{12}$	$\frac{1}{6}$
α_5	–	–	$\frac{1}{60}$

2.4.2 Verlet neighbour list

The most time-consuming part of a MD simulation is the calculation of energies or forces. In principle, the energies and forces are computed between every pair of atoms in the system, i.e., the contribution to the force on an atom i by all its neighbours has to be considered. If the interactions are not truncated, for a system with N atoms, there are $N(N-1)/2$ pair interactions. It is therefore advantageous to exclude atoms beyond a certain distance r_{cut} from the calculation. It is, hence, a common choice to use a truncated version of Eqn. (2.26)

$$E_{vdw} = \begin{cases} 4\xi \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] & r \leq r_{cut} , \\ 0 & r > r_{cut} \end{cases} \quad (2.67)$$

where r_{cut} is typically 2.5σ .

Since the force equals to zero for any $r_{ij} > r_{cut}$, evaluating distances r_{ij} that are greater than r_{cut} “wastes” computational time. This “wasted” time can, however, be saved by using a book-keeping scheme devised by Verlet [68], commonly referred to as the Verlet neighbour list. The Verlet neighbour list is used in this work to improve computational time.

In the Verlet neighbour list method, a second cutoff radius $r_{verlet} > r_{cut}$ is introduced as shown in Fig. 2.1. For each atom i , a neighbour list of neighbouring atoms that lie within a distance r_{verlet} is maintained. Therefore, the neighbour list identifies those atoms that contribute to the force on atom i . In subsequent calculation of the interactions, only those atoms in the list have to be considered. In the calculation, if the maximum displacement of the atoms is less than $r_{diff} = r_{verlet} - r_{cut}$, then the neighbour list remains unchanged. However, as soon as one of the atoms is displaced more than r_{diff} , the neighbour list has to be updated.

There are no fixed rules that determine how much larger r_{verlet} should be than r_{cut} . Clearly there is a trade-off between the two cutoffs and the frequency at which the neighbour list must be updated, with smaller r_{diff} contributing to more frequent updates of the neighbour list. However, if r_{diff} is too large, then more neighbouring atoms are involved in the computation of force on atom i , thereby decreasing the efficiency.

Fig. 2.1. A graphical depiction of the cutoff distances in a Verlet neighbour list.

Table 2.3 shows the CPU time taken for a MD simulation of a single-wall (8,8) carbon nanotube with 640 atoms. The potential computed include the Brenner REBO potential as well as the non-bonding van der Waals forces. The simulation is carried out for 1000 time steps, with r_{cut} held fixed at 2.50, and r_{verlet} varied. From the results in Table 2.3, it can be seen that employing the Verlet neighbour list will greatly enhance the computational time by as much as 5 times. In addition, as r_{diff} becomes larger, there are less updates of the neighbour list. A r_{verlet} of 2.80 will yield the least computational time

even compared to a larger r_{verlet} . This is because larger r_{verlet} has a larger neighbour list that decreases the efficiency.

Table 2.3. Time saving using a Verlet neighbour list.

r_{cut}	r_{verlet}	r_{diff}	Number of updates	CPU time (mins)
No list	—	—	—	15.80
2.5σ	2.6σ	0.1σ	8	2.98
2.5σ	2.70	0.20	4	2.83
2.5σ	2.8σ	0.3σ	3	2.80
2.5σ	3.0σ	0.5σ	1	2.93
2.5σ	3.20	0.7σ	1	2.95
2.5σ	3.50	1.00	0	3.08

2.5 Parallel computing

The CNT systems can contain as many as 20,000 atoms and it will therefore be computationally very inefficient if the simulation is to be run on a single processor. A solution to this problem is to implement parallelization technique to the computer codes. The goal of the parallel implementation is that each processor sends or receives information of atoms to the appropriate processor, such that a complete neighbour list for the evaluation of interatomic potential can be obtained. At the same time, computational efficiency should be maintained in the optimum sense.

Parallelization was achieved using the classical domain decomposition technique and the Message Passing Interface (MPI) [73,74] was used for the implementation of the parallel code, employing the well-known linked-cell method [70]. MPI is a programming technique used widely on parallel computers, particularly on Scalable Parallel Computers with distributed memory. Since its inception in 1994, MPI has become widely accepted and used. It not only provides good portability across different machines, but also being able to run transparently on heterogeneous systems. MPI was also carefully designed so as to avoid a requirement for large amount of re-coding to be done on pre-existing serial computer codes.

In the linked cell approach, the simulation domain is decomposed into equally sized cells. A linked list is then associated to each cell and stores the atoms that are located in this cell. The overall set of cells forms a three-dimensional array, where each element contains the starting address of the respective linked list.

By combining the techniques of linked-cell method [70] and Verlet neighbour list, considerable speedup can be achieved. Table 2.4 gives the measured run times for one time step of a subroutine `PIBOND`, which computes Brenner REBO potential energy [56] between atoms on SGI 3000.

It can be observed that the introduction of MPI, making use of linked-cell and Verlet neighbour list approaches will yield a nearly linear speed up. Doubling the number of processors results in about halving of the execution time. In addition, the algorithm also scales perfectly. If the number of atoms is increased by a factor of two, but additionally the number of processors is also doubled, the same absolute execution times are obtained.

Table 2.4. Parallel execution times (in seconds) for one time step of subroutine PIBOND .

No. of atoms	Processors				
	1	2	4	8	16
8000	0.450	0.230	0.110	0.058	0.029
16000	0.900	0.450	0.230	0.120	0.060
32000	1.790	0.900	0.450	0.220	0.110

2.6 Molecular dynamics computer program

A parallelized MD computer program is written in FORTRAN 77 to carry out the MD simulations in this research work. The program is based on the translation of Brenner’s REBO potential energy into the computer codes, while the Newtonian equations of motions, are approximated using finite-difference methods using the Gear’s predictor-corrector algorithm. To enhance the computational time, the Verlet neighbour list [68] is incorporated into the computer codes. The whole program consists of a total of 41 subroutines and 4 functions.

The program is divided into two main stages: the initialization stage and the production stage. A flowchart depicting the flow of the program is shown in Fig. 2.2.

During the initialization stage when $t = 0$, all parameters are first defined and variables initialized. To incorporate the Verlet neighbour list method into the program, a variable defined as UPDATE which takes the value of numeral one or zero, is needed. The value of UPDATE is dependent on the maximum displacement of the atoms. If the maximum displacement is lesser than r_{diff} , then $UPDATE = 0$ and the neighbour list

remains unchanged. However, if it is greater than r_{diff} , then $UPDATE = 1$, and the neighbour list needs to be updated. The computer program then reads the coordinates of the CNT before computing the neighbour lists for both short and long-range interactions, and the constraints. After which, the long-range van der Waals potential, and short-range Brenner REBO potential are determined. The CNT model is then minimized using the conjugate gradient method before computing the initial acceleration for all atoms. After initialization, the program proceeds to the production stage.

At production stage, $t > 0$ and using the Gear's predictor-corrector algorithm, the coordinates of the atoms are first 'predicted' based on previous run or when $t = 0$. The program then determines if it is necessary to update the neighbour list for both the short and long-range interactions based on the value of $UPDATE$. The long and short-range potential are then computed, followed by minimizing the CNT model using the conjugate gradient method, which will be performed at every interval of 50 steps to reduce the computational time. Next, the coordinates of the atoms are 'corrected' based on the Gear's predictor-corrector algorithm. After that, the program will determine the maximum displacement of the atoms. If it is lesser than r_{diff} , $UPDATE$ will be set to numeral zero. However, if it is greater than r_{diff} , then $UPDATE$ will be set to numeral one. The final step is to save any desired data for analysis. This process will repeat for every time step until the defined total number of time steps has reached or the desired data has been collected.

Fig. 2.2. A flowchart depicting the flow of the MD computer program.

CHAPTER 3

MECHANICAL PROPERTIES OF CARBON NANOTUBES

In a graphite sheet, each carbon atom is strongly bonded to three other carbon atoms, however, the adjacent sheets are only weakly bound by van der Waals forces. This makes graphite very strong in directions planar to the graphite sheet, and very weak in directions perpendicular to the plane of the graphite sheet. A good example of a product of graphite sheet is the carbon fibre, which has already been widely used to strengthen a wide range of materials and composites. Therefore, the special and unique properties of CNTs mean that they could be the ultimate high-strength fibre. This chapter concentrates on the mechanical properties of various forms of CNTs. The elastic properties of CNTs such as Young's modulus E_y , critical buckling load P_{cr} , and critical strain ε_{cr} are determined from the MD simulations.

3.1 Elastic properties

The mechanical stiffness and strength of CNTs are expected to be excellent [3,75 – 77]. Several experimental and theoretical studies have been performed to quantify the strength of CNTs by determining their elastic properties [78 – 84,88 – 97]. Since knowledge of Young's modulus E_Y , which is a measure of elastic strength, is the first step towards the mechanical study of any material, various experimental studies have been carried out to determine Young's modulus E_Y of CNTs. Generally, experimental studies yield diverging results for the elastic properties of CNTs, with the values for Young's modulus E_Y higher than those predicted by most theoretical studies.

3.1.1 Experimental results

The first Young's modulus measurement came from Treacy *et al.* [78] who obtained a Young's modulus E_Y value ranging from about 0.4TPa to 4.15TPa, with an average Young's modulus E_Y value of 1.8TPa, using thermal vibration analysis of cantilevered MWCNTs. The MWCNTs were arranged vertically on a surface such that the CNTs were fixed at the bottom and free to move at the top. A transmission electron microscope (TEM) was then used to measure the thermal vibrations of the free ends. The authors also proposed a trend for higher Young's modulus E_Y for CNTs with smaller diameters.

Krishnan *et al.* [79] have also used the same approach by observing the CNTs free-standing room temperature vibrations in a TEM and reported an average value of Young's modulus E_Y for SWCNTs of 1.25 TPa. However, the diameters and lengths of samples of the CNTs used in the technique proposed by Treacy and Krishnan and their

respective co-workers are limited to those that do not result in neither too small nor too large thermally excited vibrations. This is necessary for reliable TEM detection.

Wong *et al.* [80] have, therefore, used a different technique by making use of an Atomic Force Microscope (AFM) to determine Young's modulus E_Y of CNTs. The structurally isolated MWCNTs were anchored at one end to molybdenum disulfide surfaces. The bending force was then measured against displacement along the unfixed lengths. These experiments revealed a Young's modulus E_Y of $1.28 \pm 0.59 \text{ TPa}$ with no dependence on CNT diameters d_t .

Fig. 3.1. An AFM image of a SWCNT suspending over a pore of alumina ultrafiltration membrane [81].

Young's modulus E_Y of CNTs can also be determined experimentally by depositing the CNTs on a well-polished alumina ultrafiltration membrane as proposed by Salvétat *et al.* [81], which is shown in Fig. 3.1. A CNT will occasionally span across pores present in the membrane, forming a suspended fixed-fixed beam configuration at the nanoscale. An atomic force microscope (AFM) was used to apply a load on the suspended CNT, resulting in a deflection dependent of the applied force. Young's modulus E_Y , which is

inversely proportional to the deflection, can then be determined and was found to be 0.81 ± 0.41 TPa.

In the work of Poncharal *et al.* [82], MWCNTs were attached to a fine gold wire, which was mounted on a small electrically insulated support so that a potential could be applied to it. The whole assembly was inserted in a custom-built specimen holder of a TEM. When a potential was applied to the wire, the CNTs became electrically charged and were attracted to a grounded counterelectrode due to electrostatic force. Hence, the application of a time dependent potential to the wire will result in a time dependent force on the CNTs. The CNTs were excited at their resonant frequency, which depends on the square root of Young's modulus E_Y , caused large-amplitude deflections as shown in Fig. 3.2. This method exhibited Young's modulus E_Y ranging from 0.1 to 0.73 TPa. It was also observed that Young's modulus E_Y was very large for CNT with diameters of less than $100 \text{ \AA}$ and decreased dramatically to lower values at about 0.1 TPa for CNTs with larger diameters. Rippling of the compressed side of the CNTs was proposed as the cause of this phenomenon.

Further insights into the mechanical properties of MWCNTs are provided by Yu *et al.* [83]. Each end of a MWCNT was attached onto the opposing tips of two AFM cantilever probes as depicted in Fig. 3.3. The CNT was then stretched until it broke. Young's modulus E_Y values extracted from the resulting stress-strain curves of the MWCNTs range from 0.27 to 0.95 TPa.

Fig. 3.2. CNT response to (a) the absence of potential with slight vibration due thermal effects; (b) resonant excitation of the fundamental mode of vibration; (c) resonant excitation of the second harmonic [82].

Fig. 3.3. Micrographs of (a) a MWCNT attached between two opposite AFM tips and (b) its amplification [83].

More recently, Demczyk *et al.* [84] deposited MWCNTs on a fabricated tensile testing device by dropping via a pipette from an ultrasonically dispersed solution of MWCNTs. A thin gold film was also deposited to adhere the CNTs to the device. An AFM was used to apply a force on the CNT and Young's modulus E_Y was determined to be 0.91 TPa.

Table 3.1. Young's modulus E_Y measurement using different methods.

Research Group	Young's Modulus E_Y (TPa)	Method
Treacy <i>et al.</i> [78]	0.4 ~ 4.15	TEM – thermally vibrating beam
Krishnan <i>et al.</i> [79]	1.25	TEM – thermally vibrating beam
Wong <i>et al.</i> [80]	1.28	AFM – one end fixed
Salvetat <i>et al.</i> [81]	0.81	AFM – both ends fixed
Poncharal <i>et al.</i> [82]	0.1 ~ 0.73	TEM – electrostatic deflection
Yu <i>et al.</i> [83]	0.27 ~ 0.95	Dual AFM cantilevers
Demczyk <i>et al.</i> [84]	0.91	TEM – direct tension

Despite the disparities in the experimentally determined Young's modulus E_Y , it is believed that Young's modulus E_Y is directly related to the chemical bonding of the carbon atoms in the CNTs. Hence, for CNTs with large diameters d_t , Young's modulus E_Y (as well as other mechanical properties), should essentially correspond to those of a flat graphite sheet. This is due to the degree of sp^2 hybridisation in the $C-C$ bonds in CNTs are almost similar to those of a flat graphite sheet. For comparison purposes, Young's modulus E_Y of a graphite sheet is 1.02TPa [4]. Table 3.1 summarises the

various experimentally determined Young's modulus by various researchers discussed above.

3.1.2 Theoretical and simulation results

Different simulation studies concerning Young's modulus E_Y and its dependence on the CNT diameters d_t and chiralities have also been reported [88 – 97]. The results are found to vary with the type of method and potentials used to describe the interatomic bonding. The classical mechanics definition for Young's modulus E_Y is often taken as the second derivative of strain energy with respect to axial strain

$$E_Y = \frac{1}{V_0} \left. \frac{\partial^2 E_s}{\partial \epsilon^2} \right|_{\epsilon=0}, \quad (3.1)$$

where V_0 is the equilibrium volume, E_s is the strain energy, and ϵ is the axial strain. In essence, a SWCNT is a hollow cylinder with its volume, V_0 given by $V_0 = 2\pi l_t r_t h_t$, where l_t is the length, r_t is the radius, and h_t is the thickness of the CNT shell.

In classical approximation, Young's modulus E_Y is not expected to vary much between a graphite sheet and a CNT because the atomic structure is not taken into account [85]. Although it is generally accepted that this classical approximation to be valid for large-diameter CNTs, classical approximation may not be valid for CNTs with small diameters because the atomic structure and bonding arrangement must be included in any realistic model.

The development of many-body interatomic potentials [57,86,87] has made MD simulations of large systems possible and efficiently, though less accurately. *Ab initio* methods based on density-functional theory are also used for simulating the bonding,

electronic structure and atomic arrangement. However, *ab initio* methods are computationally very intensive and expensive. Hence, they are not recommended for models with a large number of atoms. Semi-empirical methods such as the tight-binding method lies in between empirical and *ab initio* methods in accuracy, even though they are generally limited to smaller models.

Both *ab initio* and empirical potential-based methods have been used to determine the mechanical properties, in particular Young's modulus E_Y of CNTs. Investigations that make use of empirical pair potential models [3,88–92] normally neglect the changing nature of the chemical bonding as the curvature of the CNT's diameter d_t is changed. The obtained elastic properties are also independent of the CNTs' chiralities and diameters. For instance, Young's moduli E_Y , of 0.97 TPa for all CNTs have been reported by Lu [91].

Hernández *et al.* [93], however, used a nonorthogonal tight-binding method to obtain Young's modulus E_Y in the region of 1.22 TPa and showed that Young's modulus E_Y have a slight dependence on the CNTs' chiralities and diameters. Srivastava *et al.* [94] investigated the mechanical properties of CNTs using generalised tight-binding formalism and reported a value of 1.3 TPa for Young's modulus E_Y . Accurate *ab initio* calculations have yielded 1.06 to 1.14 TPa for SWCNTs [93,95].

It is worth noting that the dependence of Young's modulus E_Y on the CNT diameter is found to be different for each model. For instance, Cornwell *et al.* [90] employed the Tersoff-Brenner empirical potential [57,86] and predicted that Young's modulus E_Y will decrease as the diameter of the CNTs increases. However, Hernandez *et al.* [93,96] reported an increasing Young's modulus E_Y with increasing CNT diameter using nonorthogonal tight-binding method. Sanchez-Portal *et al.* [97] obtained Young's

modulus E_Y with little dependence on the diameter for various SWCNTs using pseudopotential-density functional theory. Experiments of high accuracies are required to resolve this contradiction.

In this research, part of the focus is to compute Young's modulus E_Y of various forms of CNTs. MD simulations are performed to determine the factors that affect Young's modulus E_Y using the reactive empirical many-body bond order potential energy expression of Brenner *et al.* [56] discussed in Chapter 2. The factors that are tested are length l_t , diameter d_t , chirality θ_{ch} , and geometry (n, m) .

In Fig. 3.4, the values of Young's modulus E_Y have been plotted as a function of the CNT length l_t for the different types of SWCNTs, namely, armchair and zig-zag CNTs. The simulations show that there is a slight dependence of Young's modulus E_Y on the length of the CNTs. However, this dependence is only noticeable for short lengths l_t . For instance, as the length l_t of the (10,10) CNT increases, its Young's modulus E_Y decreases slowly until it reaches a steady Young's modulus E_Y value of about 1.05 TPa, which is close to the experimental results of Krishan *et al.* [79]. However, the dependence on length l_t is not as significant for zig-zag CNTs as shown in Fig 3.4. For example, at $l_t = 40 \text{ \AA}$, Young's modulus E_Y for the (10,0) CNT is about 1.1 TPa. However, increasing the length l_t to $210 \text{ \AA}$ will only cause its Young's modulus E_Y to decrease by less than 6% to about 1.03 TPa.

Fig. 3.4. Plot depicting the effect of CNT length on Young's modulus E_Y .

It can also be seen that for CNTs with larger diameters d_t , the effect of the length l_t is not so considerable. It is exemplified by at length $l_t = 23 \text{ Å}$, Young's modulus E_Y for the (20,20) SWCNT is 1.07 TPa which is approximately the same as at $l_t = 210 \text{ Å}$, where Young's modulus E_Y has decreased steadily to about 1.05 TPa. As such there is only a 3% deviation in Young's modulus E_Y from length $l_t = 23 \text{ Å}$ to $l_t = 210 \text{ Å}$. However, for the (10,10) CNT that has a smaller diameter d_t , its Young's modulus E_Y at length $l_t = 23 \text{ Å}$ is about 1.2 TPa, and at length $l_t = 210 \text{ Å}$, Young's modulus E_Y has steadily decreased by 13% to a value of 1.05 TPa.

Fig. 3.5. Plot depicting the effect of CNT diameter on Young's modulus E_Y .

Figure 3.5 shows the dependence of the CNT diameter d_t have on Young's modulus E_Y , with smaller diameters d_t having higher Young's modulus E_Y for both armchair and zig-zag CNTs. However, despite the differences in lengths l_t , as the diameter d_t increases, Young's modulus E_Y for the armchair and zig-zag CNTs are all approximately 1.05 TPa and 0.9 TPa respectively. This finding is in agreement with the general theory that as the diameter d_t of a CNT becomes larger, its Young's modulus E_Y will approach to the value of a plane graphite sheet of 1.02 TPa [4]. This is because for very large diameters d_t , the CNTs resemble closer to a graphite sheet. Furthermore, the bonds are less curved which is close to the flat bonds in a graphite sheet. It is important to note that the trend of higher Young's modulus E_Y at smaller diameters

obtained from this work agrees well with the work of Treacy *et al.* [78], Popov *et al.* [98], and Cornwell *et al.* [90] but differ from other works such as Hernández *et al.* [93,96]. The reason may be largely due to the different form of potentials employed in the simulations.

Fig. 3.6. Plot depicting the effect of chiral angle θ_{ch} on Young's modulus E_Y .

From Figs. 3.4 and 3.5, it can be seen that generally zig-zag CNTs have lower Young's modulus E_Y . CNTs can have different chiralities too, and hence, to fully understand the effect of chiralities have on the elastic properties of CNTs, MD simulations are performed on both (10,m) and (15,m) SWCNTs. From the plot in Fig. 3.6, it is observed that as the chirality of the SWCNT increases, its Young's modulus E_Y also

increases, which is also noticed in the simulations of Hernández *et al.* using nonorthogonal tight-binding method [93,96].

Young's moduli E_Y for a selected number of SWCNTs are summarised in Table 3.2. Together with Young's moduli E_Y , another mechanical property of interest is the Poisson ratio ν_p , which is given by the variation of the radius of the CNT resulting from longitudinal deformations along the tubular axis

$$\nu_t = -\frac{\Delta r_t / r_{t_0}}{\Delta l_t / l_{t_0}} = -\frac{\Delta r_t / r_{t_0}}{\varepsilon}, \quad (3.2)$$

where r_{t_0} is the equilibrium radius of the CNT, r_t represents the radius of the CNT at strain ε , l_{t_0} is the equilibrium length of the CNT, and l_t represents the length of the CNT at strain ε . In all cases the Poisson ratio ν_t is positive: an increase in strain increases the diameter d_t of the CNT. Table 3.2 presents the Poisson ratios ν_t and Young's moduli E_Y of selected armchair SWCNTs.

From Table 3.2, it can be seen that there is a slight increase in Poisson ratio ν_t with increasing diameter d_t , and a strong dependence on chirality. The Poisson ratio ν_t values using the Brenner's 'second generation' potential [56] for armchair CNTs range from 0.22 to 0.25, and a little larger for other chiralities: 0.28 to 0.30 for zig-zag CNTs. For instance, a (10,10) armchair CNT has a Poisson ratio ν_t of **0.22**, while the (10,0) zig-zag CNT has a larger Poisson ratio ν_t value of 0.28. This result is close to the value of $\nu_t = 0.26$ and 0.28 for armchair and zig-zag CNTs respectively obtained by using tight-binding calculation [96]. Furthermore, according to Table 3.2, when the chiral angle θ_{ch} increases, the Poisson ratio ν_t also increases.

Table 3.2. Structural and elastic properties of selected SWCNTs.

(n,m)	Diameter d_t (Å)	Poisson ratio ν_t	Young's modulus E_y (TPa)
(7,7)	9.63	0.22	1.09
(8,8)	10.99	0.22	1.06
(10,10)	13.71	0.22	1.05
(12,12)	16.45	0.22	1.05
(15,15)	20.54	0.21	1.05
(20,20)	27.33	0.25	1.05
(10,0)	7.99	0.28	1.03
(12,0)	9.54	0.29	0.97
(15,0)	11.89	0.29	0.90
(20,0)	15.84	0.30	0.88
(10,4)	9.84	0.26	1.04
(10,8)	12.27	0.22	1.04
(15,3)	13.13	0.28	0.95
(15,5)	14.16	0.27	0.97
(15,10)	17.10	0.24	1.00

The various Young’s modulus E_y values for SWCNTs determined in this research using MD simulation and Brenner’s ‘second generation’ empirical analytical potential function [56] ranges from from 0.88 TPa to 1.09 TPa. These values are in good agreement with the more accurate but computationally expensive *ab initio* simulations [91,93] that

yields Young's modulus E_Y values of 1.06TPa to 1.14TPa for various CNTs, and experimental values of 1.25 TPa from Krishnan *et al.* [79].

3.2 Carbon nanotubes under axial compressive load

The developments of many-body interatomic potentials have made MD simulations of large systems possible and efficient. Yakobson *et al.* [3] applied REBO potential to investigate the instability of SWCNTs under axial compression, bending, and torsional deformation, respectively. In their study, a continuum shell model is also introduced to describe the buckling and bending behaviour of CNTs in the plastic deformation regime by properly chosen parameters.

Cornwell and Wille [90,99] carried out large-scale calculation on the SWCNTs subjected to axial compression and stretched in the plastic deformation regime. Instead of using the conjugate-gradient method used by Yakobson *et al.* [3], Cornwell and Wille used finite temperature molecular dynamic simulation to examine the relaxation of the SWCNTs. The REBO potential is also employed in their work to describe the interatomic interactions.

Using the MD simulations as well as the Tersoff many-body potential energy, Erkoc [100] investigated the structural stability of SWCNTs with infinite length and the thermal behaviour of three different SWCNTs of a similar size, both in diameter and length [101]. The effect of temperature on the structure of CNTs is examined in their study. In addition, Erkoc *et al.* [102] investigated the stability of finite carbon nanorods formed from MCNTs with different chirality. Their simulation results showed that the carbon nanorod is not stable even at low temperatures.

The MD simulations on the mechanisms of buckling, bending, slipping, and elastic recovery of CNTs have been carried out by Garg *et al.* [59]. Their work investigated the effects of length and surface type of CNTs on the mechanisms of the interaction between the CNTs and the surfaces. Also Garg and Sinnot [62] studied CNT tip-surface interaction using a many-body empirical hydrocarbon potential coupled to a long-range Lennard-Jones potential. Their simulation indicated how the deformation of the rope leads to the distortion of its end, and allows for the determination of the effect of shear stress within the bundle on the buckling force of the rope.

Hertel *et al.* [103] investigated the effects of surface van der Waals forces on the shape of SWCNTs and MWCNTs using molecular mechanics simulation. Their simulation showed that the van der Waals interaction between CNTs and a substrate leads to substantial axial and radial deformations of absorbed CNTs, destroying the idealised shape of free CNTs.

Ru [104 – 107] proposed elastic shell models for buckling analyses of double-walled CNTs. The derived explicit expression for critical axial strain indicated the role of the van der Waals interaction between outer and inner tubes. His formula showed that van der Waals forces do not increase the critical axial strain for infinitesimal buckling of the double-walled CNTs.

3.2.1 Numerical simulations

The numerical simulations are carried out using the classical MD method [108] in which Newtonian equations of motion are solved numerically for a set of atoms interacting via Brenner's "second generation" reactive empirical many-body bond order potential energy

[56]. In this study, the buckling behaviours of SWCNTs and MWCNTs are simulated by solving the equations of motions using the Gear's predictor-corrector algorithm[69].

Fig. 3.7. Force is applied to the dark blue edge atoms of the CNT at z-direction.

The axial compressions of perfectly structured SWCNTs and MWCNTs are achieved by applying a rate of 20 and 10 m/s respectively at both ends. At the same time, the atoms at both ends of the CNTs are kept transparent to the interatomic forces. The end atoms are then moved inwardly along the axis by small steps, followed by a conjugate gradient minimization whilst keeping the end atoms fixed. Referring to Fig. 3.7, the dark blue atoms are the edge atoms, which are to be constrained during energy minimisation. Hence, only the light blue atoms, i.e., the non-edge atoms, are minimised. The force in the z-direction is applied to the edge atoms so that axial compression can take place.

3.2.2 Single-walled carbon nanotubes

To characterize the buckling behaviours of SWCNTs, (8,0) and (15,15) SWCNTs are used in the simulation. The SWCNTs have similar lengths $l_t = 43 \text{ \AA}$ and diameters $d_t = 6.3 \text{ \AA}$ and $20.36 \text{ \AA}$ respectively for (8,0) and (15,15) SWCNTs. Each time step used in this simulation is equivalent to 1 fs and the simulations are allowed to run for 20 000 time steps.

Figure 3.8 shows the plot of strain energy per atom, which is determined as the difference in total energy per atom of the strained and unstrained CNT, against strain, which is defined as

$$\varepsilon = \frac{l_t - l_{t_0}}{l_{t_0}} \quad (3.3)$$

where l_{t_0} is the original length of the CNT, for the (8,0) and (15,15) SWCNTs after they are compressed axially using the Brenner's "second generation" empirical potential function [56]. Additionally, for comparison, the similar strain energy calculated for (8,0) CNT using quantum generalized tight-binding molecular dynamics (GTBMD) [94] is also shown. At the elastic regime, both Brenner's second generation empirical analytical potential function and the GTBMD simulation agrees well (only with a slight difference) for the (8,0) SWCNTs. Furthermore, Brenner's second generation empirical analytical potential function shows that the (8,0) SWCNT can be compressed up to a strain $\varepsilon = 0.13$ before buckling, while the GTBMD simulation for the same SWCNT shows that buckling starts at $\varepsilon = 0.12$. Hence, generally both the GTBMD and Brenner's second generation

empirical analytical potential function agrees well with each other, validating the accuracy of the latter.

Fig. 3.8. Strain energy per atom for (8,0) and (15,15) SWCNTs using Brenner’s ‘second generation’ empirical potential (BSGEP) [56] and (8,0) SWCNT using GTBMD [94].

Figure 3.8 depicts that the (8,0) and (15,15) SWCNTs undergo elastic deformation before collapsing catastrophically at a certain critical strain. For instance the critical strain of the (8,0)SWCNT is $\epsilon = 0.13$, resulting in a 30% spontaneous drop of strain energy per atom to 0.4 eV/atom. The nature of the spontaneous plastic collapse of the SWCNT is in qualitative agreement with the experimental observations of Lourie *et al.* [109] and the simulated observation of Srivastava *et al.* [94] using the GTBMD scheme. The calculated critical stress $\sigma_{cr} = 149$ GPa for the (8,0) SWCNT in this simulation is also close to the

simulation work of Srivastava *et al.* [94] who obtained $\sigma_{cr} = 153$ GPa. From the figure, it can be seen that the (15,15) SWCNT has a lower strain energy per atom after buckling, due to the existence of highly strengthened chemical bonds between the atoms. Both the (8,0) and (15,15) SWCNTs are subjected to morphological changes during buckling. The (8,0) SWCNT undergoes acute morphological changes during buckling, hence, higher strains are found in the (8,0) SWCNT, particularly around the kinks.

Fig. 3.9. Morphological changes for (8,0) SWCNT showing high strains concentrated at the kinks. The (8,0) SWCNT at $\epsilon = 0.13$ (a) spontaneously collapse into a three-fin pattern while maintaining its straight axis (b). At $\epsilon = 0.15$, the SWCNT buckles sideways (c) before further reduction in length at $\epsilon = 0.17$ (d).

In Fig. 3.9 and Fig. 3.10, the shading indicates the strain energy per atom, equally spaced from below 0.25 eV (lightest) to above 1.25 eV (darkest). According to Fig. 3.8(a), at $\epsilon = 0.13$ the compressed (8,0) CNT maintains its cylindrical shape before spontaneously deforming into a symmetric three-fin pattern as shown in Fig. 3.8(b), leading to a plastic collapse and a net release of energy. This phenomenon has also been discussed by Srivastava *et al.* [94]. The highly symmetric morphological shape is intrinsic to the mechanics of a perfect, undisturbed CNT as reported [3,94]. Furthermore, higher strain energy per atom is found along the edges of the fin. At $\epsilon = 0.15$, the CNT continues to deform with the pinches thinning while buckling sideways, as shown in Fig. 3.9(c). It is observed that higher strain energy per atom is located across the pinch as the CNT is being compressed. Further increase in strain beyond $\epsilon = 0.17$ causes the CNT to continue to buckle sideways with further reduction in length l , as shown in Fig. 3.9(d), where higher strain energy per atom is concentrated at the kinks.

However, when the wider (15,15) SWCNT is exposed to axial compression, it first forms a “ring” pattern as shown in Fig. 3.10(a) before buckling plastically into a “chessboard” pattern [see Fig. 3.10(b)]. At $\epsilon = 0.065$, the CNT continues to deform resulting in a larger radial displacement [see Fig. 3.10(c)] prior to spontaneously collapsing into two fins perpendicular to each other as shown in Fig. 3.10(d).

Fig. 3.10. Morphological changes for (15,15) SWCNT showing slight strains. The (15,15) SWCNT first forms a “ring” pattern (a) before plastically deforms into a “chessboard” pattern (b). Larger radial displacements were found at $\epsilon = 0.065$ (c) prior to collapsing into two perpendicular fins (d).

A length/diameter (l_t/d_t) ratio of 7.7:1 is used to illustrate its relationship with the buckling loads P_{cr} of selected zig-zag and armchair SWCNTs as listed in Table 3.3. It can be seen that as the diameters d_t increase, the buckling loads P_{cr} also increase steadily until the optimum diameters of $d_t = 11.76 \text{ \AA}$ and $d_t = 20.36 \text{ \AA}$ for the zig-zag and armchair CNTs are respectively attained. Beyond these optimum diameters d_t , the buckling loads P_{cr} start to decrease instead. It is, however, important to note that at any l_t/d_t ratio, there is an optimum diameter.

Table 3.3. Buckling loads for selected zig-zag and armchair SWCNTs.

Zig zag			Armchair		
(n,m)	Diameter d_t (Å)	P_{cr} ($\times 10^{-7}$ N)	(n,m)	Diameter d_t (Å)	P_{cr} ($\times 10^{-7}$ N)
(4,0)	3.13	0.72	(4,4)	5.43	0.87
(5,0)	3.92	0.94	(5,5)	6.79	0.88
(6,0)	4.70	1.01	(6,6)	8.14	0.90
(7,0)	5.49	1.09	(7,7)	9.50	0.90
(8,0)	6.27	1.10	(8,8)	10.86	0.91
(9,0)	7.05	1.14	(9,9)	12.22	1.03
(10,0)	7.84	1.19	(10,10)	13.57	1.04
(11,0)	8.62	1.20	(11,11)	14.93	1.12
(12,0)	9.40	1.22	(12,12)	16.29	1.13
(13,0)	10.19	1.25	(13,13)	17.65	1.15
(14,0)	10.97	1.27	(14,14)	19.00	1.16
(15,0)	11.76	1.30	(15,15)	20.36	1.16
(16,0)	12.54	1.29	(16,16)	21.72	1.18
(17,0)	13.32	1.27	(17,17)	23.08	1.19
(18,0)	14.11	1.26	(18,18)	24.43	1.19
(19,0)	14.89	1.25	(19,19)	25.79	1.20
(20,0)	15.67	1.25	(20,20)	27.15	1.19
(21,0)	16.46	1.24	(21,21)	28.50	1.17
(22,0)	17.24	1.23	(22,22)	29.86	1.16
(23,0)	18.02	1.21	(23,23)	31.22	1.16
(24,0)	18.81	1.18	(24,24)	32.58	.15
(25,0)	19.59	1.16	(25,25)	33.93	.14
(26,0)	20.38	1.15	(26,26)	35.29	.12
(27,0)	21.16	1.14	(27,27)	36.65	.11
(28,0)	21.94	1.14	(28,28)	38.01	.11
(29,0)	22.73	1.13	(29,29)	39.36	.10
(30,0)	23.51	1.12	(30,30)	40.72	.09
(35,0)	27.43	1.11	(32,32)	43.44	1.09
(40,0)	31.35	1.10	(34,34)	46.15	1.09
(45,0)	35.27	1.10	(35,35)	47.5 1	1.09
(50,0)	39.18	1.09	(37,37)	50.22	1.09
(55,0)	43.10	1.09	(40,40)	54.29	1.09

Figure 3.11 shows the plot of buckling load P_{cr} against diameter d_t for zig-zag SWCNTs. As the diameter d_t of the zig-zag CNT increases, there is a rapid increase in its buckling load P_{cr} . However, as the diameter d_t reaches an optimum value $d_t = 11.76 \text{ \AA}$, any further increment beyond that will cause the buckling load P_{cr} to decrease slowly to a steady value of about 1.10×10^{-7}

Fig. 3.11. Comparison between cylindrical shell formula and MD simulation for buckling loads P_{cr} of various zig-zag SWCNTs with different diameters d_t .

It is worthy to note that the classical shell theory can be used for local buckling analysis of CNTs. For a layer of cylindrical shell with length l , radius r , thickness t , Young's modulus E_Y , Poisson's ratio ν , and m and $2n$ the longitudinal and

circumferential wave numbers, the critical stress for the buckling of the cylindrical shell is obtained as [110]

$$\sigma_{cr} = \frac{Et^2}{12(1-\nu^2)} \left\{ \frac{[n^2 + (m^2 \pi^2 r^2 / l^2)]^2}{r^2 (m^2 \pi^2 r^2 / l^2)} \right\} + \frac{E(m^2 \pi^2 r^2 / l^2)}{[n^2 + (m^2 \pi^2 r^2 / l^2)]^2}. \quad (3.4)$$

In predicting the buckling loads P_{cr} of CNTs by using the cylindrical shell model, almost all previous literatures adopted the interlayer separation of graphite, i.e. $d_{in} = 3.4 \text{ \AA}$ as the representative thickness of SWCNTs. However, the buckling loads P_{cr} obtained from Eqn. (3.4) are much larger than the results obtained from the Brenner's "second generation" reactive empirical many-body bond order potential energy MD simulation if $d_{in} = 3.4 \text{ \AA}$ is used. Here, the diameter of the carbon atom ($1.54 \text{ \AA}$) is used as the effective thickness of the CNT, as shown in Fig. 3.9(a), when the CNT is assumed to be a continuum cylindrical shell. Young modulus E_Y of 1.28 TPa is directly extracted from the experimental result of Wong *et al.* [80] for the calculation of buckling loads P_{cr} using Eqn. (3.4). Since the buckling load P_{cr} is not sensitive to the value of Poisson's ratio, it is taken as $\nu_t = 0.25$. Using the cylindrical shell formula in Eqn. (3.4) and MD simulations, buckling loads P_{cr} are computed for various zig-zag SWCNTs, as shown in Fig. 3.11. It is observed from Fig. 3.11 that the two sets of results are in good agreement with diameter d_t ranging from $5.49 \text{ \AA}$ to $43.1 \text{ \AA}$ or larger. In spite of this, the results obtained from the cylindrical shell formula [Eqn.(3.4)] for diameters d_t smaller than $5.49 \text{ \AA}$ do not agree well with that of the MD simulation. This is because the SWCNT behaves more like a rod than a cylindrical shell when diameters d_t are smaller than $5.49 \text{ \AA}$. In view of this, the buckling loads P_{cr} of zig-zag SWCNTs with fixed ends are also calculated using Euler's formula [111] and are presented in Fig. 3.11,

$$P_{cr} = \frac{4\pi^2 E_Y I}{l_t^2}, \quad (3.5)$$

where I is the moment of inertia. For the fixed length/diameter (l_t/d_t) ratio, the buckling loads P_{cr} obtained from Euler's formula for SWCNTs with fixed ends are proportional to the diameter d_t of SWCNTs, as shown in Fig. 3.11. At diameters d_t smaller than 5.49 Å, the MD simulations revealed increasing diameters d_t will lead to increasing buckling loads P_{cr} .

Fig. 3.12. Critical strains ϵ_{cr} for (10,10) SWCNTs with $d_t = 13.57$ Å at different lengths l_t .

Figure 3.12 plots the various critical strains ϵ_{cr} of a (10,10) SWCNT at different lengths l_t from 24.6 to 140.0 Å. This plot shows that as the length l_t increases, the

critical strain ϵ_{cr} decreases. This indicates that a larger l_t/d_t ratio results in a lower critical strain ϵ_{cr} .

3.2.3 Multi-walled carbon nanotubes

Comparisons are also made between MWCNTs to determine the effect of the number of layers on the properties of the MWCNTs. Three configurations of MWCNTs are considered in the simulation: the first is a two-walled (5,5) and (10,10) CNT; the second is a three-walled (5,5), (10,10), and (15,15) CNT; and the last is a four-walled (5,5), (10,10), (15,15), and (20,20) CNT. The lengths of all three MWCNTs are $l_t = 60 \text{ \AA}$, and their diameters d_t are $13.52 \text{ \AA}$, $20.36 \text{ \AA}$, and $27.15 \text{ \AA}$ for the two, three and four-walled MWCNTs respectively. In these simulations, the long-range van der Waals potential E_{vdw} is added into the short-range covalent potential for the interlayer interaction [61]

$$E_{vdw} = \begin{cases} 0.0 & r_{ij} \leq r'_s \\ c_{3,k}(r_{ij} - r_k)^3 + c_{2,k}(r_{ij} - r_k)^2 & r'_s \leq r_{ij} \leq r'_m \\ E^{LJ}(r_{ij}) & r'_m \leq r_{ij} \leq r'_b \end{cases} \quad (3.6)$$

where $c_{n,k}$ are the cubic spline coefficients and E^{LJ} is the Lennard-Jones 12-6 potential [50,51] computed as

$$E^{LJ} = 4 \frac{\xi}{\sigma} \left[\left(\frac{\sigma^e}{r_{ij}} \right)^{12} - \left(\frac{\sigma^e}{r_{ij}} \right)^6 \right] \quad (3.7)$$

where the coefficients of well-depth energy ξ and the equilibrium distance σ^e are $4.2038 \times 10^{-3} \text{ eV}$ and $3.4 \text{ \AA}$, respectively [112].

It is worthy to note that the van der Waals potential E_v will only be computed after the Brenner REBO potential is zero, i.e., when $r_{ij} > r'_s$.

The three MWCNTs are compressed axially using the same method as the SWCNTs. Each time step is equivalent to 1 fs and there are a total of 20,000 time steps, which corresponds approximately to a total strain of $\epsilon = 0.066$. The resulting plots are shown in Fig. 3.13. For MWCNTs with m layers, the total strain energy is

$$E_t = \sum_i^m E_i . \quad (3.8)$$

From Fig. 3.13 it is evident that the two-walled MWCNT manages to keep its elasticity for the longest with the largest critical strain at $\epsilon_{cr} = 0.06$, while the four-walled MWCNT has the lowest critical strain at $\epsilon_{cr} = 0.038$. Instead of a spontaneous decrease of strain energy upon buckling as evidenced in the SWCNTs, the strain energy per atom increases until all the layers in the MWCNTs are fully buckled.

The sudden increase in strain energy per atom for each layer is due to the spontaneous increase in potential energy of each atom for each layer, as shown in Fig. 3.14. From the plot, it is observed that the middle layer has the largest increment of potential energy of each atom for each layer followed by the inner layer and then the outer layer.

Fig. 3.13. Strain energy per atom for two –walled [(5,5) and (10,10) with diameter of 13.57Å], three-walled[(5,5), (10,10) and (15,15) with diameter of 20.36Å], and four-walled [(5,5), (10,10), (15,15) and (20,20) with diameter of 27.15 Å] CNTs.

Fig. 3.14. Potential energy per atom for each layer for (5,5), (10,10) and (15,15) three-walled CNT with diameter 20.36 Å.

Being sandwiched between the outer and inner layer, when the three-walled CNT starts to buckle, the atoms at the middle layer will have more nearest-neighbours than those of the outer and inner layer. This causes the formation of more chemical bonds to form, from sp^2 to sp^3 configuration. Thus it leads to a larger increase in the empirical bond order function and consequently the potential energy. And hence the middle layer has the highest strain energy per atom for each layer after buckling, as seen in Fig. 3.15.

Fig. 3.15. Strain energy per atom of each layer for (5,5), (10,10) and (15,15) three-walled CNT with diameter 20.36 Å.

Figure 3.16 depicts the distances of selective pair of atoms from different layers at $\epsilon = 0.047$ (before buckling) and $\epsilon = 0.055$ (after buckling) of the three-walled CNT. It is observed that at $\epsilon = 0.047$, the distances between the atoms from different layers are approximately 3.4 Å apart. However at $\epsilon = 0.055$, the distances between these atoms are reduced to values less than 1.6 Å. The decrease in distance allows the formation of sp^3 bond that results in a rise in the potential energy.

Fig. 3.16. Distances between atoms from different layers before buckling at $\epsilon = 0.047$ and after buckling at $\epsilon = 0.055$ for the three-walled CNT.

To further explain the phenomenon of the increase in strain energy per atom upon buckling as observed in Fig. 3.13, the plot of the strain energy per atom for each layer of the three-walled CNT against the strain ϵ is presented in Fig. 3.15. Before buckling, the three layers have the same strain energy per atom for each layer. However at $\epsilon = 0.0484$, the outer layer starts to buckle first, followed by the middle layer at $\epsilon = 0.0486$, and then inner layer at $\epsilon = 0.0493$ (see Fig. 3.15 inset for amplification).

Fig. 3.17. Three-dimensional and cross-sectional view of morphological changes for three-walled (5,5), (10,10), and (15,15) CNT with diameter 20.4 Å. At $\epsilon = 0.0484$ the outer layer deforms into a “ring” pattern (a). Further compression at $\epsilon = 0.0486$ causes the middle layer to deform too (b). At $\epsilon = 0.0493$, the inner layer also buckles (c) and at $\epsilon = 0.052$, all the three layers are deformed (d).

Figure 3.17 shows the three-dimensional and cross-sectional views of a three-walled CNT at different strains. It is evident from Fig. 3.17(a) that the outer layer starts to deform first into a ring pattern till $\varepsilon = 0.0484$, while the middle and inner layers are undeformed and their strain energies remain low. However, further compression at $\varepsilon = 0.0486$ causes the middle layer to deform too, resulting in a sudden increase in the strain energy per atom because of the increase in potential energy due to the atoms in the middle layer. Similarly at this time, the inner layer maintains the elasticity of the CNT temporarily, as shortly after at $\varepsilon = 0.0493$, the inner layer also starts to buckle, therefore increasing the overall potential energy and hence increasing the strain energy per atom further. After $\varepsilon = 0.052$, all the layers are deformed, hence there is no further abrupt increase in potential energy due to the sudden addition of nearest-neighbours.

The force-deformation plot in Fig. 3.18 shows the buckling load P_{cr} that each layer is able to withstand. Being a layer with wider diameter d_i , the outer layer of the three-walled CNT has the highest buckling load P_{cr} at about 1.18×10^{-7} N. However, it also tends to buckle fractionally earlier than the two other layers after deforming $\Delta l_i = 2.9 \text{ \AA}$. The buckling loads P_{cr} for the middle and inner layers are lower at 0.88×10^{-7} N and 0.42×10^{-7} N respectively.

Fig. 3.18. Force-deformation curves of each layer for (5,5), (10,10) and (15,15) three-walled CNT with diameter 20.4 Å.

According to Fig. 3.19, the buckling load P_{cr} increases as the number of layers in a MWCNT increases. The four-walled CNT buckles first at $\Delta l_t = 2.3 \text{ Å}$, even though it has the highest buckling load P_{cr} at $3.2 \times 10^{-7} \text{ N}$; while the three-walled CNT buckles at $\Delta l_t = 2.9 \text{ Å}$ with $P_{cr} = 2.5 \times 10^{-7} \text{ N}$. And finally, the two-walled CNT buckles last at $\Delta l_t = 3.7 \text{ Å}$ but with a lowest buckling load $P_{cr} = 1.7 \times 10^{-7} \text{ N}$. Hence the more layers a MWCNT has, the higher the buckling load P_{cr} is required.

Fig. 3.19. Force-deformation curves for two-walled [(5,5) and (10,10) with diameter of $13.57 \text{ \AA}$], three-walled [(5,5), (10,10) and (15,15) with diameter of $20.36 \text{ \AA}$], and four-walled [(5,5), (10,10), (15,15) and (20,20) with diameter of $27.15 \text{ \AA}$] CNTs.

The buckling loads P_{cr} for two and three-walled CNTs are tabulated in Table 3.4. It is observed from the table that generally MWCNTs have larger buckling loads P_{cr} . For instance, the (10,10), (15,15) two-walled CNT has a higher buckling load $P_{cr} = 2.02 \times 10^{-7} \text{ N}$ compared to the (5,5), (10,10) two-walled CNT, that has a buckling load $P_{cr} = 1.72 \times 10^{-7} \text{ N}$ (see Table 3.4). Moreover, Table 3.4 also verifies that as the number of layers in a CNT increases, its buckling load P_{cr} increases too. According to Table 3.3, the buckling load P_{cr} for a (5,5) SWCNT is $0.88 \times 10^{-7} \text{ N}$, however, if an extra outer layer is added to form a (5,5), (10,10) two-walled CNT, its buckling load P_{cr}

increases to 1.72×10^{-7} N as seen in Table 3.4. If another layer is added to form a (5,5), (10,10), and (15,15) three-walled CNT, the buckling load P_{cr} increases to 2.46×10^{-7} N.

Table 3.4. Buckling loads for selected two and three-walled CNTs.

Two-walled		Three-walled	
$(n_1, m_1) (n_2, m_2)$	P_{cr} ($\times 10^{-7}$ N)	$(n_1, m_1) (n_2, m_2) (n_3, m_3)$	P_{cr} ($\times 10^{-7}$ N)
(5,5) (10,10)	1.72	(5,5) (10,10) (15,15)	2.46
(10,10) (15,15)	2.02	(10,10) (15,15) (20,20)	2.73
(15,15) (20,20)	2.09	(15,15) (20,20) (25,25)	2.81
(20,20) (25,25)	2.10	(20,20) (25,25) (30,30)	3.05

3.3 Carbon nanotubes under axial tensile load

In contrast to the CNTs under axial compression, studies on CNTs under axial tension are limited; only a few has been reported on the plastic properties of CNTs under large tensile strains. Yakobson *et al.* [113] studied the CNTs behaviour under a high strain using Tersoff-Brenner’s reactive empirical bond-order (REBO) potential [57,87]. Large elastic deformations of CNTs under axial tension, axial compression, and torsion were investigated in their work. Xiao and Liao [114] simulated the nonlinear elastic properties of CNTs under axial tensile deformation by using the Brenner’s “second generation” potential [56]. They examined the in-plane stiffness of two groups of SWCNTs, i.e. $(n,0)$ and (n,n) CNTs. Even though CNTs possess an excellent elastic characteristic, plastic deformation does occur under sufficiently large tension strains due to the Stone-Wales

bond rotation [115]. Yakobson [116] first predicted a 90° rotation of a $C-C$ bond during the Stone-Wales bond rotation, where two pentagons and two heptagons are converted into 5-7-7-5 defects [92,117 – 119] during the extension. The plastic deformation has occurred due to the separation and glide of these 5-7-7-5 defects. In another work [120], it is stated that the elastic properties of a CNT are nearly independent of the indices, i.e., $(n,0)$, (n,n) , (n,m) , but not for the plastic deformation. The elastic limits of $(n,0)$ CNTs are nearly twice that of (n,n) CNTs with the same radius [120].

Experimental work on measuring the mechanical properties of CNTs under tension is also limited. Yu *et al.* [83] measured the tensile strengths of MWCNTs. The stress-strain curve was obtained and analysed for Young's modulus of individual MWCNT. Their experimental work revealed that the fracture first takes place at the outermost layer of the MWCNTs. From the experiment of Bozovic and Bockrath [121], they used the atomic force microscope tip to induce varying degrees of strain in the SWCNTs. Their study and experimental results showed that SWCNTs can sustain elongations as large as 30% without fracture.

Here, the elastic and plastic deformation of tensile armchair CNTs using the second-generation of reactive empirical bond-order (REBO) potential [56] are investigated. The stress-strain relation from elastic to fracture is obtained to describe the elastic and plastic behaviors of CNTs. The mechanical properties, such as Young's modulus E_Y , Poisson's ratio, Yield stress, ultimate stress and maximum strain, are obtained and presented for selected SWCNTs and MWCNTs.

3.3.1 Simulated results

Using the computational methods as described in section 2.3, Young's modulus E_Y , which is assumed to be constant, can be determined from the second derivative of potential function by fitting the potential energy into a cubic polynomial function. For CNTs, Young's modulus E_Y is dependent on strain and treated as a constant if the strain is small. In general, it is possible to obtain the derivative of a potential function in a smooth stress-strain curve in the elastic region, but not so for the elasto-plastic-failure region. This is due to the large fluctuation of stresses. Thus it is difficult to determine some mechanical properties, such as the tensile strength, elastic strain limit, maximum strain and so on, by just fitting the potential energy into a smooth stress-strain curve.

In order to describe the complete stress-strain relationship from the elastic deformation to rupture, the stress-strain curves of SWCNTs and MWCNTs under tensile deformation are obtained in the simulations by applying a rate of 20 m/s to both ends. The atoms at the end of the CNTs are then moved outwardly along the axis by small steps, followed by a conjugate gradient minimization method, while keeping them fixed in place.

In this simulation, the strain is computed as Eqn. (3.3) and the stress is given by

$$\sigma = \frac{F}{S}. \quad (3.9)$$

The axial force F is obtained by summing the interatomic force for the atoms at the end of the CNTs and the cross-sectional area is

$$S = \pi d_t h_t, \quad (3.10)$$

where h_t is the thickness of the CNT that is taken as $h_t = 0.335$ nm for (10,10) SWCNT, $h_t = 0.67$ nm for (5,5) and (10,10) two-walled CNT, $h_t = 1.005$ nm for (5,5), (10,10) and (15,15) three-walled CNT, and $h_t = 1.34$ nm for (5,5), (10,10), (15,15) and (20,20) four-walled CNT.

Since Brenner's REBO potential [56] does not account for the long-range interactions, such as the van der Waals interactions, the long-range Lennard-Jones potential is incorporated into the REBO potential to take care of the van der Waals interactions in the MD simulations. The implementation of the van der Waals interactions in the MD simulations allows a better description of the elastic and plastic deformation of CNTs.

The elasto-plastic responses of the CNTs are simulated and plotted in Figs. 3.20(a)-(h) for the length to diameter ratio (l_t/d_t) of 4.5 and 9.1. It is evident that when $0 \leq \varepsilon \leq \varepsilon_s$, the stress-strain relationship follows Hooke's law, i.e. $\sigma = E\varepsilon$. Here, ε_p corresponds to point P in Figs. 3.20(a)-(h), which is the proportional strain limit. It is observed that as the strain increases, the stress-strain curve behaves non-linearly with a decreasing gradient until it reaches the yield strain ε_s , which corresponds to yield point S in Figs. 3.20(a)-(h). Using the regression analysis, the stress-strain curve can be represented by $\sigma = (A\varepsilon + B)\varepsilon$ where $\varepsilon_p \leq \varepsilon \leq \varepsilon_s$. The values of A and B can be determined by fitting the stress-strain relationship to a smooth curve again using the regression analysis, as shown in Table 3.5 for various CNTs. At the yield point, we have $d\sigma/d\varepsilon = 0$, and thus the yield strain limit ε_s becomes $\varepsilon_s = -B/2A$. Beyond the yield point S, considerable plastic deformation occurs without a noticeable increase in the stress, i.e., in the strain region $\varepsilon_s \leq \varepsilon \leq \varepsilon_M$, the stress can be approximately expressed as $\sigma = \sigma_s$. This ductile behavior can be observed in our animated MD simulations, showing wave propagation from the center to the two ends of the CNTs and then back to the center. This phenomenon of wave

propagation displays the re-arrangement of configuration of the CNTs for strain release via the formation of the Stone-Wales defects.

Fig. 3.20(a). The transverse elastic-plastic response of a (10,10) SWCNT under axial tension with $l_t/d_t = 4.5$.

Fig. 3.20(b). The transverse elastic-plastic response of a two-walled (5,5) and (10,10) CNT under axial tension with $l_t/d_t = 4.5$.

Fig. 3.20(c). The transverse elastic-plastic response of a three-walled (5,5), (10,10) and (15,15) CNT under axial tension with $l_t/d_t = 4.5$.

Fig. 3.20(d). The transverse elastic-plastic response of a four-walled (5,5), (10,10), (15,15) and (20,20) CNT under axial tension with $l_t/d_t = 4.5$.

Fig.3.20(e). The transverse elastic-plastic response of a (10,10) SWCNT under axial tension with $l_t/d_t = 9.1$.

Fig. 3.20(f). The transverse elastic-plastic response of a two-walled (5,5) and (10,10) CNT under axial tension with $l_t/d_t = 9.1$.

Fig. 3.20(g). The transverse elastic-plastic response of a three-walled (5,5), (10,10) and (15,15) CNT under axial tension with $l_t/d_t = 9.1$.

Fig. 3.20(h). The transverse elastic-plastic response of a four-walled (5,5), (10,10), (15,15) and (20,20) CNT under axial tension with $l_t/d_t = 9.1$.

Figure 3.21 shows the formation of (5-7-7-5) defect due to a 90° rotation of a bond during the plastic deformation of a four-walled (5,5), (10,10), (15,15) and (20,20) CNT under axial tension. The initial (5-7-7-5) defect is formed at a strain of 24%. As the strain increases, more (5-7-7-5) defects are generated along the circumferential direction, as shown in Fig. 3.21. When the strain reaches the maximum strain point M at 0.256, two bonds are broken initially to form two holes, as shown in Fig. 3.22(a). This observation is in close agreement with the quantum mechanical simulated results of Dumitrică *et al.* [122], which showed that failures occurred at strains above 0.240 for armchair CNTs. As the strain increases, more bonds are broken and the holes get larger until the CNT fractures. The brittle fracture process is displayed in Fig. 3.22(a)-(d) for the outermost

layer of the four-walled CNTs. Upon reaching the maximum strain ϵ_M , the CNTs rupture very quickly and fracture completely within a short period of time, as depicted in Figs. 3.20(a)-(h). Figure 3.23 shows the entire failure process of the four-walled CNT of (5,5), (10,10), (15,15) and (20,20). When strain is at 0.263, bond breaking initially takes place in the outermost layer (first layer), while all the other three layers remain undamaged. The phenomenon whereby the outermost layer of MWCNT is the first to be damaged is consistent with the experimental result of Yu *et al.* [83]. As the strain increases to 0.268, the outermost layer is almost completely fractured, while one bond in the second layer begins to break, and the third and innermost layers remain undamaged. However, a bond is observed to have broken in the third layer as the strain increases to 0.275. At this point, the third layer is completely fractured, even though no bond breaking is found in the innermost layer (fourth layer). When strain is at 0.279, a bond starts to break in the innermost layer and the three outer layers are all completely broken. Eventually, when the strain is at 0.28, the entire four-walled CNT completely fractures. The above exemplifies that MWCNTs can sustain elongations up to 28%, which is in good agreement with the experimental result of Bozovic *et al.* [121]. The reason why the outermost layer will suffer from fracture first followed by the next inner layer can be explained in Fig. 3.24. From the plot, it can be seen that at any strain ϵ , the outermost layer is bearing the most load compared to the other three layers; while the innermost layer is bearing the least load. At $\epsilon = 0.263$, when the outermost suffers from fracture, it is carrying almost 40.6% of the total axial load; while the next innermost layer carries about 30.5% of the total axial load. The last two layers carry 19.4% and 9.5% of the total axial load respectively. Since the outermost layer has the highest load, it is therefore natural for it to fracture first, followed by the next layer with a next highest load.

Fig. 3.21. The formation of (5-7-7-5) defects in the outermost layer of a four-walled (5,5), (10,10), (15,15) and (20,20) CNT under axial tension during the plastic deformation.

(a) Strain is at 0.256

(b) Strain is at 0.263

(c) Strain is at 0.271

(d) Strain is at 0.279

Fig. 3.22. The brittle fracture process of the outermost layer of four-walled CNTs. (a) Formation of initial fracture; (b) Fracture propagation in circumferential direction; (c) Fracture propagation in the axial and circumferential direction; (d) The CNT is almost completely broken.

Innermost (4th) layer

3rd layer

2nd layer

Outermost (1st) layer

All

(a) Strain is at 0.263

(b) Strain is at 0.268

(c) Strain is at 0.275

(d) Strain is at 0.279

Fig. 3.23. The brittle fracture process of the four-walled (5,5), (10,10), (15,15) and (20,20) CNT with $l_t/d_t = 9.1$. (a) Bond breaking first takes place in the outermost layer when the strain is at 0.263; (b) The second layer starts to break when the strain is at 0.268; (c) The third layer starts to break when the strain is at 0.275; (d) the innermost layer starts to break when the strain is at 0.279; and (e) the entire four-walled CNT completely fractures when the strain is at 0.280.

Table 3.5 lists the computed Young's modulus E_Y , proportional strength, yield strength, tensile strength, proportional strain limit, elastic strain limit and maximum strain for selected single to four-walled armchair CNTs with length to diameter ratios l_t/d_t of the CNTs equal to 4.5 and 9.1. It is observed that the properties are dependent on the number of layers in the CNT. Nevertheless there are small changes in the properties of CNTs for the length to diameter ratios l_t/d_t of 4.5 and 9.1. It is evident that the effect of size on the mechanical properties of CNTs is very small and, with the same number of layers, it may be concluded that the mechanical properties of CNTs can be treated as the same for all length to diameter ratios l_t/d_t .

The simulations show that the Stone-Wales defect leads to plastic deformation. For the MWCNTs, the brittle fracture first takes place in the outermost layer. Once the outermost layer completely breaks, the next inner layer starts to fracture. This fracture process will continue until the innermost layer completely breaks. The stress-strain relation from elastic to fracture stage to describe the elastic and plastic behaviors of CNTs is also obtained. The complete mechanical properties, such as Young's modulus E_Y , Poisson's ratio, Yield stress, ultimate stress, and maximum strain, for selected SWCNTs and MWCNTs are also obtained. The simulated results show that the properties are sensitive to the number of layers in the MWCNTs. However, the effect of size on the mechanical properties of CNTs is very small, and with the same number of layers, the mechanical properties of CNTs can be treated as the same for all length-to-diameter ratios.

Fig. 3.24. Load of different layers of a four-walled(5,5), (10,10), (15,15) and (20,20) CNT with $l_t/d_t = 9.1$.

Table 3.5. Material properties of selected SWCNTs and MWCNTs.

	Single-walled CNT of (10,10)		Two-walled CNT of (5,5) and (10,10)		Three-walled CNT of (5,5), (10,10) and (15,15)		Four-walled CNT of (5,5), 10,10), (15,15) and (20,20)	
l_t/d_t	4.5	9.1	4.5	9.1	4.5	9.1	4.5	9.1
Young's modulus E , (TPa)	1.043	1.031	1.161	1.175	1.000	0.972	0.932	0.872
A (TPa)	-2.625	-2.522	-2.543	-2.810	-2.358	-2.275	-2.234	-2.132
B (TPa)	1.211	1.190	1.259	1.362	1.160	1.120	1.103	1.023
Proportional Strength ($\times 10^4$ MPa)	6.103	6.271	7.231	7.287	6.068	5.645	6.075	5.784
Yield strength ($\times 10^5$ MPa)	1.369	1.421	1.614	1.633	1.430	1.381	1.343	1.278
Tensile strength ($\times 10^5$ MPa)	1.404	1.485	1.624	1.684	1.434	1.414	1.382	1.327
Proportional strain limit	0.0585	0.0594	1.0627	0.0621	0.0605	0.0611	1.0654	0.0633
Elastic strain limit	0.231	0.236	0.247	0.242	0.238	0.246	0.235	0.241
Maximum strain	0.280	0.279	0.279	0.281	0.281	0.282	0.281	0.280

CHAPTER 4

MECHANICAL PROPERTIES OF CARBON NANOTUBE BUNDLES

Wire ropes are an important structural element and mainly used in applications in which axial tensile load is dominant as compared to bending or torsional loads. Their ability to withstand relatively large tensile loads makes them one of the oldest tools that humans have used. Carbon fibres have been used as reinforcements in high strength, light weight, high performance composites which can be found in a range of products from expensive tennis rackets to spacecraft and aircraft body parts. Recently, it is discovered that SWCNTs, in many cases, self-organize into crystalline bundles [17,123], composing of SWCNTs vertically aligned next to one another. Such CNT bundles (or CNT fibres) are often used in nanotube-reinforced composites to enhance the mechanical properties. In this chapter, a review of past research of CNT bundles is carried out. In addition, the mechanical properties of CNT bundles when subjected to axial compressive and tensile loads are also investigated.

4.1 Previous studies on carbon nanotube bundles

One of the most important opportunities for CNTs is the fabrication of CNT composite materials. This has led to significant increase in experimental work to synthesize aligned CNTs and CNT bundles (or CNT fibres). A wide variety of synthesis methods have been employed, yielding CNTs of different sizes, aspect ratios, crystallinity, crystalline orientation, purity, entanglement and straightness. For instance, Hammel *et al.* [124] had successfully produced high purity CNT fibres at low cost by a catalytic chemical vapour deposition process. Fan *et al.* [125] have synthesized regular arrays of oriented CNTs with high uniformity on substrates. Their approach involves chemical vapour deposition, catalytic particle size control by substrate design, CNT positioning by patterning, and CNT self-assembly for orientation. Vigolo and colleagues [126] devised a novel method to produce indefinitely long CNT ribbons and fibres by dispersing the CNTs in surfactant solutions, recondensing the CNTs in the flow of a polymer solution to form a CNT mesh, and then collating this mesh to a CNT fibre or ribbon. Zhu *et al.* [127] have also fabricated long strands of SWCNTs up to 20cm in length synthesized by using an alternative technique of catalytic pyrolysis of n-hexane with an enhanced vertical floating technique, while Dalton *et al.* [128] has successfully produced 100m long super tough CNT fibres by using a type of coagulation-based CNT spinning method. They subsequently spun the CNT fibres to supercapacitors and wove them into textiles (see Fig. 4.1).

Fig. 4.1. Photograph of a textile containing two CNT fibre supercapacitors woven in orthogonal directions (scale bar equivalent to 10 mm) [128].

Li *et al.* [129] developed a method of spinning bundles of CNTs directly from the chemical vapour deposition zone of a furnace using a liquid source of carbon and an iron nanocatalyst. On the other hand, well-aligned macroscopic, neat SWCNT bundles are produced by Ericson *et al.* [130] who made use of conventional spinning together with fuming sulphuric acid to promote their orderly alignment. Qin *et al.* [131], synthesized helical carbon nanofibres with a symmetric growth mode by the decomposition of acetylene with a copper catalyst as shown in Fig. 4.2.

The development of SWCNT/polyelectrolyte multilayer composites following the protocol of layer-by-layer assembly has also been presented by Mamedov *et al.* [132]. This deposition technique is reported to be able to obtain SWCNT loading as high as 50 wt%. At the same time, fabrication of carbon nanofibres-polystyrene composites by ultrasonic dispersion in a solution followed by spraying to cast films was also recently reported [133].

Fig. 4.2. Field emission SEM image of helical carbon nanofibres [131].

Yutaka Maniwa *et al.* have studied the thermal expansion of SWCNT bundles using the X-ray diffraction technique [134]. They determined the thermal expansion of the CNT diameter to be about -0.15×10^{-5} (1/K) and the lattice constant is about 0.75×10^{-5} (1/K). The coalescence property of an array of SWCNTs forming into a single MWCNT under thermal treatment was investigated by López *et al.* [135]. Their simulation results revealed the physical mechanism of single-wall to multi-wall transformation based on the patching of SWCNTs and their subsequent tearing apart, forming a MWCNT.

Various experimental and theoretical studies have also been carried out in determining the effect of the surface van der Waal forces between a number of SWCNTs. Tersoff [136], for example, discovered that the structural properties of CNTs in an ordered condensed phase will show a clear transition between two regimes with qualitatively different behaviour when the CNT diameter changes. The findings revealed that CNTs will behave as rigid cylinders if their diameters are less than $10 \text{ \AA}$; whereas the CNTs will flatten against each other under the van der Waals attraction, forming a honeycomb structure if the CNT diameters are greater $25 \text{ \AA}$. Gao *et al.* [137] had presented three stability regions based on the SWCNT diameters d_t . It was found that

SWCNTs with diameters $d_t < 20 \text{ \AA}$, are stable; while diameters $d_t > 60 \text{ \AA}$ are unstable. Hertel *et al.* [103,138] studied the strength and effect of the surface van der Waals forces on the shape of CNTs using atomic-force microscopy, continuum mechanics, and MD simulations. Their results showed that the van der Waals forces interaction between CNTs and a substrate can lead to substantial axial and radial deformation, upsetting the idealized shape of free CNTs. First principles study consisting of two crossed (5,5) SWCNTs were carried out by Yoon *et al.* [139]. They showed that the intertube contact distance is highly dependent on the applied force, and that the contact distance saturates at about $2.5 \text{ \AA}$. And very recently, detailed MD simulations for two aligned SWCNTs and a stack of three aligned SWCNTs were performed by Ma *et al.* [140]. They discovered that the van der Waals force between the SWCNTs is responsible for a small frictional force between rafts made of CNTs.

While experimental studies on CNT bundles have been extensive, the mechanical properties of CNT reinforced composites have also been investigated. Li *et al.* studied the mechanical properties of SWCNT reinforced epoxy composites with varying weight percentages (0, 1, 3, and 5 wt%) of SWCNTs measured by nanoidentation and nanoscratch techniques [141]. They discovered that the hardness, elastic modulus, and scratch resistance of SWCNT reinforced epoxy composites increase with increasing weight percentage of SWCNTs. For example, epoxy with 5 wt% SWCNT showed an increase in the elastic modulus value by 75% and hardness by 30% when compared to the pure epoxy. In Thostenson and Chou's research [142], they observed Euler-type buckling behaviour of CNTs with small diameters in a polymer composite. However, large diameter CNTs in a polymer composite showed locally sharp kinking as depicted in

Fig. 4.3. These deformation behaviours suggest a probable existence of a critical diameter for the change in buckling modes.

Fig. 4.3. TEM micrographs of CNT buckling in an aligned composite showing (a) large scale Euler-type buckling observed for CNTs with small diameters, (b) local buckling of a large diameter CNT, and (c) segmental buckling of a CNT with a large diameter at higher strain [142].

Experiments to extract the elastic properties of CNT bundles have also been performed. Salveta *et al.* have carried out experiments using atomic force microscope to obtain the elastic and shear moduli of SWCNT bundles [81]. The buckling instabilities in an array of vertically aligned MWCNTs under uniaxial compression using a nanoindenter have also been reported by Waters *et al.* [143], who found that the buckling load is of the order of 2 μN for CNTs with 250 Å outer radius, 130 Å inner radius, and heights of 500 and 1000 Å. Direct tensile tests were performed on well-aligned MWCNT strands by Li

et al. [144]. The measured average tensile strength and Young's modulus E_Y are 1.2 GPa and 16 GPa respectively.

Much theoretical studies on CNT bundles have also being carried out [145 - 150]. Most of the studies make use of nanoscale simulation methods to study the elastic properties of CNT bundles. Lu [145] determined the elastic properties of CNT bundles using empirical force-constant model and found that the elastic moduli are insensitive to structural details such as the helicity, radius, and the number of walls. Ru [146] made use of a modified honeycomb model to study the elastic buckling of CNT bundles under high pressure and predicted the critical pressure is about 1.8 GPa for SWCNT bundles with diameters about 13 Å. The finding is in good agreement with the results from other works [151 - 153]. By making use of Monte Carlo simulations, Kwon *et al.* [147] discovered that orientational dislocations or twistons may exist in twisted CNT bundles because of the competition between anisotropic intertube interactions and torsion rigidity. Pipes and Hubert [148], however, made use of a traditional textile-mechanics approach whereby the CNT was treated as a continuous textile fibre, and an utilized anisotropic elasticity theory to examine the effective elastic properties of helical arrays of CNTs. Elliot *et al.* [149] performed a series of MD simulations and demonstrated that SWCNT bundles undergo a discontinuous collapse transition under hydrostatic pressure. They also found out that the diameter of the SWCNT is the key parameter determining the transition pressure since chirality appears to be insignificant. The structural and elastic properties of CNT fibres were also studied by Wei and Srivastava [150]. They have developed a general analytical expression from continuum elastic theory for the computation of Young's modulus E , for a range of CNT fibres.

Many other interesting works related to CNT bundles were also carried out, such as, capturing images of the early stages of carbon nanofibre growth using high-resolution transmission electron microscopy *in situ* [154]. The team showed images revealing the events that lead to carbon nanofibre growth and the observations are in good agreement with Density-functional theory calculations. Interestingly, Hinds *et al.* made use of an array of aligned CNTs across a polymer film to form a well-ordered membrane structure [155]. As CNT bundles are held together by van der Waals interaction, the CNTs can easily slide over each other, resulting in a low shear modulus which is an obstacle in the fabrication of macroscopic fibres composed of CNTs. To solve this problem, Kis and colleagues introduced stable links between neighbouring CNTs within the bundles, using moderate electron-beam irradiation inside a transmission electron microscope [156]. Measurements of the mechanical properties show a 30-fold increase of the bending modulus, owing to the formation of stable crosslinks that effectively eliminate sliding between the CNTs. Qian *et al.* [157] used molecular mechanics and MD simulation methods to study the nature of load transfer in a CNT bundle and realized that twisting can significantly enhance the load transfer between the neighbouring SWCNTs.

4.2 Non-twisted carbon nanotube bundles

The excellent mechanical properties of CNTs have made CNT bundles a good candidate to be used in CNT-reinforced nanocomposites. Here, non-twisted CNT bundles are investigated using MD simulations to further understand how different configurations of non-twisted CNT bundles will affect their compressive and tensile properties.

4.2.1 Numerical simulations

Schematic cross-sectional views of non-twisted CNT bundles involving three and seven (10,10) SWCNTs respectively, that were studied are shown in Fig. 4.4. The SWCNTs in the CNT bundle are spaced $d_{in} = 3.4 \text{ \AA}$ apart and their lengths are $l_t = 123.1 \text{ \AA}$. The diameter of each (10,10) SWCNT is $d_t = 13.57 \text{ \AA}$. A full MD simulation via the short-range Brenner's "second generation" reactive empirical many-body bond order potential energy [56] is carried out on these two CNT bundles.

Fig. 4.4. Schematic cross-sectional diagram of CNT bundle of (a) three (10,10) SWCNTs and (b) seven (10,10) SWCNTs, with the diameter of each SWCNT is $d_t = 13.57 \text{ \AA}$ and the length $l_t = 123.1 \text{ \AA}$.

As the Brenner's "second generation" reactive empirical many-body bond order potential energy [56] is a short-range model and does not account for the non-bonding interactions between atoms, therefore in this work, the intertube spacing interaction between the SWCNTs in the bundles are computed using the long-range van der Waals

potential in the form of Lennard-Jones (12,6) potential [50,51]. The coupling between the short and long-range potential is discussed in section 2.3.

In the MD simulation, the non-twisted CNT bundles are subjected to axial compressions and tensions by applying a rate of 50 m/s and 20 m/s respectively at both ends. At the same time, the atoms at both ends of the non-twisted CNT bundles are not subjected to the interatomic forces. The end atoms are then moved inwardly along the axis by small steps, followed by a conjugate gradient minimization method to relax the CNT bundle, whilst keeping the end atoms fixed.

4.2.2 Non-twisted carbon nanotubes bundles under axial compressive load

When compressed, the non-twisted CNT bundles will undergo structural deformation. Fig. 4.5 shows the morphological changes at various stages of the compression process. Fig. 4.5(a) shows the non-twisted CNTs at strain $\epsilon = 0.0$, where there is no deformation. Further compression until strain $\epsilon = 0.04435$, will cause the non-twisted CNT bundle of three (10,10) SWCNTs to spontaneously collapse into a three fin pattern, while the non-twisted CNT bundle of seven (10,10) SWCNTs are bent slightly outwards from the center SWCNT. At strain $\epsilon = 0.05175$, the non-twisted CNT bundle of three (10,10) SWCNTs continue to deform. However, the non-twisted CNT bundle of seven (10,10) SWCNTs begins to buckle forming three-fin patterns in each of the SWCNTs. Finally at strain $\epsilon = 0.1536$, the non-twisted CNT bundle of three (10,10) SWCNTs buckles sideways in the same direction, while the SWCNTs in the non-twisted CNT bundle of seven all buckle outwards from the center SWCNT forming a ‘birdcage’ pattern.

Fig. 4.5. Morphological structural deformation of non-twisted CNT bundle of three (10,10) SWCNTs and seven (10,10) SWCNTs at different strains.

Figure 4.6 shows the force-deformation curves for the two non-twisted CNT bundles and, for comparison purposes, the force-deformation curve of a (10,10) SWCNT is included in the plot. From the plot, it is evident that the more SWCNTs there are in a bundle, the higher buckling load P_{cr} is required to cause the non-twisted CNT bundle to collapse. For instance, a (10,10) SWCNT has a buckling load $P_{cr} \approx 1.0 \times 10^{-7}$ N, while the non-twisted CNT bundle with three (10,10) SWCNTs has a higher buckling load $P_{cr} \approx 2.4 \times 10^{-7}$ N. And finally the non-twisted CNT bundle of seven (10,10) SWCNTs has the highest buckling load $P_{cr} \approx 6.6 \times 10^{-7}$ N.

Fig. 4.6. Force-deformation curves for non-twisted CNT bundles of seven and three (10,10) SWCNTs and a (10,10) SWCNT.

Further simulations were also carried out for non-twisted CNT bundles composing three and seven (5,5), (12,12), (15,15) and (18,18) SWCNTs. The intertube spacing

between each individual SWCNTs in the non-twisted CNT bundles remains at $d_{in} = 3.4 \text{ \AA}$ and the length of each non-twisted CNT bundle is the same at $l_t = 123.1 \text{ \AA}$. Figure 4.7 shows the plot of critical buckling load P_{cr} against the diameters d_t of the SWCNTs, where the solid and dash lines are fitted to aid in the reading of the plot. It shows from the plot that as the diameter d_t of the SWCNTs in the non-twisted CNT bundle increases, the critical buckling load P_{cr} also increases exponentially. From the plot, it can be seen that the critical buckling load P_{cr} of the non-twisted CNT bundles of three tend to reach a maximum value of $P_{cr} \approx 3.0 \times 10^{-7} \text{ N}$ despite further increases in the SWCNT diameters d_t .

Fig. 4.7. Critical buckling loads P_{cr} for various non-twisted CNT bundles of three and seven SWCNTs.

However, when the non-twisted CNT bundle contains seven SWCNTs, the critical buckling load P_{cr} is about two to three times higher than the non-twisted CNT bundles of three SWCNTs. As the diameter d_t of the SWCNTs in the non-twisted CNT bundle increases, the difference in critical buckling loads P_{cr} between the non-twisted CNT bundle of the three and seven SWCNTs also increases. For instance, at diameter $d_t = 6.79 \text{ \AA}$, the critical buckling load P_{cr} of the non-twisted CNT bundle of seven (5,5) SWCNTs is about 2.1 times larger. However, when the diameter increases to $d_t = 24.43 \text{ \AA}$, the critical buckling load P_{cr} of the non-twisted CNT bundle of seven (18,18) SWCNTs is about 2.4 times larger.

Fig. 4.8. Critical strains ϵ_{cr} for various non-twisted CNT bundle of three and seven SWCNTs.

The critical strains ϵ_{cr} of the various non-twisted CNT bundles were also investigated. Figure 4.8 depicts that, in general, as the diameter d_t of the SWCNTs in the non-twisted CNT bundle increases, the critical strain ϵ_{cr} will decrease. Furthermore, the critical strain ϵ_{cr} of the non-twisted CNT bundle of seven SWCNTs is generally higher than that of non-twisted CNT bundle of three SWCNTs. For example, the critical strain ϵ_{cr} of the non-twisted CNT bundle of seven (10,10) SWCNTs is $\epsilon_{cr} = 0.05175$, while the critical strain ϵ_{cr} of the non-twisted CNT bundle of three (10,10) SWCNTs is lower at $\epsilon_{cr} = 0.04435$. This is due to the existence of more SWCNTs in the non-twisted CNT bundle of seven, giving rise to higher strength and thus higher resistance to buckling. However as the diameter d_t increases, the difference between critical strains ϵ_{cr} of both the non-twisted CNT bundle of seven and three SWCNTs becomes smaller.

The mechanical properties, in particular the critical buckling loads P_{cr} and critical strains ϵ_{cr} , of different configurations of non-twisted CNT bundles, using MD simulations, were studied and it was found that the critical buckling loads P_{cr} of non-twisted CNT bundles are much higher than that of a SWCNT. At the same time, the bigger the non-twisted CNT bundle (composing more SWCNTs) the higher buckling load P_{cr} it will have. Though with a higher buckling load P_{cr} , non-twisted CNT bundles have lower critical strain ϵ_{cr} than individual SWCNTs. Additionally, bigger non-twisted CNT bundles with more SWCNTs are expected to have higher critical strains ϵ_{cr} than non-twisted CNT bundles with less SWCNTs. And the difference between the two critical strains ϵ_{cr} will diminish further as the diameter d_t increases.

4.2.3 Non-twisted carbon nanotubes bundles under axial tensile load

MD simulations were also carried out by applying a tensile load at both ends of the CNT bundles. The results of the critical failure loads P_f and critical strains ϵ_{cr} for bundles of three (5,5) SWCNTs; seven (5,5) SWCNTs; three (10,10) SWCNTs; and seven (10,10) SWCNTs are tabulated in Table 4.1.

Table 4.1. Critical failure loads P_f and strains ϵ_{cr} of a single, bundle of three, and bundle of seven (5,5) and (10,10) SWCNTs.

	Critical failure load P_f (N)	Critical strain ϵ_{cr}
Single (5,5) SWCNT	0.8×10^{-7}	0.28
Bundle of three (5,5) SWCNTs	2.8×10^{-7}	0.36
Bundle of seven (5,5) SWCNTs	6.5×10^{-7}	0.36
Single (10,10) SWCNT	1.6×10^{-7}	0.28
Bundle of three (10,10) SWCNTs	4.9×10^{-7}	0.30
Bundle of seven (10,10) SWCNTs	12.8×10^{-7}	0.36

It is observed from Table 4.1 that the failure load P_f increases as the number of SWCNTs in a CNT bundle increases. For example, a single (5,5) SWCNT will fail at a load of $P_f = 0.9 \times 10^{-7}$ N, while a bundle of three and seven (5,5) SWCNTs will fail at a load of about three times and seven higher respectively. Expectedly, having a larger diameter d_t , the (10,10) CNT bundles will collapse at larger failure load P_f . From the

table, it is also observed that the CNT bundles tend to fail at higher critical strains E_c , than a single SWCNT.

4.3 Twisted carbon nanotube bundles

Qin and Iijima [158] has reported that there are some cases when SWCNT bundle will naturally assume a twisted form, which is similar to the wire ropes at continuum scale. Recently, Li *et al.* [129] produced continuous twisted CNT bundles by adding a rotating wind-up rod and through careful selection of the reaction conditions. According to continuum mechanics analysis of wires or fibres, twisting the wires or “weaving” the fibres can lead to a cable or rope having much better tensile properties than a straight bundle would have [159]. This motivates the study on the effect of twisting on the compressive and tensile properties of twisted CNTs. The understanding developed from the MD simulations will serve as a feedback in developing a deeper understanding of twisted CNT bundles.

4.3.1 Numerical simulations

A schematic cross-sectional view of a single CNT bundle involving six (5,5) SWCNTs surrounding a core (5,5) SWCNT being studied is shown in Fig. 4.9. The SWCNTs in the CNT bundle are spaced $d_{in} = 3.4 \text{ \AA}$ apart and the length of the CNT bundle is $L = 123.1 \text{ \AA}$. The diameter of each (5,5) SWCNT is $d_t = 6.79 \text{ \AA}$ and each CNT bundle contains 7000 atoms. A twisting load is then applied on six surrounding SWCNTs around the centre of the core SWCNT at $1^\circ/\text{fs}$. The twist angle θ_t is quantified as the relative

twist between the two ends of the CNT bundle. A total of eight cases have been studied, which correspond to total twisting angles θ_t of 0° , 15° , 30° , 60° , 75° , 90° , 100° , and 120° . Similarly, a full MD simulation via the short-range Brenner's "second generation" reactive empirical many-body bond order potential energy [56], coupled with the long-range non-bonded van der Waals forces F_{vdw} characterized by the Lennard Jones (12,6) potential [50,51] was implemented.

Fig. 4.9. Schematic cross-sectional diagram of CNT bundle of six (5,5) SWCNTs surrounding a core (5,5) SWCNT, with the diameter and length of each SWCNT at $d_t = 6.79 \text{ Å}$ and $l_t = 123.1 \text{ Å}$ respectively.

MD simulations were carried out on twisted CNT bundles under axial compression and tension force. The CNT bundles were fully relaxed by a conjugate gradient minimization method before the axial compressive and tensile loads are applied. After relaxation, the intertube distances d_{in} for different twisting angle θ_t of CNT bundles vary from 3.2 Å to 3.4 Å . The axial compressive and tensile loads are achieved by applying a rate of 50 m/s and 20 m/s respectively at both ends of the CNT bundles. The atoms at both ends of the CNT bundles are made transparent to the interatomic forces and are then

moved inwardly or outwardly along the axis in small steps. The CNT bundles are relaxed again at every 50 time steps interval.

4.3.2 Twisted carbon nanotubes bundles under axial compressive load

When a twisted CNT bundle is subjected to axial compression, the surrounding six SWCNTs will expand and contract radially along the centre axis of the CNT bundle. To quantify the radial expansion and contraction morphological changes, the van der Waals forces F_{vdw} acting on the centre SWCNT is computed and shown in Fig. 4.10.

Fig. 4.10. van der Waals forces F_{vdw} acting on the core SWCNTs of CNT bundles twisted at various angles θ_t during axial compression.

Figure 4.10 depicts the total intertube van der Waals forces F_{vdw} acting on the core SWCNTs of various CNT bundles twisted at angles $\theta_t = 0^\circ, 30^\circ, 60^\circ$, and 90° . From the graph, it can be seen that the total intertube van der Waals forces F_{vdw} will go through a cyclic pattern during compression. When the six surrounding SWCNTs are expanding radially along the centre axis of the CNT bundle, the total intertube van der Waals forces F_{vdw} acting on the core SWCNT will be lower, as shown by the “valleys” of the plots in Fig. 4.9. However, when the six surrounding SWCNTs are contracting radially, the total intertube van der Waals forces F_{vdw} acting on the core SWCNT will be higher, which is shown by the “peaks” of the plots in Fig. 4.10.

Fig. 4.11. Critical buckling loads P_{cr} of CNT bundles twisted at different angles θ_t .

Twisted CNT bundles are expected to have lower critical buckling loads P_{cr} and critical strains than non-twisted CNT bundles due to the curved geometry of the six surrounding SWCNTs formed by twisting. Figure 4.11 depicts the plot of the critical buckling loads P_{cr} against the angle of twist θ_t in the CNT bundle. As the twist angle θ_t increases from 0° to 60° , the critical buckling load P_{cr} will decrease about 5% from 3.25×10^{-7} N to 3.08×10^{-7} N. Further increase in the twist angle θ_t from 60° to 120° will however result in a larger drop of about 42% in the critical buckling load P_{cr} from 3.25×10^{-7} N to 1.88×10^{-7} N.

Fig. 4.12. Morphological changes of a twisted CNT bundle (twisting angle $\theta_t = 60^\circ$) due to compressive load at different strains.

Additionally, due to the curved geometry in the six surrounding SWCNTs, they will buckle earlier than the core SWCNT. The morphological changes of the CNT bundles twisted at an angle of $\theta_t = 60^\circ$ at three different strains ϵ are shown in Fig. 4.12. At the initial stage when strain $\epsilon = 0$, the whole CNT bundle is relaxed, and the helical angle θ_{he} formed due to the twisting of the six surrounding SWCNTs is about 77° . Upon further compression till strain $\epsilon = 0.048$ [see Fig. 4.12(b)], the six surrounding SWCNTs buckle outwards from the centre axis fractionally earlier forming a “birdcage” pattern; while the core SWCNT remains unbuckled. The fully buckled CNT is shown in Fig. 4.12(c).

Fig. 4.13. Forces F acting on the core SWCNT and a surrounding SWCNT of a 60° twisted CNT bundle during axial compression.

To gain further insight on the load P each SWCNTs is experiencing in the 60° twisted CNT bundle, the force F acting on each individual SWCNT in the CNT bundle during compressive loading, is plotted against its deformation in Fig. 4.13. As the axial force F acting on the six surrounding SWCNTs is the same, therefore only the axial force F acting on one surrounding SWCNT and the core SWCNT is plotted. From the plot, it is evident that the surrounding SWCNT will buckle slightly earlier than the core SWCNT and at a lower critical buckling load P_{cr} . It is also interesting to note that the core and surrounding SWCNTs carry 15.5% and 84.5% of the total axial compressive load.

4.3.3 Twisted carbon nanotubes bundles under axial tensile load

Contrary to wire ropes that provides better structural reliability and mainly used in applications in which tensile load is dominant, twisted CNT bundles tend to underperform compared to non-twisted CNT bundles when subjected to axial tensile force. Due to the twist, the six surrounding SWCNTs are brought closer to each other in a helical angle, forming junctions between the neighbouring SWCNTs. During axial tensile loading, the six surrounding SWCNTs are further pulled closer to the core SWCNT causing the intertube distance d_{in} between individual SWCNTs to decrease. Figure 4.14 shows the plot of intertube distance d_{in} against strain ϵ . The plot clearly shows that the larger amount of twisting angle θ_t will cause the intertube distance d_{in} to decrease as the strain ϵ grows larger. For instance, at a deformation of $\Delta l_t = 0.16$, the intertube distance d_{in} in a 90° twisted CNT bundle has decreased from 3.2 Å to 1.9 Å. However, the intertube distance d_{in} remains at around 3.2 Å in the 30° twisted CNT bundle even after a deformation of $\Delta l_t = 0.16$. The reason why a larger twisting angle will lead to a reduction in intertube distance d_{in} can be attributed to the fact that being twisted at a larger angle

θ_t , the six surrounding SWCNTs are more closely intertwined together with their curved geometry. Therefore when a tensile load is applied at both ends of the CNT bundles, the curved geometry of each of the six individual surrounding SWCNTs tends to be straightened out leading to a reduction in the intertube distances d_{in} . Figure 4.15 shows a diagram of a curved SWCNT which when subjected to axial tensile load, will tend to be straightened and therefore reducing the intertube distance d_{in} .

Fig. 4.14. The intertube distances d_{in} for CNT bundles twisted at different angles θ_t at different strains ϵ .

Fig. 4.15. A SWCNT with curved geometry will straighten out when axial tensile load is applied.

Fig. 4.16. Total intertube van der Waals forces F_{vdw} acting on the core SWCNTs of CNT bundles twisted at various angles θ_t during axial tension.

As the intertube distance d_{in} changes, the intertube van der Waals forces F_{vdw} will also vary. This phenomenon can be seen in Fig. 4.16 in which the total van der Waal forces F_{vdw} acting on the core SWCNT at different strains ϵ are plotted for CNT bundles twisted at 0° , 30° , 60° , and 90° .

When the tensile load is applied to the CNT bundles, the total intertube van der Waal forces F_{vdw} acting on the core SWCNT will increase for larger twisting angle θ_t , or in other words, there is a decrease in the intertube distance d_{in} between the surrounding six SWCNTs and the core SWCNT. For instance, the total intertube van der Waal forces F_{vdw} acting on the core SWCNT for the 90° twisted CNT bundle will increase to a maximum value at a deformation of $\Delta l_t \approx 0.14$, after which, the total intertube van der Waal forces F_{vdw} will decrease slowly. Here, the decrease in the total intertube van der Waal forces F_{vdw} acting on the core SWCNT is not a result of an increase in the intertube distance d_{in} between the six surrounding SWCNTs and the core SWCNT, instead it is an indication of an increase in repulsive energy (which will be explained later in this section).

According to Fig. 4.17, and contrary to the theory of wire ropes in continuum domain, twisted CNT bundles will not produce better tensile properties. When the twisting angle θ_t is greater than 75° , the failure load P_{ft} actually decreases sharply. An investigation to the cause of this was carried out. It was realised that when a CNT bundle with twisting angle θ_t greater than 75° is subjected to axial tension, the intertube spacing d_{in} between the seven SWCNTs decreases to lower than $2.0 \text{ \AA}$. This constitutes to an increase in the repulsive forces F_{rep} between the seven SWCNTs, which is similar to graphite, and the SWCNTs will repel each other at the junction area when the intertube distance d_{in} is below $3.4 \text{ \AA}$. As a result, these CNT bundles tend to fail at the junctions with lower load and strain. This is in qualitative agreement with previous work [103,137 – 140] where

investigations found that the dangling C – C bonds formed between SWCNTs when they are brought close together are not strong enough to withstand bending and axial forces.

Fig. 4.17. Critical failure loads P_f of CNT bundles twisted at different angles θ_t due to axial tensile force.

Figures 4.18 and 4.19 show the total intertube van der Waal forces F_{vdw} and intertube repulsive forces F_{rep} around mid-length of the 0° and 90° twisted CNT bundles respectively. The mid-length is chosen because it is where the twisted SWCNTs meet at a helical angle, forming a junction where the SWCNTs overlap. In Fig. 4.18, we can see that there is a steady increase in the total van der Waals forces F_{vdw} as the deformation Δl_t becomes larger for the 90° twisted CNT bundle due to the closer intertube distance d_{in} . However, the total van der Waals forces F_{vdw} for the 0° twisted CNT bundle weakens

steadily due to the elongation of the CNT bundle during tension instead of a reduction in the intertube distances d_{in} (as seen in Fig. 4.14). At the same time, the plot also reveals that higher van der Waals forces are present in the 90° twisted CNT bundle than the 0° twisted CNT bundle.

Fig. 4.18. Total intertube van der Waals forces F_{vdw} around mid-length of 0° and 90° twisted CNT bundles.

Similarly, the plot of total intertube repulsive force F_{rep} against deformation Δl_t is shown in Fig. 4.19. Throughout the whole tension process, the 0° twisted CNT bundle do not have any intertube repulsive force due to the large intertube spacing d_{in} . Likewise, there isn't any intertube repulsive force F_{rep} present in the 90° twisted CNT bundle up to $\Delta l_t = 0.185$. However, after $\Delta l_t > 0.185$, the intertube distance d_{in} for the 90° twisted

CNT bundle reduces to less than $2.0 \text{ \AA}$, which sees a sudden increase in the intertube repulsive force F_{rep} while its intertube van der Waals force F_{vdw} begins to decrease as shown in Figs. 4.16 and 4.17. It is worthy to note that these intertube van der Waal forces F_{vdw} and repulsive forces F_{rep} are acting radially on neighbouring SWCNTs and therefore as a result of the sudden surge in intertube repulsive forces F_{rep} , the junction area where the SWCNTs overlap are weakened severely. At the same time, tensile load is being applied on the CNT bundle and therefore the collapse often occurs at the junction area (see Fig. 4.20).

Fig. 4.19. Total intertube repulsive forces F_{rep} around mid-length of 0° and 90° twisted CNT bundles.

As a consequence of the sudden increase in repulsive force F_{rep} at the junction areas where the individual SWCNTs overlapped, CNT bundles that are twisted at a larger angle

Fig. 4.21. Critical strains ϵ_{cr} of CNT bundles twisted at different angles θ_t due to axial tensile force.

Figure 4.22 shows the cross-sectional view of two CNT bundles with a twisting angle of 0° and 120° respectively at different strains. From the figure, it is evident that the 120° twisted CNT bundle suffers a large amount of distortion in the individual SWCNT as compared to the 0° twisted CNT bundle. The SWCNTs in the 120° twisted CNT bundle lose their cylindrical shapes at higher strains resulting in a dislocation of the hexagonal arrangement of the *C* atoms. The distortion of individual SWCNTs in the CNT bundle is manifested by the compressive van der Waal forces as well as the repulsive forces between the seven SWCNTs. Moreover, the attractive van der Waal forces at opposite

faces of each individual SWCNT also contribute to the collapse of the twisted CNT bundle.

Fig. 4.22. Cross-sectional view of CNT bundles twisted at 0° and 120° at different strains ε .

MD simulations were performed on non-twisted and twisted CNT bundles under axial compression and tension. Non-twisted CNT bundles, composing three and seven SWCNTs aligned parallel to one another and spaced $d_{in} = 3.4 \text{ \AA}$ apart from one another, have superior buckling loads P_{cr} compared to their single CNT counterpart. Non-twisted CNT bundles also exhibit excellent tensile properties with failure loads P_{fl} about three to seven-fold greater than their single CNT counterpart.

Each twisted CNT bundle that was simulated, contains seven (5,5) SWCNTs, of which six of them are surrounding a core SWCNT. The six surrounding SWCNTs were twisted at various angles. Due to the curve geometry of the six surrounding SWCNTs, twisted CNT bundles do not have good compressive properties. Results show that larger twist angles θ_t will lead to lower critical buckling load P_{cr} and strain ϵ_{cr} . Twisted CNT bundles also do not demonstrate good tensile properties as opposed to twisted wire ropes which are useful in applications where the tensile force is dominant. As the twisted CNT bundles are subjected to axial tension force, the intertube distances d_{in} decrease giving rise to an increase in the intertube van der Waals forces F_{vdw} . The repulsive forces F_{rep} between the seven SWCNTs then suddenly increase due the decline in intertube distances d_{in} . The sudden surge in the repulsive forces F_{rep} cause the SWCNTs to repel one another at the junction area where the SWCNTs overlap when the intertube distance d_{in} is below $3.4 \text{ \AA}$. As a result, these CNT bundles tend to fail at the junction areas with lower failure load P_{fl} and strain ϵ_{cr} .

CHAPTER 5

THERMAL PROPERTIES OF CARBONNANOTUBES

Since their discovery [12] in the early 1990s, CNTs have attracted much attention due to their excellent mechanical properties. One area of investigation is the study of CNTs' thermal properties. Hone *et al.* [160] measured the thermal conductivity of SWCNTs by comparing the temperature drops across the SWCNT samples and a constantan rod. Their results indicated a thermal conductivity κ of between 60 and 180 W/m-K at 30K. Yang *et al.* [161] investigated the thermal conductivity of MWCNTs using the pulsed photothermal reflectance technique. Their results showed that the thermal conductivity of MWCNTs is about 15 W/m-K at room temperature. Vavro *et al.* [162] compared the thermal conductivity of SWCNTs and C₆₀-filled SWCNTs and found that the magnitude of the thermal conductivity of C₆₀-filled SWCNTs is generally 20% higher than that of an 'empty' SWCNTs. At room temperature the thermal conductivity κ of empty SWCNTs is approximately 15 W/m-K, while the thermal conductivity κ of C₆₀-filled SWCNTs is about 18 W/m-K. More recently, Schelling and Keblinski [163] analysed the thermal

expansion of CNTs using the Grüneisen theory [164]. Their results showed a negative thermal-expansion coefficient for long CNTs. Additionally, The coalescence property of an array of SWCNTs forming into a single MWCNT under thermal treatment has been investigated by López *et al.* [135].

Although the thermal expansion coefficient of CNTs has been widely studied, no studies have focused on the atomic structural stability and changes of the CNTs at various temperatures. In this work, we incorporate the Berendsen thermostat scheme [165] into the MD simulation to determine the atomic structural changes and stability of various CNTs at different temperatures. The Berendsen thermostat scheme is widely used even though it does not reproduce a canonical ensemble. The scheme usually gives the same results as other rigorous methods, and it permits the system to fluctuate about the desired temperature.

5.1 Molecular dynamics at constant temperature

In MD simulations, if temperature considerations are not taken into account, one measure of the accuracy of the integration of motion for the atoms is that the total energy for the system is conserved. In thermodynamic terms, the simulations are said to have been performed in the microcanonical or NVE ensemble. In other words, the number of atoms N , the volume V , and the energy E of the system are constants.

Although MD within the microcanonical ensemble is easiest to perform, if the aim of the simulation is to mimic the conditions under which the systems are investigated experimentally, then the microcanonical ensemble might not be appropriate. In particular, it is common to carry out experiments under conditions in which the ambient temperature

is constant. The thermodynamic ensemble that corresponds to such a condition is known as canonical or NVT ensemble.

Researchers have devised different schemes to perform MD at constant temperature T . Each of the schemes has its own advantages and disadvantages. The following section will discuss the more important schemes in detail, two of which represents true microcanonical condition, while another two are simpler to implement but not resembling truly microcanonical condition.

5.1.1 Andersen thermostat

In the constant-temperature method proposed by Andersen [166], the system is coupled to a heat bath that imposes the desired temperature. The coupling to a heat bath is represented by stochastic impulsive forces that act occasionally on randomly selected atoms. Between stochastic collisions, the system is simulated at constant energy according to the normal Newtonian laws of motion and so the overall effect is equivalent to a series of microcanonical simulations, each performed at a slightly different energy. The stochastic collisions ensure that all accessible constant-energy shells are visited according to their Boltzmann weight.

By calculating the energy change due to a stochastic collision, the mean rate ν at which an atom would be subjected to a stochastic collision is given by

$$\nu = \frac{2aK}{3k_B N_d^{1/3} N^{2/3}}, \quad (5.1)$$

where a is a dimensionless constant, κ is the thermal conductivity, k_B is the Boltzmann constant, and N_d is the number density of the atoms. If the thermal conductivity κ is not known, the mean rate $\bar{v}$ can be obtained from the interatomic collision frequency ν_c

$$\bar{v} = \frac{\nu_c}{N^{2/3}}. \quad (5.2)$$

If the collision rate $\bar{v}$ is too low, then the system does not sample from a canonical distribution of energies. However, if it is too high, then the temperature control algorithm dominates and the system does not show the expected fluctuations in kinetic energy E_K . One major drawback of the Andersen thermostat, however, is that it does not generate a smooth trajectory.

5.1.2 Nosé-Hoover thermostat

Extended system methods, originally introduced for performing constant temperature MD by Nosé [167] and subsequently developed by Hoover [168], consider the thermal reservoir to be an integral part of the system. The reservoir is represented by an additional degree of freedom s , which has a conjugate momentum p_s . The real velocities of the atoms is given by

$$\mathbf{v} = s \frac{d\mathbf{r}}{dt} = \frac{\mathbf{p}}{ms}. \quad (5.3)$$

An extra potential energy $\mathcal{U}_s$ is associated to the additional degree of freedom s , such that

$$\mathcal{U}_s = (N_f + 1)k_B T \ln s, \quad (5.4)$$

where N_f is the number of degrees of freedom in the physical system and T is the desired temperature. The kinetic energy E_{Ks} is

$$E_{Ks} = \frac{Q}{2} \left(\frac{ds}{dt} \right)^2 = \frac{p_s^2}{2Q}, \quad (5.5)$$

where Q is the thermal inertia parameter and its magnitude determines the coupling between the reservoir and the real system, and hence influences the temperature fluctuations. If Q is too large, the energy flow will be slow between the system and the reservoir. However if Q is too small, long-lived and weakly damped oscillations of energy occur, resulting in poor equilibration. Nosé [167] suggested that Q should be proportional to $N_f k_B T$; the constant of proportionality can then be obtained by trial and error, so as to achieve satisfactory damping of these correlations.

5.1.3 *Ad hoc* velocity scaling

A convenient definition of the temperature in a many-body system makes use of the equipartition of energy over all degrees of freedom that enter quadratically in the Hamiltonian of the system. In particular, the average kinetic energy per degree of freedom is

$$\langle E_K \rangle = \left\langle \frac{1}{2} m v_\alpha^2 \right\rangle = \frac{1}{2} k_B T, \quad (5.6)$$

where m is the mass, v_α is the x, y , and z component of the velocity of a given atom, and T is the temperature. In practice, the total kinetic energy of a system with N atoms can be computed by multiplying Eqn. (5.6) with the number of degrees of freedom

$N_f = 3N - 3$. As a result, for any dimensional system, the total kinetic energy can be written as

$$\langle E_K \rangle = \left\langle \frac{1}{2} m \sum_i^N v_{i\alpha}^2 \right\rangle = \frac{1}{2} k_B N_f T \quad (5.7)$$

As such, at any time t , the instantaneous temperature T , is

$$T(t) = \sum_i^N \frac{m_i v_{i\alpha}^2(t)}{k_B N_f}. \quad (5.8)$$

Since there are only carbon atoms in a three-dimensional CNT, Eqn. (5.8) can be rewritten as

$$T(t) = \frac{m}{3Nk_B} \sum_i^N v_{i\alpha}^2(t), \quad (5.9)$$

assuming $N_f \approx 3N$. From this, it is clear that the instantaneous temperature $T(t)$ can be adjusted to match the desired temperature T by scaling all velocities with a factor $\sqrt{T/T(t)}$. Since

$$\frac{v_{i\alpha}^{new}}{v_{i\alpha}^{old}} = \sqrt{\frac{T}{T(t)}}, \quad (5.10)$$

therefore the velocities can be scaled accordingly to

$$v_{i\alpha}^{new} = v_{i\alpha}^{old} \times \sqrt{\frac{3Nk_B T}{m \sum_i^N v_{i\alpha}^2(t)}} \quad (5.11)$$

Although the *ad hoc* velocity scaling method yields the desired kinetic energy, it does not correspond to any known ensemble. Nevertheless it is useful for the preliminary studies on the effect of thermal properties on CNTs.

5.1.4 Berendsen thermostat

An alternate way to maintain temperature is to couple the system to an external heat bath, which is fixed at a desired temperature [165]. The bath acts as a source of thermal energy, supplying or removing heat from the system as appropriate. The velocities are scaled at each time step, such that the rate of change of temperature is proportional to the difference in temperature between the bath and the system

$$\frac{dT(t)}{dt} = \frac{1}{\tau} [T_{bath} - T(t)], \quad (5.12)$$

where τ is the coupling parameter whose magnitude determines how tightly the bath and the system are coupled together. A larger τ will give a weaker coupling, while a smaller τ will give a stronger coupling. This method gives an exponential decay/growth of the system towards the desired temperature. The change in temperature between successive time steps is

$$\Delta T = \frac{\delta t}{\tau} [T_{bath} - T(t)], \quad (5.13)$$

and therefore the scaling factor λ for the velocities is

$$\lambda = \sqrt{1 + \frac{\delta t}{\tau} \left[\frac{T_{bath}}{T(t)} - 1 \right]}. \quad (5.14)$$

From Eqn. (5.14), it can be seen that if the coupling parameter τ equals to the time step δt , then the Berendsen scheme is equivalent to the simple *ad hoc* velocity scaling method. A coupling constant τ of approximately 0.4 ps [165] has been suggested as a suitable value to use when the time step is 1 fs, thereby giving $\delta t/\tau \approx 0.0025$. The advantage of this approach is that it permits the system to fluctuate about the desired temperature.

Although this method does not reproduce a canonical ensemble, it is widely used, and usually gives the same results as other more rigorous methods discussed above. However, caution must be taken using the Berendsen thermostat. It reproduces the correct average energy, but the distribution is wrong. Therefore, their averages are usually correct, but not their fluctuations.

5.2 Thermal stability of carbon nanotubes

In order to simulate the thermal stability of CNTs, in this thesis, the Berendsen thermostat [165] is employed. Although the fluctuations of energy are incorrect, this scheme is easy to apply, with only slight modifications to the computer codes, and it is robust.

As mentioned in Section 5.1.4, the Berendsen thermostat method [165] gives an exponential increase of the system towards the desired temperature. The plot in Fig. 5.1 illustrates a (10,10) SWCNT heated to temperature $T = 300\text{K}$ over 100,000 time steps.

Fig. 5.1. Exponential growth in temperature T to 300K when applying the Berendsen thermostat method.

To apply the Berendsen thermostat [165] to the studies of CNTs, the atoms are first given random initial velocities uniformly distributed over the interval $[-1,+1]$. Since no external forces act on the CNT, the total linear momentum should be conserved. Therefore

$$v_{i\alpha}^{new} = v_{i\alpha}^{old} - \frac{1}{N} \sum_i^N v_{i\alpha}^{old}, \quad (5.15)$$

where α represents the x , y , and z -directions. These velocities are then rescaled to achieve the desired temperature T by using the scaling factor in Eqn. (5.14) for all directions.

From these initially assigned velocities, Maxwell velocity distribution should develop during equilibration. The Maxwell-Boltzmann law [169] is used to evaluate the Maxwell velocity distribution analytically and is defined as

$$f(\mathbf{v})d\mathbf{v} = \frac{N(\mathbf{v})d\mathbf{v}}{N}, \quad (5.16)$$

which measures the fraction of N atoms having velocity within an interval $d\mathbf{v}$ of a particular value $\mathbf{v}$. From Eqn. (5.16), the Maxwell velocity distribution can then be evaluated analytically as

$$f(v_\alpha)dv_\alpha = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_\alpha^2}{2k_B T}\right) dv_\alpha. \quad (5.17)$$

The distribution is Gaussian with standard deviation $\sigma_{sd} = (k_B T / m)^{1/2}$ about the mean value $\langle v_\alpha \rangle = 0$. Figure 5.2 shows the Maxwell velocity distribution of a (10,10) SWCNT exposed to various temperatures T at 100K, 200K, 300K and 400K employing the Berendsen thermostat [165]. It can be seen that as the temperature T increases, the standard deviation σ_{sd} approaches uniformity.

Fig. 5.2. Effect of temperature on the distribution of the velocity of (10,10) SWCNT, as computed from the Maxwell velocity distribution in Eqn. (5.17).

Fig. 5.3. The velocity distribution averaged over 100,000 time steps of the run (points) compared to the Maxwell distribution (line) for the (10,10) SWCNT at temperature $T=300\text{K}$.

To verify if the Maxwell velocity distribution has developed, the velocity distribution $f(v_\alpha)$ time averaged over a number of time steps is compared with the Maxwell velocity distribution at the same kinetic energy. Figure 5.3 shows the comparison for the (10,10) SWCNT at temperature $T=300\text{K}$. The plot shows good agreement and signifies the equilibrium state is achieved.

During the simulation, it is good to follow the development of the Maxwell distribution (and, hence the approach to equilibrium) by monitoring the time behaviour of the kinetic portion of Boltzmann's celebrated H -function [169], expressed as

$$H_\alpha(t) = \int_{-\infty}^{\infty} f(v_\alpha) \ln(v_\alpha) dv_\alpha. \quad (5.18)$$

Since $f(v_\alpha)$ is a positive fraction, its logarithm is negative, and therefore H_α is negative. For a simulation started from an arbitrarily assigned nonequilibrium situation and undergoing mixing dynamics, $H_\alpha(t)$ decreases to its equilibrium value provided by the Maxwell distribution in Eqn. (5.17). And hence, for x -, y - and z -components, the H -function can be written as

$$H = \frac{1}{3}(H_x + H_y + H_z). \quad (5.19)$$

Figure 5.4 shows the instantaneous H -function computed during the equilibration of the (10,10) SWCNT at temperature $T=300\text{K}$. In the figure, the horizontal line at $H = -0.00505$ is the value of the H -function for the Maxwell velocity distribution at the kinetic energy of the simulation. After about 3000 time steps, the instantaneous H -function converge to the Maxwell's value of H -function, indicating that the Maxwell distribution is developed within about 3000 time steps. Above 3000 time steps, the instantaneous H -function fluctuates along the Maxwell's value of H -function, and hence the system is considered to be in equilibrium after 3000 time steps.

Fig. 5.4. Approach to equilibrium for the (10,10) SWCNT at temperature $T= 300\text{K}$ based on H-function.

At equilibration, the potential energy and kinetic energy E_K should fluctuate about a steady value. Figure 5.5 shows that at temperature $T = 300\text{K}$, equilibrium is reached for the (10,10) SWCNT. The kinetic energy E_K fluctuates around 9.0 eV while the binding energy E_b fluctuates around -7230 eV over 4000 time steps. The plot also signifies that the total energy is conserved.

Fig. 5.5. Plot of kinetic energy and binding energy for the (10,10) SWCNT at temperature $T = 300\text{K}$ after equilibration.

In the section, the simulation methodology, together with the results, are discussed with focus on the relationships between different CNT geometries and their ability to withstand thermal loads. Both close-capped and open-capped SWCNTs are initially investigated to determine the influence of the caps on the CNTs. Next, the thermal stabilities of various CNTs are determined. All the CNTs are ensured to adhere to the Maxwell velocity distribution, and the H-function to confirm their equilibrium state.

5.2.1 Close-capped single-walled carbon nanotubes

Three different lengths l , of (5,5) close-capped SWCNTs are investigated. The lengths l are 122 Å, 183 Å, and 244 Å. Figure 5.6 shows that a 122 Å long (5,5) close-capped SWCNT remains undeformed at temperatures T from 300K up to 2000 K. At $T = 2000$ K, the close-capped SWCNT begins to deform slightly at its body and disintegrates completely at $T = 3489$ K.

Fig. 5.6. The relaxed structures of close-capped (5,5) SWCNT ($l_t = 122\text{Å}$) at various temperatures.

A similar simulation is carried out on a $183\text{ \AA}$ long (5,5) close-capped SWCNT as shown in Fig. 5.7. The longer close-capped SWCNT begins to deform structurally at temperature $T = 2000\text{ K}$ before breaking down completely at a lower temperature $T = 3333\text{ K}$.

Similarly, atomic structural deformation is evident for the $244\text{ \AA}$ long (5,5) close-capped SWCNT before collapsing at $T = 2946\text{ K}$.

Fig. 5.7. The relaxed structures of close-capped (5,5) SWCNT ($l_t = 183\text{ \AA}$) at various temperatures.

5.2.2. Open-capped single-walled carbon nanotubes

As a comparison to close-capped (5,5) SWCNTs, different lengths $l_t = 122 \text{ \AA}$, $183 \text{ \AA}$, and $244 \text{ \AA}$ of open-capped (5,5) SWCNTs are also investigated. The relaxed CNTs at various temperatures are shown in Figs. 5.8 to 5.9.

Fig. 5.8. The relaxed structures of open-capped (5,5) SWCNT ($l_t = 122 \text{ \AA}$) at various temperatures.

It can be seen in Fig. 5.8 that the ends of the $122\text{ \AA}$ long open-capped (5,5) SWCNT begins to flange slightly at temperature $T = 300\text{ K}$. As the temperature increases to $T = 1000\text{ K}$, the open-capped (5,5) SWCNT begins to deform structurally. And when the temperature increases to $T = 3000\text{ K}$, the CNT bends, before disintegrating at $T = 3582\text{ K}$. The bending-induced thermal contraction causes the end-to-end distance to shrink, and agrees with the findings of Schelling *et al.* [163].

Fig. 5.9. The relaxed structures of open-capped (5,5) SWCNT ($l_t = 183\text{ \AA}$) at various temperatures.

Deformation at the ends of the 183 Å long open-capped (5,5) SWCNT is apparent at temperature $T = 1000\text{K}$, as shown in Fig. 5.9. The CNT starts to bend from $T = 2000\text{K}$ to 3000K, causing a reduction of the end-to-end distance. At $T = 3337\text{ K}$, the 183 Å long open-capped (5,5) SWCNT can no longer withstand the thermal load and disintegrates.

A 244 Å long open-capped (5,5) SWCNT is also modelled and simulated thermal load is applied to it. The results show that it collapses after it reaches a temperature of $T = 2798\text{ K}$.

From Figs. 5.6 to 5.9, it can be seen that the atomic structural deformation defers between close-capped and open-capped (5,5) SWCNTs. For open-capped CNTs, the end atoms begin to deform first, while the body of the close-capped CNTs will deform first when subjected to thermal load. The former is due to the unsatisfied bonds present at the ends, and the deformation process started (and driven) by end atoms is to satisfy their bonds, by bonding to other carbon atoms at the end. However, the maximum critical temperatures of both the open-capped and close-capped CNTs can withstand before breaking down are less of than 5% different (see Fig. 5.10). Hence for the ease of modelling, further (10,10) and (12,12) SWCNTs that are open-capped are investigated.

It is observed that the close-capped CNTs will deform, while the open-capped CNTs will bend when subjected to thermal load. Further studies are needed to determine why significant bending can be observed in open-capped CNTs, while deformation is observed in close-capped CNTs.

The response to temperature for the open-capped (10,10) and (12,12) SWCNT is included in Fig. 5.10. From the plot, all the SWCNTs tend to have lower thermal stability as their lengths l_t increase. For instance at length $l_t = 122\text{ Å}$, the (10,10) SWCNT can

resist up to $T = 3350$ K before collapsing. However, the maximum temperature a $244 \text{ \AA}$ long (10,10) SWCNT can withstand is lower, at $T = 2798$ K.

Fig. 5.10. Plot depicting the maximum temperature T various SWCNT of different lengths can resist before collapsing.

Additionally, as the diameter d_t of the SWCNT decreases, its ability to withstand thermal load is higher. This is exemplified by the maximum temperature $T = 2868$ K the (12,12) SWCNT can withstand as compared to the higher maximum temperature $T = 3337$ K for the (5,5) SWCNT, when both their lengths $l_t = 183 \text{ \AA}$.

According to Fig. 5.10, it is evident that the length of the SWCNT affects its response to temperature T . Figure 5.11 helps in explaining the cause of this phenomena using the (10,10) SWCNT as an example. Compared to the shorter $61.55 \text{ \AA}$ (10,10) SWCNT that is shown in Fig. 5.10, it can be deduced that longer SWCNTs tend to break down at a lower

temperature than the shorter SWCNTs. This can be explained by the plot in Fig. 5.11. Although both lengths of (10,10) SWCNT have very close kinetic energy E_K per atom at a certain temperature T , the potential energy E_{POT} per atom is different. The longer (10,10) SWCNT has lower potential energy E_{POT} per atom compared to the shorter (10,10) SWCNT at all temperatures T . When subjected to heat, the chemical bonds from the longer SWCNT break down easier, because each atom from the longer (10,10) SWCNT has lower potential energy E_{POT} . Consequently, the longer (10,10) SWCNT collapses at a lower temperature T than the shorter (10,10) SWCNT.

Fig. 5.11. Plot depicting the kinetic energies E_K and potential energies E_{POT} for the short ($l_t = 61.55$ Å) and long ($l_t = 122.0$ Å) (10,10) SWCNTs at various temperatures T .

5.2.3. Open-capped multi-walled carbon nanotubes

The responses of MWCNTs with different geometries and at different temperatures T are also investigated. In this study, two MWCNTs namely, the (5,5) and (10,10), and (10,10) and (15,15) MWCNTs with same lengths $l_t = 61.55 \text{ \AA}$ are considered. The relaxed MWCNTs at various temperatures T are shown in Fig. 5.12 and 5.13. All of the MWCNTs adhere to the Maxwell velocity distribution and the H -function to satisfy their equilibrium state.

Figure 5.12 depicts the morphological changes of the (5,5) and (10,10) MWCNT when subjected to increasing temperature T from 0K to 3000K. At $T = 300\text{K}$, the MWCNT is similar to that of an ideal structure. However, at $T = 1000\text{K}$, both layers start to deform. Significant flanges at both ends of the outer layer of the MWCNT are also observed, and the ends of the inner layer start to close together. Before the MWCNT collapses after $T = 2000\text{K}$, more deformation occurs at both layers. Due to the high temperature, the atoms at both layers vibrate more and collide with one another, resulting in the disintegration of the MWCNT

Fig. 5.12. The relaxed structures of (5,5) and (10,10) MWCNT at various temperatures.

When exposed to increasing temperatures T , the second (10,10) and (15,15) MWCNT deforms as shown in Fig 5.13. Like all of the MWCNTs, the (10,10) and (15,15) MWCNT maintains its overall geometry at $T = 300\text{K}$. Flanges at both ends of the MWCNT are formed from $T = 1000\text{K}$ until $T = 2300\text{K}$, when the ends of both layers begin to close. On further increases in temperature T , the bonds break and the MWCNT eventually collapses.

Fig. 5.13. The relaxed structures of (10,10) and (15,15) MWCNT at various temperatures.

In conclusion, MD simulation, together with the Berendsen thermostat scheme, was used to analyze the atomic structural stability and changes of SWCNTs and MWCNTs. Close-capped SWCNTs are first modelled and simulated together with open-capped SWCNTs. It is found that there is less than 5% different in the temperatures T with which they can resist from deformation. Further CNTs are then modelled as open-capped. The results show that SWCNTs with smaller diameters d_t and shorter lengths l_t are able to withstand thermal loads better than those with larger diameters d_t . Longer SWCNTs tend to bend, causing the end-to-end distance to shrink.

The MWCNTs are, however, not as thermally stable as SWCNTs due to the presence of more than one layer in MWCNTs. When a MWCNT is subjected to thermal load, the atoms from different layers are thermally excited and begin to vibrate. At higher

temperatures T , the vibrations become larger and the atoms from one layer collide with the atoms from the neighbouring layers, which causes the MWCNTs to disintegrate easier and faster than SWCNTs.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

This chapter summarizes the major achievements and contributions of the present research project. Part of the work composes of the review of the progress made on the theoretical and computational fronts. Major part of the focus in this thesis has also been to address the particularly promising mechanical characteristics of CNTs as indicated in numerous experiments and simulations, with emphasis on the mechanical and thermal properties of such nanostructures.

This chapter also outlines the possible future directions for these areas of research.

6.1 Mechanical properties

The discovery [12] and the development of successful methods for the synthesis of high quality CNTs [123] have led to world-wide research efforts in the field of CNTs. In this thesis, two main properties of CNTs are studied, viz the mechanical and thermal properties. For mechanical properties, the elastic properties of various CNTs are examined through MD simulations. One of the most important mechanical properties of any material is Young's modulus E_Y . Part of the research work involves computing Young's moduli E_Y for different CNTs by making use of MD simulations.

6.1.1 Elastic modulus of carbon nanotubes

It is observed that Young's modulus E_Y of CNTs is dependent on various factors. At short CNT lengths l_t , Young's moduli E_Y for different CNTs are different and are generally higher than those with longer lengths l_t . However at longer lengths l_t , Young's moduli E_Y for the different CNTs decrease steadily to 1.05TPa and 0.9TPa for armchair and zig-zag CNTs respectively. Any further increase in length l_t has insignificant effect on Young's moduli E_Y .

The diameter d_t of a CNT will also affect its Young's modulus E_Y . MD simulation results reveal that CNTs with smaller diameters d_t generally have lower Young's modulus E_Y . As the diameter d_t increases, its Young's modulus E_Y will approach 1.05TPa and 0.9 TPa for armchair and zigzag CNTs respectively, which is close to Young's modulus E_Y value of 1.02GPa [4] of a plane graphite sheet. This is because the C – C bonds in the CNTs with larger diameters d_t are less curved which resembles closer to that of a flat graphite sheet. The trend of higher Young's modulus E_Y at smaller

diameters d_t obtained from this work agrees well with the work of Treacy *et al.* [78], Popov *et al.* [98], and Cornwell *et al.* [90] but differ from other works such as Hernandez *et al.* [93,96]. The reason may be largely due to the different form of potentials employed in the simulations.

Young's moduli E_Y of CNTs are also slightly dependent on its chirality. A larger chiral angle θ_{ch} will give rise to a higher Young's modulus E_Y . Generally, armchair CNTs are found to have higher Young's moduli E_Y than zigzag CNTs. This behaviour is also observed in the simulations of Hernandez *et al.* using nonorthogonal tight-binding method [93,96].

6.1.2 Carbon nanotubes under axial compressive load

The buckling behaviour of various geometries of SWCNTs was also explored. When buckled, the strain energy decreases due to the release of energy. Upon compression, CNTs will form kinks and higher strain energies are found around these regions. Typically, when a SWCNT is subjected to axial compression, it will deform into a three-fin pattern that leads to plastic collapse. Further compression will cause the SWCNT to buckle sideways until the $C - C$ bonds break and the whole structure disintegrates.

SWCNTs with smaller diameters d_t buckle into a three-fin pattern before buckling sideways. This deformation is similar to the work reported by Yakobson *et al.* [3]. However, SWCNTs with larger diameters d_t will first deform slightly into a "ring" pattern prior to plastically deforming into a "chessboard" pattern. Further compression will then cause the SWCNT to buckle into a three-fin pattern.

The buckling behaviour of MWCNTs is, however, more complicated. Due to the presence of different layers, there will be a sudden increase in strain energy upon

buckling. This is due to the sudden increase in the number of atoms from neighbouring layers in the nearest-neighbour configuration. The binding energy E , then increases, resulting in an increase of strain energy too as more C – C change from sp^2 to sp^3 configurations.

The buckling loads P_{cr} for various zigzag and armchair SWCNTs were determined. The calculations show that as the diameter d_t of the SWCNTs increases, the buckling load P_{cr} increases rapidly up to an optimum buckling load P_{cr} . However, any further increase beyond the optimum diameter d_t will result in a slow decline in the buckling load P_{cr} up to a steady value. Using the cylindrical shell formula [110], the buckling loads P_{cr} of zigzag SWCNTs were computed and the results show good agreement with that from MD simulations with diameters d_t ranging from 5.49 Å to 43.1 Å. The results obtained from classical cylindrical shell model for diameters d_t smaller than 5.49 Å do not agree well with MD simulations because the SWCNTs behave more like a rod than a cylindrical shell with thickness/radius (t/r) ratio greater than 0.66.

The buckling loads P_{cr} for MWCNTs were also determined. It is observed that generally MWCNTs have larger buckling loads P_{cr} . For instance, the (10,10), (15,15) two-walled MWCNT has a higher buckling load $P_{cr} = 2.02 \times 10^{-7}$ N compared to the (5,5), (10,10) two-walled MWCNT, that has a buckling load $P_{cr} = 1.72 \times 10^{-7}$ N. Moreover, as the number of layers in a MWCNT increases, its buckling load P_{cr} increases too. For example, the buckling load P_{cr} for a (5,5) SWCNT is 0.85×10^{-7} N, however if there is an extra outer layer forming a (5,5), (10,10) two-walled MWCNT, its buckling load P_{cr} increases to 1.72×10^{-7} N. If a third layer is further added forming a (5,5), (10,10), and (15,15) three-walled MWCNT, the buckling load P_{cr} will rise to 2.46×10^{-7} N.

6.1.3 Carbon nanotubes under axial tensile load

The elastic to plastic deformation of SWCNTs up to four-walled MWCNTs when subjected to axial tensile force was also studied. The elasto-plastic responses of CNTs were also computed in the form of stress-strain relationship. It is found that at small strains ϵ , the stress-strain relationship follows the classical Hooke's law. However, as the strain ϵ increases, the stress-strain curve behaves non-linearly with a decreasing gradient until it reaches the yield strain ϵ_y . Ductile behaviour of CNTs was also observed from the animated MD simulations, showing wave propagation from the centre to both ends of the CNTs, and then back to the centre. This phenomenon of wave propagation shows the rearrangement of configuration of the CNTs from strain release via the formation of Stone-Wales defects.

From the MD simulations, it was observed that the Stone-Wales defect will lead to the plastic deformation of the CNTs. When axial tensile load is applied to MWCNTs, fracture will first take place at the outermost layer. After the outermost layer has completely broken, the fracture will begin in the next inner layer. This process will continue until the innermost layer completely breaks.

The mechanical properties, such as the ultimate stress and maximum strain, were also computed. The MD simulated results show that these properties are sensitive to the number of layers in the CNTs. It is, however, realised that the geometrical size of the CNTs has insignificant effect on these properties.

6.1.4 Non-twisted carbon nanotube bundles under axial load

The critical buckling loads P_{cr} , failure loads P_{fl} , and critical strains ϵ_{cr} of different configurations of non-twisted CNT bundles, using MD simulations, were studied. Non-twisted CNT bundles composing of three and seven SWCNTs, aligned parallel to one another and spaced $3.4 \text{ \AA}$ apart, and subjected to axial compressive load were studied and it was found that the buckling loads P_{cr} of non-twisted CNT bundles are much higher than that of a SWCNT. At the same time, the bigger the non-twisted CNT bundle (composing more SWCNTs), the higher buckling load P_{cr} it will have. Additionally, bigger non-twisted CNT bundles with more SWCNTs are expected to have higher critical strains than CNT bundles with less SWCNTs. And the difference between the two critical strains will diminish further as the diameter d_t increases.

Non-twisted CNT bundles also exhibit excellent tensile properties with failure loads P_{fl} about three to seven-folds greater than their single CNT counterpart.

6.1.5 Twisted carbon nanotube bundles under axial load

In the study of twisted CNT bundle, each twisted CNT bundle simulated contains seven (5,5) SWCNTs, of which six of them are surrounding a core SWCNT. The six surrounding SWCNTs are twisted at various angles. It is observed from the MD simulations that the twisted CNT bundles do not have good compressive properties. Results indicate that larger twist angle θ_t will lead to lower critical buckling load P_{fl} and strain ϵ_{cr} , due to the curve geometry of the six surrounding SWCNTs.

Twisted CNT bundles also do not demonstrate good tensile properties. As the twisted CNT bundles are subjected to axial tension force, the intertube distances decrease giving rise in the intertube van der Waals forces F_{vdw} . The repulsive forces F_{rep} between the seven SWCNTs then suddenly increase due the decline in intertube distances. The sudden surge in the repulsive forces F_{rep} has caused the SWCNTs to repel one another at the junction area where the SWCNTs overlap when the contact distance is below $3.4 \text{ \AA}$. As a result, these CNT bundles tend to fail at the junction areas with lower failure loads P_f and strains ϵ_{cr} .

6.2 Thermal properties

MD simulation, together with the Berendsen thermostat scheme, was used to analyze the atomic structural stability and changes of SWCNTs and MWCNTs. It was found that the maximum temperature T , which both close-capped and open-capped SWCNTs can withstand before breaking down is less than a 5% different. As such further CNTs are then modelled open-capped. The simulated results revealed that SWCNTs with smaller diameters d_t and shorter lengths l_t are able to withstand higher thermal loads than those with larger diameters d_t and longer lengths l_t . Longer SWCNTs tend to bend, causing the end-to-end distance to shrink.

The MWCNTs are, however, not as thermally stable as SWCNTs due to the presence of more than one layer in multi-walled CNTs. When a MWCNT is subjected to thermal load, the thermally excited atoms from different layers start to vibrate. At high temperature T , the vibrations become larger, and the atoms from one layer collide with the atoms from the neighbouring layers, which cause the MWCNTs to disintegrate.

6.3 Recommendations for future work

The field of nanoscale science and technology is advancing rapidly and it is conceivable that the discovery of CNTs will have a great impact in the field of engineering and technology. The high expectations on CNTs have led many theoretical and experimental works in determining their properties, ranging from their mechanical, electrical, chemical, and thermal characteristics. However, there remains much to be investigated and many challenges to overcome. In the face of these challenges, future work includes the following:

- (1) Currently, many experimental works are carried out in fabricating CNT-reinforced nanocomposites [132,133]. However, the theoretical studies via simulations of CNT-reinforced nanocomposites have been so far neglected due to the large model demanded. The modelling of CNT-reinforced nanocomposites has also been made difficult by the interfacial interactions between the CNT and the matrix material. Conceivably, it will deepen the understanding of the properties and mechanics of CNT-reinforced nanocomposites by performing MD simulations.
- (2) Before the successful synthesization of helical carbon nanofibres [131], nanosprings are usually fabricated by silicon-based materials such as silicon carbide nanosprings [170] and silicon oxide nanosprings [171]. It is proposed to investigate the properties of helically coiled CNTs via MD simulations to further understand their mechanics and properties to determine their suitability for various potential applications.

- (3) The mechanics related to the twist of CNTs also need to be further investigated [172 – 174]. Thus far, MWCNTs have been used as torsional springs but are stiffened by repeated flexing [173,174]. It is, however, unclear what causes the stiffening.
- (4) Currently the parallelization is implemented using the MPI standards. It is however found that the computational time taken to calculate the van der Waals forces characterized by the Lennard Jones (12,6) model took exceptionally long due to the large number of neighbouring atoms to be considered. As such, it is useful to enhance the parallelization codes by making use of OpenMP [175].

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To gain further insight on the load P each SWCNTs is experiencing in the 60" twisted CNT bundle, the force F acting on each individual SWCNT in the CNT bundle during compressive loading, is plotted against its deformation in Fig. 4.13. As the axial force F acting on the six surrounding SWCNTs is the same, therefore only the axial force F acting on one surrounding SWCNT and the core SWCNT is plotted. From the plot, it is evident that the surrounding SWCNT will buckle slightly earlier than the core SWCNT and at a lower critical buckling load P_{cr} . It is also interesting to note that the core and surrounding SWCNTs carry 15.5% and 84.5% of the total axial compressive load.

4.3.3 Twisted carbon nanotubes bundles under axial tensile load

Contrary to wire ropes that provides better structural reliability and mainly used in applications in which tensile load is dominant, twisted CNT bundles tend to underperform compared to non-twisted CNT bundles when subjected to axial tensile force. Due to the twist, the six surrounding SWCNTs are brought closer to each other in a helical angle, forming junctions between the neighbouring SWCNTs. During axial tensile loading, the six surrounding SWCNTs are further pulled closer to the core SWCNT causing the intertube distance d_{in} between individual SWCNTs to decrease. Figure 4.14 shows the plot of intertube distance d_{in} against strain ϵ . The plot clearly shows that the larger amount of twisting angle θ_t will cause the intertube distance d_{in} to decrease as the strain ϵ grows larger. For instance, at a deformation of $\Delta l_t = 0.16$, the intertube distance d_{in} in a 90" twisted CNT bundle has decreased from 3.2 $\text{\AA}$ to 1.9 $\text{\AA}$. However, the intertube distance d_{in} remains at around 3.2 $\text{\AA}$ in the 30" twisted CNT bundle even after a deformation of $\Delta l_t = 0.16$. The reason why a larger twisting angle will lead to a reduction in intertube distance d_{in} can be attributed to the fact that being twisted at a larger angle

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