Computer simulation studies of carbon nanotube and its interactions with water

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Computer Simulation Studies of Carbon Nanotube and its Interactions with Water

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ABSTRACT

Recent discoveries of various forms of nano-materials have stimulated research on their applications in diverse fields. Of particular mention is the carbon nanotubes (CNTs) whose unique mechanical and physical properties has triggered a wide-spread research interest in a broad range of innovative application in a number of fields such as nano-electronics, nano-fluidics, biosensors, marine, biological and medical applications. Design of CNT based nano-drug delivery devices have also been a rapidly emerging research in the field of nano-biotechnology. Most of these applications involve interaction of CNTs with water and water based solutions. Much of the underlying physical phenomena such as the effect of water interaction dynamics on the mechanical properties of CNTs remains to be investigated. A thorough knowledge on the influence of water molecule interactions on the mechanical and transport properties of CNTs is useful to determine the lifetime and stability of CNT based nano-fluidics and NEMS devices.

In view of this, the major focus of this thesis is to study and understand the mechanical properties of CNTs interacting with water molecules by employing molecular dynamics (MD) simulation. The mechanical properties of single-walled CNTs (SWCNTs) interacting with water molecules have been studied by subjecting the SWCNT to four forms of mechanical loading conditions – compression, tension, torsion and shear. The results indicate that the mechanical performance of SWCNT is strongly affected due to interaction of the surrounding water molecules. In addition, the influence of the SWCNT geometry on the mechanical properties of water submerged SWCNTs is examined. The MD simulations show that SWCNTs with large diameter performs better than SWCNTs with small diameter under mechanical loading. The results also demonstrate that in

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addition to defect concentration, the location of defects in SWCNT will also affect the mechanical properties of water submerged SWCNT. For the case of capped SWCNTs, it was found that the concentration of water molecule encapsulated inside the SWCNT strongly affects the elastic properties of the SWCNT.

Another study involved the transport characteristics of water molecules in CNTs using MD simulation. The transport properties of water molecules in a nano-scale channel such as CNTs is critical for its key role in designing the next generation CNT based nano-fluidic devices. The effect of channel diameter, defects and the inter-layer spacing on the transport of water molecules is studied by subjecting the flow of water molecules through CNTs under pressure. The findings show that the efficiency of water transport can be improved by deploying bigger SWCNTs that have wide channel diameter. It was however found that defects in the nano-fluidic system will reduce the transport efficiency of water molecules. The results also show that the inter-layer spacing in a double-walled CNTs (DWCNTs) has a significant influence on the transport efficiency of water molecules. The investigations and conclusions obtained from this thesis is expected to further compliment the potential applications of CNTs in nano-fluidics and NEMS devices.

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LIST OF SYMBOLS

(n,m)	Pair of chiral indices that represent the number of unit vectors along two directions in the hexagonal lattice structure of graphene
$\mathbf{a}_{1,2}$	Unit cell base vectors of graphene sheet
b_0	Equilibrium bond length
b_i	Actual bond length
b_{ij}	Reactive empirical bond order between atoms i and j
C	Vacancy defect concentration in single walled carbon nanotube
d_{sys}	Dimensionality of system
D	Diameter of single walled carbon nanotube
e_c	Electron charge
E	Energy
E_{ab}	Potential energy between two water monomers a and b
E_{AIREBO}	AIREBO potential energy
E_b	Potential energy due to bonded interactions
E_{bend}	Bending energy of water molecule
E_{bond}	Bond strength energy of water molecule
E_{FPC}	FPC potential energy
E_{LJ}	Lennard-Jones (12–6) potential
E_{nb}	Potential energy due to non-bonded interactions
$E_{non-bond}$	Non-bonded potential energy between water molecules and carbon atoms
E_{pot}	Total potential energy

LIST OF SYMBOLS

E_{REBO}	REBO potential energy
E_{SWCNT}	Strain energy of single walled carbon nanotube
E_{TORS}	Torsional potential energy
F_n	Torsional force constant
F_{TORS}	Torque of single walled carbon nanotube
$\vec{F}_{ij}$	Gradient of potential energy between atoms i and j
G	Vacancy defect concentration in graphene sheet
$G_{torsion}$	Torsional modulus of single walled carbon nanotube
h	Planck constant
h_{beam}	Thickness of Euler-Bernoulli beam
h_{cyl}	Thickness of continuum cylinder
h_t	Thickness of single walled carbon nanotube
k_B	Boltzmann constant
k_{bend}	Force constant for bending
k_{bond}	Force constant for the bond
K_{cyl}	Torsional stiffness of continuum cylinder
K_{FF}	Torsional stiffness of free form single walled carbon nanotube
k_θ	Angular force constant
K_{WS}	Torsional stiffness of water submerged single walled carbon nanotube
L	Length of single walled carbon nanotube
L_{cyl}	Length of continuum cylinder
m_i	Mass of atom i
m_b	Amplitude of bent in an imperfectly straight single walled carbon nanotube

LIST OF SYMBOLS

N	Total number of atoms in a system
n_b	Number of bents in an imperfectly straight single walled carbon nanotube
N_f	Degree of freedom
n_p	Periodicity
P	Pressure
P_{sys}	Momentum of a system
P_{water}	Pressure on water molecules
q_i	Charge on atom i
q_j	Charge on atom j
R	Radius of single walled carbon nanotube
r_{CNT}	Radial distance from the center of a single walled carbon nanotube
r_{cut}	Cutoff distance
R_{cyl}	Radius of continuum cylinder
r_{ij}	Scalar distance between atoms i and j
r_{skin}	Skin distance
r_{verlet}	Verlet neighbor list cutoff radius
t	Time
T	Temperature
V	Volume
V_0	Equilibrium volume of single walled carbon nanotube
V_A	Attractive energy
V_{cyl}	Volume of continuum cylinder
v_i	Velocity of atom i

LIST OF SYMBOLS

V_k	Torsional coefficient
V_R	Repulsive energy
V_{TORS}	Torsional energy
w_{ij}	Weighted contribution of bond between atoms i and j
x_{new}	Computed x coordinate of a carbon atom in an imperfectly straight single walled carbon nanotube
x_{orig}	x coordinate of a carbon atom in a perfectly straight single walled carbon nanotube
Y	Young's modulus of single walled carbon nanotube
z_{orig}	z coordinate of carbon atom in a perfectly straight single walled carbon nanotube
z_{min}	Minimum z coordinate of carbon atom in a perfectly straight single walled carbon nanotube
$\alpha_{1,2,3}$	Angles formed by central carbon atom with three other carbon atoms in the lattice of the single walled carbon nanotube
ε	Strain
ε_0	Permittivity of free space
ε_{cr}^{CS}	Critical compressive strain of cylindrical shell
ε_{cr}^{EBB}	Critical compressive strain of Euler-Bernoulli beam
ζ	Well depth parameter
γ	Angular phase
$\gamma_{torsion}$	Torsional strain of single walled carbon nanotube
σ	Equilibrium distance between two atoms
θ_0	Equilibrium angle
θ_{cyl}	Torsional angle of continuum cylinder

LIST OF SYMBOLS

θ_i	Actual angle
θ_{SWCNT}	Torsional angle of single walled carbon nanotube
μ	Chemical potential
ω	Dihedral angle
ω_t	Torsional angle

LIST OF PUBLICATIONS

The following SCI journal publications are related to the present research:

1. **V. Vijayaraghavan** and C. H. Wong, “Torsional characteristics of single walled carbon nanotube with water interactions by using molecular dynamics simulation,” *Nano-Micro Letters* (accepted for publication, in press).
2. **V. Vijayaraghavan** and C. H. Wong, "Transport characteristics of water molecules in carbon nanotubes investigated by using molecular dynamics simulation," *Computational Materials Science* 89, pp.36-44, 2014.
3. **V. Vijayaraghavan** and C. H. Wong, “Compressive characteristics of single walled carbon nanotube with water interactions investigated by using molecular dynamics simulation,” *Physics Letters A* 378, pp. 570, 2014.
4. **V. Vijayaraghavan** and C. H. Wong, “Shear deformation characteristics of single walled carbon nanotube with water interactions by using molecular dynamics simulation,” *Physica E: Low-dimensional Systems and Nanostructures* 54, pp. 206, 2013.
5. **V. Vijayaraghavan** and C. H. Wong, “Nanomechanics of single walled carbon nanotube with water interactions under axial tension by using molecular dynamics simulation,” *Computational Materials Science* 79, pp. 519, 2013.
6. **V. Vijayaraghavan** and C. H. Wong, “Temperature, defect and size effect on the elastic properties of imperfectly straight carbon,” *Computational Materials Science* 71, pp. 184, 2013.
7. C. H. Wong and **V. Vijayaraghavan**, “Nanomechanics of free form and water submerged single layer graphene sheet under axial tension by using molecular dynamics simulation,” *Materials Science & Engineering A* 556, pp. 420, 2012.
8. C. H. Wong and **V. Vijayaraghavan**, “Nanomechanics of non-ideal single and double walled carbon nanotubes,” *Journal of Nanomaterials* 2012, Article ID 490872, 2012.
9. C. H. Wong and **V. Vijayaraghavan**, “Nanomechanics of imperfectly straight single walled carbon nanotubes under axial compression by using molecular dynamics simulation,” *Computational Materials Science* 53, pp. 268, 2012.

CHAPTER 1

INTRODUCTION

The development of high performance computers and new computation methods has triggered significant research in the field of nano-materials. Of particular mention is in the use of computers for theoretical characterization of carbon nanotubes (CNT) due to its remarkable mechanical, thermal and electrical properties. CNTs compose entirely of carbon atoms and it is formed by wrapping around an atom layer thick graphite sheet into a cylinder. CNTs have become the subject of intensive research in the field of nanotechnology due to its extraordinary properties for promising applications. Notably, CNTs today have forayed into the emerging fields such as nano-fluidics, biosensors, marine, biological and medical applications. In addition, the transport properties and nano-confinement effects of molecules in CNTs have gained a lot of interest with particular regard to water and water based solutions in the field of nano-fluidics and nano-biotechnology. In this thesis, the elastic properties of CNTs subjected to various forms of mechanical loading while interacting with water have been comprehensively studied using the molecular dynamics approach. In addition, the influence of various factors that govern the transportation properties of water molecules in CNTs has also been analyzed. The mechanical and transport properties of CNTs under various forms of water interactions have been systematically studied and the findings are presented in this thesis.

This chapter begins with an introduction of CNTs and a brief description of water molecule and its properties. The applications of CNTs are outlined next followed by its specific applications in water technology. The motivation and objective of this thesis are detailed next. Finally, the chapter concludes with the scope of this thesis.

1.1. Carbon nanotubes

CNTs are the molecular-level cylindrical form of the graphene sheets which possess superior qualities. The unique characteristics of the carbon nanotubes are their high strength and stiffness. The remarkable qualities of the CNT have generated a huge commercial interest especially in the core regions of electronics and bio-engineering. This has triggered extensive researches to be conducted on them by industry and academia.

Fig. 1.1. A TEM image of a MWCNT (magnification scale of 3 nm : 1 cm) as reported in Ref [1].

The structure of the CNT which was first reported by Iijima [1], was made up of series of nested cylinders in telescopic form. This form of CNT is referred as the multi-walled carbon nanotubes (MWCNTs). The length of the MWCNTs can range from as short as a few angstroms [2] to as lengthy as many micrometers [3]. The outer diameter of the MWCNT varies from about 25 Å to 300 Å. The transmission electron microscope (TEM) image of an MWCNT is shown in Fig. 1.1, which indicates a layered arrangement of rolled up sheets forming a concentric MWCNT pattern.

1.1.1. Synthesis of carbon nanotubes

The single-walled carbon nanotube (SWCNT) was first synthesized independently by two research groups at the NEC Corporation Laboratories, Japan [4] and the IBM Almaden Research Center, USA [5] in 1993. The synthesized SWCNT often curls up into nanoropes because of the van der Waals forces. These SWCNT were seldom straight and come with a looped or bundled up structure. The scientists at the IBM Almaden Research Center followed up their initial work with other group of physicists from the California Institute of Technology and the Virginia Polytechnic and State University to synthesize the SWCNT by using catalysts [6]. The studies showed that the diameter of the CNTs can be widened by inclusion of sulphur to the cobalt anode. Similarly, inclusion of the lead and bismuth [7] will also yield the fabrication of larger diameter CNTs.

In 1997, a group of French and American scientists demonstrated that mass production of SWCNT can be achieved by means of electric arc-discharge method [8]. This method is almost identical to that of the work reported in ref.[5] except that the reactor they used had a different geometry and the catalyst used in the experiment was a nickel/yttrium

mixture. The concentration of the SWCNT was found to be highest around the cathodic deposit in diameters of 14 Å, resulting in a collar shaped structure. The yields of the SWCNT thus obtained were estimated in between 75 to 95%.

A different approach to mass produce the SWCNTs was accomplished by researchers from Du Pont, Delaware [9] in association with workers from SRI International. The electric arc-discharge of the gadolinium-impregnated electrodes [9] results in the soot formation that contains the SWCNT which results from the particles of gadolinium carbide. Therefore, the length of the SWCNTs formed were actually shorter compared to those of [8] but the diameters were almost equal. Subsequent researchers also indicated the use of other metals such as the yttrium [10] and lanthanum [11] for the production of radial SWCNTs.

The SWCNTs can also be fabricated independently by means of catalytic method. This method [12] consists of alumina supported molybdenum particles placed inside a tube furnace. At the temperature of 1200 °C, carbon monoxide was passed through the mix, which results in the catalytic synthesis of nanotubes. The mechanism of growth consists of formation of a single layered cap, which grows away from the catalytic particles. This results in the formation of a nanotube. The SWCNTs thus produced often had small particles that were attached to its end. The catalytic particle that is used for the fabrication of SWCNT determines the diameter. The advantage of this technique is that it is possible to produce distinct SWCNT as compared to that of the grouped or bundled system that were produced by the electric arc-discharge method.

In addition to the processes described above, SWCNTs can also be fabricated by means of induction thermal plasma method [13]. In this process, the metal catalysts and carbon

containing substances is vaporized at high temperature by using ionized gas. The flowing ionized gas maintains high frequency oscillating currents in a coil that induces the thermal plasma. This process typically involves feeding of carbon black and metal catalysts in the plasma which is later cooled down to form SWCNTs.

1.2. Structure of carbon nanotubes

The structure of SWCNT is formed by rolling up a single layer graphene sheet to form a seamless cylinder. There are many ways to roll up the graphene sheet to form a cylinder. The manner in which the graphene sheet is rolled up can be mathematically represented by a pair of chiral indices (n,m) , where the integers n and m represent the number of unit vectors along two directions in the hexagonal lattice structure of graphene. If $\mathbf{a}_1$ and $\mathbf{a}_2$ represents the unit cell base vectors of graphene sheet, then the hexagonal lattice structure of graphene sheet with atoms labeled using the indices (n,m) is represented in Fig. 1.2.

Fig. 1.2. Hexagonal lattice structure of graphene sheet defined using indices (n,m) .

1.2.1. Single walled carbon nanotube

It can be noted from Fig. 1.2 that the graphene sheet can be rolled non-helically in two mutually perpendicular directions such that the graphene lattices at the top and bottom of the SWCNT are parallel. The resulting structure will give rise to two types of SWCNTs which are named as ‘armchair’ and ‘zigzag’ SWCNT. The structure of an armchair and zigzag SWCNT is shown in Fig. 1.3. We can see from this figure that the cross-sectional rings at the end of the SWCNTs resemble an ‘armchair’ and ‘zigzag’ pattern. In an armchair SWCNT, the C–C bonds in the opposite sides of the hexagonal graphene lattice is perpendicular to the axis of the SWCNT. In a zigzag SWCNT, the C–C bond is parallel to the axis of the SWCNT.

(a) (10,10) armchair SWCNT

(b) (10,0) zigzag SWCNT

Fig. 1.3. Structure of (a) (10,10) armchair SWCNT and (b) (10,0) zigzag SWCNT. The dashed line represents the axis of the SWCNT.

If the graphene sheet is rolled helically, then the C–C bonds will lie at an angle to the axis of the SWCNT. This type of SWCNT is known as a chiral SWCNT. Fig. 1.4. illustrates a chiral SWCNT.

Fig. 1.4. Structure of (8,3) chiral SWCNT. Only front part of the SWCNT is shown for clarity. The dashed line represents the axis of the SWCNT.

The structure of the SWCNT is defined by its chirality, which strongly affects the mechanical [14] and electrical properties [15] of SWCNT. For a given SWCNT structure defined by its chiral indices (n,m) , the SWCNT is metallic if $n = m$ and is semiconducting if the difference between the chiral indices, i.e. $(n - m)$ is a multiple of 3. For all other cases, the SWCNT behaves as a moderate semiconductor.

1.2.2. Multi-walled carbon nanotube

The structure of MWCNT consists of two or more SWCNTs which are concentrically nested one inside another. Hence, a MWCNT consisting of two layers of SWCNT is defined as a double-walled CNT (DWCNT) and those with three layers is defined as a triple-walled CNT (TWCNT) and so on.

In an MWCNT, the inter-layer separation distance between the adjacent walls of the SWCNTs is about $3.4 \text{ \AA}$, which is taken to be the van der Waal's diameter of the carbon atom [16] and are weakly bonded by van der Waal's forces. Fig. 1.5. depicts a structure of a (10,10)@(15,15) MWCNT, formed by concentrically nesting a (10,10) SWCNT

inside a (15,15) SWCNT. This kind of arrangement results in the inter-layer separation distance between the two SWCNTs to be 3.4 Å.

Fig. 1.5. Structure of (10,10)@(15,15) MWCNT. The (10,10) SWCNT is shown in red and (15,15) SWCNT is shown in blue.

1.3. Properties of carbon nanotubes

1.3.1. Mechanical properties

CNTs have excellent tensile strength and high elastic modulus. The high strength of CNT is attributed due to the strong covalent sp^2 bonds between the carbon atoms in the CNT. Literature studies point out that CNTs are strong in the axial direction [17]. Literature studies on strength of CNT indicate that the Young's modulus is on the order of 270 ~ 1350 GPa and tensile strength is about 11 ~ 120 GPa [18-20].

CNTs subjected to high tensile elongations show plastic deformation, after which the CNT cannot be reverted back to its original shape. Generally, a plastic deformation is said to occur in CNTs at strains of approximately 5% [21]. This deformation increases to a maximum and will result in fracture of the CNT by releasing the accumulated strain energy. However, it is worth noting that the mechanical strength of CNTs under compression are not generally high. This is because the hollow cylindrical geometry with

high aspect ratio causes it to undergo buckling under compressive or bending loading condition [22].

1.3.2. Kinetic properties

The kinetic properties of CNTs can be envisioned from MWCNTs consisting of SWCNTs nested inside each other. This results in a telescopic arrangement where the smooth, frictionless wall of SWCNTs results in formation of an atomic level linear or rotational bearing. This property of CNTs have been extensively researched and studied by researchers based at University of California, Berkeley to build world's smallest rotational motor [23].

1.3.3. Electrical properties

The electrical properties of CNTs are strongly influenced by the geometry of the CNT [24]. It can be seen from section 1.2.1 that the chirality of SWCNT determines if the SWCNT is metallic, semiconducting or moderately semiconducting material. Theoretical studies on electrical conductivity of CNT indicate that metallic SWCNTs are able to carry an electric current density of $4 \times 10^9 \text{ A/cm}^2$ [25].

The electrons transport in SWCNT involves quantum effects and occurs only along the tube axis due to nanoscale cross-section. The maximum electrical conductance of a SWCNT is $4e_c^2/h$ where, e_c is the electron charge and h is Planck constant [26].

1.3.4. Thermal properties

The SWCNTs exhibit high thermal conductivity along the tube axis and behave as insulators along the radial direction of the tube [27]. At room temperature, a SWCNT exhibits thermal conductivity of about $3500 \text{ Wm}^{-1}\text{K}^{-1}$ along the tube axis [28]. This is much higher when compared to that of copper which exhibits thermal conductivity of $385 \text{ Wm}^{-1}\text{K}^{-1}$, which is highest among metals [29]. Additionally, the room temperature thermal conductivity of SWCNT in radial direction is about $1.52 \text{ Wm}^{-1}\text{K}^{-1}$ which is comparable to that of soil [30]. Furthermore, CNTs exhibit temperature stability of about 750°C in air and up to 2800°C in vacuum [31].

1.3.5. Electromagnetic wave absorption properties

Research on microwave absorption has gained momentum in the field of wave absorption properties of MWCNTs. An advancement in this research holds great promise for the application of CNTs to be employed as radar absorbing materials in defense technology [32]. Until recently, researchers were able to increase the absorption effectiveness of MWCNTs by using filler metals such as nickel, cobalt and iron [33, 34]. Hence, the absorption properties of CNTs can be further improved and shows a promising future.

1.3.6. Defects

CNTs, like other materials can exhibit defects in the crystal lattice which affects the properties of CNTs. The most common defects in CNTs are either vacancy defects or Stone-Thrower-Wales (STW) defects. Vacancy defects in CNT occur due to missing of one or several atoms on the lattice structure of CNT. High concentration of vacancy

defects can result in the reduction of mechanical strength by up to over 75% [35]. Similarly, electrical conductivity of CNT decreases due to missing atom. Specifically, the defects can cause the armchair CNTs, which are natural conductors of electricity, to be semi-conducting materials [36]. An SWCNT with a vacancy defect due to single missing atom is depicted in Fig. 1.6(a).

STW defect is a bond rotation defect of a C–C bond in the hexagonal crystal lattice of CNT as shown in Fig. 1.6(b) [37]. The rotation of bond will result in the formation of pentagon-heptagon pair caused by rearrangement of atoms in the CNT lattice structure. Large scale STW defects are shown to scatter the phonons to a wide range of frequencies which affect the thermal conductivity of CNTs [38].

Fig. 1.6. Structure of SWCNT showing (a) vacancy defect and (b) STW defect.

1.4. Applications of carbon nanotubes

CNTs have many commercial applications due to its excellent properties. The electronic properties of CNTs are remarkable, which make them suitable for nano-electronics applications. The single-molecule field effect transistor [39] based on a single semiconductor SWCNT was fabricated by the Delft group. Because of the high strength and excellent elastic properties, CNTs can be used for reinforcing the polymer composites. By using CNT, it is also possible to achieve high strength interfaces of the order of few hundred megapascals [40]. The CNTs are ideal candidates for fabrication of composite polymers since the nanotubes do not break during processing.

CNTs can also be used as nano-probes for applications that require high-resolution imaging. Experiments have been performed to demonstrate that the individual SWCNT and MWCNT are used as probing elements of atomic force microscopy (AFM) and scanning transmission microscopy (STM) for lithography [41] and imaging [42]. Since the tip of the CNT is in the order of nanometers or angstroms, it is possible to image even the intricate features of the substrate, which cannot be normally achieved when using silicon or metal tips as they are large and blunt. The CNT tips also possess high elasticity and this makes them immune to fracture as the impact of the CNT with the substrate will induce buckling and the CNT reverts back to its original shape within the elastic limits.

The partially aligned CNT films are used as field emission electron source [43]. The CNT field emitters can be used in applications such as lamps [44], flat panel displays [45] and x-ray generators [46]. The most important application of the CNT in the recent days is in the domain of energy storage and production. The catalytically grown CNTs have many desirable properties required for the high-power electrochemical capacitors [47]. Since

the intake of hydrogen by the CNT does not induce adsorption, high energy storage efficiency can be achieved by choosing an optimum tube diameter for the intake and release of hydrogen. CNTs are also used in the microenvironments as carbon nano-thermometers [48].

1.5. An introduction to water molecule

The water molecule, H_2O , is a very simple and most stable molecule. It displays a discrete but nevertheless exceptional property that has far-reaching consequences, one of them being that without it life would not exist. At ambient conditions, water remains in liquid form. It is however possible for different phases of water to co-exist in nature. A classical example is being that water exists in solid form as ice in Polar Regions and as water vapor and clouds in places of hot, humid temperature such as desert. Water also exhibits a liquid crystalline phase [49] at the proximal regions of hydrophilic surfaces. As an element, it has many unique biological properties that make it ideal for survival of various life forms on earth.

1.5.1. Properties of water

The major physical and chemical properties of water are described in this section. At standard temperature and pressure, water exists in a liquid form. Water in its normal form has no odor and taste. The color of water and ice can be characterized by a slight blue color although it can be agreed that it is mostly colorless and takes the color of the container or reflecting surface (such as the sky). Water vapor, which is gaseous form of water, is invisible. In the visible region of the electromagnetic spectrum, water is

transparent. This enables the sun light to pass through the layers of water which is essential for survival of aquatic life forms. Water also absorbs the infrared and ultra violet light rays.

The molecular structure of water consists of two hydrogen atoms covalently bonded to the oxygen atom forming a triangulated structure. A single oxygen atom has twice the negative charge of the two hydrogen atoms which give the charge neutrality of the water molecule. This results in polar nature of the water molecule carrying an electrical dipole moment. Water exhibits a very high surface tension. Since water molecule can form a large number of intermolecular hydrogen bonds; a molecule of water can form up to four bonds of hydrogen. This property also enables water to exhibit capillarity, an action defined by the tendency of water to move up against the gravitational force in a tube of narrow diameter. All vascular functions in biological systems such as nerves, absorption of ground water by the plants and trees relies on this exceptional quality of water.

Water is a naturally occurring good solvent that can dissolve almost all biological substances and elements. It is therefore normally considered as a universal solvent. Water is used by living beings to dissolve essential elements such as sugars, salts, alkalis and gases such as oxygen and carbon dioxide. Based on the reactivity with water, all molecules can be classified as either hydrophilic, i.e., those substances that can mix well with water and hydrophobic, those that do not. Water is also used to dissolve the cell components such as DNA, proteins and polysaccharides.

The electrical conductivity of pure water is very low. However, addition of small concentrations of ionic compounds such as sodium and potassium results in substantial increase in the electrical conductivity. As like other liquids, the atmospheric pressure

influences the boiling point of water. Hence, we expect a variation in the boiling point of water depending on the region of its presence. For instance, water boils at 341 K (68 °C) at the top of Mt. Everest. At the sea level, the boiling point of water is 373 K (100 °C). Water that is found in the geothermal vents at Deep ocean levels take hundreds of temperatures to reach the boiling point and can still remain in liquid form.

Water has the highest heat of vaporization ($40.65 \text{ kJ mol}^{-1}$) of all known materials due to the network of hydrogen bonding between its molecules. The specific heat capacity of water is second highest (4181.3 J/kg K) after ammonia. Because of these unusual thermodynamic properties, it is possible for water molecule to buffer the large temperature fluctuations, which allows it to moderate the climate in the earth's surface.

When water is cooled to form ice, it becomes less dense. This is contrary to other materials that becomes denser by shrinking in volume. The maximum density of water occurs at 277 K (4 °C) which is 1000 Kg/m^3 [50]. The volume of water expands by about 9% during cooling, which explains why ice floats on liquid water. In the gaseous phase, the water vapor is completely miscible with atmospheric air.

The electrolytic process of water results in its fragmentation to form hydrogen and oxygen. Since water is an oxide of hydrogen, it is always formed as a by-product in a chemical reaction that involves reaction of hydrogen containing elements with oxygen or in elements undergoing oxidation. Water always results as a combustible product of hydrogen. It should also be noted that the energy required in combining the oxygen and hydrogen to form a water molecule [51] is far lower than that is required to split the water molecule by means of electrolysis.

1.6. Carbon nanotube applications in water technology

The nanoscale dimension combined with exceptional properties makes CNTs a promising candidate for a variety of applications in technology involving water. Notably, CNTs have shown great potential for water treatment applications in reverse osmosis (RO) desalination plants [52, 53]. The hydrophobic walls of CNT enable frictionless movement of water molecules and hence consume less power compared to conventional RO water treatment plants. In addition, CNTs when combined with boron can be used to clean oil spills from water [54]. It has been demonstrated that a sponge of hydrophobic CNT can float on water and can attract oil droplets. The oil thus absorbed in the CNT sponge can be squeezed off and the sponge can be reused many times due to the excellent elastic properties of CNT.

CNTs have also been used to fabricate inexpensive nano-sensor to detect the presence of microbes in water [55]. In this technique, CNTs are at first bound to antibodies that are sensitive to the toxins in water. The CNT-antibody dispersion is then dip coated on the surface of paper which changes its conductance and can detect the microbes in water. Furthermore, polymer and surfactant functionalized CNTs when dissolved in water can form CNT ink [56] which can then be printed on paper and plastic surfaces. Printing of electrically conductive CNTs on papers or fabric has extensile applications in flexible electronics. In addition, this technique can be used to print tracking tags on objects which needs to be traced and tracked.

1.7. Motivation and objective

The extraordinary properties of CNTs combined with the nano-scale geometry makes CNTs an attractive choice for engineering nano-fluidic devices important for technologies such as drug delivery [57], fluid separation [53] and biological channels [58]. These applications require CNTs to operate in hydrodynamics or aqueous environment and are subjected to mechanical forces by the surrounding fluid flow. In addition, the application of CNT as nano-scale flow channel has attracted an enormous research attention for transport of water, macromolecules, ions and protons in the field of nano-fluidics and nano-biotechnology [59, 60]. The interaction and transportation of molecules in a nano-flow channel is an emerging research in chemistry and biology [61]. An understanding of the interaction and transport of water molecules with CNTs is necessary for applications involving the diffusion, flow and selective adsorption of water and other bio-molecules. Furthermore, a thorough study and investigation of transport of water molecules and its influence on the mechanical properties of CNT is key to realize the full potential of CNTs for its promising applications in nano-fluidics and nano-biotechnology.

Hence, the main objective of this thesis is to study the elastic characteristics of CNTs while interacting with a surrounding water medium using molecular dynamics (MD) simulation method. The investigation of elastic properties of CNTs in water is highly important in order to gain a comprehensive and satisfactory understanding of the mechanical response of CNTs in various forms of water interaction. Furthermore, the influence of geometrical characteristics and the effect of defects on the elastic properties of a CNT in water medium present an important and crucial design input for fabricating

CNT based nano-level drug delivery and nano-fluidic NEMS devices. This thesis also presents a detailed investigation on the influence of topological defects in nanoscale flow channel on the transport characteristics of water molecules which has not been studied well in the literature. The mechanical and transport properties of SWCNTs under various forms of water interaction have been comprehensively studied using MD simulation and presented in this thesis. The investigations and analyses carried out in this thesis are expected to provide valuable insights for the application of CNTs for nano-level processes involving water molecules such as nano-bio devices, NEMS, and drug delivery devices.

1.8. Scope of the thesis

An introduction to CNTs and their properties and applications have been presented in Chapter 1. In addition, the science of water molecule, its phases and its properties have been discussed. The motivation and objective of the PhD thesis has been outlined in Chapter 1.

Chapter 2 is devoted to computer simulation of nanoscale materials. This chapter describes the modeling of nanostructures based on MD simulations. The nanoscale simulation method employed in this thesis is presented along with techniques to reduce computation time.

Chapter 3 deals with the mechanical properties of CNTs. A thorough literature review on the mechanical properties of CNTs determined by analytical experimental methods is given. Following this, the mechanical properties of CNT under compressive and tensile loading are studied.

Chapter 4 discusses the compressive and tensile loading properties of CNTs interacting with water molecules. Chapter 5 focuses on the torsional and shear loading properties of CNTs interacting with water molecules. CNTs are subjected to various forms of water interaction and the elastic properties due to interaction of water molecules is thoroughly studied and presented in these chapters.

Chapter 6 concentrates on the transport properties of water molecules in CNT. The effect of channel geometry and topological defects of CNTs on the transport of water molecules is determined. The mechanism of water transport through DWCNT is also discussed.

The final chapter concludes the thesis and outlines further extensions of the research work and goals for the future work.

CHAPTER 2

COMPUTER SIMULATION OF NANOSCALE MATERIALS

MD refers to the computer simulation of physical motion of atoms and molecules using approximate finite difference equations of Newtonian mechanics. This technique was first introduced by Alder and Wainwright in 1957 to study the bulk properties of hard spheres [62]. MD simulation can be further classified into quantum mechanical calculations and molecular mechanics. Quantum mechanical calculations are further classified into *ab initio* or semi-empirical methods and is used to obtain the solution of physical systems with the former being more accurate. Molecular mechanics method is based on the principles of classical mechanics equations and describes the system based on the interactions within the atoms. Atomic and molecular level simulations have become a fast expanding domain of research in academia and industry alike. MD simulation has evolved as a powerful tool of study investigation in the field of physics, chemistry and materials science. It is employed to understand the material properties at the atomic level.

This chapter outlines the principles and procedure of MD simulation technique and discusses about the important features in the MD simulation method. Additionally, the inter-atomic potential models that define the force field equations which form the crux of MD simulation is also discussed. Finally, this chapter concludes with an overview of the MD computer program that is deployed in this project.

2.1. Principle of molecular dynamics simulation

MD simulation is one of the principal tools that is used for investigation and analysis in the field of theoretical physics, materials science and modeling of biological molecules. MD simulation is a pure computational method that describes the time dependent properties of a material system by depicting insights into an atomic scale motion. MD simulations can be used in applications of molecular biology such as *ab initio* prediction of proteins and nucleic acids, thermodynamics and structure of biological molecules and their complexes.

In predicting the movement of a system of atoms, MD simulation makes use of the interactive forces and appropriately assumed boundary conditions. The whole idea of an MD simulation is based on the Newton's second law, which defines the relationship between the force applied on a system to its mass and acceleration. The basic steps involved in the MD simulation are depicted as a flowchart shown in Fig. 2.1. The initialization phase consists of defining the initial position and velocities of all atoms in the system. The inter-atomic potential energy models are used to compute the interactive forces between the atoms. The differential equations of atomic motion are then solved by numerical integration to obtain the position and velocities of the atoms at succeeding time steps. This is followed by repeated monitoring of the state of the system until equilibrium is reached or the loading process is completed.

Fig. 2.1. Flow chart representing the typical steps involved in MD simulation.

Inter-atomic potential energy models are used to define the interactive forces that act in between the atoms. The potential energy model is a mathematical equation representing state of the system, which involves the atomic positions. Normally, experimental methods are used to derive the parameters that are involved in the potential energy function. At a complex level, quantum mechanics approach, which is used to study the electronic structure of atoms, is also incorporated in the energy interaction function.

2.2. Important features of molecular dynamics simulation

The essential features of the MD simulation in the context of mechanical modeling of general solids will be discussed in this section. Important features of an MD simulation include the initial configuration of the system, invoking the boundary conditions, controlling the temperature of simulation system, the criteria of bond-breaking, extraction of necessary information from the simulation process, and visualization of materials modeling process.

2.2.1. Initial configuration of the system

In order to begin the MD simulation, we need to assign initial position and velocities to all atoms in the system to be simulated. For simulating a crystalline structure, the initial positions are determined by making use of its lattice positions, while a random method can be used for cases that are amorphous. The positions of atoms should be determined in such a way that it is compatible with the system which needs to be simulated. It is also important to specify the initial velocities of all atoms in the system. The initial velocities may be specified randomly using uniform or Gaussian distribution method [63]. The magnitude of the initial velocities is then scaled such that it conforms to the required temperature, such that there is no overall momentum. This can be represented mathematically as [63],

$$P_{sys} = \sum_{i=1}^N m_i v_i = 0 \quad (2.1)$$

where P_{sys} is the momentum of the system, m_i and v_i are the mass and velocity of atom i and N is the total number of atoms in the system.

2.2.2. Periodic boundary conditions

MD simulation is used for simulating small systems which consist of up to millions of atoms or molecules. In MD simulation, periodic boundary conditions (PBC) are applied in simulating bulk gases, liquids, crystals and mixtures. The PBC are a set of boundary conditions which are used for simulating a larger system by performing simulations on a smaller part that is far from the edge [63]. The PBC is deployed in MD simulation by defining a primary cell via constructing a volume consisting of atoms with defined initial positions and velocities as described in section 2.1.1. Now, the primary cell is surrounded by its exact replicas to model a macroscopic system in space. During the process of simulation, when the molecule moves in the primary cell, its periodic image in each of the replica cells also moves exactly in the same way. A two-dimensional PBC system is shown in Fig. 2.2. The cells in the PBC system are separated by open boundaries with no walls so that the particles can freely enter and exit any cell. Hence, it can be seen from Fig. 2.2. that when a molecule leaves the primary cell, one of the images of the molecule will enter through the opposite face. By this method, the number density of the primary cell and hence, the entire system is conserved. It is however, useful to note that this method cannot be applied in all cases due to the non-periodic nature of some structures.

Fig. 2.2. PBC in a two-dimension system in which the primary cell represented by the central square (grey color) is surrounded by eight exact replicas. Molecules can enter and leave the square across each of the four edges of the central square.

2.2.3. Temperature control

The instantaneous temperature of a system in a conventional MD simulation is evaluated based on the particle kinetic energy statistics [63] given by

$$T(t) = \frac{1}{k_B N_f} \sum_{i=1}^N m_i v_i^2(t), \quad (2.2)$$

where the instantaneous temperature at time t is given by $T(t)$, $v_i(t)$ represents the velocity of atom at time t , the Boltzmann constant is given by k_B , and the degree of freedom is depicted by N_f . The degree of freedom is given by the minimum number of coordinates required to specify the atom. Thus, a single atom in a plane will have two degrees of freedom whereas an isolated atom in space will have three translational degrees of

freedom, and two bonded atoms in space will have six degrees of freedom (three translational and three rotational) and so on.

Temperature stability is achieved by controlling the particle velocity such that the canonical ensemble is obeyed at a given temperature. The MD simulation makes use of various techniques to control the system temperature. In Andersen thermostat, the system is coupled to a bath of stochastic impulsive forces that act on random particles [64]. In Berendsen's thermostat technique, the thermostat suppresses the fluctuations in kinetic energy of the system such that the deviation in system temperature exponentially decays with time [65]. Another method is the velocity rescaling technique [66] where the velocity of atom is rescaled to achieve the set temperature.

The frequently used technique to control the system temperature in MD simulation is by using the Nose-Hoover thermostat [67, 68]. In Nose-Hoover thermostat, the thermal reservoir is considered to be an integral part of the system. The reservoir in Nose-Hoover thermostat is represented by an additional degree of freedom s . If p_s denote the conjugate momentum associated with the additional degree of freedom s in the Nose-Hoover thermostat, the real velocities of atoms in the Nose-Hoover system, v_{NH} is given by

$$v_{NH} = s \sum_{i=1}^N \frac{dr_i}{dt} = \sum_{i=1}^N \frac{p_s}{m_i} \quad (2.3)$$

where m_i and r_i represents the mass and position vector of particle i respectively.

For a system thermally equilibrated using Nose-Hoover thermostat technique, an extra potential energy, P_{NH} will be associated with the additional degree of freedom s , represented by

$$P_{NH} = (N_f + 1)k_B T \ln s \quad (2.4)$$

2.2.4. Integration algorithms

The potential energy model is a mathematical function that describes the positions of atoms in the system comprising the simulation domain. The complexity of the potential energy function requires numerical integration, which makes use of several integration algorithms to provide information regarding trajectory of interacting particles evolved over time. Several numerical algorithms have been developed for integrating the equations of motion. The most popular algorithm used in MD simulation is the Verlet algorithm, which assume the positions, velocities and accelerations of atoms approximated by a Taylor series expansion given by [63]

$$r(t + \delta t) = r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 + \frac{1}{6}b(t)\delta t^3 + O(\delta t^4) \quad (2.5)$$

$$r(t - \delta t) = r(t) - v(t)\delta t + \frac{1}{2}a(t)\delta t^2 - \frac{1}{6}b(t)\delta t^3 + O(\delta t^4) \quad (2.6)$$

Adding Eq. (2.3) and (2.4) yields,

$$r(t + \delta t) = 2r(t) - r(t - \delta t) + a(t)\delta t^2 + O(\delta t^4) \quad (2.7)$$

where r , v , a and b denotes the position, velocity, acceleration and third derivative of position respectively with respect to time t .

The main advantages of the Verlet algorithm are that it is accurate, stable and simple to implement. However, the Verlet algorithm does not facilitate direct computation of velocity of atoms. The velocities of atoms are sometimes required to compute the kinetic energy of atoms which is used to achieve the energy conservation of the system. This problem can be overcome by implementing velocity Verlet algorithm, which is an improved variant of Verlet algorithm. In velocity Verlet algorithm, the positions, and velocities of atoms are given by [63]

$$r(t + \partial t) = r(t) + v(t)\partial t + \frac{1}{2}a(t)\partial t^2 \quad (2.8)$$

$$v\left(t + \frac{\partial t}{2}\right) = v(t) + \frac{1}{2}a(t)\partial t \quad (2.9)$$

2.2.5. Ensemble selection

An ensemble is defined as a collection of all possible systems which have different microscopic states but share an identical macroscopic or thermodynamic state. The purpose of adopting an ensemble method is to match the condition of simulation to those that can be experienced in real world experiments. In addition to manipulating the simulation temperature, ensemble techniques also facilitate to avoid the energy drifts caused by accumulation of numerical errors. Different ensemble methods are available with different characteristics. The common thermodynamic ensembles are microcanonical ensemble, canonical ensemble, isobaric-isothermal ensemble and grand canonical ensemble.

The thermodynamic state represented by microcanonical ensemble is characterized by a fixed number of atoms N , a fixed volume V , and a fixed energy E . The microcanonical ensemble corresponds to an isolated system. A canonical ensemble is represented as a collection of all systems in which the thermodynamic state is characterized by a fixed number of atoms N , a fixed volume V , and a fixed temperature T . This ensemble is suitable for simulating systems where the temperature and the system volume need to be conserved throughout the simulation process. The isobaric-isothermal ensemble is characterized by a fixed number of atoms N , a fixed pressure P , and a fixed temperature T . This ensemble is useful in simulating a molecular system in which the system

temperature and pressure needs to be conserved. A grand canonical ensemble is characterized by a fixed chemical potential μ , a fixed volume V , and fixed temperature T .

2.2.6. Bond breaking criteria

The criterion of bond breaking is an important issue to be considered in the atomistic simulation of materials. The simulation time and the computational cost involved in MD simulations can be minimized by terminating the simulation once bond breaking or fracture has been observed. For example, in determining the mechanical property of CNTs by tension, the cessation of simulation is marked by the fracture and breaking of bonds between the covalently bonded carbon atoms. A distance-based approach is normally adopted by most of the MD simulations. For example in CNT, a bond in between any two atoms is considered to have broken when the scalar distance between the atoms exceeds 2 Å [69]. Detection of bond-breaking can also be based on energy of the system. This can be done by monitoring the potential energies of individual atoms in the system, in which bond-breaking and fracture results in release of irregularly high energy or observed by a drop of force and strain energy [70, 71].

2.2.7. Information extraction

The MD simulation is used to track the trajectory of atoms and its velocities at a given instance of time. Using this basic information with the relevant loading and geometric conditions, useful and critical information regarding the properties of material can be obtained. For example, system deformation and propagation of defects can be obtained by monitoring the position of atoms directly. The basic information is then further

subjected to post-processing to extract information such as forces, thermal conductivity, total energy of the system, and fracture toughness etc.

2.2.8. Visualization of materials modeling

It is also helpful to have a good visualization interface apart from the numerical calculations. The material behavior generated by the MD simulations can be explored effectively by visual inspection methods, particularly for those systems consisting of large number of atoms. Visual environment interface and digital movies provide greater understanding and direct insight of the behavior of the system being simulated.

2.3. Force fields

The most time-consuming part of the MD simulation is the computation of forces due to the involvement of a large number of atoms. Computation of forces from the force field is often an approximation since the force fields are empirical, which means that no accurate form for a force field exists. A diversified range of force field functions exists in literature [72-79]. The total potential energy E_{pot} of a system is the sum contribution due to the bonded E_b and non-bonded E_{nb} interactions. The respective mathematical functions for N system of atoms are given as [66],

$$E_b = \sum_{bonds} \frac{k_{bond}}{2} (b_i - b_0)^2 + \sum_{bonds} \frac{k_\theta}{2} (\theta_i - \theta_0)^2 + \sum_{torsions} \frac{F_n}{2} [1 + \cos(n_p \omega_i - \gamma)] \text{ and} \quad (2.10)$$

$$E_{nb} = \sum_i \sum_j \frac{q_i q_j}{r_{ij}} + \sum_i \sum_j \xi_{ij} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (2.11)$$

The harmonic bonding energy (Eqn. (2.3)) is given by the first term on the right hand side of the bonded energy function. This term consists of the equilibrium bond length b_0 , the actual length of bond between atoms b_i , and the force constant k_{bond} . The variation in the energy due to distortion in bond angle is depicted in the second term, which consists of the angular force constant k_θ , the equilibrium angle θ_0 , and the actual angle θ_i between the atoms that defines the angle. The energy due to torsional rotations is given in the third term, which again comprises the force constant F_n , the actual torsion angle ω_i , the angular phase γ , and the periodicity n_p .

The non-bonded energy function given by Eqn. (2.4) is the summation of the electrostatic potentials given by the coulomb potential and the Lennard-Jones (12-6) potential function [80]. The ζ and σ terms defines the well depth parameter and the equilibrium distance between atoms respectively, while the charge on atoms i and j is represented by q_i and q_j . The scalar distance between the centers of atoms i and j is given by r_{ij} and is defined as

$$r_{ij} = |r_i - r_j|. \quad (2.12)$$

2.3.1. Potential models

The chemical bonds between the atoms in a material will dictate its mechanical, thermal, and physical properties. The inter-atomic potential models are used to mathematically explain the governing inter-atomic forces in a system. Accurate description of the interaction effects is obtained by quantum mechanical approach of solving the Schrödinger wave equation that analytically describes the electron probability states. However, this method is not suitable for systems that involve large number of atoms due

to limitations in computational resources. Hence, classical potential models have since been developed and used extensively in the field of MD simulations.

A large number of inter-atomic potentials have been developed and reported in the literature. Each potential model is usually developed to suit a particular system or class of materials. These potential functions may be simple or could be complicated that incorporates the effect of bond orders, bond angles, and the local electron densities, etc. The empirical isotropic pair potentials such as the Lennard-Jones [80] and the Morse potential [81] were among the earliest potentials that were used in computational modeling studies. These potentials represent the pair interactions in gases and liquids by describing the interaction of closed-shell atoms. Isotropic functions were used during the early years of materials simulation. These potential functions are used to obtain the basic properties such as the lattice structure, metallic defects [82, 83], and fracture investigation [84, 85]. The simplicity of these potential models enables them to be widely used until today.

To consider the effect of local electron density, many-body potential functions such as the embedded atom method (EAM) potential [86, 87], the Finnis-Sinclair potential [88], the Sutton-Chen potential [89], etc. have been developed. These classes of potentials have the ability to incorporate the approximate variation of bond strength with the electron density [90]. However, neither the isotropic pair potentials nor many-body potentials incorporate the angle formed in between the bonds of atom. Hence, these potentials is not suitable for simulation of materials containing covalent bonds in their structure. This discrepancy can be overcome by the Stillinger-Weber potential [91] that is effectively used to model the diamond-cubic structure and liquid state of silicon. The

potential is modeled by making use of empirical parameters obtained from the properties of silicon determined by experiments. Since the atomic configurations obtained for the amorphous phase of silicon are not reproduced accurately when compared to those of the experiments, this potential is not useful for systems that undergo significant change such as material failure.

The bond energy variations due to changes in the number of nearest neighboring atoms has been effectively modeled by complex bond order potentials such as the Tersoff [92, 93], Brenner's potential function [94] and adaptive intermolecular reactive empirical bond order potential (AIREBO) [95]. The AIREBO potential is used in our study on the MD simulation of CNTs and is described further in section 2.4.

The environment dependent inter-atomic potential (EDIP) [96] model for silicon and carbon are obtained by fitting the parameters to the cohesive energy curves obtained by *ab initio* calculations, but not the experimental data. The cohesive energy calculated by the *ab initio* method is inversed to obtain the potential energy. Even though the fundamental form of the equation is the same as the Stillinger-Weber potential, they are more complicated than the many-body potential equations. The elastic properties of covalently bonded solids are analyzed to determine the cohesive forces. Originally developed to investigate the bulk studies of silicon, the EDIP model has since been extended for cases involving fracture simulation [97].

2.3.2. Potential models for solutions and liquids

Liquid water and aqueous solutions in the field of computational chemistry are commonly modeled by means of classical water models. The most fundamental forms of water models are the TIP3P [98], TIP4P [99], TIP5P [100], SPC [101], and SPC/E [65].

These water models are based mainly on the number of interaction sites used to define the model that includes the Lennard-Jones interaction between oxygen atoms and electrostatic interaction between charged species. To date, about 46 different water models have been developed which are based on the improvements and re-parameterization of the above mentioned water models.

The transferable intermolecular potentials (TIP) remain by far the most popular form of potential for water simulations [102] though many alternatives have been proposed thereafter. The main purpose of introducing the transferable potentials for aqueous solutions is to improve the ease of constructing potential functions for many different systems based on one set of parameters for an atom or its group. The transferable intermolecular potential was originally computed using the Monte Carlo (MC) simulations [103] and it is imperative that the computational time depends on the number of interaction sites in a molecule. In addition, the TIP water models describe the water molecule with a rigid geometry.

The earliest form of intermolecular potential functions is the TIP3P [98] model, which consists of three interaction sites in the water molecule (consisting of two hydrogen atoms and an oxygen atom). This form of TIP potential consists of charge sites located exactly at one oxygen and two hydrogen sites which make the water molecule. The oxygen atom carries negative charge while the hydrogen atoms are positively charged. The summation of the total charges on the oxygen atom and two hydrogen atoms in a water monomer equals to zero. In addition, the Lennard-Jones parameters for the hydrogen (H) to hydrogen (H) interaction, namely σ_{HH} and ϵ_{HH} is set to zero. The three site models are very popular for MD simulations because of their simplicity,

computational efficiency and better compatibility between the experiment and the simulated values [102]. The TIP3P model of a water molecule is depicted in Fig. 2.3, where r_{OH} describes the inter-atomic distance between the oxygen (O) and hydrogen (H) atoms. The angle formed between the two hydrogen atoms and the centre oxygen atom is given by $\angle HOH$.

Fig. 2.3. A three site water model, the red circle represents oxygen and the two grey circles denote hydrogen atoms.

The TIP3P water model describes the water molecule with a rigid geometry which means that additional computational cost will be associated with keeping the water structure rigid. This can be overcome by using flexible three site water models. One such flexible water model is a flexible fixed point charge water (FPC) model [104] which is used in our simulation. The FPC water model is used in our study to model the water molecules in our simulation and is described further in section 2.4.

The TIP4P potential [99] is an extended class of the TIP3P which models water as a rigid structure consisting of 3 atoms and an additional mass less site. The negative charge associated with the oxygen atom is placed on this site. The mathematical form of the potential is very much similar to that of the three site interaction potential model. The bonded interactions are calculated by the electrostatic potential function with the

Lennard-Jones interaction in between the oxygen atoms account for inter-molecular interaction. The water molecule modeled as a TIP4P model is depicted in Fig. 2.4, where r_{OM} describes the inter-atomic distance between the oxygen and the dummy mass-less site. The inclusion of the dummy site in the TIP4P water model improves the electrostatic distribution around the water molecule and the oxygen to oxygen partial radial distribution function predicted by TIP4P is in good agreement with the results predicted using neutron diffraction data [102]. It should however be noted that the oxygen to hydrogen and hydrogen to hydrogen partial distribution functions predicted by the TIP4P water model do not agree well with the experimental data [105]. In addition, the presence of an additional interaction site increases the simulation time and computational cost required to simulate the water molecule.

Fig. 2.4. A four site water model, with a dummy mass-less site (M) represented by the blue circle. The oxygen (O) and the hydrogen (H) atoms are denoted by the red and grey circles respectively.

The computational statistical mechanics of the interaction potentials of liquid water was subjected to intensive research focused on improving and understanding the properties of liquid water at a range of thermodynamic state points. To better describe the density anomaly of liquid water, a new model, TIP5P, has been developed that consists of five interaction sites [100]. As depicted in Fig. 2.5, in a TIP5P model, three particles represent the three atoms in water, while the remaining two sites correspond to oxygen lone pairs. In this model, r_{ON} describes the inter-atomic distance between the oxygen and the oxygen lone pairs. The angle formed between the two lone pairs and the centre oxygen atom is given by $\angle NON$. The TIP5P water model results in a more tetrahedral structure of water. It therefore produces a better reproduction of the structure factors as comparable to the neutron diffraction studies. However, increasing the charge sites in water molecule will result in substantial increase in computational time.

Fig. 2.5. A five site water model, with two dummy mass-less sites (N) represented by the blue circles. The oxygen (O) and the hydrogen (H) atoms are denoted by the red and grey circles respectively.

The Simple Point Charge (SPC) water model [101] employs three interaction sites that correspond to the three atoms in the water molecule. In this potential, a point charge is assigned to each of the three atoms and the Lennard-Jones parameter is added to the oxygen atom. The point charges on the hydrogen atoms are positive with an excess negative charge on the lone oxygen atom. This configuration results in an incorrect value for the water dipole moment [106]. It is for this reason that the bond angle between the H-O-H is given as 109.47° , resulting in an ideal tetrahedral shape. The SPC/E (extended simple point charge model) [65] is a slight re-parameterization of the SPC model of water, with a modified value for the negative charge on the oxygen atom. The water molecule is modeled as a rigid isosceles triangle with charges situated on each of the three atoms. Since the SPC class of water models employ only 3 sites of water molecule, they are well suited for carrying out computation of large systems of atoms at constant temperature dynamics [107]. Furthermore, the SPC water model includes corrections for self energy term that results in better correlation of the measured radial distribution function, diffusion and density to the observed experimental values [65, 108].

The mathematical form of the above mentioned potentials of water is given by

$$E_{ab} = \sum_i^a \sum_j^b k_c \frac{q_i q_j}{r_{ij}} + \left(\frac{A}{r_{oo}^{12}} - \frac{B}{r_{oo}^6} \right), \quad (2.13)$$

where, E_{ab} represents the interaction potential between any two water monomers a and b , r_{ij} represents the scalar distance between atoms i and j , q denotes the charges acting on each atom, A and B represent the Lennard-Jones parameters, k_c is the electrostatic constant that has a value of $332.1 \text{ \AA kcal/mol}$ [109], and r_{oo} indicates the equilibrium distance between the two oxygen atoms. It should also be noted that the geometry of the water molecule is fixed in all water models described above, so there is no bond

stretching or angle bending. The parameter values depicted in Fig. 2.3-2.5 and Eqn. (2.13) are represented in Table 2.1.

Table 2.1. Parameters for the commonly used water molecular models.

Parameter	SPC [101]	TIP3P [98]	SPC/E [65]	TIP4P [99]	TIP5P [100]
r_{OH} (Å)	1.0	0.9572	1.0	0.9572	0.9572
r_{OM} (Å)	NA	NA	NA	0.15	NA
r_{ON} (Å)	NA	NA	NA	NA	0.70
$\angle HOH$ (degrees)	109.47	104.52	109.47	104.52	104.52
$\angle NON$ (degrees)	NA	NA	NA	NA	109.47
q_O	-0.82	-0.834	-0.8476	NA	NA
q_H	+0.41	+0.417	+0.4238	+0.52	+0.241
q_M	NA	NA	NA	-1.04	NA
q_N	NA	NA	NA	NA	-0.241
$A \times 10^{-3}$ (Kcal Å ¹² mol ⁻¹)	629.4	582.0	629.4	600.0	544.5
B (Kcal Å ⁶ mol ⁻¹)	625.5	595.0	625.5	610.0	590.3

2.4. Nano-scale simulation model employed in our research

2.4.1. Potential model for simulating carbon atoms

Carbon is one of the most versatile elements on the periodic table in terms of the number of compounds it may form. It may form virtually an infinite number of compounds due to the types of stable bonds it can form in both sp^2 and sp^3 configurations. An accurate modeling of structures in these hybridization configurations and in between transition structures calls for a suitable empirical potential. The AIREBO potential developed by Stuart et al [95] is used in the thesis to study the mechanical characterization of CNTs using MD simulation. The AIREBO potential consists of the Brenner's second generation reactive empirical bond order (REBO) potential [94] to describe the short range carbon to carbon interaction. In addition, it also includes a torsional term to describe the various dihedral angle preferences and to include the interaction due to bond rotation, and the standard Lennard-Jones (12-6) potential to compute the potential energy of the long range non-bonded interactions. The description of each of the above mentioned potential energy terms are described below.

The Brenner's second generation potential energy model [94] describes the interactions in between the carbon atoms. The second-generation REBO potential energy model [94] hereafter represented as REBO potential, is an improved version of the first generation Brenner's potential energy function for hydrocarbon systems [110]. The improvement is achieved by including mathematical terms that account for breaking and forming of bonds with adequate changes in the hybridization of atoms in the REBO potential. This feature of REBO potential leads to better description of the bond energies, force constants, bond lengths, interstitial defect energies, surface energies and elastic

properties. A variety of applications in CNTs [111-115] have been successfully modeled by making use of the REBO potential.

In the REBO potential, the chemical binding energy derived from chemical pseudo-potential theory [116] is expressed as a summation over the nearest neighboring atoms and is given as [116]

$$E_{REBO} = V_R(r_{ij}) - b_{ij}V_A(r_{ij}), \quad (2.14)$$

where $V_R(r_{ij})$ and $V_A(r_{ij})$ are the repulsive and attractive pair terms, b_{ij} term is used to include the reactive empirical bond order between the atoms i and j , and r_{ij} represents the scalar distance between the atoms i and j .

The torsional interaction due to the rotation about single bonds is also included in the calculation of potential energy in simulating the mechanical testing of CNTs [95]. The torsional interaction is given by V_{TORS} , which is given by the cosine power series in dihedral angle ω [95]

$$V_{TORS} = \frac{1}{2} \sum_{k=1}^3 V_k [1 - (-1)^k \cos(k\omega)]. \quad (2.15)$$

The coefficients V_k are chosen for each individual molecule based on the relative energies and barriers to rotation of the bonds and atom k refers to the covalently bonded neighbor of atom i [95].

The torsional potential given in Eq. (2.8) is implemented in addition to the REBO potential for all dihedral angles in the system, in proportion to the bond weights $w_{ij}(r_{ij})$ that contribute to the dihedral angle. The complete form of torsional potential, E_{TORS} is therefore an explicit 4-body potential that describes various dihedral angle preferences in hydrocarbon configurations [117]. The torsional potential E_{TORS} is given by [95]

$$E_{TORS} = \frac{1}{2} \sum_i \sum_{j \neq i} \sum_{k \neq i, j} \sum_{l \neq i, j, k} w_{ij}(r_{ij}) w_{jk}(r_{jk}) w_{kl}(r_{kl}) \times V_{TORS}(\omega_{ijkl}), \quad (2.16)$$

where atoms k and l are covalently bonded neighbors of atoms i and j . The bond weight w_{ij} is a number ranging between 0 to 1, which indicates the nature of bonding between two atoms given by i and j . The bonded weight terms ensures a smooth transition from bonded to non-bonded interaction during the dissociation of a molecule. The atom pairs can hence be identified as bonded ($w_{ij} = 1$), partially dissociated ($0 < w_{ij} < 1$) or non-bonded ($w_{ij} = 0$) [95].

The REBO potential does not account for the non-bonded interaction in between the carbon atoms. The non-bonded interaction must be considered when we need to simulate an array of SWCNT or any MWCNT system. For this reason, we compute the long range interactions by employing the Lennard-Jones (12-6) potential which is mathematically expressed as [80]

$$E_{LJ} = 4\xi \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (2.17)$$

where $\xi = 4.55$ meV is the well depth parameter and σ is the equilibrium distance between two atoms i and j .

Hence, the combined form of the total potential as described by the AIREBO potential to model the CNT in our work is given by [95, 117]

$$E_{AIREBO} = E_{REBO} + E_{TORS} + E_{LJ} \quad (2.18)$$

2.4.2. Potential model for simulating water molecules

The interaction between the water molecules in our simulation is described using the FPC water model [104]. The basic structure of the FPC water model is based on the TIP3P water model in which the water molecule is represented by three sites, viz. two hydrogen atoms and one oxygen atom. Unlike the rigid TIP3P water model, the water molecule is fully flexible in FPC model. This results in substantial reduction in the additional computation cost associated with keeping the structure constrained. Furthermore, in FPC water model, the Lennard-Jones potential of hydrogen atom is added to the total potential energy of the system. The inclusion of Lennard-Jones energy of hydrogen atom in FPC water model improves the dielectric properties and diffusion of water molecule at ambient conditions. The FPC water model is also capable of accurately reproducing the properties of water for different ranges of pressure, temperature, integration time steps and system sizes. The predicted properties of water using the FPC water model are listed in Table 2.2 [104]. It can be seen from this table that the FPC water model can predict the properties of water model which are comparable to those predicted by the SPC/E or the computationally expensive TIP4P water models. The simple three site representation of the FPC water model and its accuracy in predicting water properties makes it ideal for MD computations of biological systems involving large number of water molecules [118].

Table 2.2. Comparison of predicted properties of water molecule using FPC [104], TIP4P [99] and SPC/E model [65] with those obtained from experiments [119].

Parameter	TIP4P [99]	SPC/E [65]	FPC [104]	Experiment [119]
Bond distance, r_{OH} (Å)	0.9572	1.0	0.9611	0.970
Bond angle, θ_{HOH} (°)	104.52	109.47	109.4712	106
Critical pressure (bar)	112	148	213 ± 6	220.64
Critical density (g/cm ³)	0.313	0.295	0.325 ± 0.004	0.322
Critical compressibility	0.232	0.172	0.220	0.236

The FPC water model is described mathematically as [104]

$$E_{FPC} = E_{bond} + E_{bend} + E_{LJ} + E_{els}, \quad (2.19)$$

where E_{bond} and E_{bend} are intra-molecular potential function that represents the bond strength energy and bending energy in a water molecule respectively. They are defined respectively as [104],

$$E_{bond} = \frac{1}{2} k_{bond} (r_{ij} - r_{eq})^2 \text{ and} \quad (2.20)$$

$$E_{bend} = \frac{1}{2} k_{bend} (\theta_{ijk} - \theta_{eq})^2 \quad (2.21)$$

where r_{ij} , r_{eq} , θ_{ij} and θ_{eq} are the measured bond length, equilibrium bond length, measured bending angle and equilibrium bending angle respectively. K_{bond} and K_{bend} are the force constants for bonding and bending respectively.

The terms E_{els} and E_{LJ} in Eq. (2.12) denote the electrostatic potential and Lennard-Jones (12-6) potential between water molecules respectively. They are defined respectively as [104]

$$E_{els} = \frac{1}{4\pi\epsilon_0 r_{ij}} q_i q_j \quad (2.22)$$

$$\text{and} \quad E_{LJ} = 4\xi_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2.23)$$

where ξ_{ij} , σ_{ij} , q_i , q_j and ϵ_0 are the potential well-depth, equilibrium distance, partial charges and permittivity of free space respectively for pairs of atoms i and j .

The parameter values for the hydrogen and oxygen terms of the FPC water model as defined in Eqs. (2.12) to (2.16) are listed in Table 2.3.

Table 2.3. FPC water model parameters as described in Eqs. (2.12) to (2.16) from ref. [104].

$r_{OH} (\text{\AA})$	0.9611	$K_{bond} (\text{kJ}/(\text{mol } \text{\AA}^2))$	1480
$\theta_{HOH} (^{\circ})$	109.4712	$K_{bend} (\text{kJ}/(\text{mol } \theta^2))$	353
$q_H (\text{e})$	0.4238	$\epsilon_H (\text{kJ}/\text{mol})$	0.0324
$q_O (\text{e})$	-0.8476	$\epsilon_O (\text{kJ}/\text{mol})$	0.6287
$\sigma_O (\text{\AA})$	3.1169	$\sigma_H (\text{\AA})$	0.98

2.4.3. Potential model for simulating carbon atom to water molecule interactions

The non-bonded interactions between the carbon atoms of CNTs and the water molecule are typically modeled using a Lennard-Jones potential function [120, 121]. This is because the Lennard-Jones potential is able to accurately describe the short-range electron repulsion and long-range electron attraction that is sufficient to describe the interactions between the CNT and water molecules [120-122]. The Lennard-Jones potential is tuned using the parameters obtained from ref [123] to accurately describe the experimentally observed water-graphene contact angle. The non-bonded interactions between the carbon atoms and the water molecule is given by [123]

$$E_{non-bond} = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (2.24)$$

where $\epsilon_{CO} = 0.3135$ kJ/mol, $\epsilon_{CH} = 0.253$ kJ/mol which is the well depth parameter, $\sigma_{CO} = 0.319$ nm, and $\sigma_{CH} = 0.282$ nm denote the collision diameter between carbon to oxygen and carbon to hydrogen respectively [123].

2.5. Efficiency of molecular dynamics computer program

The MD simulation of a CNT–water system is computationally expensive and time consuming. The efficiency of the computer program is improved by incorporating the Verlet neighbor list feature [124] for carbon atoms in the MD simulations.

2.5.1. Verlet neighbor list

The computation of the potential energies and the inter-atomic forces is time consuming in the computer simulation of nano-scale materials. In the nano-scale simulation of material properties, the forces and energies in every pair of atoms are computed to determine the contribution of force on an atom by all its neighbors. For a system of N atoms, if the inter-atomic pair potential is not truncated, then $N(N - 1)/2$ pair interactions have to be considered. The computation efficiency can be improved by excluding atoms which are beyond a certain cutoff distance, r_{cut} . Hence, in an MD simulation it is a normal practice to use pair potentials with a truncated cutoff distance. The truncated version of Eq. (2.10) can be written as

$$E_{LJ} = \begin{cases} 4\xi \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] & r \leq r_{cut} \\ 0 & r > r_{cut} \end{cases} \quad (2.25)$$

where r_{cut} is typically 2.5σ .

It can be seen from Eq. (2.18) that evaluating the Lennard-Jones energy for distances greater than r_{cut} will increase the computation time even though the Lennard-Jones energy is zero and will not alter the result. This increase in computation time can be saved by using a book-keeping scheme devised by Verlet [124], known as Verlet neighbor list. In Verlet neighbor list, a second cutoff radius $r_{verlet} = r_{cut} + r_{skin}$ is introduced to keep track of neighboring atoms that lie within the distance r_{verlet} (Fig. 2.6). Generally, a smaller skin distance will result in more frequent building of the neighbor list. However, if the skin distance r_{skin} is larger, the neighbor lists are built less frequently, but more pairs must be checked for possible force interactions thereby decreasing the efficiency. Hence, there is clearly a trade-off in determining the skin distance, r_{skin} and the frequency in which the neighbor list needs to be updated.

Fig. 2.6. Depiction of cutoff distances in a Verlet neighbor list.

The CPU time taken for MD simulation of a (5,5) SWCNT consisting of 820 atoms equilibrated at 300 K using the Lennard-Jones potential function as given in Eq. (2.10) is shown in Table 2.4. The simulation is carried out for 50000 time steps, with each time step equal to 1 fs. The r_{cut} is kept constant at 2.5σ while the skin distance r_{skin} is varied. It can be clearly seen from this table that incorporating a neighbor list in the computer simulation will greatly reduce the computation time. It can also be noted that increasing the skin distance will result in fewer updates of the neighbor list. Similarly, a smaller skin distance will result in a smaller neighbor list. Hence this will reduce the computation time that ultimately improves the efficiency.

Table 2.4. Computation statistics using the Verlet neighbor list.

r_{cut}	r_{skin}	Number updates	of	Average neighbors/atom	CPU time (min)
No list	—	NA		NA	7.87
2.5σ	0.1σ	4979		116.16	1.23
2.5σ	0.2σ	1905		121.58	1.18
2.5σ	0.3σ	470		125.85	1.16
2.5σ	0.5σ	1		142.90	1.16
2.5σ	0.7σ	0		151.99	1.23
2.5σ	1.0σ	0		170.06	1.46

2.6. Molecular dynamics computer program

The MD computer program was written in LAMMPS open source software [117] to carry out the simulations described in this thesis. LAMMPS is an acronym for “Large Scale Atomic/Molecular Massively Parallel Simulator” and is based on C++ programming language. The computer program involves incorporation of the potential energy functions of the CNT, water and CNT–water interactions as described in section 2.4. The required trajectory of atoms at various time steps is computed using the velocity Verlet algorithm [124]. LAMMPS makes use of the neighbor list to keep track of nearby particles to improve computational efficiency. In addition, LAMMPS adopts spatial decomposition technique to implement parallel processing using MPI-library. In the spatial decomposition method, the simulation domain is partitioned into small 3 dimensional sub-domains and each sub-domain is assigned to a processor. These processors then communicate and store the neighboring atom information for atoms that border their sub-

domain. The computational statistics of equilibration of a CNT–water system at 300 K for various system sizes (number of atoms) using Nose-Hoover thermostat [67, 68] is listed in Table 2.5. The execution time required to equilibrate a CNT interacting with 6300 water molecules using a single processor is 4.37 minutes. However, if two processors are used, the execution time is reduced by half. Increasing the number of processors proportionally decrease the computation time. Hence, considerable speed-up can be achieved by making use of parallel computing technique in MD simulation.

Table 2.5. Computation statistics using the parallel processing by implementing MPI-library.

Number of atoms			Execution time (in minutes) for number of processors			
Water		CNT				
Oxygen	Hydrogen	Carbon	1	2	4	8
6300	12600	1640	4.37	2.18	1.10	0.55
12600	25200	1640	8.73	4.35	2.19	1.09
25200	50400	1640	17.48	8.74	4.35	2.18

A plot of the variation of temperature in a CNT-water system consisting of (10,10) SWCNT submerged in simulation box consisting of 7248 water molecules with time during system equilibration using Nose-Hoover thermostat is depicted in Fig. 2.7. It can be noted from this plot that the convergence of system is attained by fixing the average temperature of the system under simulation, but at the same time allowing for a fluctuation of the temperature with Gaussian distribution [117].

Fig. 2.7. Convergence plot of (10,10) SWCNT submerged in water depicted as a variation of temperature with time during equilibration process.

The MD computer program consists of two main stages: the initialization stage and production stage. The flowchart of the computer program described in this thesis is shown in Fig. 2.8. During the initialization stage (when time $t = 0$), initial parameters such as the position of atoms, number of processors required and the desired neighbor list cut off distance are defined. A simulation box of dimension $40 \text{ \AA} \times 40 \text{ \AA} \times 150 \text{ \AA}$ is deployed in this work and the water molecules are arranged randomly inside the simulation box before it is subjected to equilibration. Thereafter, the CNT is positioned at the geometric center of the simulation box. PBCs are then applied on all three directions

of the simulation box to simulate the interaction of CNT with the water molecules. Then, the required potential models to be deployed in the current simulation are defined. The computer program then scans and reads the coordinates of the CNT and water molecules from the given input data file before computing the neighbor list and the selected atoms to be constrained. The total potential of the system is then computed using the potential energy functions as described in section 2.4. The long range electrostatic interactions of the water molecules are computed by using particle-particle-particle-mesh (PPPM) solver [63] available in LAMMPS software. The system is then equilibrated at the desired temperature using Nose-Hoover thermostat [68, 125]. Following equilibration, the new positions of the atoms are then computed using the velocity Verlet algorithm [124]. The program then proceeds to the production stage.

In the production stage (when time $t > 0$) the program decides if it is required to compute a new neighbor list based on the new positions of atoms after initial equilibration. After this decision, the interactions between the atoms in the system is calculated using the potential energy functions (section 2.4), again followed by the equilibration of the system using Nose-Hoover thermostat [68, 125]. The equilibration is carried out for every 1000 time steps, following which the next new positions of atoms are determined using the velocity Verlet algorithm [124]. The program then computes the maximum displacement of atoms. If this displacement exceeds the skin distance r_{skin} , a new neighbor list will be generated. However, if the maximum displacement does not exceed r_{skin} , the calculated position of atoms computed in the earlier step is saved. The desired properties of the system are also extracted in this step. This process will repeat for every time step until the defined total number of steps has been reached or the desired data has been collected.

Fig. 2.8. Flowchart depicting the MD computer program used in this work.

2.7. Summary

In this chapter, the fundamental features of MD simulation were discussed and presented. The selection of an appropriate potential energy is important in the MD simulation. This is necessary to accurately describe the mechanical, thermal and physical properties of the system. Though MD simulation can be time consuming, the computational efficiency can be increased by incorporating Verlet neighbor list and parallel computing using MPI-library. CNTs have enormous potential to be used for complex applications involving water molecules. Theoretical analyses based on MD simulation have become a major tool in the study of mechanical properties of CNTs. The fundamental nature of MD simulation offers an advantage for simulating the material properties at of CNTs at nano-scale.

CHAPTER 3

MECHANICAL PROPERTIES OF CARBON NANOTUBES

CNT has attracted numerous attention and has been the focus of research due to its exceptional mechanical properties. The special and unique qualities of CNTs has been established and quantified by analytical and experimental modes of research. The elastic properties of CNT determined by experimental [126-128] and analytical [129-131] methods indicate that the elastic modulus of CNT can be as high as 1 TPa. Furthermore, CNTs can withstand tensile loading by exhibiting a large strain to the order of 15% [6, 132]. The CNTs are flexible to buckling and bending, and they are robust for applications that involve high temperatures.

This chapter is organized as follows. In the first part of this chapter, literature on mechanical properties of CNTs is reviewed. The second part focuses on the effect of axial curvature on the mechanical properties of CNTs. Additionally, the curvature and defects have been modeled into the CNT structure to assess the extent to which these imperfections can affect the elastic properties of CNT. The effects of size and temperature on the mechanical properties of these imperfectly straight CNTs are also systematically studied using MD simulations and presented.

3.1. Review of existing literature

3.1.1. Elastic properties of carbon nanotubes determined by theoretical methods

Many studies aimed to investigate the mechanical characterization of CNT through experimental and theoretical means. The material properties of CNTs are more often investigated by using computer simulation approach that employs numerical models to describe and compute the force-field interactions between the atoms in CNT. The existing literature studies in which the CNTs were modeled using computer simulation can be broadly classified into the following major types - *ab initio* method, MD simulation method, continuum mechanics approach and finite element modeling. A vast majority of the research that focuses on the theoretical investigation of elastic properties of CNTs are based on MD simulation. As described in the previous chapter, MD techniques involves computation of the inter-atomic forces as a function of the bond energies described by various empirical pair potentials [94, 95, 116]. Yakobson et al. [133] made use of the REBO potential [94] to study the effect of morphological patterns on CNT subjected to large deformations and its role in high stiffness. They incorporated a cylindrical shell model to describe the bending and buckling effects on the CNT. Liew et al [134] studied the elastic properties of CNTs using MD simulation by making use of REBO potential. They found that the onset of plastic deformation is marked by the formation of STW defects which ultimately leads to fracture and failure of CNTs. Cornwell and Wille [135] investigated the elastic properties of free standing CNTs using MD simulation method. They investigated the response of CNT to compression and found that CNTs could be compressed to a critical strain value until they show formation of kinks and fins. Halicioglu [136] made use of REBO potential to study the atomic stress

of CNTs under tension and compression. The results showed that the CNTs can withstand up to 10% elongation and 5% compression. Yao and Lordi [131] made use of MD simulation to investigate the factors that affect the Young's modulus of CNT. The studies showed that Young's modulus of CNT is not merely a material property and it varies depending on the radius and helicity of CNT. Belytschko et al [129] studied the fracture of CNTs using MD simulation method. They found that while the computed fracture strain agrees well with experimental observations, the computed fracture stress is considerably higher than the experimental values. Wei et al [130] investigated the strain rate and temperature dependence of SWCNT using MD simulation. They found that a defect free micrometer long SWCNT at 300 K elongated at strain rate of 1%/hour fails at $9 \pm 1\%$ tensile strain. Ozaki et al [137] studied the axial deformation in a SWCNT using tight-binding large scale MD simulation method. They found out that the axial stress of SWCNT depends greatly on the chirality of the SWCNT. Dereli and Özdoğan [138] studied the structural stability of SWCNT using tight-binding MD simulation method. It was observed that a (10,10) SWCNT can withstand a tensile strain of 0.23 and compressive strain of 0.06. Dereli et al [139] applied tight-binding MD simulations to simulate tensile elongations of SWCNTs. In this study, it was found that the armchair SWCNT exhibits better tensile strength than the zigzag SWCNT.

The *ab initio* simulation method involving quantum mechanical mechanics calculations were also deployed to study the mechanical properties of CNTs. Peng et al [140] employed *ab initio* method to study the elastic properties of CNTs. They showed that the value of Young's modulus of a CNT depends very weakly on its diameter. Similarly, the elastic properties of CNT was also studied by Sanchez-Portal et al [141] using *ab initio*

techniques. They found that the Young's modulus of CNTs is almost similar to that of a graphene sheet. Fereidoon et al [142] investigated the mechanical properties of CNTs under axial tension and torsion by employing the first-principle based *ab initio* technique. It was observed from their results that the CNTs capped with carbon atoms show better Young's modulus than the hydrogen capped CNTs. Xia et al [143] studied the elastic properties and tensile strength of CNTs using *ab initio* electronic structure calculations. Their studies indicated that the CNTs undergo elastic deformation at small values of strain and subsequently undergo plastic deformation and fracture at large strain values. Hernandez et al [144] predicted the elastic properties of CNTs using *ab initio* studies. The studies predicted that small diameter CNTs exhibit high C–C bond curvature which can reduce its Young's modulus. However, the Young's modulus of bigger CNTs is relatively high and is comparable to that of defect free graphene sheets.

Apart from MD simulation and *ab initio* methods, continuum mechanics and finite element (FE) approach were also deployed to investigate the elastic properties of CNTs using computer simulation. Chandraseker and Mukherjee [145] developed an atomistic-continuum based approach to study the elastic properties of CNTs. They found that the elastic properties of CNTs using the developed approach are comparable to those determined using classical MD simulation methods. Meo and Rossi [146] proposed FE modeling to investigate the elastic properties of CNTs. It was demonstrated that the calculated variation of elastic properties of zigzag and armchair CNTs were in good agreement with the variation observed in experiments. Guo et al [147] developed a nanoscale quasi-continuum constitutive model to determine the mechanical properties of SWCNTs. The constitutive model developed by them predicted that at low temperatures,

the Young's moduli do not have any significant variation with the chirality of SWCNTs. Giannopoulos [148] adopted a semi-continuum FE analysis (FEA) to determine the Young's modulus of CNTs of various diameters. In this study, the CNT was considered as a cylindrical representative volume. They found that the CNTs exhibit very high Young's modulus and the predicted values of Young's modulus are comparable to that of experimental and analytical procedures.

Ye et al [149] developed molecular mechanics based numerical algorithms to predict the mechanical properties of CNTs. They found that the Young's modulus of CNTs has a strong dependence on the diameter of the CNT and it converges to the value of Young's modulus of a plane graphene sheet. Chen et al [150] made use of structural mechanics based computational study to evaluate the effect of thermal fluctuation on the Young's modulus of CNTs. They found that the Young's modulus of CNT decreases at high temperatures. Sears and Batra [151] made use of molecular mechanics simulations to study the axial deformation properties of SWCNTs. They modeled the SWCNT as a continuum tube made of linearly elastic isotropic material. They predicted the value of Young's modulus of SWCNTs to be about 2.56 TPa. They also found that the failure strain of SWCNT predicted using their proposed model do not match well with those derived from the Donnell shell theory and Euler buckling formula.

To summarize, computer simulation of modeling material properties of CNTs have gained popularity due to the nano-scale dimension of CNTs. A brief survey of the studies undertaken to explore the mechanical properties of CNTs using analytical approach is presented in Table 3.1, with the corresponding literature references enclosed in square brackets.

Table 3.1. Mechanical characterization of CNTs using analytical methods.

Potential Employed	Length (Å)	Diameter (Å)	Young's Modulus (TPa)	Ultimate strength (GPa)
<i>Ab initio</i> method [140]	NA	6.8 ~ 15.67	1.29 ~ 1.35	NA
<i>Ab initio</i> method [141]	PBC	6.0 ~ 14.0	0.5 ~ 0.82	NA
<i>Ab initio</i> method [142]	23.0 ~ 124.0	6.9	0.83 ~ 0.92	NA
<i>Ab initio</i> method [143]	NA	6.80	0.83 ~ 3.02	NA
<i>Ab initio</i> method [144]	NA	8.0 ~ 20.0	0.8 ~ 1.22	NA
Atomistic-continuum [145]	NA	6.8 ~ 7.8	1.7 ~ 6.9	35.2 ~ 42.7
EAM potential [131]	100.0	4.0 ~ 34.0	0.97 ~ 1.20	NA
FE modeling [146]	9.7 ~ 27.0	0.4 ~ 2.7	0.912	NA
Molecular mechanics [149]	100.0	5.0 ~ 40.0	0.17 ~ 1.44	NA
Molecular mechanics[151]	15.62	12.526	2.56	NA
Morse potential [129]	NA	16.0	NA	65.0 ~ 93.0
Quasi-continuum [147]	NA	13.6 ~ 14.1	0.79 ~ 1.0	NA
REBO potential [134]	30.0 ~ 120.0	6.9 ~ 13.6	NA	130.0 ~ 170.0
REBO Potential [133]	60.0	9.48	NA	NA
REBO Potential [135]	NA	24.0 ~ 33.0	0.4 ~ 0.8	NA
REBO Potential [136]	PBC	4.0 ~ 22.0	0.5	NA
Semi-continuum FEA [148]	NA	4.0 ~ 16.0	0.4 ~ 0.5	NA
Structural mechanics [150]	41.35	6.8 ~ 13.6	0.62 ~ 0.72	NA
Tersoff Potential [130]	60.0	4.0 ~ 22.0	1.0	40.0 ~ 50.0
Tight binding [137]	140.0	13.0	0.98	NA
Tight binding [138]	NA	13.6	0.311	4.92
Tight binding [139]	20.0 ~ 25.0	6.8 ~ 14.1	0.4	NA

3.1.2. Elastic properties of carbon nanotubes determined by experimental methods

The strength of CNT has also been established by means of experiments. Wagner et al [40] proved that the strength of CNT under compression is higher than any known reinforcing material. They indicated that the tube geometry influences the stress behavior of the CNTs. Wong et al [152] deployed AFM to study the mechanical properties of structurally isolated MWCNTs. Molybdenum disulphide was used to anchor one end of the MWCNTs and the bending force is then measured against displacement along the free end of the CNT. Lourie et al [128] made use of experimental observation to examine the compressive characteristics of MWCNTs embedded in a polymeric matrix using TEM analysis. It was found from their experiments that the compressive strength of MWCNTs are much higher than that of any known engineering fiber. Yu et al [17] measured the mechanical response of 15 SWCNTs ropes under tensile loading. For this purpose, they built a manipulation tool that can be operated inside a scanning electron microscope (SEM). It was found from their experiments that the average tensile strength of SWCNTs range from 13 to 52 GPa. Demczyk et al [126] conducted pulling and bending tests on individual CNTs in-situ in a TEM. It was found from these experiments that CNTs can withstand a maximum tensile strength of 150 GPa. They also found from their experiments that prior to failure; the CNTs do not undergo any obvious reduction in its cross-sectional area.

Treacy et al [19] deployed the thermal vibration analysis and obtained the Young's modulus of CNTs to be 1.06 to 3.70 TPa. The apparatus consisted of free standing MWCNTs which were fixed at the bottom and free to move at the top. The thermal vibrations at the free end of the tubes were measured by using TEM. Poncharal et al [20] induced static and dynamic mechanical deflections in cantilevered MWCNT to measure the

mechanical strength of SWCNTs. It was observed that when CNTs are excited at resonant frequency, their fundamental frequency corresponds to those of an elastic cantilever beam. In addition, they also found from their analysis that the Young's moduli of MWCNTs vary from 0.1 to 0.73 TPa.

Krishnan et al [127] used thermal vibration analysis to detect the Young's modulus of free standing room temperature vibrations of CNTs in TEM. Electron micrograph from TEM was used to monitor the dimensions and vibration amplitude of CNTs. The CNTs used in their experiment have diameters ranging from 10 to 15 Å and reported the value of Young's modulus to be 1.25 TPa. Salvetat et al [153] made use of AFM technique to determine the Young's modulus of CNT. In their experiment, the CNTs were deposited on a well polished alumina substrate and were subjected to mechanical loading. It was found from this experiment that the Young's modulus of CNTs was measured to be about 0.81 TPa. Li et al [154] measured the mechanical properties of aligned DWCNTs by performing direct tensile tests using a stress-strain puller. They found that individual DWCNTs exhibit Young's modulus and tensile strength of about 6 GPa and 1.2 GPa respectively. For the case of DWCNT bundle, the corresponding elastic values show a significant increase of 80 GPa and 6 GPa respectively. Zhang et al [155] measured the failure mechanisms of CNT fibers under different strain rates. They were able to produce strong and uniform CNT fibers synthesized from pure ethylene using argon as a carrier gas. The mechanical properties of CNT fibers thus produced were measured using a precise micro-loading device and recorded a maximum tensile strength of around 1.2 GPa.

A collection of the existing literature data on the mechanical properties of CNTs determined by experimental methods is given in Table 3.2 with the corresponding literature enclosed in the square brackets.

Table 3.2. Mechanical characterization of CNTs using experimental methods.

Experiment Description	Young's modulus (TPa)	Ultimate tensile strength (GPa)
Nanotube-polymer interface tested in tension using Instron 4502 apparatus [40].	1.8	55
AFM was used to bend the CNT that was pinned at one end to molybdenum disulphide surface [152].	1.28 ± 0.59	14.2 ± 8.0
MWCNTs are embedded in a polymeric matrix. Compressive stress is developed due to shrinkage of the polymer resin [128].	NA	135.0 ~ 147.0
Tensile loading of MWCNTs undertaken using a manipulation tool built by authors operating inside an SEM [17].	0.27 ~ 0.95	13.0 ~ 52.0
Tensile and bending tests conducted on a SWCNT inside a transition electron microscope [126].	0.9	150.0
The Young's modulus of SWCNTs are measured in TEM by amplitude of their intrinsic thermal vibrations [19].	1.06 ~ 3.70	NA
Static and dynamic mechanical deflections electrically induced in MWCNT in a TEM [20].	0.1 ~ 0.73	NA
Stiffness of SWCNT estimated by observing their room temperature vibrations in TEM [127].	1.25	NA
CNTs are deposited on a well-polished alumina ultra-filtration membrane and is subjected to deflections by AFM probe tip [153].	0.81 ± 0.41	NA
Direct tensile measurement on DWCNTs using stress-strain puller. Deformation and fracture process were examined to determine Young's modulus [154].	0.53 ~ 0.7	NA
Elastic properties of vertically aligned long CNT fibers measured by micro-loading device [155].	0.05 ~ 0.27	0.3 ~ 1.3

3.2. Simulation details

The first part of our results will focus on the computation of Young's modulus of SWCNT. The MD simulations are performed using LAMMPS open source software [117] to determine the effect of aspect ratio and chirality on the Young's modulus of SWCNT. Here, aspect ratio is defined as the ratio of the length L to diameter D of the SWCNT. The inter-atomic interactions between the carbon atoms in the SWCNT is modeled using AIREBO potential [95], which has been discussed in detail in Chapter 2. As described in chapter 2, the AIREBO potential is capable of accurately describing the covalent bond breaking and formation, in addition to non-bonded interactions in the SWCNT. The additional advantages of AIREBO includes its suitability for simulating large systems with reasonable computation times while maintaining the accuracies of semi-empirical and *ab initio* simulation methods [156].

3.2.1. Computation of Young's modulus

In classical mechanics, the Young's modulus of a material is obtained from the second derivative of the quadratic plot of variation of strain energy of SWCNT represented by E_{SWCNT} , with strain ε from the strain-strain energy curve using polynomial curve fitting. The Young's modulus of the SWCNT is hence given by [157]

$$\left\{ \begin{array}{l} E_{SWCNT} = c_0 + c_1\varepsilon + c_2\varepsilon^2 + c_3\varepsilon^3 + \dots \\ Y = \frac{1}{V_0} \left| \frac{\partial^2 E_{SWCNT}}{\partial \varepsilon^2} \right|_{\varepsilon=0} \end{array} \right., \quad (3.1)$$

where E_{SWCNT} is determined as the difference in total energy of the strained and unstrained SWCNT, V_0 is the equilibrium volume of the SWCNT, c_j ($j=0,1,2,3,\dots$) the

coefficient of the fitted polynomial. Since the SWCNT is a hollow cylinder, the equilibrium volume V_0 is computed as [157]

$$V_0 = 2\pi LRh_t, \quad (3.2)$$

where L and R represents the initial length and the radius of the SWCNT respectively and h_t denotes the thickness of SWCNT shell and is assumed to be equal to 3.4 Å [134].

3.2.2. Results and Discussion

This section will focus on the determination of Young's modulus of SWCNT. For this purpose, we chose two sets of armchair SWCNTs, viz. (5,5) and (10,10) and two sets of zigzag SWCNTs, viz. (10,0) and (18,0) respectively. The variation of Young's modulus with aspect ratio for the selected armchair and zigzag SWCNTs is depicted in Fig. 3.1. We can see from this figure that the Young's modulus shows a gradual dependence on the aspect ratio of SWCNT. At high aspect ratios, the value of Young's modulus of armchair SWCNTs approaches a steady value of about 1.03 TPa. This value is in good agreement with the experimental results reported in previous studies [126, 127]. It can be further noted that for the case of zigzag SWCNTs, the variation in Young's modulus with aspect ratio is almost negligible. The Young's modulus of (18,0) SWCNT at aspect ratio 5 is 0.99 TPa. Increasing the aspect ratio to 20 results in an Young's modulus value of 0.97 which is a variation of less than 3%.

The variation of Young's modulus with aspect ratio becomes insignificant for large diameter SWCNTs. For example, the value of Young's modulus of a (10,10) SWCNT at aspect ratio of 5 is 1.05 TPa. The corresponding value of Young's modulus at aspect ratio 20 is 1.01 TPa. This results in a variation of about 4%. However, for the case of (5,5)

SWCNT which has a smaller diameter, the Young's modulus at aspect ratios 5 and 20 is 1.17 and 1.02 respectively which translates to a difference of about 13%. We can also see from Fig 3.1 that when the diameter of the SWCNT increases, the value of Young's modulus of armchair and zigzag SWCNTs approach the values of 1.01 TPa and 0.99 TPa respectively. This value is very close to the Young's modulus of a plane graphene sheet of 1.02 TPa [158]. This phenomenon can be explained as follows. The curvature of SWCNT is inversely proportional to the diameter of the SWCNT. Hence, a large diameter SWCNT exhibits a lesser curvature compared to that of a small diameter SWCNT and it resembles almost a plane graphene sheet.

Fig.3.1. Plot of the variation of Young's modulus Y with aspect ratio of SWCNT.

From the figure, we note that the Young's moduli of the SWCNTs vary with different aspect ratios. These results are in good agreement with experimental results reported in refs. [19, 127]. Furthermore, the Young's moduli of zigzag SWCNTs are lower than that of the armchair SWCNTs which agrees well with the previous simulation results described in refs. [159, 160].

The Young's moduli of selected SWCNTs of armchair and zigzag configurations with varying aspect ratios has been computed using the MD simulation method and they vary between 0.92 TPa to 1.17 TPa. The values obtained from our simulations are in close agreement with the more accurate however computationally expensive *ab initio* simulations [140, 142] which predict the value of Young's modulus of armchair SWCNTs to be 1.29 TPa and zigzag SWCNTs to be 0.92 TPa for various types of SWCNTs used in their studies and experimental results of 1.25 TPa as given in ref. [127].

3.3. Imperfectly straight single walled carbon nanotubes

The elastic properties of SWCNTs with an axial curvature (imperfectly straight) of single and double bents were presented in this section. It would be interesting to observe from section 3.1.1. that almost all of the computer simulation results suggest that SWCNTs possess high mechanical strength and good elastic properties. On the contrary, we observe from section 3.1.2. that the experimental studies on SWCNTs present a wide scatter of data on the reported mechanical properties of SWCNTs. Much of the earlier simulation studies on characterizing the mechanical properties of SWCNTs assumed that the SWCNTs were pristine, straight structures. This could be a major factor for the discrepancy that is observed between the elastic properties determined by computer

simulations and laboratory experiments. This is due to the reason that CNTs in experiments are not pristine and perfectly straight. The environment temperature can be another major factor that can affect the mechanical properties of SWCNTs. In view of this, computer simulation studies on the elastic properties of SWCNTs including the temperature effects have also been extensively investigated [161-164]. The discrepancies observed between experiment and simulation results could be attributed to the additional possible reason that the SWCNTs used in experiments have imperfections in the form of defects. To account for this factor, researchers have also investigated the elastic properties of SWCNTs by constructing various forms of defects such as vacancy defects [35, 164, 165] and STW defects [166-168] in the structure of SWCNTs.

It is noteworthy to mention that almost all theoretical investigation of the elastic properties model the CNTs to be perfectly straight cylindrical structure with no bents or curvature along the tube axis, resulting in the ideal and excellent mechanical properties of CNTs. It is generally agreed that the CNTs when fabricated exhibit an induced bent or curvature defect [1, 169]. This curvature results in the CNT to exhibit imperfection in the degree of straightness. Some studies were conducted to analyze the effect of curvature on the electronic properties of SWCNTs. Gülseren et al [170] conducted *ab initio* studies on the effect of curvature on the energetics and variation of band gap of the zigzag SWCNTs. They found that the band gap energy of the C–C bond length of axially curved SWCNTs are different from the perfectly straight SWCNTs. The electronic velocity and the effective mass of the lowest conduction band of SWCNTs with curvatures were computed by Wei et al [171]. They found that the low-bias transport of electrons in a zigzag SWCNT is more sensitive to the curvature effect. The above mentioned literature

explains the influence of the SWCNT curvature on the electronic properties of SWCNT. However, the influence of curvature on the mechanical properties of imperfectly straight SWCNTs is yet to be investigated.

Hence the aim of our present study is to understand the effect of curvature on the elastic properties of imperfectly straight SWCNT under compressive and tensile loading conditions. In this work, the performance of the CNT with curvature has been compared with that of the perfectly straight CNT. In addition, we incorporated a single vacancy defect in the imperfectly straight SWCNT model to determine the extent to which the elastic properties can be affected. The effect of size, chirality and temperature on the elastic properties of these imperfectly straight SWCNT were also systematically studied and presented.

3.3.1. Description of carbon nanotubes used in the study

An imperfectly straight SWCNT can be modeled by introducing bents along its tube axis. This can be done by performing the following transformation on the x (or y) co-ordinate of the carbon atoms in a SWCNT used in the computer simulation, such that

$$x_{new} = x_{orig} - m_b \sin\left(n_b \pi \frac{z_{orig} - z_{min}}{L}\right), \quad (3.3)$$

where x_{new} is the new coordinate of the bent SWCNT, x_{orig} and z_{orig} are the original x and z coordinates of the carbon atoms in a perfectly straight SWCNT computer model, z_{min} is the minimum z coordinate of the carbon atom in the SWCNT, and L is the length of the SWCNT. The angle or amplitude of the bent is defined by m_b which can either be an

integer or a real number, and the number of bents in a SWCNT can be controlled by varying n_b , which is an integer.

Based on Eq. (3.3), three types of SWCNTs can be obtained by the following n values:

1. $n_b = 0$, perfectly straight SWCNT (referred to as P – SWCNT)
2. $n_b = 1$, SWCNT with one bent along its axis (referred to as C – SWCNT, since it resembles the letter ‘C’)
3. $n_b = 2$, SWCNT with two opposite facing bents along its axis (referred to as S – SWCNT, since it resembles the letter ‘S’)

All these three classes of SWCNTs used in our study are depicted in Fig. 3.2. We used a value of $m_b = 1$ for all the three cases of SWCNT described above. Although the value of m_b can be suitably varied, if it is increased beyond 1, the initial minimization of the SWCNT will relax the SWCNT to either a perfectly straight structure or a SWCNT structure with minimum amplitude bent. This is because increasing the curvature will result in a significant change in the equilibrium inter-atomic bond distance of the carbon atoms – especially near to where the bent is. This change in the equilibrium bond distance will give rise to attractive or repulsive forces that will force the atoms to shift back to their equilibrium positions during the energy relaxation procedure. Hence, the obtained mechanical properties of those SWCNTs with higher m_b values are almost identical to that of the pristine SWCNT. Furthermore, this phenomenon also holds true if the value of n_b is increased beyond 2 (i.e., a SWCNT with 3 or more bents along its axis). It should be noted that the length of the SWCNT is unchanged despite increasing the number of bents in the SWCNT. Hence, the inclusion of 3 or more bents in a SWCNT will affect the equilibrium inter-atomic distance significantly. We found that subsequent

energy relaxation will result in a SWCNT with perfectly straight structure or a SWCNT with a single bent (i.e. a ‘C’ shaped SWCNT).

Fig. 3.2. Representative shapes of the CNT variants used in the study. (a) Perfectly straight SWCNT (P – SWCNT), (b) ‘C’ shaped SWCNT (C – SWCNT) and (c) ‘S’ shaped SWCNT (S – SWCNT). The degree of bent is exaggerated in this illustration to make the curvature look obvious. The dashed line represent the axis of the SWCNT.

The effect of chirality on the elastic properties of imperfectly straight SWCNT is accounted by considering various armchair and zigzag SWCNTs. The size of the SWCNTs is accounted by varying the aspect ratios of SWCNTs. We used aspect ratios of

15, 17.5 and 20. This choice of aspect ratios allows the SWCNT to sustain the bents even after the SWCNT structure is equilibrated. Apart from the bents, we also studied the combined effect of bents and defects by introducing a single vacancy defect approximately at the center along the length of the SWCNT. The temperature effect is considered by carrying out the simulation at four different temperatures, namely 0 K, 300 K, 600 K and 900 K.

3.4. Computer simulation of elastic properties of single walled carbon nanotube

This section describes the computer simulation procedure carried out to investigate the elastic properties of SWCNT. Before the SWCNT is subjected to mechanical loading, the structure is thermally equilibrated in an NVT ensemble at the desired temperature using Nose-Hoover thermostat [67, 68]. Following equilibration, the end atoms in the SWCNT are fixed and is subjected to constant displacement (strain rate = 0.001 ps^{-1}) in either inward or outward direction to effect compressive and tensile loading respectively (see Fig. 3.3). The end atoms are then shifted to a new position at every 1 ps by calculating the velocity of atoms based on Verlet algorithm [124]. The remaining atoms are then equilibrated in the NVT ensemble after which the required data (energy, temperature, force etc.) is extracted. This procedure is repeated until we observe the compressive or tensile failure of SWCNT. As an illustration, the equilibrated structures of a (5,5) SWCNT with aspect ratio 15 attained after 200 ps of equilibration at different temperatures used in our simulation are depicted in Fig. 3.4.

Fig. 3.3. Procedure of loading of a SWCNT in MD simulation. The end atoms enclosed within the rectangles are fixed and given a constant inward or outward displacement to effect (a) compression or (b) tension.

(i)

(ii)

(iii)

(iv)

(a)

(i)

(ii)

(iii)

(iv)

(b)

(i)

(ii)

(iii)

(iv)

(c)

Fig. 3.4. The equilibrated structures of (a) P – SWCNT, (b) C – SWCNT and (c) S – SWCNT at temperatures (i) $T = 0$ K, (ii) $T = 300$ K, (iii) $T = 600$ K and (iv) $T = 900$ K respectively. Thermal equilibration at high temperatures distorts the P – SWCNT structure which makes it morphologically similar to that of the imperfectly straight SWCNTs.

3.4.1. Compressive loading characteristics of single walled carbon nanotubes

In this section, we will focus on the MD simulation of the compressive characteristics of the imperfectly straight SWCNTs. Fig. 3.5(a) depicts the plots of the variation of strain energy (calculated as the difference between the final and initial energy levels) against strain of different configurations of (5,5) SWCNTs without vacancy defects of length $L = 100 \text{ \AA}$ (aspect ratio = 15) at temperature $T = 0 \text{ K}$. We observe from this figure that the strain energy of the P – SWCNT increases under compression up to the point of collapse at a strain value of $\varepsilon = 0.04$. The corresponding values of maximum compressive strain for the C – SWCNT is $\varepsilon = 0.037$ and for the S – SWCNT is $\varepsilon = 0.035$ respectively. This would mean that the imperfectly straight SWCNTs exhibit lower values of elastic limit than the pristine straight SWCNT under compression. At this point, we observe a sharp decrease in the value of strain energy. Furthermore, we find from this figure that at low values of strain, the C – and S – SWCNT always exhibit slightly higher values of strain energies during the process of compression. This indicates that the presence of bents in an otherwise perfectly straight SWCNT (P – SWCNT) will increase the strain energy of CNTs. This increase in strain energy results in the imperfectly straight SWCNT to fail faster under compression. It is also evident from the plot that the threshold values of the strain energy at which the C – and S – SWCNT fail are lower than those of the P – SWCNT. Hence, inclusion of bents in a P – SWCNT lowers the energy needed for the SWCNT to fail under compression, hence favoring its quick failure.

The decline in the threshold strain energy limit that results in the deterioration of compressive properties is also useful to investigate the compressive properties of SWCNTs with vacancy defect. As described in section 3.3.1, in addition to the curvature,

we also introduced a single vacancy defect approximately at the center of the SWCNT. The strain energy characteristics of the SWCNTs with single vacancy defect density are shown in Fig. 3.5(b). We see from this figure that the strain energy at failure is much lower than that of their non-defective counterparts. The maximum compressive strain of the defective P – SWCNT is about $\varepsilon = 0.027$, which is a 33% drop in the elastic limit compared to that of its pristine counterpart. It should further be noted that the combination of vacancy defects with the imperfections in the degree of straightness can further deteriorate the compressive elastic properties of SWCNT. The defective C – and S – SWCNT fail at $\varepsilon = 0.025$ and $\varepsilon = 0.023$ respectively. This is clear indication that the combination of vacancy defects with bents will significantly deteriorate the properties of SWCNT under compression.

(a)

(b)

Fig. 3.5. Strain energy plot of (5, 5) SWCNTs (a) without defects and (b) with single vacancy defect of length $L = 100 \text{ \AA}$ subjected to compression at $T = 0 \text{ K}$.

The effect of size on the compressive properties of imperfectly straight SWCNT is investigated by varying the aspect ratio while maintaining same degree of curvature of the SWCNT. The variation in the compressive force of the defect-free and defective SWCNTs at 0 K is shown in Fig. 3.6. We can see from this figure that the variation in the compressive forces due to the curvature in the SWCNT decreases while increasing the

aspect ratio (L/D). It should be noted that increasing the aspect ratio of SWCNT increases the length of the SWCNT. As the radius of curvature in an SWCNT is inversely proportional to the length of the SWCNT, SWCNT with large aspect ratio will be more straight compared to that of an SWCNT with small aspect ratio.

Fig. 3.6. Plot of the compressive properties of defect free and defective (5,5) SWCNTs at temperature $T = 0$ K at various aspect ratios.

We can also observe from Fig. 3.6. that increasing the aspect ratio substantially decreases the elastic properties of SWCNT under compression. Similar results have also been

obtained by earlier researchers as can be seen in refs. [161-164, 172]. This is due to the reason that for a given SWCNT diameter, SWCNT with large aspect ratio will be more slender compared to that of an SWCNT with small aspect ratio which would be stocky. This means that the long slender SWCNT would be able to bend much easier compared to that of the small stocky SWCNT. Similar conclusions have been drawn earlier by Lu et al [172]. Hence the elastic properties of long SWCNTs become inferior in contrast to short length SWCNTs under compression. We can further observe from Fig. 3.6 that although the effect of curvature can be ignored for long SWCNTs, the presence of defects still presents an impact the mechanical properties of SWCNT under compression.

The variation in the compressive properties of selected armchair and zigzag SWCNTs is shown in Fig. 3.7. It can be observed from this figure that regardless of chirality or diameter, the compressive properties decrease with increasing aspect ratio. Additionally, we also observe that for all SWCNTs, the variation in the elastic properties of P – , C – and S – SWCNT is greatly reduced due to an increase in the length of the SWCNT. It can hence be concluded from this observation that though the curvature affects the compressive properties of SWCNT, the variation can be minimized by selecting a suitably long SWCNT.

(a)

Fig. 3.7 Plot of the compressive properties of (a) armchair and (b) zigzag SWCNTs at temperature $T = 0$ K for different aspect ratios considered in our study.

Additionally, Fig 3.7 shows that for a given chirality, the maximum compressive force increases with the diameter of the SWCNT. This observation is consistent with the previous simulation results of Liew et al [69]. This is because the surface area of SWCNT increases with increasing diameter of the SWCNT. This increase in surface area offers the bigger diameter SWCNT with more number of bonds that can resist the forces of compression. Furthermore, it can be noticed from Fig. 3.7 that the zigzag SWCNTs are

able to withstand a much larger compressive force when compared to that of the armchair SWCNT. This observation is consistent with the previous simulation results on buckling of SWCNTs by Zhang et al [164]. This is because the vertical bonds in a zigzag SWCNT is able to offer the zigzag SWCNTs with a greater resistance to compression compared to that of an armchair SWCNT [164].

It is also useful to observe the effect of temperature on the elastic properties of imperfectly straight SWCNTs. The variation of the maximum compressive force with temperature of the (5,5) and (10,10) SWCNTs of aspect ratio = 15 is given in Fig. 3.8. We note from this figure that the increase in temperature significantly impacts the elastic properties of SWCNTs under compression. This is because high temperature causes a greater thermal movement which increases the thermal stress of atoms as proven in previous studies [162-164]. Additionally, we also observe from Fig. 3.8 that the difference in the mechanical performance between P –, C – and S – SWCNT shows a significant decline at elevated temperatures. We note from Fig. 3.4 that equilibrating the perfectly straight SWCNT at high temperatures ($T = 600$ K, $T = 900$ K) causes disorientations and distortions along the tube axis that makes it morphologically similar to its imperfectly straight SWCNT counterparts. Hence, the effect of axial imperfection on the elastic properties of SWCNT under compression becomes negligible at very high temperatures.

Fig. 3.8. Plot of the compressive properties of armchair SWCNTs at aspect ratio, $(L/D) = 15$ for different temperatures considered in our study.

3.4.2. Analysis of carbon nanotube compression with continuum mechanics theory

It is worthy to note that the classical continuum mechanics models can be used for predicting the elastic properties of SWCNT under compressive loading. For the case of SWCNT modeled as a Euler-Bernoulli beam (EBB) model, the critical compressive strain ϵ_{cr}^{EBB} is given as a function of the length and diameter of the beam defined as [173]

$$\epsilon_{cr}^{EBB} = \pi^2 \frac{(D^2 + h_{beam}^2)}{2L^2} \quad (3.4)$$

where D and L represents the diameter and length of the SWCNT and h_{beam} in EBB model denotes the thickness of the beam, which is usually taken to be 0.066 nm [173].

Similarly, the critical buckling strain of a SWCNT modeled as a cylindrical shell (CS) defined by continuum mechanics is given as an inverse function of the diameter D of the SWCNT [133]

$$\varepsilon_{cr}^{CS} = \frac{0.0776}{D}. \quad (3.5)$$

In predicting the variation of compressive strain with aspect ratio using the continuum mechanics theory, we employed perfectly straight (5,5) and (10,10) armchair SWCNTs. These SWCNTs were simulated at temperature 300 K. As stated in ref. [173], predicting the compressive behavior of SWCNTs at room temperature allows the MD simulation results to be directly compared with the continuum models results. The compressive strains calculated using the continuum mechanics equations (Eqns. (3.4) - (3.5)) and MD simulation method is calculated and is shown in Fig. 3.9. It is observed from this figure that the MD simulation results are in good agreement with the values predicted using the EBB continuum mechanics model. However, the results obtained by the CS model do not agree well with that of the MD simulation results. This is because in the CS model, the compressive strain of the SWCNT is only given as a function of the diameter (Eq. (3.5)). Hence the compressive strain values predicted using Eq. (3.5) are independent of the length of the SWCNTs for various aspect ratios. Additionally, we note that the CS model show good agreement with SWCNTs of higher aspect ratios. It can hence be concluded from this analysis that for SWCNTs with small aspect ratio, the EBB model which takes into account the length and the diameter of the SWCNT is more suitable for predicting the compressive elastic strain of the SWCNT.

Fig. 3.9. Comparison between classical elastic model equations [173] and MD simulation for compressive strain of (5,5) and (10,10) armchair SWCNTs.

The MD simulation method has been employed in our study to investigate the effect of axial curvature as a defect in the compressive properties of SWCNT. The simulation results show that the presence of bends in an SWCNT will reduce the elastic properties of SWCNT. Combination of vacancy defect and curvature can cause a significant deterioration of the elastic qualities of SWCNT, which can be minimized by selecting a long SWCNT. A summary of the MD simulation results by various researchers along with the results obtained from our present simulation is shown in Table 3.3.

Table 3.3. A summary of compressive strains of SWCNTs obtained using MD simulation methods in literature.

Authors	Potential	Equilibration Technique	SWCNT		Compressive strain
			Chirality	Aspect ratio (L/D)	
Cornwell and Wille [135]	Tersoff potential [93]	0.005 K by velocity scaling	(16,16)	NA	0.0381
			(19,19)	NA	0.0312
			(24,24)	NA	0.0256
Wang et al [174]	REBO potential [94]	0.01 K using Nose Hoover method [68, 175]	(8,8)	9.02	0.053
			(11,11)	6.56	0.042
			(17,17)	4.24	0.032
			(23,23)	3.15	0.0225
Liew et al [69]	REBO potential [94]	Conjugate Gradient	(10,10)	7.7	0.055
Zhang et al [173]	REBO potential [94]	300 K by velocity rescaling	(5,5)	7.93	0.0550
			(5,5)	17.15	0.0193
			(7,7)	18.71	0.0151
			(10,10)	3.00	0.0429
			(16,16)	2.96	0.0285
Batra and Sears [176]	Molecular mechanics	Molecular mechanics	(16,0)	13.75	0.0267
			(16,0)	16.12	0.0212
			(16,0)	20.57	0.0125
Present simulation	AIREBO potential [95]	300 K by Nose Hoover method [68, 175]	(5,5)	15.05	0.024
			(10,10)	14.96	0.0235
			(5,5)	17.51	0.017
			(10,10)	17.50	0.0165
			(5,5)	20.12	0.013
			(10,10)	20.04	0.0126

3.4.3. Compressive loading characteristics of carbon nanotube array system

From the earlier section, it is evident that the elastic properties of imperfectly straight SWCNT under compression depend strongly on the number of bents present in the CNT, aspect ratio and temperature. Based on this understanding, we perform the compressive characteristics on the CNT array comprising of SWCNT variants discussed above. Two sets of arrays are used for the study. The first array comprises SWCNTs of uniform variant, i.e., two similar SWCNT variants form a CNT array. The second array comprises SWCNT that has dissimilar SWCNT variants, i.e., two different SWCNT variants form a CNT array. For the case of uniform array system, we have three models. The first array consists of two pristine SWCNTs (hereafter, we denote it with P – P array), while the second consists of two ‘C’ shaped SWCNTs (hereafter, known simply as C – C array), and finally the third includes two ‘S’ SWCNTs (hereafter, represented as S – S array). Using the same naming convention, the non-uniform array system consists of three models, viz. the P – C array, P – S array, and C – S array.

We selected an array comprising two (10,10) SWCNTs of lengths $L = 200 \text{ \AA}$ (aspect ratio = 15) that are vertically aligned next to each other, and an inter-spacial gap of $3.4 \text{ \AA}$ in between the tubes along the x -axis (Fig. 3.10). It is also important to note that when imperfectly straight SWCNTs are coupled to form an array system, the inter-atomic distance between the atoms in the adjacent facets of the SWCNT (region marked by dashed rectangle in Fig. 3.10) will either be less or more than the carbon to carbon equilibrium van der Waal's distance of $3.4 \text{ \AA}$ [114]. This variation in the inter-atomic distance will give rise to repulsive or attractive forces which will straighten the individual component SWCNTs in the array. This would mean that regardless of curvature in the array system, the equilibration of imperfectly straight SWCNTs will result in P – P array system.

Fig. 3.10. The long range non-bonded interaction acting in between the adjacent facets of the SWCNT array system will result in straightening of the component SWCNTs that will convert any form of curvature array into P – P array system.

The force-strain plot of the P – P array system is depicted in Fig. 3.11. We have also included the compressive loading characteristics of a single pristine SWCNT in Fig. 3.11 for comparison. It can be seen from this plot that the SWCNT array system outperforms the mechanical characteristics of the single pristine SWCNT under compression. The maximum compressive force that can be withstood by the P – P array is 95.92 nN which is about 1.6 times higher than that of the single pristine SWCNT. Additionally, the SWCNT array system possesses improved elastic strain compared to that of a single pristine SWCNT.

Fig. 3.11. Force-strain plot of the SWCNT array system at aspect ratio (L/D) = 15 at temperature $T = 0$ K considered in our study.

To gain an insight of and to explain the compressive characteristics exhibited by the SWCNT array, we need to analyze the van der Waal's interaction that act in between the non-bonded carbon atoms in the SWCNT array. The van der Waal's interactions are repulsive forces that act in between the layers of SWCNT array [177] or MWCNT [134]. For the case of SWCNT loaded in compression, the inter-layer van der Waal's interaction must be overcome in order to induce compressive failure of the SWCNT array. In this section we present a quantitative analysis of the measured van der Waal's interaction acting in between the two SWCNTs of the array system.

Fig. 3.12. Total van der Waal energy vs. strain plot of the P – P array consisting two pristine (10, 10) SWCNTs.

Figure 3.12 illustrates the van der Waals energy of the P – P array at different strain values. It can be seen from the figure that the total van der Waals energy drops steadily as the strain increases. The high frequency fluctuation of van der Waal's energy at strain range 0 to 0.04 might be attributed to the increased vibration of atoms while compressing the large aspect ratio SWCNT array. The total van der Waals energy of the SWCNT array will reach its minimum at the failure strain where the SWCNT undergoes compression. It is hence clear from this observation that the non-bonded van der Waal's interaction in a SWCNT array exerts a strengthening effect on the compressive properties of SWCNT array. Similar conclusions have been drawn in earlier observations of Liew et al [134, 177]. We can hence conclude from our observation that the compressive strength of the SWCNT array depends strongly on the long range van der Waals interactions in a CNT array.

The morphological characteristics of the P – P array under compression is given in Figure. 3.13. It can be seen from this figure that when no external loading is applied, the SWCNT array maintains its stable equilibrium pristine form (Fig. 3.13(a)). Subsequent application of compressive forces results in compression of the SWCNT array resulting in the formation of kinks and fins as seen in Fig. 3.13(b).

Fig. 3.13. Morphological structural deformation of P – P array at (a) strain $\varepsilon = 0.00$, and (b) $\varepsilon = 0.041$.

3.4.4. Tensile loading characteristics of single walled carbon nanotubes

The effect of curvature on the elastic properties of SWCNTs under an axial tensile loading is discussed in this section. As illustrated in Fig. 3.3(b), the tensile loading is effected on SWCNT by subjecting the end atoms to constant outward displacement. At first, we focus on the effect of bents on the tensile elastic properties of SWCNT. The force-strain plot of the P –, C – and S – (5,5) SWCNTs at temperature $T = 0$ K is shown in Fig. 3.14. We can see from this plot that at lower values of strain, the force increases almost linearly with strain. At higher values of strain ($\varepsilon > 0.15$), the slope of the curve decreases and the force exhibits a non-linear relation with the strain. This region marks the plastic deformation region of the SWCNT. A sudden drop in force after the plastic region is observed which indicates the failure of SWCNT.

Fig. 3.14. Force-strain plot of perfectly straight and imperfectly straight (5, 5) SWCNTs of length $L = 100$ Å under axial tension at temperature $T = 0$ K.

The investigation of the tensile mechanical properties of SWCNTs shows that the presence of bents in an SWCNT has little or almost no impact on the maximum tensile force that can be withstood by the SWCNT. Additionally, we note from Fig. 3.14 that the percentage variation of the maximum tensile strain between C – and P – SWCNT and S – and P – SWCNT is 3.2% and 5.3% respectively. This is relatively lower when compared to the corresponding percentage differences (7.5% and 12.5%) that we observed in the case of compressive loading of imperfectly straight SWCNT.

Furthermore, it is interesting to observe that the maximum tensile strains of the imperfectly straight SWCNTs are slightly improved when compared to that of the pristine, perfectly straight P – SWCNT. This is due to the reason that application of tensile force at small strain values (during the initial stages of tension) straightens out the imperfectly straight SWCNT. This ‘straightening effect’ imparts the additional elasticity to the imperfectly straight SWCNT. The S – SWCNT possess slightly higher tensile strain than the C – SWCNT, which indicates that the tensile elastic limit increases with the number of bents. The snap shots of the tensile loading process of the C – and S – SWCNT at $T = 0$ K is given in Fig. 3.15. We note from this figure that at $\varepsilon = 0.0$, when no load is applied, the SWCNTs were able to retain the geometrical imperfections (i.e., the curvature) in their shapes. Subsequent application of tensile load straightens and elongates the SWCNT until at a certain point of maximum tensile strain where failure occurs due to fragmentation and bond breaking of the SWCNT.

(i)

(ii)

(a)

Fig. 3.15. The morphological changes of (a) (5,5) C – SWCNT at strain (i) $\varepsilon = 0.00$ and (ii) $\varepsilon = 0.287$, and (b) (5,5) S – SWCNT at strain (i) $\varepsilon = 0.00$ and (ii) $\varepsilon = 0.295$ under tension at temperature $T = 0$ K. Application of tensile forces causes the imperfectly straight SWCNTs to straighten, which effectively increases the elasticity. The dashed lines indicate the axis of the SWCNT.

The tensile loading properties of the (5,5) SWCNTs with different aspect ratios are depicted in Fig. 3.16(a). It is clear from this figure that the variation of aspect ratio in an SWCNT has little or no impact on the mechanical properties of the SWCNTs under tensile loading. This observation is in good agreement with the results reported in previous studies [69, 133, 178]. Additionally, we also observe that the mechanical properties of the SWCNT loaded in tension is much superior compared to that of the observed elastic properties in compression (please refer section 3.4.1). This observation is

consistent with the earlier simulation reports on the elastic properties of SWCNT as can be seen in refs. [35, 179].

(a)

Fig. 3.16. Plot of the tensile properties of (a) (5,5) SWCNTs and (b) (10,10) SWCNTs at various aspect ratios.

The variation in the mechanical properties of (10,10) SWCNT at various aspect ratios is given in Fig. 3.16(b). It is useful to observe from this figure that the maximum tensile load that the (10,10) SWCNT can withstand is almost double that of a (5,5) SWCNT since the diameter of the (10,10) SWCNT is double that of the (5,5) SWCNT. This increase in diameter increases the cross-sectional area of SWCNT which ultimately

results in a proportional increase in the maximum tensile load. This information is useful to compute the maximum tensile load of any SWCNT with varying diameters without performing expensive computer simulations on the elastic properties of SWCNTs loaded in tension. This observation is in quantitative agreement with the results published by Liew et al [134] who predicted that the maximum tensile force exhibits a linear relation with the diameter of the SWCNT. It can also be observed from Figs. 3.16(a) and (b) that the maximum tensile strain at which the SWCNTs fail are insensitive to the diameter of the SWCNT.

We also investigated the tensile mechanical properties of imperfectly straight zigzag SWCNTs, viz. (10,0) and (18,0) SWCNT. The plot of the mechanical properties of zigzag SWCNTs with varying aspect ratios is given in Fig. 3.17. Based on the aforementioned discussions, we can see that the presence of bents in the zigzag SWCNT has no major impact on the mechanical properties of zigzag SWCNT. Fig. 3.17 also shows that the (18,0) SWCNT ($D = 1.409$ nm) possesses a much larger maximum tensile force than that of (10,0) SWCNT ($D = 0.78$ nm). Increasing the diameter of SWCNT effectively increases the cross-sectional area of the SWCNT which increases the maximum tensile load of the (18,0) SWCNT.

(a)

Fig. 3.17. Plot of the tensile properties of (a) (10,0) SWCNTs and (b) (18,0) SWCNTs at various aspect ratios.

It is also useful to compare the tensile elastic properties of armchair and zigzag SWCNTs depicted in Fig. 3.16 and 3.17 respectively. We note that the zigzag SWCNTs are weaker in tension compared to that of an armchair SWCNT. This finding is in quantitative agreement with the results reported by earlier work [134, 160]. This phenomenon can be explained by observing the deformation of the lattice structure of armchair and zigzag SWCNT loaded in tension. Fig. 3.18 illustrates the lattice structure of the armchair and

zigzag SWCNTs respectively. In this figure, angles α_1 , α_2 and α_3 represent the angles formed by the central carbon atom with three other carbon atoms in the lattice of the SWCNT. The plot of the variation of these dihedral angles when the armchair (10,10) SWCNT and zigzag (18,0) SWCNT is loaded in tension is shown in Fig. 3.19. At the beginning of tensile loading, the dihedral angles at strain $\varepsilon = 0$ is given by $\alpha_1 = 119.73^\circ$, $\alpha_2 = 119.93^\circ$ and $\alpha_3 = 120.34^\circ$. For the case of (18,0) SWCNT loaded in tension, the dihedral angles at a particular strain, say $\varepsilon = 0.15$ is given by $\alpha_1 = 123.92^\circ$, $\alpha_2 = 117.63^\circ$ and $\alpha_3 = 118.45^\circ$. The corresponding values for the case of an (10,10) SWCNT loaded in tension at same strain, $\varepsilon = 0.15$ is given by $\alpha_1 = 128.59^\circ$, $\alpha_2 = 115.63^\circ$ and $\alpha_3 = 115.78^\circ$. It can be seen that the bonds in (10,10) SWCNT can be twisted to large angles compared to (18,0) SWCNT. This means that the arrangement of bonds in the armchair (10,10) SWCNT allows it an increased flexibility and extension in the direction of tensile loading of SWCNT. This flexibility results in superior elastic properties of armchair SWCNTs compared to that of the zigzag SWCNTs when they are loaded in tension.

Fig. 3.18. Lattice definition of an armchair and zigzag SWCNTs. The angle formed by the center carbon atom with three other neighboring carbon atoms is represented by α_1 , α_2 and α_3 .

Fig. 3.19. Variation of the dihedral lattice angles of the (10,10) and (18,0) SWCNT as a function of strain during tensile loading of the SWCNTs.

We also studied the effect of temperature on the tensile elastic properties of imperfectly straight SWCNTs. The variation in the elastic properties of selected armchair SWCNTs with aspect ratio $(L/D) = 15$ is shown in Fig. 3.20. It can be noted from this figure that the influence of curvature on the elastic properties of SWCNTs decreases at elevated temperatures. As explained in section 3.4.1, the high temperature results in disorientations and distortions in the perfectly straight SWCNT structure. Due to this reason, a perfectly straight SWCNT exhibits a similar morphology compared to its

imperfectly straight counterparts (Fig. 3.4). These distortions in the form of kinks in the perfectly straight SWCNT results in the mechanical properties similar to bent SWCNTs at high temperature.

(a)

Fig. 3.20. Plot of the tensile properties of (a) (5,5) SWCNTs and (b) (10,10) SWCNTs at various temperatures.

3.4.5. Tensile loading characteristics of carbon nanotube array system

The tensile studies indicate that unlike compression, the effect of straightness of a SWCNT has no marked impact on the general tensile behavior. Additionally, we note from section 3.4.3 that initial equilibration of an array of imperfectly straight SWCNTs will revert the configuration to a P – P array system. Based on this, we perform tensile characteristics on the P – P array. The force-strain plot of a (10,10) P – P array under

tension at temperature $T = 0$ K is shown in Fig. 3.21. Similar to our observation in compression (section 3.4.3), the tensile properties of the SWCNT array are much superior when compared to that of the SWCNT. Increasing the number of SWCNTs in an array increases the cross-sectional area which effectively increases the force required to pull the ends of SWCNT array under tensile loading.

Fig. 3.21. Force-strain plot of P – P SWCNT array under tensile load.

3.5. Summary

In this work, we employed MD simulation to study the mechanical performance of imperfectly straight SWCNTs subjected to compressive and tensile loads. We focused our investigation on the effect of size, defects and temperature on the mechanical properties of SWCNT with bends. From our results, we find that the axial curvature along with defects significantly impact the elastic properties of the SWCNT. The presence of curvature increases the elasticity of SWCNT under tension while decreasing the elasticity under compressive loading. Moreover, at high temperatures, the effect of curvature can be ignored for all modes of loading. However, at low temperatures, the impact of curvature on the compressive properties can be controlled by increasing the length of the CNT. Our studies show that although the bends in an SWCNT affect the mechanical properties, the variation can be suitably controlled by making use of longer CNTs.

CHAPTER 4

COMPRESSIVE AND TENSILE ELASTIC PROPERTIES OF CARBON NANOTUBE WITH WATER INTERACTIONS

The mechanical characteristics of SWCNT with surrounding water interactions are studied in this chapter using MD simulation method. The effect of chirality, geometry of the SWCNT and the presence of end caps on water submerged SWCNT is investigated by subjecting the SWCNT to axial loading conditions. The findings show that the presence of surrounding water molecules will reduce the mechanical strength of SWCNT. Our findings also show that the location and concentration of defects will strongly affect the mechanical strength of water submerged SWCNT. Furthermore, the mechanical strength of free form and water submerged capped SWCNTs encapsulated with varying concentrations of water molecules are also investigated. This is particularly useful to determine the stability and strength of the SWCNTs for potential applications such as nano-fluidic or NEMS devices. The mechanical characteristics of SWCNTs with various forms of water interaction have been systematically and comprehensively studied using the MD simulations and the discussions are presented in this chapter.

4.1. Introduction

Research in CNTs has generated significant interest in materials science and nanotechnology due to its remarkable physical and mechanical properties [180]. The unique combination of ultra-light weight and high strength of CNTs makes it a promising candidate for applications in nano-level drug delivery [181], nanoelectromechanical systems (NEMS) [182, 183], nano-fluidic devices [133, 184] and nano-level filtration systems [185]. These attractive applications of CNTs for its use in nano-level biological devices and NEMS require a critical investigation of the mechanical properties in a biological medium. Extensive studies on the mechanical properties of free standing CNTs determined by theoretical or experimental methods have been widely reported in the literature. A collection of these literature studies have been discussed in detail in chapter 3. It is further evident that while numerous studies were conducted to explore the mechanical properties of CNTs, the mechanical characteristics of CNTs in an hydrodynamic environment (interacting with water) is yet to be investigated.

CNTs have enormous potential to be used as a nano-fluidic device in nano-level flow channels or as nano-level drug delivery devices in biological environment [184, 186]. When the CNTs are operating in nano-fluidic or hydrodynamics environment, they are subjected to mechanical forces by the surrounding fluid flow. Hence, the main objective of this chapter is to study the elastic characteristics of SWCNTs while interacting with a surrounding water medium. This chapter also investigates the influence of geometrical characteristics and the effect of defects on the elastic properties of a SWCNT interacting with water molecules. In addition, this chapter also provides an insight on the elastic properties of capped SWCNTs with varying densities of water molecules. The mechanical properties of SWCNTs under various forms of water interaction have been comprehensively studied and the results are presented in this chapter.

4.2. Computational model

The work described in this chapter is carried out entirely by using classical MD simulation method where interactive pair potentials are used to describe the potential energy between the individual atoms. Three forms of interaction are considered here – interaction between the carbon atoms of SWCNT, the interaction between the water molecules and interaction between the water molecules and the carbon atoms of SWCNT. As described in Chapter 2, the AIREBO potential is used to describe the interaction between the carbon atoms in the SWCNT. The non-bonded interactions between the carbon atoms and the water molecules is described by the Lennard-Jones (12-6) potential with force-field parameters described in [123] which accurately describes the experimentally observed wetting properties and the density distribution of water molecules with graphene surfaces. Finally, the interaction between the water molecules is described using the FPC water model [104]. The complete details of the potential functions described in this chapter are discussed in detail in Chapter 2.

4.3. Simulation details

The work described in this chapter can be classified into two parts, viz. mechanical characteristics of uncapped and capped SWCNTs. The method of uni-axial loading applied on an SWCNT in our study has been defined in Fig. 3.3 (Chapter 3). The end atoms are fixed and are given a constant displacement in either inward or outward direction to effect compression or tension respectively. The effect of surrounding water molecule is studied by submerging the SWCNT in a simulation box filled with water molecules of density 0.997 g/cm^3 (approximately 1 g/cm^3). The simulation box has

dimensions of $40 \text{ \AA} \times 40 \text{ \AA} \times 150 \text{ \AA}$. PBC is applied along all directions of the simulation box. This allows the water molecule that leaves the simulation box through one face of box will always enter the simulation box through the opposite face. This would ensure that the density of water molecule remains constant throughout the simulation. The effect of size and chirality of SWCNTs on the elastic properties is studied by employing armchair and zigzag SWCNTs of varying aspect ratios. The investigation of the elastic properties of a defective SWCNT is carried out by constructing a single vacancy defect along the center of the SWCNT. In order to study the effect of location and density of defect, the vacancy defect is expanded along the axial or circumferential direction as shown in Fig. 4.1.

Fig. 4.1. Morphology of the defect description in the SWCNT employed in our study. A single vacancy defect is constructed at the center and the defect is expanded along the axial (indicated by red arrow) or circumferential (indicated by blue arrow) direction. Only the front part of the SWCNT is shown.

Before we subject the SWCNT to uni-axial loading, the system is first thermally equilibrated in an NVT ensemble to release any residual stresses. The simulations are carried out by maintaining the system temperature at 300 K and the density of water molecules at 0.997 g/cm^3 . The temperature stability of the system is attained by using the Nose-Hoover thermostat [67, 68]. Following equilibration, the SWCNT is subjected to elastic loading by applying a constant displacement (strain rate = 0.001 ps^{-1}) on the atoms at both ends of the SWCNT (Fig. 3.3). The system is allowed to relax after every 1000 time steps such that the atoms attain the favorable minimum energy positions. The velocity and the trajectories of end atoms are calculated and the atoms are subsequently shifted to the new position. The remaining atoms are relaxed in the NVT ensemble and the procedure is repeated until failure occurs. We used a total of 600,000 time steps (including 200,000 time steps for initial equilibration) with each time step equivalent to 1 fs.

4.4. Structure and dynamics of water molecule interactions with carbon nanotube

The structure and dynamics of water molecules around the SWCNT when it is submerged in a simulation box consisting of water molecules is described next. As described in section 4.3, the effect of water interactions on the elastic properties of SWCNT is carried out by submerging a (10,10) SWCNT in a simulation box filled with water of density 0.997 g/cm^3 . The system is then equilibrated at 300 K and the corresponding equilibrated system is shown in Fig. 4.2(a). The radial density function (RDF) of oxygen and hydrogen atoms from the center of the SWCNT is depicted in Fig. 4.2(b). We observe

from this figure that inside the SWCNT, the water molecules tend to form a confined structure as can be seen in the two distinct peaks. It can further be noted from the figure that the RDF drops down to zero for radial distances exceeding above 0.4 nm from center of SWCNT. This characteristic is due to the strong hydrophobic behavior of water molecules with the carbon atoms of SWCNT. This observation is similar to the results obtained by earlier researchers [120, 187]. It can further be noted from Fig. 4.2(b) that at radial distance $r_{CNT} = 0.4$, the RDF for hydrogen atom is about 1.81 and for oxygen atom, the RDF value is about 0.45. This large value of RDF for hydrogen atom means that the hydrogen atoms are slightly closer to the SWCNT surface than the oxygen atoms. This phenomenon as observed in [122, 123] is due to the reason that the hydrogen atoms are slightly hydrophilic when compared to that of the oxygen atoms to the SWCNT surface. Additionally, a third characteristic peak can be observed outside the wall of the SWCNT at around 1 nm which is consistent with the simulated result of Nakamura and Ohno [120]. The smooth hydrophobic wall of the CNT results in the formation of a circular water surface on the exterior of the CNT. To summarize, the above system dynamics study helps us to confirm the accuracy of our simulation model.

(a)

(b)

Fig. 4.2. (a) Snap shot of an equilibrated structure of SWCNT submerged in water where the carbon atoms of CNT are depicted by the blue balls and the water molecules represented by red and white balls, and (b) Plot describing the RDF of the water molecules from the center of the SWCNT.

4.5. Free form and water submerged uncapped single walled carbon nanotubes

4.5.1. Effect of surrounding water molecules

The effect of surrounding water interactions on the elastic properties of a SWCNT without end caps when submerged in water medium is described in this section. This is accomplished by submerging a (10,10) SWCNT in a simulation box filled with water molecules of density 0.997 g/cm^3 . Three lengths of SWCNT are considered here and they are $L = 50 \text{ \AA}$, $75 \text{ \AA}$ and $100 \text{ \AA}$. These lengths correspond to aspect ratios (L/D) of 3.69, 5.53 and 7.37 respectively. The compressive and tensile properties of the free form and water submerged (10,10) SWCNT is shown in Fig. 4.3(a) and (b) respectively. It is worthy to observe that the maximum compressive force of the free form SWCNT decreases with increasing the aspect ratio of the SWCNT. This observation is similar to the results obtained by previous researchers [164, 173] on the compressive characteristics of SWCNT. However, the effect of aspect ratio has almost no influence on the elastic properties of SWCNTs under tension. This observation is also in good agreement with previous studies on the tensile loading properties of SWCNTs as can be seen in refs. [134, 160]. Additionally, it can be observed from Fig. 4.3 that a reduction in the mechanical strength of SWCNTs is observed due to interaction of surrounding water molecules.

(a)

Fig. 4.3. Plot of the mechanical characteristics of free form and water submerged (10,10) SWCNTs under (a) compression and (b) tension at temperature $T = 300$ K.

The negative impact of the influence of water molecules on SWCNT can be described by observing the variation of strain energy with strain during the elastic loading process. The plot of the strain energy of the free form and water submerged SWCNT plotted against strain is illustrated in Fig. 4.4(a). It can be seen from this figure that the strain energy of water submerged SWCNT is higher than the free form SWCNT at smaller strain levels. The interaction of water molecules surrounding the SWCNT increases the strain on the SWCNT surface which causes the SWCNT to buckle faster when compared to that of the freeform SWCNT. Additionally, we can also see from this figure that the presence of water molecules surrounding the SWCNT decreases the threshold strain energy (and hence, the lower compressive force) required to induce plastic collapse in the SWCNT due to the mechanical loading. It is also worthy to note that SWCNTs under tension could exhibit both brittle and plastic behavior [188] and the presence of water molecules may play a hidden role in deciding brittle over plastic mechanisms of SWCNT. Hence, the interaction of surrounding water molecules decreases the mechanical strength of SWCNTs when it is submerged in water.

The energy of interaction between the water molecules and the (10,10) SWCNT (defined by Eqn. (2.17)) of aspect ratio 7.37 is depicted in Fig. 4.4(b). It can be noted from this figure that the interaction energy of water molecules rises until the point of compression of the SWCNT. The application of compressive loading in the SWCNT increases the energy of carbon atoms under compression. The hydrophobic nature of SWCNT results in increasing the interaction energy of water molecules, which require greater energy to repel the carbon atoms with higher energy due to the compressive loading. This increase in the interaction energy until the point of compression attributes to the increased rate of

strain energy of the water submerged SWCNTs resulting in its weaker compressive properties. Hence, we can conclude from this section that the compressive characteristics of SWCNT will be weakened due to the presence and interaction of the surrounding water molecules.

(a)

(b)

Fig. 4.4. Plot of the (a) strain energy of the free form and water submerged (10,10) SWCNT with aspect ratio $(L/D) = 7.37$ and (b) interaction energy between the water molecules and carbon atoms of (10,10) SWCNT with aspect ratio $(L/D) = 7.37$.

The morphological characteristics of a (10,10) SWCNT of length $L = 100 \text{ \AA}$, submerged in water under tensile loading is shown in Fig. 4.5. From this figure, we find that during equilibrium when no load is applied, the SWCNT is able to maintain its stable structure. Subsequent application of tensile load causes the SWCNT to stretch resulting in bond breaking and fragmentation, which mark the tensile failure of the SWCNT.

(a)

(b)

Fig. 4.5. Morphological characteristics of the water submerged (10, 10) SWCNT submerged in under uni-axial tensile loading at strain (a) $\varepsilon = 0.00$ and (b) $\varepsilon = 0.21$. Carbon atoms are represented by the black balls, while water molecules are represented by the red and grey balls.

4.5.2. Effect of size and chirality of single walled carbon nanotube

In this section, we will focus on the influence of size and chirality on the compressive characteristics of water submerged SWCNT. The effect of chirality is analyzed by investigating the compressive characteristics of armchair and zigzag SWCNT. The effect of size is analyzed by varying the aspect ratios of the considered SWCNTs. The SWCNTs employed in this study and their respective geometries is given in Table 4.1. The SWCNTs are then submerged in a simulation box filled with water molecules of density 0.997 g/cm^3 and then subjected to elastic loading.

Table 4.1. Geometry of SWCNTs considered in this study.

Chirality	Type of SWCNT	Diameter D of SWCNT (nm)	Length L of SWCNT (nm)	Aspect ratio (L/D)
Armchair	(5,5)	0.678	25.0	3.69
			37.5	5.53
			50.0	7.37
	(10,10)	1.356	50.0	3.69
			75.0	5.53
			100.0	7.37
Zigzag	(10,0)	0.693	25.6	3.69
			38.3	5.53
			51.2	7.37
	(18,0)	1.387	51.2	3.69
			76.7	5.53
			102.2	7.37

The variation in the compressive characteristics of the armchair and zigzag water submerged SWCNTs is shown in Fig. 4.6. It can be seen that the zigzag water submerged SWCNTs possess higher compressive strength when compared to that of its armchair counterpart. This phenomenon as explained in ref. [164] that the vertical bonds (to the direction of compression) in zigzag SWCNT offer higher resistance to compression than the horizontal bonds (to the direction of compression) in the armchair SWCNT.

Fig. 4.6. Plot of the variation of maximum compressive force of the armchair and zigzag water submerged SWCNTs with aspect ratio (L/D) of the SWCNTs.

It can be seen from Fig. 4.6 that at aspect ratio $(L/D) = 7.37$, small SWCNTs, such as (5,5) and (10,0) SWCNT show huge drop in the maximum compressive force when compared to that of the bigger (10,10) and (18,0) SWCNTs respectively. The small radius of (5,5) and (10,0) SWCNTs (refer Table 4.1) are approximately similar to that of the nominal thickness of SWCNT (assumed to be $3.4 \text{ \AA}$ [134]). Hence, this would mean that these small SWCNTs are more solid-like compared to that of the SWCNTs with bigger radius which will be substantially more hollow. At large aspect ratios, compression of a solid tube will begin to show a slender rod-like bending behavior that will reduce its ability to undertake pure axial compressive loads.

The decrease in the maximum compressive force of small SWCNTs of large aspect ratios can further be confirmed by analyzing the post buckling shapes of the armchair and zigzag water submerged SWCNTs of aspect ratio 7.37 as depicted in Fig. 4.7. In this figure, only the carbon atoms of the SWCNT is shown and the water molecules surrounding the SWCNT have been omitted for clarity. We see from this figure that the (5,5) and (10,0) SWCNTs begin to bend sideways when compared to that of (10,10) and (18,0) SWCNT which show pattern of pure axial compression.

(a)

(b)

(c)

(d)

Fig. 4.7. Post buckling shapes of the water submerged (a) (5,5), (b) (10,10), (c) (10,0), and (d) (18,0) SWCNTs at strain $\varepsilon = 0.031$. The SWCNTs with small diameters, namely (5,5) and (10,0) shows lateral bending compared to (10,10) and (18,0) SWCNT which is marked by formation of kinks and fins. The water molecules are not shown in this figure for clarity.

The tensile loading characteristics of water submerged armchair and zigzag SWCNTs is shown in Fig. 4.8. We note from this figure that the armchair SWCNT can withstand high tensile force compared to zigzag SWCNT. As can be seen in Fig. 4.9, the zigzag arrangement of carbon atoms in the armchair SWCNT (in the direction of tensile loading) enables it to expand and offers greater flexibility to deform under tension. Hence, the armchair SWCNT performs better than the zigzag SWCNT under tension. Furthermore, for the case of tensile loading, the maximum tensile load of water submerged SWCNT will decrease proportionately due to the decrease in the diameter of the SWCNT (Fig. 4.8). This is due to the reason that reducing the diameter of SWCNT decreases its cross-sectional area which will ultimately reduce the maximum tensile load of the SWCNT. This observation is consistent with the findings of Liew et al. [189], who predicted a linear relationship between the tensile load and the diameter of a freeform SWCNT. Similar to the observations in a free form SWCNTs [134, 189], for a given chirality, the maximum tensile force of the water submerged SWCNTs is also relatively insensitive to the aspect ratio of the SWCNT.

The Young's modulus of the free form and water submerged SWCNTs of aspect ratio 7.37 is computed using Eqn. (3.1) and is presented in Table 4.2. It can be observed that the interaction of the surrounding water molecules decreases the Young's modulus of SWCNTs. Additionally, the computed Young's modulus values of the free form SWCNTs obtained from our MD simulation are in good agreement with experimental results reported in refs. [19, 127] and with the simulation results described in refs. [159, 160].

Fig. 4.8. Tensile loading characteristics of water submerged armchair and zigzag SWCNTs.

Fig. 4.9. Morphological characteristics of a (10,10) armchair SWCNT under tension. It can be seen that the zigzag bonds parallel to the axis of the CNT offers greater flexibility and elongation under tension. The dashed line indicate the axis of the SWCNT.

Table 4.2. Young's modulus of free form and water submerged SWCNTs.

Geometry	Free form SWCNT (TPa)	Water submerged SWCNT (TPa)	Percentage variation (%)
(5,5)	1.10	1.00	9.1
(10,10)	1.07	1.01	5.6
(10,0)	0.93	0.86	7.5
(18,0)	0.98	0.92	6.1

4.5.3. Effect of location and number of defects on single walled carbon nanotubes

The effect of location and number of defects on elastic properties of water submerged SWCNT is studied by considering (5,5) and (10,10) SWCNTs of aspect ratio $L/D = 7.37$. The defects are located and constructed in the water submerged SWCNTs as described in section 4.3. The elastic properties of the water submerged SWCNTs with different defect densities under compressive and tensile loading is shown in Fig. 4.10(a) and (b) respectively. The presence of defects strongly impact the elastic properties of water submerged SWCNTs which is consistent with the observations on free form SWCNTs [162, 164]. We can see from Fig. 4.10(a) and (b) that the mechanical properties of SWCNTs decrease rapidly with the increase in the number of defects either along the axial or circumferential direction. Furthermore, the reduction in the maximum compressive force of a (5,5) SWCNT with 3 defects along axial direction is about 37%. This drop in compressive loading is more significant than that of a (10,10) SWCNT with same defect configuration which suffers a drop of about 31%. Similarly for the case of SWCNT under tensile loading, the drop in maximum tensile force of a (5,5) SWCNT with 6 vacancy defects along the axial direction is about 9% which is more significant

compared to the 1% drop in a (10,10) SWCNT. This is due to the reason that the (5,5) SWCNT has a smaller diameter and the defect region occupies a much larger portion when compared to that of the (10,10) SWCNT with a bigger diameter.

The effect of defect location on the elastic properties of water submerged SWCNT is also investigated. This is done by constructing a single vacancy defect on the SWCNT and expanding it along the circumferential direction as described in section 4.3. From Fig. 4.10(a) and (b), we can see that increasing the defects along the circumferential direction of the two SWCNTs shows significant reduction in the elastic properties of the SWCNT. From Fig. 4.10(a), the drop in the maximum compressive load of the (10,10) SWCNT with 3 vacancy defects along the circumferential direction is about 51%. This reduction is significant compared to that of the (10,10) SWCNT with same number of defects in the axial direction. This observation also holds true for the case of SWCNT under tensile loading (Fig. 4.10(b)). The drop in the maximum tensile load of the (10,10) SWCNT with 6 vacancy defects along the circumferential direction is about 6% which is significant compared to that of the (10,10) SWCNT with same number of defects in the axial direction.

(a)

Fig. 4.10. Variation of (a) maximum compressive force and (b) maximum tensile force for water submerged SWCNTs of aspect ratio $(L/D) = 7.37$ with increasing the vacancy defect concentration along the axial and circumferential direction.

It is important to note that the influence of circumferential defects on the mechanical strength of water submerged SWCNTs are more sensitive to the diameter of the SWCNT. Fig. 4.10(a) indicates that placing 3 vacancy defects in the circumferential direction of a (5,5) SWCNT submerged in water will reduce its compressive loading by about 70%. We also note from Fig. 4.10(b) that placing 6 vacancy defects along the circumferential

direction of the (5,5) SWCNT reduces the maximum tensile load by about half. This phenomenon is however understandable since the placement of defects along the circumferential direction of the SWCNT is similar to breaking the SWCNT into two halves [35, 121]. Expansion of defects along the circumferential direction of SWCNT result in a smaller number of bonds holding the two halves together which will yield a greater drop in the elastic properties of the SWCNT under compression. Hence, adequate care must be taken to ensure that the circumferential defects in the SWCNT should be kept to a minimum while designing SWCNT based nano-biological and nano-fluidic devices.

4.6. Free form and water submerged capped single walled carbon nanotubes

4.6.1. Effect of density of encapsulated water molecules

This section focuses on the elastic properties of the free form capped SWCNT encapsulated with varying densities of water molecules. Theoretical studies on NEMS based nano-fluidic devices and nano-level drug delivery devices have focused on designing a CNT encapsulated with bio-molecules or water as can be seen in ref [190, 191]. Hence, determining the elastic properties of capped SWCNT with encapsulated water molecules are of utmost importance in the field of nano-drug delivery devices. For SWCNTs which operate in hydrodynamic environment, the SWCNT based nano-fluidic devices will also be subjected to compressive and tensile forces due to surrounding fluid flow.

In order to test the elastic properties of an SWCNT encapsulated with water molecules, we employed a capped (10,10) SWCNT of aspect ratio $(L/D) = 7.37$. This capped SWCNT is filled with water molecules of density 0.49 g/cm^3 and 0.98 g/cm^3 which we define as the ‘half-filled’ and ‘fully-filled’ states of the capped SWCNT respectively. For the purpose of comparison, we also tested the mechanical properties of a capped SWCNT without encapsulated water molecule defined as an empty SWCNT.

The capped SWCNTs with varying quantities of encapsulated water molecule is at first subjected to thermal equilibration followed by compressive or tensile loading as described in section 4.3. The elastic loading characteristics of the free form capped SWCNTs with varying densities of encapsulated water molecules is shown in Fig. 4.11(a) and (b). We note from this figure that for the case of capped SWCNT under compressive loading (Fig. 4.11(a)), the compressive load increases almost linearly with compressive strain until it reaches a point of maximum compressive load. After this point, the compressive load shows a drastic decrease which is caused by the release of strain energy. This phenomenon is almost similar to the compressive loading in a freeform SWCNT (please see Fig. 4.4(a)). For the case of capped SWCNT loaded in tension, the tensile load increases almost linearly with tensile strain for smaller values of strain ($\epsilon < 0.15$). At larger strain values, the tensile force doesn't show any appreciable increase which marks the plastic deformation of the SWCNT.

It can be inferred from Fig. 4.11(a) and (b) that the density of encapsulated water molecules has a significant effect on the compressive and tensile loading response of the SWCNT. Additionally, it can be noted from this figure that an increase in the density of water encapsulation will reduce the mechanical properties of the free form capped

SWCNTs. The maximum compressive force of a fully-filled SWCNT is about 20% lower than that of an empty SWCNT. Similarly, for the case of SWCNT under tension, the maximum tensile force of a fully filled SWCNT is about 7% lower than that of an empty SWCNT.

(a)

(b)

Fig. 4.11. Force-strain plot of a capped (10,10) SWCNT of aspect ratio $(L/D) = 7.37$ with varying water concentrations encapsulated inside the SWCNT under (a) compression and (b) tension.

The effect of encapsulated water molecules on the mechanical properties of capped SWCNT can be explained by observing the variation of strain energy of the capped SWCNT under mechanical loading. A plot of the variation of strain energy against strain of capped SWCNTs with varying densities of encapsulated water molecules under tension is shown in Fig. 4.12. From this plot, it can be observed that for smaller values of strain, the half-filled and fully-filled SWCNTs exhibit higher values of strain energy when compared to that of the

empty SWCNT. This is caused by the forces of encapsulated water molecules acting on the walls of the SWCNT. This increase in the rate of strain energy increases the system instability of the SWCNT with encapsulated water which decreases the elastic properties of capped SWCNTs under compression or tension. Additionally, it should further be noted from Eq. (2.17) that the interaction energy between the water molecules and the carbon atoms of SWCNT is directly related to the number of water molecules. Hence, the variation in the concentration of water molecule will further affect the strain energy threshold at which the SWCNT will fail.

Fig. 4.12. Strain energy plot of a capped (10,10) SWCNT of aspect ratio $(L/D) = 7.37$ under tensile loading with varying water concentrations filled inside the SWCNT.

The phenomenon of the weak compressive resistance of SWCNTs with increasing water encapsulation can be further explained by analyzing the snap shot of post buckling shapes of the capped SWCNTs (Fig. 4.13). From the figure, we observe that the empty and half-filled SWCNT compresses axially with response to the axial compression marked by the formation of kinks and fins. However, we note that the fully-filled SWCNT bends laterally in response to compression. The axial compression of end caps of SWCNT compresses the water molecules further towards the center of the SWCNT. Since it is impossible to compress the water molecules further, therefore the water molecules have nowhere to escape, but to force the CNT to bend. Based on section 4.5.2, though a large diameter SWCNT can withstand large axial compression, dense filling of such a SWCNT can substantially change the buckling characteristics.

(a)

(b)

(c)

Fig. 4.13. Snap shot of the buckling shapes at strain $\varepsilon = 0.03$ exhibited by capped SWCNTs encapsulated with water molecules of varying densities. It can be observed that an (a) empty SWCNT and (b) half-filled SWCNT show axial compressive mode. However (c) fully-filled SWCNT bends laterally in response to compression.

The morphological characteristics of the fully filled capped SWCNT under tension are shown in Fig. 4.14. From this figure, we observe that when no force is applied on the capped SWCNT, the capped SWCNT maintains a stable structure that completely prevents the flow of water molecules from the interior of the SWCNT. Subsequent application of force results in fracture and fragmentation of the SWCNT that leads to the release of water molecules from the capped SWCNT.

Fig. 4.14. The morphological changes of a fully filled capped (10,10) SWCNT with water at strain (a) $\varepsilon = 0.00$, where the end caps and the walls of SWCNT completely confine the water molecules inside SWCNT after equilibration, and (b) $\varepsilon = 0.23$. Further application of tensile forces result in the release of water molecule from the SWCNT (c).

4.6.2. Effect of interaction of surrounding water molecules

It is also useful to investigate the mechanical properties of water-encapsulated capped SWCNTs submerged in water. The capped SWCNTs with varying water encapsulated densities (empty, half-filled and fully-filled) are submerged in a simulation box filled with water molecules of density 0.997 g/cm^3 to determine its elastic properties under mechanical loading. The variation in the mechanical characteristics of the water submerged capped SWCNTs are compared with that of the free form SWCNTs as shown in Fig. 4.15. The reduction in the mechanical properties of the water submerged capped SWCNTs due to water encapsulation follows the same trend as observed in an uncapped SWCNT as can be observed in Fig. 4.3. Fig. 4.15 also indicates that the effect of surrounding water molecules reduces the mechanical properties of water encapsulated SWCNTs. Based on the foregoing discussion, presence of surrounding water molecules increases the strain of the capped SWCNT thereby accelerating its failure to mechanical forces. Additionally, it can be observed from the plot that a water submerged fully-filled SWCNT shows a huge drop in the elastic properties compared to that of an empty or half-filled SWCNT. This suggests that dense filling of water molecules in capped SWCNT will continue to affect the mechanical properties of the SWCNT submerged in water. Nevertheless, the capped SWCNTs containing water molecules exhibit high resistance to mechanical forces which can be observed from the values of maximum compressive and tensile forces.

(a)

Fig. 4.15. Force-strain plot of the (a) compressive and (b) tensile loading conditions of the capped (10,10) SWCNTs filled with varying water concentrations submerged in water at temperature $T = 300$ K.

Fig. 4.16 shows the structural characteristics during tensile loading of the water-filled capped (10,10) SWCNT in water. For better visualization of the movement of water from the interior of the SWCNT to the exterior, only the cross-sectional view across the region where the tensile failure of the SWCNT occurs is shown. We see from this figure that after equilibration, the wall of the SWCNT clearly prevents the flow of water

molecule from inside the SWCNT. However, application of tensile forces on the capped SWCNT causes the failure of SWCNT which results in breaking and fragmentation of the walls of SWCNT. Hence, the fracture of SWCNT walls result in the release of water molecules from the interior of SWCNT to the outside water medium. This process that releases the enclosed water molecules to the surrounding water is of primary interest in the field of design of bio-nano devices. Additionally, we note that the release of water molecule in a capped SWCNT can be effected upon by a simple application of tensile forces on the ends of the capped SWCNT.

(a)

(b)

Fig. 4.16. The morphological changes of a water-filled capped SWCNT at temperature $T = 300$ K shown across the cross-sectional area of the SWCNT at strain (i) $\varepsilon = 0.00$, and (ii) $\varepsilon = 0.19$. Breaking of the capped SWCNT under tensile loading causes the release and subsequent mixing of water molecules from the inside of the SWCNT to the water molecules in the exterior of the SWCNT surface.

4.7. Summary

In this chapter, the mechanical characteristics of water submerged SWCNT under compressive and tensile loading has been studied using MD simulation method. The understanding of elastic properties of SWCNT in hydrodynamics environment such as water is of significant importance in the field of nano-fluidics and nano-biotechnology. The studies show that the elastic properties of SWCNTs under compression and tension are generally reduced due to the presence of surrounding water interaction. It is also found that the elastic properties of uncapped SWCNT that is submerged in water are more sensitive to the diameter than the length of the SWCNT. Furthermore, the effect of chirality and the vacancy defects significantly affect the elastic properties of the water submerged SWCNT.

CHAPTER 5

TORSIONAL AND SHEAR ELASTIC PROPERTIES OF CARBON NANOTUBE WITH WATER INTERACTIONS

The torsional and shear characteristics of SWCNT with water interactions are studied in this chapter using MD simulation method. The elastic properties of CNTs in hydrodynamic environment such as water under torsion and shear loading conditions are critical for its key role in determining the lifetime and stability of CNT based nano-fluidic devices. The effect of chirality, defects and the density of water encapsulation is studied by subjecting the SWCNT to torsional loading. The findings show that the interaction of water molecules and defect density and distribution will reduce the mechanical strength of the SWCNT. Additionally, for the case of water molecules encapsulated inside the SWCNT, the elastic response depends on the density of packing of water molecules. This chapter also includes studies to determine the effect of chirality and density of encapsulated water molecules in capped SWCNT on the shear loading properties of SWCNT. The elastic characteristics of SWCNTs under torsion and shear with various forms of water interaction have been comprehensively studied using the MD simulations and the discussions are presented in this chapter.

5.1. Introduction and literature review

Research in CNTs has gained enormous interest in nanotechnology and materials science due to its remarkable physical and mechanical properties [180]. CNTs possess a unique combination of high strength and ultra-light weight that makes it promising for applications in nanoelectromechanical systems (NEMS) such as springs [192], and oscillators [193]. These applications require a critical understanding of the torsional properties of CNTs. In addition, CNTs have also demonstrated the potential to be used in the field of nano-fluidics [184, 194] and NEMS devices [180]. Hence, understanding the torsional and shear elastic properties of CNTs in hydrodynamic environment is important to optimize the performance of CNTs for its use in NEMS and nano-level biological devices.

Many studies have been aimed to investigate the torsional elastic properties of CNTs by means of experimental or theoretical based approaches [195-197]. Lu and Zhang [198] proposed a hybrid nanoscale continuum theory to investigate the effect of SWCNT geometry on the torsional properties of SWCNT. They found that the torsional modulus increases with diameter of the SWCNT. Wang et al [196] deployed MD simulation technique to determine the mechanical properties of CNTs under torsion. They found that the shear modulus of CNT increases with increasing the radius of CNT. Zhang et al [197] studied the effect of various types of defects and temperature on the torsional responses of defective SWCNT. The studies showed that the torsional strength is strongly dependent on the chirality, type of defects, and temperature. Hall et al [195] deployed *in situ* SEM to experimentally characterize the torsional properties of SWCNT. They obtained the value of shear modulus of SWCNT to be about 0.41 ± 0.36 TPa. Jeong et al

[199] studied the torsional responses of DWCNTs, fullerenes and gases. Their investigations revealed that the torsional responses of SWCNTs will be distinct which depends on the density and nature of the filling material. In addition, Wang et al studied the torsional characteristics of CNTs filled with copper [200]. It was found that inclusion of deformable elements such as copper in SWCNTs increases the torsional rigidity of SWCNTs.

It can be seen from the above mentioned literature studies that the torsional properties of the CNTs have been well studied and investigated in free form and those filled with gases and metal atoms. However, it should be noted that the torsional and shear strength of CNTs in hydrodynamic environment remains to be investigated. Hence, the main objective in this chapter is to investigate the torsional and shear characteristics of free form and water submerged SWCNT. The torsional and shear properties of SWCNTs under various forms of water interaction have been comprehensively studied and the results are presented in this chapter.

5.2. Simulation details

The description of various pair potentials used in the MD simulation of SWCNT and water molecule is described in detail in Chapter 2. The work described in this chapter is divided into two parts. The first part of the chapter focuses on the torsional elastic characteristics of SWCNTs interacting with water. The shear elastic properties of SWCNTs with water interactions are discussed in the second part. Fig. 5.1 illustrates the method of torsional and shear loading condition applied in SWCNT considered in our study. To investigate the effect of geometry on the elastic properties of SWCNT, we

considered armchair and zigzag SWCNTs of varying aspect ratios. Furthermore, the effects of defect density and distribution on the torsional properties were also investigated in this chapter. In order to accomplish this, we first constructed a single vacancy defect approximately at the center of the SWCNT. This vacancy defect is then expanded in the radial or axial direction to form a bigger defect (please see Fig. 4.1). This method of defect reconstruction facilitates to study the role of defect distribution on the torsional properties of SWCNT [35, 201].

Fig. 5.1. The procedure of (a) torsional and (b) shear loading of the SWCNT in our study. For torsion loading, the end atoms enclosed within the red rectangle are fixed rigidly and atoms enclosed inside the black rectangle is subjected to anti-clockwise rotational displacement (strain rate = 0.001 ps^{-1}) to effect torsion. For shear loading, the atoms at the top and bottom end of SWCNT are subjected to constant outward displacement (strain rate = 0.001 ps^{-1}).

At the beginning of the simulation, we equilibrate the system to release the residual stresses by achieving thermal equilibrium in an NVT ensemble. The simulations are carried out by maintaining a constant system temperature of 300 K and the density of water molecules at 0.997 g/cm^3 . The temperature stability of the system is achieved by employing Nose-Hoover thermostat [67, 68]. Following this, the elastic loading is applied on the SWCNT as defined in Fig. 5.1. After every 1000 time steps, the system is allowed to relax such that the atoms attain the favorable minimum energy positions. The end atoms are subsequently shifted to a new position after calculation of the inward velocity and the trajectories of atoms based on Verlet algorithm [124]. The remaining atoms are relaxed in an NVT ensemble and the procedure is repeated until failure occurs. A 1 fs time step was used in all MD simulations described in this chapter.

5.3. Validation of the simulation model

The elastic properties of a free form SWCNT under torsional loading is discussed in this section. In order to validate the computational model employed in the current study, we subjected the same SWCNT model (a (10,10) SWCNT of length 100 Å) as used in ref. [199] simulated using the AIREBO potential function under NVT ensemble as described in Chapter 2. The torsional elastic response of the (10,10) SWCNT is depicted in Fig. 5.2. It can be seen from this figure that the strain energy per atom, which is determined as the difference in total energy of the strained and unstrained SWCNT, against strain, during the torsion process increases non-linearly with strain until when the torsional strain value is about 0.07. Additionally, the torque (measured as the product of torsional force and the radius of the SWCNT) increases linearly with strain until it reaches the same torsional

strain $\gamma_{torsion} \approx 0.07$. After this point, we note that the nature of the curve deviates markedly from its linear behavior. This change in curve is due to the elastic to plastic transition of the SWCNT under torsion, which is in good agreement with results reported in earlier research [197]. It can be seen from this figure that the SWCNT can withstand a maximum torque of 14.698 nN nm at torsional strain of $\gamma_{torsion} = 0.078$. This values are in good agreement with previous MD simulation results of Jeong et al [199], who obtained a maximum torque of 13.75 nN nm at torsional strain of $\gamma_{torsion} = 0.081$ by using REBO potential.

Fig. 5.2. Torque-strain and strain energy plot of the (10,10) SWCNT of length 100 Å at 300 K.

5.4. Elastic properties of single walled carbon nanotubes under torsion

5.4.1. Effect of surrounding water molecules

This section focuses on the effect of surrounding water molecules on the torsional properties of SWCNT. This is accomplished by submerging a (10,10) SWCNT in a simulation box filled with water molecules of density 0.997 g/cm^3 . Three lengths of the SWCNT are considered here, viz. $L = 50 \text{ \AA}$, $75 \text{ \AA}$ and $100 \text{ \AA}$. These lengths correspond to aspect ratios (L/D) of 3.69, 5.53 and 7.37 respectively. Fig. 5.3 shows the torsional characteristics of the free form and water submerged (10,10) SWCNT. It can be noted from this figure that the maximum torque decreases while the torsional angle increases with the aspect ratio of the SWCNT, which is similar to results reported previously [199, 200]. This is because SWCNTs with small aspect ratio are stocky which would require larger torque, while SWCNTs with large aspect ratio are slender that can be twisted easily to large angles. Furthermore, this dependence is in agreement with the continuum elastic definition of torque F_{TORS} given by [199],

$$F_{TORS} = \frac{K_{cyl} \theta_{cyl}}{L_{cyl}} \quad (5.1)$$

where K_{cyl} is the torsional stiffness of continuum tube, θ_{cyl} and L_{cyl} are the torsional angle and length of the tube respectively.

Fig. 5.3. Plot of the variation in the torsional response for free form and water submerged (10,10) SWCNTs of different aspect ratios.

It can be seen from Fig. 5.3 that the effect of interacting water molecules decreases the torsional performance of the SWCNT. This can be explained as follows. The plot of the strain energy of the free form and water submerged SWCNT plotted against strain is illustrated in Fig. 5.4. It is observed from this figure that the strain energy of water submerged SWCNT is higher than the free form SWCNT at smaller strain levels. The interaction of water molecules surrounding the SWCNT increases the strain on the SWCNT surface which reduces the torsional performance of the SWCNT. Additionally,

we can also see from this figure that the presence of water molecules surrounding the SWCNT decreases the threshold strain energy required to induce elastic to plastic transition in the SWCNT due to torsional twisting. This observation is similar to the elastic properties of water submerged SWCNT under tension and compression as described in section 4.5.1.

Fig. 5.4. Plot of the strain energy of the free form and water submerged (10,10) SWCNT of aspect ratio $(L/D) = 7.37$.

It is also worthwhile to note from Fig. 5.4 that at the onset of plastic deformation, there is a sharp change in the non-linear behavior of the strain energy curve with torsional strain. Thereafter, the strain energy increases slowly with increasing torsional angle in the plastic stage. This gradual change of the strain energy after plastic transition is different to the drastic drop in strain energy for the case of SWCNTs under tensile or compressive loading (please see section 4.5.1). This phenomenon as explained in ref.[197] is due to the reason that the elastic to plastic transition in SWCNT under torsion results in small structural changes compared to that of the tensile or compressive loading. This is further confirmed by analyzing the snap shots of the torsional deformation of water submerged SWCNT as shown in Fig. 5.5. In this figure, only the carbon atoms comprising the SWCNT are shown and the water molecules surrounding the SWCNT have been omitted for clarity. It can be seen from this figure that the SWCNT maintains its stable structure when no torsional twisting is applied at the end atoms of the SWCNT. When the end atoms of the SWCNT are subjected to torsion of 30° , the resulting structure shows small changes compared to that of the initial SWCNT before torsion. At higher torsional angles, twisting of SWCNT takes place which results in screw twisted configurations of the SWCNT.

Fig. 5.5. Snapshots of the torsional deformation of a water submerged (10,10) SWCNT with aspect ratio, $(L/D) = 7.37$ at torsional angle (a) 0° , (b) 30° , (c) 60° , and (d) 90° . The water molecules are not shown in this figure for clarity.

5.4.2. Effect of geometry of single walled carbon nanotube

In this section we investigate the effect of SWCNT geometry on the torsional properties of SWCNT submerged in water. The effect of chirality is analyzed by investigating the torsional characteristics of armchair and zigzag SWCNT. The effect of size is analyzed by varying the aspect ratio of the considered SWCNTs. The SWCNTs employed in this study and their respective diameters are given in Table 4.1. The SWCNTs are then submerged in a simulation box filled with water molecules of density 0.997 g/cm^3 and subjected to torsion. The variation in the torsional characteristics of the armchair and zigzag water submerged SWCNTs is shown in Fig. 5.6. We note from this figure that SWCNTs with small diameter, namely (5,5) and (10,0) SWCNTs withstand smaller torque compared to that of SWCNTs with bigger diameters, namely (10,10) and (18,0) SWCNTs. This is because small diameter SWCNTs has smaller cross-sectional area which ultimately reduces the maximum torque of the SWCNT. Fig. 5.6 also shows that the zigzag water submerged SWCNTs can withstand slightly higher torque compared to that of its armchair counterpart. This observation is in quantitative agreement with the study on torsional properties of free form SWCNTs reported by Zhang et al [197]. This is because the application of torsional loading in SWCNTs induces contraction of bonds that are arranged along the radial circumference of the SWCNT. Hence, the horizontal bonds in an armchair SWCNT (which are arranged parallel to the direction of torsional loading) help in resisting the contraction of bonds which ultimately increases the torque to resist the torsional deformation in an armchair SWCNT.

Fig. 5.6. Torsional characteristics of armchair and zigzag SWCNTs submerged in water at temperature $T = 300$ K.

5.4.3. Effect of location and number of defects on single walled carbon nanotube

The effect of location and number of defects on elastic properties of water submerged SWCNT is discussed in this section. For this purpose we considered (5,5) and (10,10) SWCNTs of aspect ratio 7.37 under torsional loading as shown in Fig. 5.1. The mechanical characteristics of the water submerged SWCNTs with different defect density is shown in Fig. 5.7. The presence of defects strongly impact the torsional properties of

water submerged SWCNTs which is consistent with the observations on free form SWCNTs in ref.[197]. Additionally, it can be seen that the dependence of torque on the presence of vacancy defects is more sensitive to the diameter of SWCNT. For instance, the percentage drop in maximum torque for a (5,5) SWCNT due to presence of 3 vacancy defects in axial direction is about 41%. This drop is significantly much larger than that of a (10,10) SWCNT with similar vacancy defects configuration that experiences a drop of about 16%. This is because the (5,5) SWCNT has a smaller diameter and the defect region occupies a much larger portion when compared to that of the (10,10) SWCNT with a bigger diameter.

The effect of defect location on the torsional response of water submerged SWCNTs is also investigated. By varying the defects along the axial or circumferential direction of SWCNT (Fig. 4.1), the dependence of defect distribution on the torsional response can be studied. We note from Fig. 5.7 that the defects placed along the circumferential direction of SWCNT has a significant impact on the torsional response of SWCNT compared to the axial defects. Defects along the circumferential direction are arranged parallel to the loading direction, which will aid in breaking and shear of SWCNTs more easily in contrast to that of the axial defects that are perpendicular to the torsional loading direction.

Fig. 5.7. Torsional properties of (10,10) and (5,5) SWCNTs of aspect ratio (L/D) = 7.37 with increasing the vacancy defect concentration along the axial and circumferential direction.

5.4.4. Analysis of carbon nanotube torsion with continuum mechanics theory

The torsional stiffness K_{SWCNT} of the SWCNTs in our study is computed in MD simulation method by obtaining the variation of strain energy E_{SWCNT} with the torsional angle θ_{SWCNT} . The torsional stiffness is then calculated by [163, 199]

$$K_{SWCNT} = L \frac{d^2 E_{SWCNT}}{d\theta_{SWCNT}^2} \quad (5.1)$$

where L is the length of the SWCNT.

The torsional stiffness of the free form and water submerged (10,10) and (5,5) SWCNTs of aspect ratio 7.37 is computed using Eq. (5.1). The results are then plotted against the respective radius of the (10,10) and (5,5) SWCNTs and is presented in Fig. 5.8. It can be noted from this figure that the torsional stiffness varies marginally due to the presence of surrounding water molecules. This observation is consistent with the results reported in earlier studies [200, 202] for the case of SWCNTs interacting with various gases and metals. For the case of freeform SWCNTs, the torsional stiffness of (10,10) SWCNT has increased by 670% compared to that of (5,5) SWCNT. Similar percentage variations can also be observed for the case of (10,10) and (5,5) SWCNTs that are submerged in water.

The torsional stiffness K_{SWCNT} is heavily dependent on the radius R of the SWCNT. It shows a relation of $K_{FF} \sim R^{2.95}$ and $K_{WS} \sim R^{3.07}$ where the subscripts 'FF' and 'WS' refers to 'free form' and 'water submerged' states of SWCNTs respectively (Fig. 5.8). It is worthy to note that the variation is consistent with the prediction of linear elasticity in continuum mechanics theory. In continuum mechanics theory, the strain energy of a thin walled cylinder is defined as [163, 199]

$$E = \frac{1}{2} G_{torsion} \int_{V_{cyl}} \gamma_{torsion}^2 dV_{cyl} = G_{torsion} \pi h_{cyl} R_{cyl}^3 \frac{\theta^2}{L_{cyl}} \quad (5.2)$$

where $G_{torsion}$ is the torsional modulus, $\gamma_{torsion}$ is the torsional strain, V_{cyl} is the volume of the cylinder, θ is the critical torsional angle, L_{cyl} is the length of the cylinder, h_{cyl} and R_{cyl} describes the thickness and radius of the cylinder respectively.

Fig. 5.8. Torsional stiffness of free form (K_{FF}) and water submerged (K_{WS}) SWCNTs.

The torsional stiffness of the thin walled cylinder K_{cyl} is then computed from Eq. (5.1) and Eq. (5.2) and is expressed as

$$K_{cyl} = L_{cyl} \frac{d^2 E}{d\theta^2} = 2G_{torsion} \pi h_{cyl} R_{cyl}^3. \quad (5.3)$$

From Eq. (5.3) we can see that the torsional stiffness of the thin walled cylinder varies as $K_{cyl} \sim R_{cyl}^3$, which is in good agreement with the relation ($K_{FF} \sim R^{2.95}$ and $K_{WS} \sim R^{3.07}$) obtained for SWCNTs using the MD simulation approach.

The torsional modulus G_{SWCNT} of SWCNT can be obtained from the quadratic plot of variation of strain energy E_{SWCNT} with torsional strain $\gamma_{torsion}$ using polynomial curve fitting, which is defined as [163, 203]

$$G_{SWCNT} = \frac{1}{2\pi RLh_t} \frac{\partial^2 E_{SWCNT}}{\partial \gamma_{torsion}^2} \quad (5.4)$$

where R is the radius of the SWCNT, h_t is the thickness of SWCNT and is assumed to be 3.4 Å [134].

The computed torsional modulus of various free form and water submerged SWCNTs of aspect ratio 7.37 is depicted in Table 5.1. It can be observed that the interaction due to surrounding water molecules decreases the torsional modulus of SWCNTs. It is important to note that the trend of torsional modulus variation for free form SWCNTs agrees well with the earlier results obtained MD simulation studies [196, 197, 199]. However, the computed torsional modulus is lower than that predicted using continuum theory [198] and experiment [195]. The corresponding shear modulus values obtained in these literature studies is given in Table 5.2.

Table 5.1. Torsional modulus of freeform and water submerged SWCNTs.

Geometry	Free form SWCNT (TPa)	Water submerged SWCNT (TPa)	Percentage variation (%)
(10,10)	0.378	0.351	7.1
(5,5)	0.335	0.304	9.2
(18,0)	0.367	0.338	7.9
(10,0)	0.329	0.302	8.2

Table 5.2. A summary of torsional modulus of free form SWCNTs reported in literature.

Authors	Employed technique	Torsional modulus (TPa)
Zhang et al [197]	MD simulation	0.381
Jeong et al [199]	MD simulation	0.338
Wang et al [196]	MD simulation	0.36 ~ 0.48
Lu and Zhang [198]	Nanoscale continuum theory	0.41 ~ 0.54
Hall et al [195]	Experimental method	0.41 ± 0.36
Present work	MD simulation	0.329 ~ 0.378

5.5. Torsional properties of capped single walled carbon nanotube

5.5.1. Free form capped single walled carbon nanotube

The torsional properties of capped SWCNTs encapsulated with water molecules is discussed in this section. For this purpose, we chose a (10,10) capped SWCNT with aspect ratio of 7.37. This capped SWCNT is filled with water molecules of density 0.49 g/cm^3 and 0.98 g/cm^3 which we define as the ‘half-filled’ and ‘fully-filled’ states of the capped SWCNT respectively. For the purpose of comparison, we also tested the mechanical properties of a capped SWCNT without encapsulated water molecule defined as an empty SWCNT.

Fig. 5.9. Torsional response of a capped (10,10) SWCNT with aspect ratio $(L/D) = 7.37$ with varying water concentrations encapsulated inside the SWCNT.

The torsional properties free form capped SWCNTs encapsulated with varying concentrations of water molecules are shown in Fig. 5.9. We note from this figure that the torsional characteristics of water submerged SWCNTs depend strongly on the density of encapsulated water molecules in the SWCNT. To understand why, we examine the interaction force exerted by water molecules on the capped SWCNT for the case of half-filled and fully-filled SWCNTs which is depicted in Fig. 5.10. It can be seen from this plot that for the case of fully filled SWCNT, the interaction force marginally increases with application of torsional strain. It should be noted that torsional loading in SWCNT

results in radial contraction of the SWCNT. Furthermore, the dense packing of water molecules in a fully-filled SWCNT decreases the mobility of water molecules inside the SWCNT. This results in an increase in hydrophobic repulsive force exerted by water molecules on the fully filled capped SWCNT. However, the interaction force exerted by water molecules on half-filled SWCNT is much smaller compared to that of the fully-filled SWCNT. This could be due to the reason that the water molecules have much greater mobility in a half-filled SWCNT compared to that of a fully filled SWCNT. Hence, the application of torsional loading in a half-filled SWCNT does not result in any appreciable increase in the hydrophobic repulsive force exerted by water molecules on SWCNT.

Fig. 5.10. Interaction force exerted by water molecules on (10,10) SWCNTs encapsulated with water molecules of densities 0.49 g/cm^3 and 0.98 g/cm^3 .

It can be also be observed from Fig. 5.9 that for the case of a fully-filled SWCNT, the torsional response shows a marked difference compared to that of the empty and half-filled SWCNTs. Additionally, the fully-filled SWCNT can withstand more torque compared to that of an empty and half-filled SWCNT prior to torsional buckling. This observation is consistent with the earlier reports of the torsional response of SWCNTs filled with SWCNTs [199], gases [202] and metals [200]. It is worth noting that at the point of buckling, there is a sudden drop in torque of a fully-filled SWCNT in contrast to

that of empty and half-filled SWCNTs. This can be explained by analyzing the snap shot of the torsional deformation of fully-filled SWCNTs as depicted in Fig. 5.11 at torsional angle $\theta_{SWCNT} \approx 22^\circ$. The torsional twisting of SWCNT results in contraction and twisting of tube walls in the radial direction of the SWCNT. This contraction results in compression of water molecules. As it is impossible to compress the water molecules further, therefore the water molecules have nowhere to escape, but to break open the walls of SWCNT which results in sudden drop in the torsional response of the fully-filled SWCNT.

(a)

(b)

(c)

Fig. 5.11. Snap shot of the twisted shapes exhibited by capped SWCNTs encapsulated with water molecules of varying densities at torsional angle $\theta_{SWCNT} \approx 22^\circ$. It can be observed that an (a) empty SWCNT and (b) half-filled SWCNT do not fracture when it is subjected to torsion. However a (c) fully-filled SWCNT breaks in response to torsion.

5.5.2. Water submerged capped single walled carbon nanotube

It is also useful to investigate the torsional response of water-encapsulated capped SWCNTs submerged in water. The variation in the torsional response of the water submerged capped SWCNTs are compared with that of the free form SWCNTs as shown in Fig. 5.12, which indicates that the surrounding water molecules reduces the torsional properties of water encapsulated SWCNTs. Based on our discussion in section 5.4.1, presence of surrounding water molecules increases the strain of the capped SWCNT which affects the torsional resistance of capped SWCNT. It can hence be concluded from this study that dense packing of water molecules can result in breaking and fracture of capped SWCNTs. Furthermore, the interaction of water molecules outside the capped SWCNT can affect the overall torsional response of capped SWCNTs irrespective of the filling concentrations.

Fig. 5.12. Torsional properties of the capped (10,10) SWCNTs filled with varying water concentrations submerged in water at temperature $T = 300$ K.

5.6. Elastic properties of single walled carbon nanotubes under shear

5.6.1. Shear elastic properties of uncapped single walled carbon nanotubes

The elastic properties of open ended SWCNTs with different geometries submerged in water medium are described in this section. The shear force characteristics of the free form and water submerged (10,10) SWCNT of length $L = 100$ Å is shown in Fig. 5.13(a). It can be noted from this figure that for small strain values ($\epsilon < 0.02$), the shear force

increases almost linearly. At larger strain values, the shear force begins to show a parabolic transition, which marks the plastic stage of deformation of the SWCNT. Additionally, we also note from this figure that the interaction of surrounding water molecules decreases the shear force characteristics of the SWCNT. The plot of strain energy of free form and water submerged SWCNT subjected to shear deformation is depicted in Fig. 5.13(b). We observe from this figure that the interaction of surrounding water molecules decreases the threshold strain energy at which shear failure occurs in SWCNT. This decrease in strain energy results in a decrease in shear force of the water submerged SWCNT. Hence, the interaction of surrounding water molecules reduces the resistance to shear loading of the SWCNT.

(a)

(b)

Fig. 5.13. Plot of the variation of (a) shear force and (b) strain energy of free form and water submerged (10,10) SWCNTs of length $L = 100 \text{ \AA}$.

The mechanical characteristics of the water submerged armchair ((10,10) and (5,5)) and zigzag ((18,0) and (10,0)) SWCNTs of length $L = 100 \text{ \AA}$ is shown in Fig. 5.14. We note from this figure that regardless of chirality, the maximum shear load decreases with decreasing diameter of the SWCNT. This is due to the reason that reducing the diameter of SWCNT decreases its cross-sectional area which ultimately reduces the maximum shear load of the SWCNT. It can also be noted from this figure that the armchair SWCNTs possess superior resistance to axial shear when compared to that of zigzag SWCNTs.

Fig. 5.14. Plot of shear response for water submerged SWCNTs of varying geometries.

The strain energy plot of the armchair and zigzag SWCNTs is shown in Fig. 5.15(a). We note from this plot that the maximum strain energy at failure for the zigzag SWCNTs are much lower than that of armchair SWCNTs. This is due to the reason that the horizontal bonds in a zigzag SWCNT (Fig. 5.15(b)) makes it much easier for the SWCNT to slip and shear when subjected to uni-axial shear loading. Hence, the threshold energy required for a zigzag SWCNT to fail under axial shear loading gets reduced and this subsequently results in the inferior performance of zigzag SWCNT under shear loading.

(a)

Fig. 5.15. Strain energy-strain plot (a) of the SWCNTs submerged in water at temperature $T = 300$ K and (b) arrangement of bonds in a zigzag SWCNT parallel to the shear loading direction results in inferior elastic properties of zigzag SWCNT.

5.6.1. Shear elastic properties of capped single walled carbon nanotubes

This section will focus on the shear elastic properties of the water interactions on the elastic properties of capped SWCNTs. As described in section 5.5.1, we deployed a (10,10) SWCNT of varying water encapsulated densities. The shear loading characteristics of the free form and water submerged capped SWCNTs is shown in Fig. 5.16. It can be seen that the density of encapsulated water molecules in a capped SWCNT will affect the shear elastic properties of SWCNT. For example, an empty capped (10,10) SWCNT can withstand maximum shear force of about 54.7 nN. However if a capped SWCNT is encapsulated with water molecules of density 0.98 g/cm^3 , the maximum shear force is reduced to about 43.9 nN. Fig. 5.16 also indicates that water submerged capped

SWCNTs shows weaker shear resistance compared to that of the free form capped SWCNTs. Based on the previous discussion on torsion, the presence of surrounding water molecules increases the strain of the capped SWCNT thereby accelerating its failure to shear forces.

Fig. 5.16. Force-strain plot of the capped (10,10) SWCNTs filled with varying water concentrations submerged in water.

It is also useful to observe the variation in the interaction energy between the water molecules and the SWCNT during the shear loading process. It is clear from Eq. (2.17) that the dominant interaction between water and the SWCNT should be the van der Waals interaction, which significantly influences the shear deformation characteristics of the SWCNT. The variation in the van der Waal's energy between the water molecules and SWCNT for the case of free form water filled capped SWCNT is shown in Fig. 5.17. We can observe from this figure that the van der Waal's energy in a fully filled SWCNT is higher than the half filled SWCNT. In a fully filled SWCNT, the dense packing of water molecules result in larger van der Waal's energy in a fully filled SWCNT compared to the half filled SWCNT. We also note that during the onset of shear failure, a drop in the energy is observed, which is attributed to the escape and release of water molecules from the capped SWCNT.

Fig. 5.17. Variation in the van der Waal's energy in a free form capped SWCNT with half filled and fully filled water molecules.

5.7. Summary

In this chapter, the torsional characteristics of water submerged SWCNT has been studied using MD simulation method. The studies show that the torsional properties of SWCNTs weaken due to the interaction of surrounding water molecules. The results also indicate that the torsional properties of SWCNTs with defects are more sensitive to the defect distribution and diameter of the SWCNT. Furthermore, for the case of capped SWCNTs, dense filling of water molecules in an SWCNT will result in breaking and fracture of SWCNT under torsion resulting in release of encapsulated water molecules. In addition, the shear elastic response of uncapped and capped SWCNTs submerged in water is also presented in this chapter. It is found that the shear elastic properties of SWCNTs are independent of the length, while a marked variation is observed depending on the diameter and geometry of SWCNT.

CHAPTER 6

TRANSPORT CHARACTERISTICS OF WATER MOLECULES IN CARBON NANOTUBES

The transport characteristics of water molecules in CNTs are studied in this work using MD simulation method. The transport properties of water molecules in a nano-scale channel such as CNTs is critical for its key role in designing the next generation CNT based nano-fluidic devices. The effect of channel diameter, defects and the inter-layer spacing on the transport of water molecules is studied by subjecting the flow of water molecules through CNTs under pressure. The findings show that the efficiency of water transport decreases in SWCNTs of narrow channel diameter which can be overcome by deploying bigger SWCNTs. In addition defects in the nano-fluidic system will also reduce the transport efficiency of water molecules. We also conducted studies on the transport properties of water molecules in DWCNTs. It is found that the inter-layer spacing in a DWCNT has a significant influence on the rapid transport of water molecules. The transport characteristics of water molecules in CNTs have been systematically and comprehensively studied using the MD simulations and the discussions are presented in this chapter.

6.1. Introduction

The application of CNTs as a medium for fluid transport is significant to understand the nano-level fluidic processes, which are important for technologies such as drug delivery [121, 194], fluid separation [204], and biological channels [184, 205]. A significant amount of research has been performed recently to investigate the role of CNTs as nano-scale flow channels for transport of water, macromolecules, ions, and protons in the field of nano-fluidics [206] and nano-biotechnology [190]. Numerous studies have been conducted to investigate the transport properties of water molecules in CNTs [207, 208]. The flow characteristics of a freshly fabricated membrane consisting of aligned MWCNTs, with graphitic inner cores which would mimic a biological flow channel were studied by Majumder et al [207]. The studies conducted by them showed that liquid flow through a membrane composed of an array of aligned CNTs is four to five orders of magnitude faster than the predicted values on conventional fluid-flow theory. Myers [208] studied the enhanced flow in CNTs using an analytical based approach adopting a mathematical model. It was found that no noticeable enhancement is observed in large tubes. Additionally, an enhancement in flow is observed with a decrease in radius of the CNT for smaller CNTs. Reddy et al [209, 210] conducted analysis on the structural vibrational properties of the fluid conveying SWCNTs and they quantified the description of mass flow rate inside the SWCNT as a function of the natural frequency of SWCNT. The interfacial friction of water molecules with graphitic surfaces of various topological features were studied by Falk et al [211]. Their studies showed that the frictional coefficient decreases with CNT radius for water inside, but increases for water outside. However, the frictional coefficient was independent of topology for the case of graphene

slab. Additionally, the frictional coefficient was also found to diminish below a threshold diameter for armchair CNTs, which results in enhanced flow rate of water molecules through CNTs. Thomas and McGaughey [212] made use of MD simulations to investigate the pressure-driven flow enhancement of water molecules through armchair CNTs of varying diameters. The studies showed that the enhancement decreases with increasing CNT diameter and are lower than previously reported experimental results. It was also hypothesized in their investigation that the discrepancy could have arisen due to a miscalculation of the available flow area and/or the presence of an uncontrolled external driving force (such as an electric field) in the experiments. As an extension to this work, they also investigated the behavior of water near carbon surfaces and explored the nature of water flow through CNTs and carbon nanopipes [213]. The MD simulation studies also pointed out that further measurement of water flow through CNTs are required to understand the magnitude of the flow enhancement and its variation with CNT diameter. It was also found that since atomically smooth and defect-free CNTs were used in MD simulations, the discrepancies with experiments were to be likely caused by differences in the chemistry of the carbon surface. Recently, Walther et al [214] made use of large scale MD simulations to study the flow of water molecules in micrometer long CNTs. The length scale of the CNT membranes used in their simulations enabled them to replicate the lengths used in the experiments. The results suggest that the reported superfast water transport rates must be attributed to effects other than hydrodynamic interactions of water with pristine CNTs.

6.2. Significance and importance of present study

The review of literature studies on the transport properties of water molecules through CNTs clearly indicate that the CNTs have enormous potential to be used for applications involving nano-level fluid flow. However, the transport characteristics of water molecules in a nano-fluidic flow channel with topological defects (such as vacancy defect) are not well studied in literature. Furthermore, for the case of water flow through DWCNTs, the influence of inter-layer spacing on the transport properties is still yet to be investigated. It is also widely recognized that the geometry of the CNT will have a considerable influence on the entry and transport of water molecules. Hence, the main objective of this chapter is to investigate the transport properties of water molecules in SWCNTs in response to the geometrical characteristics of the SWCNT. The influence of concentration and the location of defects on the transport properties of water molecules in a nano-fluidic flow channel are also investigated. The transport properties of water molecules through DWCNT are further analyzed to understand the effect of inter-layer spacing on the flow characteristics of the water molecules through DWCNT. The transport properties of water molecules under pressure driven flow have been comprehensively studied and the results are presented in this chapter.

6.3. System specification

In this chapter, the transport of water molecules through the CNTs is achieved by using a pressure control model [215]. The system specification is shown in Fig. 6.1. The system consists of a reservoir of dimensions $62.52 \text{ \AA} \times 65.22 \text{ \AA} \times 50 \text{ \AA}$ filled with 6300 water molecules. The water molecules are held in the reservoir by two planar graphene sheets –

GS1 and GS2. The two sheets GS1 and GS2 are initially separated by a vertical distance of 50 Å. Pressure is applied on the water molecules by downward displacement (along z direction) of GS1 that contains a hole which has the same size as that of the diameter of the CNT of length $L = 100$ Å. All carbon atoms belonging to the SWCNT and two parallel graphene sheets are fixed in the simulation and are not allowed to evolve over time. At the beginning, the rigid CNT is displaced vertically downward inside the reservoir for a distance of 30 Å with a constant velocity of 10 m/s. After this, GS1 is pushed vertically downward with a velocity of 10 m/s until it is displaced by a distance of 20 Å from its initial position. The downward displacement of GS1 increases pressure on the water molecules that enables rapid transport of water molecules through the CNT core.

6.3.1. Calculation of pressure and force on water molecules

The pressure on water molecules (P_{water}) is obtained by computing the stress on entire system of water molecules and is computed as [117]

$$P_{water} = \frac{Nk_B T}{V} + \frac{\sum_i^N \mathbf{r}_{ij} \cdot \mathbf{F}_{ij}}{d_{sys} V} \quad (6.1)$$

where N is the number of atoms in the system, k_B is the Boltzmann constant, T is the temperature, d_{sys} is the dimensionality of the system (2 or 3 for 2 and 3 dimension respectively), and V is the system volume.

The force on atom i due to interaction with atom j , F_{ij} is defined as the gradient of potential energy which is computed as [117]

$$F_{ij} = - \left(\frac{dE_{pot}(r_{ij})}{dr_{ij}} \right) \quad (6.2)$$

where r_{ij} is the distance between the atoms i and j and $E_{pot}(r_{ij})$ is the potential between the atoms i and j .

Fig. 6.1. The specification of the system used to analyze the transport properties of water in our study. The water molecules are enclosed in a reservoir bound by two graphene sheets, GS1 and GS2. The carbon atoms of CNT and graphene sheets are depicted by the blue balls and the water molecules represented by red and white balls.

6.4. Simulation details

The description of various pair potentials used in the MD simulation for describing interactions between CNT, graphene sheet and water molecules is described in Chapter 2. The work described in this chapter consists of two parts. In the first part, we focus on the transport properties of water molecules through SWCNTs. The effect of channel diameter on the transport characteristics is studied by varying the diameter of the SWCNT. Three types of armchair SWCNTs are considered in our study, viz. (5,5), (7,7) and (10,10) SWCNT. In addition, the transport characteristics of water molecules are also investigated with vacancy defects either in the graphene sheet (GS1) or in the SWCNT. To adequately understand the effect of vacancy concentration on the transport properties, we used a system consisting of 4 different vacancy defect concentrations – 6, 12, 18 and 24 defects. A hexagonal defect is first reconstructed by removing 6 carbon atoms from a hexagon (Fig. 6.2). This defect is then expanded circumferentially to form a bigger vacancy defect in GS1 or the CNT. This method of defect reconstruction helps us to study the role of defect density and location on the transport properties of water molecules through the SWCNT [35]. In the second part of our study, we focus on the transport properties of water molecules through DWCNTs. Two DWCNTs are deployed in our study, viz. (5,5)@(15,15) and (10,10)@(15,15). This choice of DWCNT configuration helps us to effectively understand the role of the inter-layer spacing on the transport properties of DWCNT. It should also be noted that the CNTs (SWCNTs/DWCNTs) and the graphene sheets (GS1 and GS2) are rigid in the present simulation.

Fig. 6.2. Morphology of the defect description in the system employed in our study. A hexagonal defect is first reconstructed by removing 6 carbon atoms that form a hexagon (red circle). This defect is then expanded circumferentially to form a vacancy of bigger defect (blue circle) consisting of 24 missing atoms in GS1 or the CNT.

Before the CNT is subjected to downward displacement, the system is first equilibrated to release any residual stresses by achieving thermal equilibrium in an NVT ensemble. The temperature stability of the system is achieved by employing the Nose-Hoover thermostat [67, 68] and the long-range electrostatic forces are handled using Ewald summation method [66]. The temperature of the system is maintained at 300 K. After every 1000 time steps, the system is allowed to relax such that the atoms attain the favorable

minimum energy positions. The atoms are subsequently shifted to a new position after calculating the velocities and the trajectories of atoms based on the velocity Verlet algorithm [124]. The remaining atoms are relaxed in an NVT ensemble and the procedure is repeated until end of the simulation. We used a total of 650,000 time steps (including 200,000 time steps for initial equilibration) with each time step equivalent to 1 fs.

6.5. Validation of the simulation model

The transport properties of water molecules through SWCNTs under capillary action are discussed in this section. For this purpose, we considered the simulation regime when SWCNTs are dipped inside the water reservoir at a height of 20 Å from GS2 but prior to the application of downward displacement on GS1. We computed the filling velocities of water molecules inside three SWCNTs viz. (7,7), (10,10) and (15,15) SWCNTs. These SWCNTs correspond to radius of 4.74 Å, 6.78 Å and 10.17 Å respectively. Fig. 6.3 shows the variation in the filling velocities of water molecules with the SWCNT radius R . From this plot, we observe that the filling velocities decrease slightly with increasing radius of SWCNT. The nature of the decrease in velocity of water molecules is similar to earlier studies on filling of SWCNTs with water molecules [216, 217]. It can be noted from Table 6.1 that the variation of filling velocities of water molecules with radius of SWCNTs in our simulation is also in good agreement with the MD simulation of Joly [217]. Hence, from the above comparison studies, we confirm the accuracy of our MD simulation.

Fig. 6.3. The velocity of filling of water molecules inside SWCNTs for different radii of SWCNTs.

Table 6.1. Filling velocity of water molecules in SWCNTs of selected radii.

Present simulation		Simulation results of Joly [217]	
Radius of SWCNT (Å)	Filling velocity (m/s)	Radius of SWCNT (Å)	Filling velocity (m/s)
4.74	47 ± 4	5.13	40
6.78	36 ± 3	8.51	33
10.17	33 ± 3	11.94	32

6.6. Transport properties of water molecules in single walled carbon nanotubes

The transport properties of water molecules through SWCNTs with different channel diameters using pressure control method [215] is described in this section. As described in section 6.4, we considered (5,5), (7,7) and (10,10) SWCNTs in this study. The process of transport of water molecules through the (7,7) SWCNT at various heights of GS1 is depicted in Fig. 6.4. It should be noted that in our system, two factors influence the transport of water molecules in the SWCNT: the pressure of the water molecules in response to the downward movement of GS1 and the competition arising between the water molecules in entering the SWCNT channel. Water molecules experience increasing competition for SWCNTs with narrow channel diameter, which would hinder their rapid transport. However, the pressure of water molecules exerted by GS1 enhances the rapid transport of water molecules. The water

molecules can be transported rapidly through the SWCNT by continuously increasing the pressure on water molecules. The pressure of water molecules P_{water} as a function of the height of GS1 for (5,5), (7,7) and (10,10) SWCNTs is shown in Fig. 6.5. We can see that when GS1 moves down, the volume of the reservoir decreases which increases the pressure of water molecules. It is also worthwhile to note that the pressure of water molecules rises more rapidly for the case of (5,5) and (7,7) SWCNT compared to that of (10,10) SWCNT. This is because as GS1 is pushed down, the water molecules face more competition in entering the narrow diameters of (5,5) and (7,7) SWCNT. However, the bigger diameter of (10,10) SWCNT permits an enhanced freedom of movement of water molecules that facilitates the easy transportation of water molecules through the SWCNT and correspondingly the lower pressure of water molecule.

Fig. 6.4. Snap shot of the various stages of transport of water molecules through the (7,7) SWCNT when GS1 is displaced downward by (a) 0 Å, (b) 10 Å, (c) 15 Å and (d) 20 Å from its initial position. It can be noted that downward movement of GS1 increases pressure on the water molecules in the reservoir that enables its rapid transport through the SWCNT.

Fig. 6.5. Pressure P_{water} acting on water molecules depicted as a function of downward displacement of GS1.

The transport characteristics of water molecules through SWCNTs can further be investigated by analyzing by the number of water molecules N_{water} flowing through the SWCNT as a function of displacement of GS1 (Fig. 6.6). It can be noted from this figure that the efficiency of water transport is strongly dependent on the entrance diameter of the SWCNT. For the case of (5,5) and (7,7) SWCNTs, the narrow diameter of the SWCNT restricts the easy movement of water molecules through the SWCNT. This result in increasing the competition of water molecules that enter and get transported

through the SWCNT. However, the transport efficiency increases greatly for the (10,10) SWCNT with bigger diameter. The number of water molecules transported per unit cross-sectional area M_{water} of the SWCNT is also higher for the (10,10) SWCNT (Fig. 6.6). Additionally, we note from Fig. 6.6 that the number of water molecules flowing through the SWCNT levels off after a certain displacement of GS1. We note from Fig. 6.4 that the vertical displacement of GS1 results in transport and release of water molecules through the SWCNT. Hence, when the water molecules exit the SWCNT, they will be continuously replaced by water molecules that enter the SWCNT due to the downward displacement of GS1. As a result, the number of water molecules flowing through the SWCNT region remains more or less constant once the water molecules begins to flow outside of the SWCNT until the reservoir is empty.

Fig. 6.6. Plot of the number of water molecules transported through the SWCNT (N_{water}) and the number of water molecules transported per unit cross-sectional area of SWCNT (M_{water}) depicted as a function of downward displacement of GS1.

It is useful to analyze the repulsive force exerted by carbon atoms at the entrance of the SWCNT on the water molecules. Fig. 6.7(a) depicts a schematic representation which defines two groups of atoms: the water molecules in the reservoir and the carbon atoms at the entrance of SWCNT which are marked red in color. The force between these two groups of atoms is then computed using Eq. (6.2) in which, if atom i represents the carbon atom at the entrance of SWCNT (red), then atom j represents the oxygen and

hydrogen atoms of the water molecules in the reservoir. Fig. 6.7(b) shows a plot of variation in the repulsive force exerted by carbon atoms at the entrance of SWCNT on the water molecules when GS1 has been displaced vertically displaced downward by 20 Å. It can be clearly seen from this plot that the repulsive force exerted by carbon atoms in an SWCNT with wide diameter is substantially lesser compared to narrow diameter SWCNT. This results in continuous rapid water transport through the (10,10) SWCNT. Our results are also in qualitative agreement with the water flowing through bigger diameter SWCNTs as be seen in refs. [218, 219]. However for small diameter SWCNTs, the restriction in mobility combined with the hydrophobic behavior results in a single-file water transport through the SWCNT. As an illustration, the single-file movement of water molecules through (5,5) SWCNTs due to increase in pressure of water molecules achieved by downward displacement of GS1 is depicted in Fig. 6.8. It is hence evident from this study that the flow of water molecules through the SWCNTs can be suitably controlled by varying the diameter of the SWCNTs.

(a)

(b)

Fig. 6.7. (a) Schematic that defines the group of atoms for the purpose of force computation, viz. the carbon atoms at the entrance of SWCNT, marked in red color and water molecules in the reservoir, which are not shown for clarity and (b) force exerted by carbon atoms at the entrance of SWCNT on the water molecules when GS1 has been vertically displaced downward by 20 Å.

Fig. 6.8. Single file transport of water molecules in a (5,5) SWCNT under pressure when GS1 is displaced in vertically downward direction. Figure depicted in cross-section for clarity.

6.7. Effect of location and number of defects

The effect of location and number of defects on transport properties of water molecules is investigated next. In this study, we investigated the effect of location of defects by constructing vacancy defects in GS1 and the SWCNT. The method of vacancy defect reconstruction is illustrated in Fig. 6.2. The number of water molecules transported per unit cross-sectional area (M_{water}) of the SWCNT when GS1 is displaced downward by 20 Å from its initial position is depicted in Fig. 6.9(a) and (b). The presence of defects strongly impacts the transport properties of water molecules through the SWCNTs. In addition, increasing the number of vacancy defects will further decrease the number of water molecules transported per unit cross-sectional area of the SWCNT. The variation in the pressure of water molecules in the reservoir with the vacancy defect concentration when GS1 has been displaced downward by 20 Å is shown in Fig. 6.9(c). It can be noted from this figure that increasing the defect concentration in GS1 decreases the pressure in water molecules. According to section 6.6, the downward displacement of GS1 increases the pressure of water molecules which is crucial for uptake of water molecules through the core of SWCNT. Hence, the decrease in pressure of water molecules due to defects in GS1 reduces the ability of water molecules to flow up through the core of SWCNT, which in turn decreases the efficiency of water transport. The snap shot of the flow of water molecules in the system consisting of defects in GS1 and SWCNT is shown in Fig. 6.10. It can be seen from this figure that defects in the system causes leakage of water molecules which ultimately reduces the efficiency of water transport in the system.

(a)

(b)

(c)

Fig. 6.9. Plot of the number of water molecules transported per unit cross-sectional area of SWCNT (M_{water}) for various vacancy defect concentration in (a) GS1 and (b) SWCNT, and (c) pressure variation in water molecules for the downward displacement of GS1 with various vacancy defect concentrations.

Fig. 6.10. Snap shots depicting the losses of water molecules in the system due to defects in (a) GS1 and (b) SWCNT that reduces the efficiency of water transport in the SWCNT.

The percentage loss in the number of water molecules transported through the SWCNTs of different geometries due to defects in GS1 and SWCNT is illustrated in Tables 6.2 and 6.3 respectively. It can be noted that the loss in water molecules transported through the SWCNT is strongly dependent on the radius of the SWCNT. For instance, a concentration of 24 vacancy defects in GS1 will produce a loss of 35.48 % in (5,5) SWCNT in contrast to 6.68 % in (10,10) SWCNT (Table 6.2). As mentioned in section 6.6, both (5,5) and (7,7) SWCNTs possess much smaller entrance openings compared to that of the (10,10) SWCNT. Hence, as GS1 is pushed vertically downwards, the water

molecules can escape more easily through the region of vacancy defect instead of the narrow entrance in small diameter SWCNTs. Similarly, we also note from Table 6.3 that the vacancy defects in (5,5) and (7,7) SWCNTs exhibit greater losses in the transport of water molecules compared to that of the (10,10) SWCNT. This is due to the reason that the (5,5) and (7,7) SWCNTs have smaller diameters and the defect region occupies a much larger portion when compared to that of the (10,10) SWCNT with a bigger diameter. It is hence clear from the foregoing discussion that the transport losses due to defects in the system can be kept to a minimum by suitably considering a bigger diameter SWCNT.

Table 6.2. Percentage loss (%) in the number of water molecules transported through the SWCNT for various vacancy defect concentrations (G) in GS1 when GS1 has displaced vertically down by 20 Å.

Geometry	$G = 0$	$G = 6$	$G = 12$	$G = 18$	$G = 24$
(5,5) SWCNT	0	1.16	12.91	25.83	35.48
(7,7) SWCNT	0	0.74	5.02	9.65	13.11
(10,10) SWCNT	0	0.53	1.68	3.52	6.68

Table 6.3. Percentage loss (%) in the number of water molecules transported through the SWCNT for various vacancy defect concentrations (C) in SWCNT when GS1 has displaced vertically down by 20 Å.

Geometry	$C = 0$	$C = 6$	$C = 12$	$C = 18$	$C = 24$
(5,5) SWCNT	0	3.23	12.90	22.58	29.03
(7,7) SWCNT	0	2.04	7.49	10.63	14.71
(10,10) SWCNT	0	0.41	3.89	6.48	9.51

6.8. Transport properties of water molecules in double walled carbon nanotubes

The transport properties of water molecules in DWCNTs are discussed in this section. The main objective of this study is to investigate the effect of inter-layer spacing on the transport qualities of water molecules in DWCNT. For this purpose, we replaced the SWCNT in our system (see Fig. 6.1) with a (10,10)@(15,15) DWCNT of length $L = 100$ Å. At the beginning, the DWCNT is pushed vertically downward such that the bottom of the DWCNT is located at a distance of 30 Å from GS2. Following this, the GS1 is pushed vertically downward by a displacement of 20 Å from its initial position, which results in flow of water molecules through the SWCNT. The stages of water transport through the (10,10)@(15,15) DWCNT when GS1 is displaced at various heights from GS2 is depicted in Fig. 6.11. We can see from this figure that when GS1 is pushed vertically down, it results in flow and transport of water molecules through the core of the

DWCNT. The number of water molecules transported through the inner core of (10,10)@(15,15) DWCNT when GS1 is gradually pushed vertically downwards is depicted in Fig. 6.12. We have also included the corresponding transport characteristics through the (10,10) SWCNT for comparison. It can be noted from Fig. 6.12 that when GS1 is pushed down, the water molecules begin to rise up in the CNT which can be seen by the rise in the number of water molecules. After GS1 has been displaced to certain height, the water molecules begin to flow out of the tube. During this phase the water molecules which are released from the CNT, are replaced by water molecules that enter the CNT due to the continuous downward movement of GS1.

Fig. 6.11. Snap shot of the various stages of transport of water molecules through the (10,10)@(15,15) DWCNT when GS1 is displaced downward by (a) 0 Å, (b) 10 Å, and (c) 20 Å from its initial position.

Fig. 6.12. Plot of the number of water molecules transported (N_{water}) through the inner core of $(10,10)@(15,15)$ DWCNT and $(10,10)$ SWCNT at various displacements of GS1 and the corresponding variation in the repulsive force exerted by carbon atoms at the entrance of CNTs on water molecules.

It is interesting to note that the efficiency of water transport decreases in the $(10,10)@(15,15)$ DWCNT in comparison with the $(10,10)$ SWCNT (Fig. 6.12). Similar phenomenon was earlier reported for the case of transport of liquid mercury through DWCNTs [215]. This is due to the reason that the entrance of the $(10,10)@(15,15)$

DWCNT has more carbon atoms that block the flow of water molecules when compared to that of the (10,10) SWCNT. This is also further evident from the fact that the repulsive force exerted by carbon atoms at the entrance of DWCNT on water molecules rises more rapidly for the case of (10,10)@(15,15) DWCNT in contrast to (10,10) SWCNT. Hence, water molecules entering the inner core of (10,10)@(15,15) DWCNT face more competition compared to that of the same diameter in a (10,10) SWCNT.

It is also useful to investigate the flow of water molecules through DWCNTs by increasing the inter-layer spacing in the DWCNT. For this purpose, we simulated the flow of water molecules through (5,5)@(15,15) DWCNT. The transport characteristics of water molecules through the (5,5)@(15,15) DWCNT is studied and depicted in Fig. 6.13. It is clear from this plot that the efficiency of water transport through the (5,5)@(15,15) DWCNT is greatly enhanced when compared to (10,10)@(15,15) DWCNT. The snapshot of the flow of water molecules through the (5,5)@(15,15) DWCNT is given in Fig. 6.14. It shows that the water molecules enter the inter-layer spacing between the two walls of the DWCNT when GS1 is displaced vertically downwards. Additionally, we note that the water molecules also get transported through the inner core of the (5,5) SWCNT. It should be noted that the inter-layer spacing between the walls of (5,5)@(15,15) DWCNT is 6.38 Å which is twice the radius of the inner (5,5) SWCNT. Correspondingly, the inter-layer spacing is also equal to the radius of the (10,10) SWCNT. Based on our analysis from section 6.6, large inter-layer spacing in DWCNTs reduces the competition of water molecules entering the DWCNT. This reduction in competition facilitates rapid transport of water molecules through DWCNTs of large inter-layer distances.

Fig. 6.13. Plot of the number of water molecules transported through the DWCNT (N_{water}) and the number of water molecules transported per unit cross-sectional area of DWCNT (M_{water}) depicted as a function of function of downward displacement of GS1.

Fig.6.14. Cross-sectional snap shot of the transport of water molecules through the (5,5)@(10,10) DWCNT. The large inter-layer separation between the walls of the DWCNT facilitates the rapid transport of water molecules.

6.9. Summary

In this chapter, the transport characteristics of water molecules through SWCNTs by pressure control model have been studied using MD simulation method. The understanding of transport properties of water molecules through SWCNTs of varying geometries is of significant importance in the field of bio-materials and nanobiotechnology. The studies show that the diameter of the SWCNT greatly influences the flow of water molecules through the SWCNT. Bigger SWCNTs can conduct and transport water more easily compared to that of the narrow diameter SWCNTs. Our studies also indicate that the efficiency of water transport decreases due to the defects in the SWCNT channel or the graphene plunger due to pressure loss in the system. Further studies on the flow of water molecules through DWCNTs were also conducted to understand the influence of inter-layer spacing on the transport qualities of DWCNTs. Our studies show that while closely spaced layers of DWCNTs reduce the efficiency of water transport, an enhancement can be achieved by deploying DWCNTs of wide inter-layer spacing.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

This chapter gives a summary of the main conclusions and contribution arising out of the PhD project. In addition, this chapter also outlines the future work that will be useful to widen the scope of research work based on the conclusions arising from this thesis. A major focus on this thesis has been to address the unique mechanical properties of CNTs interacting with water molecules. MD simulation method has been deployed in the current research to study and understand the mechanical properties of CNTs subjected to various forms of mechanical loading conditions. The retrospective of the thesis indicates a significant dependence of the mechanical performance of CNTs due to interaction of surrounding water molecules. This thesis has also addressed the influence of geometry, defects and inter-layer wall spacing on the transport properties of water molecules through CNT.

7.1. Conclusion

CNTs have attracted widespread research attention in the field of nanotechnology and materials science due to its excellent physical and mechanical properties. The application of CNTs in diversified environments necessitates the need to understand its properties in different medium. Notably, CNTs have demonstrated their enormous potential to be used in NEMS and nano-fluidics devices. These applications require an understanding of properties of CNTs while interacting with water molecules. The major focus of this thesis is to study and understand the elastic properties of SWCNTs interacting with water. The elastic properties of SWCNTs interacting with water molecules subjected to four forms of mechanical loading conditions – compression, tension, torsion and shear are investigated. The transport properties of water molecules in CNTs are also studied. The findings and conclusions obtained from this thesis is expected to further compliment the potential applications of CNTs in NEMS, nano-fluidics and nano-drug delivery devices.

Chapter 1 presents an introduction and properties of CNTs and water molecules. The chapter has also highlighted the need to study the mechanical and transport characteristics of CNTs interacting with water molecules. Chapter 2 has provided a detailed discussion of the principle and procedure of computer simulation of nanoscale materials using MD simulation. An overview of MD computer program used in this thesis has also been discussed.

A detailed literature review of the mechanical properties of CNTs determined by using computer simulation and experiments has been provided in Chapter 3. The investigation of the elastic properties of the free form SWCNT using MD simulation were systematically studied and presented in this chapter. It was found that at low temperature,

the presence of bends along the axis of an SWCNT in addition to defects will affect the mechanical properties of SWCNT. The negative impact of the bends on elastic properties of SWCNT can however be overcome by deploying long SWCNTs. At high temperatures, not much difference is observed between the mechanical properties of pristine SWCNT and those with a bent. Additionally, the mechanical properties of SWCNT array have also been studied. It was found that the elastic properties of SWCNT array are much superior compared to that of a free standing SWCNT.

In Chapter 4, the mechanical properties of water submerged SWCNTs are studied under compression and tension. The interaction of SWCNT with water molecules is brought about by submerging SWCNT in a simulation box filled with water molecules. The studies show that the elastic properties of SWCNTs are reduced due to the presence of surrounding water interaction. The mechanical properties of SWCNTs under tension are influenced more strongly by the diameter rather than the length of the SWCNT. It was also found that the compressive properties of SWCNTs decrease due to increasing the length of SWCNT. However, better compressive properties can be achieved by increasing the diameter of SWCNT. In terms of chirality of SWCNTs, we found that armchair SWCNTs performs better than a zigzag SWCNT under tension while it is vice versa for the case of compression. For SWCNT with defects, circumferential defects cause a greater impact on the elastic properties of SWCNTs compared to axial defects. In addition the mechanical properties of capped SWCNTs encapsulated with varying densities of water molecules were also studied. It was found that the failure of capped SWCNT under tensile loading results in release of encapsulated water molecule that could prove to be a useful mechanism in drug-delivery devices.

In Chapter 5, the mechanical properties of water submerged SWCNTs under torsion and shear has been studied. The studies show that the torsional and shear characteristics of SWCNTs reduce due to the interaction of surrounding water molecules. SWCNTs with bigger diameter possess better torsional and shear elastic properties compared to that of SWCNTs with small diameter. The results also indicate that the torsional properties of SWCNTs with defects are more sensitive to the defect distribution and diameter of the SWCNT. Furthermore, for the case of capped SWCNTs, dense filling of water molecules in an SWCNT under torsion and shear will also result in fracture of SWCNT which results in release of encapsulated water molecules. This mechanism could be useful in the design of SWCNT based nano-drug delivery devices.

In Chapter 6, the transport characteristics of water molecules through SWCNTs by pressure control model have been studied using MD simulation method. The studies show that the diameter of the SWCNT greatly influences the flow of water molecules through the SWCNT. Bigger SWCNTs can conduct and transport water more rapidly compared to that of the narrow diameter SWCNTs. Additionally, our studies indicate that the efficiency of water transport decreases due to the defects in the SWCNT channel or the graphene plunger due to pressure loss in the system. Further studies on the flow of water molecules through DWCNTs were also conducted to understand the influence of inter-layer spacing on the transport qualities of DWCNTs. It was found that closely spaced layers of DWCNTs reduce the efficiency of water transport. However an enhancement in the efficiency of water transport can be achieved by deploying DWCNTs of wide inter-layer spacing. This observation holds a great promise in the design of CNT based nano-fluidic devices.

7.2. Main contributions arising from this thesis

The main contributions from this thesis are listed in this section:

- (1) The effect of bends on the mechanical properties of SWCNTs has been investigated. It is found that though the presence of bends influences the elastic properties of SWCNTs, it can be overcome by deploying long SWCNTs.
- (2) Investigating the tensile mechanical properties of SWCNTs interacting with water molecules. The tensile properties of SWCNTs are insensitive to length of SWCNT. Increasing the diameter will proportionally increase the tensile properties of SWCNT.
- (3) Compressive elastic properties of SWCNTs interacting with water molecules. Small diameter SWCNTs with large aspect ratio bend in response to compression, whereas bigger diameter SWCNTs compress axially and show superior compressive properties.
- (4) Torsional elastic properties of SWCNTs interacting with water molecule are investigated. Bigger SWCNTs possess better torsional rigidity compared to that of small SWCNTs. The elastic properties of SWCNT under torsion are sensitive to both length and diameter of the SWCNT.
- (5) The shear elastic properties of SWCNTs interacting with water molecules are investigated. SWCNTs with large diameter possess better shear loading characteristics compared to that of SWCNTs with small diameter.
- (6) Investigation of the effect of concentration and location of defects on the mechanical properties of water submerged SWCNTs. Increasing defect concentration will drastically reduce the elastic properties of SWCNTs. The

elastic properties of SWCNTs are more sensitive to circumferential defects compared to that of axial defects.

- (7) Transport characteristics of water molecules in CNTs. It was found that better transport efficiency can be obtained by deploying large diameter SWCNTs. Defects in nano-system can cause leakage of water molecules and can hence reduce the transport efficiency of SWCNTs.

7.3. Future works

Research in CNT for their potential applications in novel and innovative technologies is advancing rapidly. With the development of state-of-art laboratories and advent of high performance computers, we can expect an increasing scope of exploring novel properties of CNTs. It is also obvious that some challenges are required to be overcome in order to fully realize the potential of CNTs for applications in nano-fluidics or nano-biotechnology. In light of these challenges, we recommend the possible direction for future work as listed below:

- (1) The high mechanical strength combined with excellent electrical properties of CNTs has led to the rise of CNT metal matrix composites (CNT – MMCs) [220-222]. Opportunities exist for CNT – MMCs to be used for potential applications in marine and underwater defense technologies. It is hence proposed to investigate the mechanical properties of CNT – MMCs interacting with water molecules. This study will also be helpful to widen the understanding of the novel properties of CNT – MMCs at nanoscale dimension.

- (2) In studying the interactions of CNT with water molecules using MD simulations, almost all of the literature work models the interaction between carbon atom and water molecules using standard Lennard-Jones potential. New potential models are required to be developed to model the chemical interaction between carbon atoms and water molecules, which would be prominent especially at higher temperatures.
- (3) There exists a scope for improving the *ab initio* technique for simulating large systems of atoms such as CNTs interacting with water molecules or biomolecules. These improved *ab initio* techniques can be used to study the effect of perturbations in a quantized field, i.e. Casimir forces and for analyzing the quantum effects due to the interaction of water molecules with CNT.
- (4) Currently, many studies have focused on investigating the transport properties of water molecules in CNTs [212-214]. CNTs have enormous potential to be used for applications in biotechnology or novel biomedical devices. It would be useful to characterize the transport characteristics of macromolecules such as proteins, lipids and nucleic acids in CNTs using MD simulations.
- (5) For the case of CNTs in drug delivery applications, the simulation model would involve encapsulating a capped SWCNT with drugs while it is submerged in a simulation box consisting of blood. The main challenge remains in modeling the complex interactions between the carbon atoms of CNT and drug, drug and blood and carbon atoms of CNT and blood. It would be interesting to figure out the mechanics of CNT interaction in such a simulation domain.

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