Molecular dynamics simulations of biomolecules and metal atoms in carbon nanotube channels

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**MOLECULAR DYNAMICS SIMULATIONS OF
BIOMOLECULES AND METAL ATOMS IN
CARBON NANOTUBE CHANNELS**

MELVIN LIM CHOON GIAP

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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2012

ABSTRACT

The usages of the carbon nanotube (CNT) as a delivery system for nanomaterials and as a template for nanowires are exciting topics to be explored. Although many studies involving the flow in carbon tubules have been carried out, the possible usages of CNT channels with junctions for various applications are not well established. This is due to the poor understanding of the flow phenomena of the encapsulated materials in these CNT channels, and also the difficulties involved in the experimental work in this area. The focus of this thesis is thus to present the novel studies of the flow of biomolecules and metal atoms along CNT channels using molecular dynamics (MD) simulations. The Chemistry at HARvard Molecular Mechanics program is used to assist the in-depth studies of the flow of a 3-base oligonucleotide in CNT channels induced by a pressure difference, whereas simulation programs based on MATLAB have been developed for the detailed investigations of copper atoms flowing along CNT channels. A new method of deriving the velocity rescaling is also developed to calculate the flow velocities of copper atoms due to electromigration in MD simulations. According to our new studies, the junction of a (8,8)-(12,12) CNT channel is found to be able to filter a solvated 3-base oligonucleotide from water molecules. The results also show that the narrowing of the CNT junctions not only aids in speeding up the flow velocities, which improve delivery processes, but also causes the oligonucleotide to fold, which reduces the overall length of the delivered oligonucleotide. Apart from that, the new results for the flow of copper atoms along a CNT channel have shown that the CNT junction acts as a buffer area for the reconfiguration of copper atoms to occur. The results also indicate that the right combination of the temperature, bias voltage, CNT junction size and CNT chirality eases the flow of copper atoms along the channel junctions. The spiral flow phenomenon of copper atoms in the downstream of CNT channels is newly found. The degree of rotation in the spiral flow suggests the way a copper mass can be formed in the channel as copper atoms flow downstream. The study also reveals that a CNT channel with a semiconductor-semiconductor junction results in a better hybrid structure of copper atoms and the downstream section of the CNT channel compared to that with a metal-metal junction, in terms of the compactness of copper atoms in the channel.

PUBLICATION LIST

Journal Papers

- [1] M.C.G. Lim, Q.X. Pei, Z.W. Zhong, Translocation of DNA oligonucleotide through carbon nanotube channels under induced pressure difference, *Physica A: Statistical Mechanics and its Applications*, 387 (2008) 3111-3120. (*Impact factor: 1.521*) (*Times Cited: 10*) (*ISI Q2 Journal*)
- [2] M.C.G. Lim, Z.W. Zhong, Molecular dynamic analyses of an Al(110) surface, *Physica A: Statistical Mechanics and its Applications*, 388 (2009) 4083-4090. (*Impact factor: 1.521*) (*Times Cited: 7*) (*ISI Q2 Journal*)
- [3] M C.G. Lim, Z.W. Zhong, Effects of fluid flow on the oligonucleotide folding in single-walled carbon nanotubes, *Physical Review E*, 80 (2009) 041915-1-8. (*Impact factor: 2.352*) (*Times Cited: 5*) (*ISI Q1 Journal*)
- [4] M C.G. Lim, Z.W. Zhong, Atomic arrangement of copper atoms in a carbon nanotube channel under electromigration conditions, *Chemical Physics Letters*, 500 (2010) 49-53. (*Impact factor: 2.280*) (*ISI Q2 Journal*)
- [5] M C.G. Lim, Z.W. Zhong, Dynamical behavior of copper atoms in a carbon nanotube channel, *Carbon*, 49 (3) (2011) 996-1005. (*Impact factor: 4.893*) (*ISI Q1 Journal*)
- [6] M C.G. Lim, Z.W. Zhong, The junction size effect on the electromigration flow of copper atoms through carbon-nanotube junctions, *Physica E: Low-Dimensional Systems and Nanostructures*, 43 (4) (2011) 862-868. (*Impact factor: 1.304*)

- [7] M C.G. Lim, Z.W. Zhong, Effects of electromigration on copper in carbon nanotube channels, *Physica A: Statistical Mechanics and its Applications*, 390 (5) (2011) 963-971. (*Impact factor: 1.521*) (*ISI Q2 Journal*)

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LIST OF ABBREVIATIONS

CHARMM	Chemistry at HARvard Molecular Mechanics
CMS	Cylindrical MultiShell
CNT	Carbon NanoTube
COM	Centre Of Mass
CVD	Chemical Vapour Deposition
DNA	DeoxyriboNucleic Acid
EAM	Embedded Atom Method
FPM	Fluidized Piston Model
GCMC	Grand Canonical Monte Carlo
HMS	Helical Multi-Shell
IPM	Ice Piston Model
LEED	Low-Energy Electron Diffraction
LJ	Lennard-Jones
MD	Molecular Dynamics
MPCVD	Microwave Plasma-assisted Chemical Vapour Deposition
MWCNT	Multi-Walled Carbon NanoTube
NAMD	a parallel molecular dynamics code
PME	Particle Mesh Ewald
PLL	Poly (L-lysine)
RNA	RiboNucleic Acid
RPM	Reflecting Particle Method
ssDNA	single stranded DNA
SWCNT	Single-Walled Carbon NanoTube
VMD	Visual Molecular Dynamics

LIST OF SYMBOLS

a	acceleration
a_0	lattice parameter
A, C	atom-type dependent constants
b	bond length
B	arbitrary constant
D	effective dielectric function
D_c	diffusion coefficient
e	electron charge
E	energy
E_{bonded}	bonded term
$E_{bond-stretch}$	bond energy
$E_{bond-angle}$	bond angle energy
E_c	cohesive energy
$E_{electrostatic}$	electrostatic energy
$E_{non-bonded}$	nonbonded term
$E_{torsion-angle}$	torsion angle energy
$E_{van-der-Waals}$	van der Waals energy
E_v^f	vacancy formation energy
f_e	scaling constant
F	electron density embedded function
F_0, F_1	constants for the embedded function

LIST OF SYMBOLS

g	gravity
$G(q)$	energy-wave-number characteristic
h	channel width
H	enthalpy
k_b	Boltzmann constant
k_m	temperature independent quantity for electromigration
K	reciprocal lattice vibration vector
K_b, K_θ, K_Φ	force constants
m	mass of an atom
n_l	the number of atoms in the l^{th} atomic layer
N	a fixed number of atoms
P	pressure
q	charges of atom
q_w	wave number
r	distance between two atoms
r_c	centre of mass
r_e	equilibrium nearest distance
r_v	radius vector
r_p	position of an atom
R_a, α, β, χ	parameters for pure element systems
S	entropy
S_l	layer structure factor

LIST OF SYMBOLS

t	time
T	temperature
T_m	melting temperature
u, v, w	velocities
V	volume
V_f	electric field
w_0	bulk velocity
Z_d	direct force
Z_w	wind force

Greek Letters

γ	resistivity
γ_f	frictional coefficient
δ	slip length
η	viscosity
θ	bond angle
λ	coefficient of symmetry
μ	a fixed chemical potential
ξ	force on an atom
ξ_{em}	driving force on an atom
ρ	electron density of individual atoms
ρ'	fluid density

LIST OF SYMBOLS

$\sigma_d(r)$	direct interaction between ions
$\sigma_{ind}(r)$	ion-electron-ion interaction (indirect ion-ion interaction)
ζ	host electron density
ζ_e	host electron density at equilibrium
Φ	dihedral angle
ψ	random force
Ω_0	specific volume
φ	pair potential
φ_v	van der Waals type interaction

CHAPTER 1

INTRODUCTION

1.1 Research background

The molecular dynamics (MD) method is one of the principal tools for the studies of biological molecules and engineering problems on the micron or nanoscale. MD was first introduced by Alder and Wainwright in the late 1950's to study the interactions of hard spheres [1]. There were many important insights related to the behaviour of simple liquids that emerged from their studies. Since then, MD simulation has been used vastly to study behaviours of molecules for science, engineering and also for the combination of both areas. Using MD simulation, extensive studies of molecules are carried out in order to justify results from theoretical calculations and experimental results.

Deoxyribonucleic acid (DNA) molecules and carbon nanotubes (CNTs) are nanostructures that have been of interest in recent studies of nanotechnology. The studies on structural and dynamical properties of DNA and ribonucleic acid (RNA) molecules in various chemical environment are pursued actively because there is much potential for these molecules to be used in delivery systems for treatments of human diseases [2].

An oligonucleotide is a short sequence of DNA molecules. Usually it is made up of twenty or fewer bases. Uses of oligonucleotides include molecular electronics, molecular sensors, electronic DNA sequencing, etc. Oligonucleotides are also often used as probes for detecting complementary DNA or RNA because of their ability to bind readily to their complements. Hence, the efficiency of transporting the oligonucleotides

for gene therapy is becoming essential and many improvements are investigated [3]. One of the promising components that can be considered for transporting DNA molecules for the applications as mentioned above is the CNT.

CNTs were first discovered by Radushkevich and Lukyanovich [4], which was published in the Russian Journal of Physical Chemistry. Throughout the years, there were many discoveries of CNTs; but none was as well-known as Iijima's discovery of CNTs [5]. Since then, the study of CNTs has escalated and played a part in many areas such as nanoelectromechanical systems, material engineering, nanotechnology and biotechnology.

The areas of CNT applications cover a wide range, from diagnostic tools and devices, to biopharmaceutics, implantable materials and devices, and surgical aids [6]. Numerous studies have focused on properties and functionalities of CNTs, due to the vast potential of CNTs as modal structures. Molecular transporters, DNA detectors and sensors are a few of the many potential biomedical applications [2, 3, 7-10]. A hybrid system of biomolecules and CNTs has also shown promising prospect for bioelectronics, nanocircuitry etc [11]. One of the growing interests in the application of CNTs is to use a CNT as a flow channel for biomolecules and fluid [12]. The nanoscale behaviour of fluid flow in a CNT has much to be explored before practical applications can be realized.

CNTs can naturally behave as nanoscale channels. The investigation of the differences in the flow inside nanotubes is important from the viewpoint of controlling the behaviour of molecules at the nanoscale. Recent MD simulations demonstrated that a single wall carbon nanotube (SWCNT) could be utilized as a molecular channel for the insertion of DNA molecules [13]. The dynamics processes of encapsulating the

molecules depend on the combined actions of the van der Waals and hydrophobic interaction forces between DNA molecules and CNTs.

The main purpose of studying the functionalization of CNTs with nanoscale materials is to develop a better understanding of the effects of confinement of DNA molecules in CNTs. The results from these studies could benefit the creation of new types of miniature devices and hopefully someday it can contribute to the applications for biology and chemical fields.

Molecular transport in CNTs can be determined by various factors [14]. For example, pore size and hydrophobicity play a crucial role in the speed of molecular transportation and the ease of the molecule to enter the nanotube [15]. Molecules such as DNA, RNA, peptides and methanol [15-18] are a few of the many nanomaterials that are essential for simulation cases of nanoscale flow in CNTs. DNA, in particular, has attracted attention in recent studies especially on its behaviour under forces [19, 20], dynamical behaviour during the translocation processes [21, 22] and conformation in nanofluidic channels [23, 24]. The possibility of encapsulating a single stranded DNA molecule into a single-walled CNT has been demonstrated by Okada *et al.* [25]. Water molecules, on the other hand, are often integrated into CNTs as the fluid molecules that solvate the biomolecules of interest during simulations. Thus, the behaviour of water molecules in a CNT channel provides insightful information regarding the fluid-fluid and fluid-channel wall interactions. Striolo [26] has performed the simulation of water diffusion through an infinitely long, narrow CNT, which shows that the concerted motion of water molecules depends not only on the interactions between water-water and water-carbon, but also on the number of molecules and the temperature of the system. These

conditions affect the speed of the diffusion and also the effectiveness of the diffusion. Hummer *et al.* [27] also suggested that a CNT might be exploited as a unique molecular channel for water and protons.

The application of forces to a system of molecules is often performed in MD simulations such that various methods of driving fluid flow are induced to the system of interest. However, in some cases, the driving force such as a pressure or density gradient is achieved through a source and sink relationship [28]. The source is maintained at a constant density and temperature by introducing the required particles, while the sink region is maintained in a vacuum. Other methods that use a pressure gradient to drive fluids include the Reflecting Particle Method (RPM) [29], the Fluidized Piston Model (FPM) and the Ice Piston Model (IPM) [30].

Although studies had been done on the encapsulation of DNA and movement of water molecules in carbon nanochannels [31, 32], no studies have yet reported the effect of interaction of CNT channels with an oligonucleotide and water molecules contained together within the channels, under the influence of a pressure difference. Hence, MD simulations have been established in this thesis to investigate the flow properties of water molecules and an oligonucleotide within a CNT channel.

The realization of nanowires is becoming more important because the scale of technology is reducing greatly and the applications of nanowires in semiconductor and other devices are growing [33, 34]. By using simulation techniques similar to that in the studies of biomolecules, MD can be applied to the simulation of capillary filling of metal atoms in CNTs [35] and the simulation of premelting phenomena for various materials. The filling of CNTs with metal atoms has been demonstrated by many studies as a

process to create nanowires [36, 37]. MD simulation by Hwang *et al.* has demonstrated the filling and flow process of copper atoms in CNT channels [38].

Premelting is an important research topic which has attracted much attention for many years. Various efforts have been made to establish a better understanding of the phenomenon involving the diffusion of atoms on the surfaces of different materials [39]. Diffusion on the surface affects film growths, adsorption, catalyst reactions, evaporations, desorption etc. In fact, nanotechnology advances have pushed the importance of surface science [40] to even a greater height, which includes the study of surface diffusion [41].

Premelting of materials, in particular, has associated with the phenomenon of surface diffusion. Due to the weak bonding of atoms on the surface, melting on the material surface was observed below the bulk melting temperature [42, 43]. Experiments have also revealed that different surface conditions would affect the validity of the melting process on the surface [44]. It was found that a Pb surface with the (111) orientation does not favour the premelting phenomenon to occur. The melting behaviour was not found on Au(111) surfaces [45].

On the other hand, the structure and dynamics of Al(110) surfaces with the effect of temperature variations have been investigated [46]. It was reported that at temperatures up to 620 K, the effective root-mean-square vibrational amplitude of aluminium atoms near the surface is larger than the amplitude in the bulk by a factor of 1.3, according to measurements using low-energy electron diffraction (LEED). The properties of Al(110) surfaces were further established by Gobel *et al.* through LEED experiments [47]. Al(110) surfaces at temperatures between 40 and 890 K were tested in order to find out the temperature dependence of the interlayer spacings. They concluded that the negative

expansion coefficient for the first interlayer spacing occurred at temperatures ranging from 0 K up to $0.4 T_m$ ($T_m = 933$ K). At temperatures above 0.4 to $0.5 T_m$, thermal expansion of the surface begins. This explains that contraction of the Al(110) surface occurs at temperatures between 0 K and $0.4 T_m$. Results also show that anharmonic effects occur at low temperatures.

Due to the complexity of carrying out experiments to understand phenomena of the surface, MD simulations are often performed to provide reasonable predictions of the atomic behaviour. Surface diffusion of noble-gas (Kr) at the outer layer of a slab was demonstrated by Schommers *et al.* using MD simulations [48, 49]. They reported that the outermost surface layer has a premelting phenomenon at temperatures below the melting point. Atoms at the outermost layer perform a diffusive motion parallel to the surface. In order for premelting to occur, delocalization normal to the surface is required. Salacuse *et al.* further elaborated the dynamic structure factor using MD simulations [50].

The premelting of Al(110) surfaces was reported to occur when surface energy [51] and surface vacancies [52] were increased due to elevated temperatures. The results were obtained using the potential for Al derived from effective medium theory. Another study of Al(110) surfaces has also been reported using a more general pseudopotential [53]. This model consists of the direct ion-ion potential and the ion-electron pseudopotential, which are determined based on the consideration of the interactions of van der Waals type.

Besides the potentials mentioned above, there are other potentials that have been used in MD analyses of surface melting. These studies include the use of lattice theory with fcc (face-centred cubic) Lennard-Jones (LJ) crystal [54], effective medium theory

[42, 55], etc [49]. Although LJ potential is often used in organic molecules [56, 57], experiments and theoretical studies [58] have shown that LJ interactions are able to predict MD phenomena of the surface metallic atoms well enough based on activation energies and cohesive energy. These LJ parameters were set based on the lattice constants at the room temperature and the cohesive energy [59]. LJ potential is also used in numerical calculations for analyzing the premelting phenomenon based on Frenkel type defects [60]. To our best knowledge, no study has yet reported the surface melting phenomenon of Al(110) surfaces using the embedded-atom method (EAM) potential. The EAM potential developed by Cai *et al.* [61] has been used to describe the atomic interactions in liquid aluminium for the investigation of the transport properties of the metal [62]. The results from the study have shown that the transport properties calculated with the EAM potential may be as reliable as experimental data. Therefore, the EAM potential has been chosen in this study to analyze the premelting of an Al(110) surface. The purpose of using this potential is to mainly compare the results obtained from using the EAM potential with the results reported by Schommers [63]. Other works [64-68] are also examined in this study so that a better understanding of the effect of the EAM potential on the premelting phenomenon of the Al(110) surface can be established. The outcomes of these comparisons are essential in providing a better understanding of the bonding strength of the Al atoms using different potentials, especially for the atomic mobility at the surface.

Due to the various applications in the field of medical and engineering, the encapsulation of metal atoms in CNTs has also been gaining much attention over the years [69, 70]. Particularly, SWCNTs are interesting materials for the encapsulation of

metal atoms [71, 72]. The production of SWCNTs has been demonstrated by Iijima and Ichihashi [73], and Bethune *et al.* [74]. In many experiments, defects in CNTs are observed [75, 76]. A SWCNT possesses well defined morphologies, thickness and other interesting characteristics, which makes this material an interesting structure for the encapsulation of metal atoms. The chiral vector of SWCNTs determines the chirality (mirror symmetric of two CNT tubules) and the diameter of the tubules [77]. Besides that, the electronic structure of a SWCNT can also be defined as metallic or semiconducting, through the identification of the indices in the chiral vector of the tubules [78]. Kinks and nanotube junctions are some of the defects found in CNTs [79, 80]. Another example is the pentagon-heptagon pairs defect that exists in the network of the CNT [81]. However, a pentagon-heptagon pair defects can also occur when two CNTs of dissimilar diameters are joined together, as that demonstrated by Jin *et al.* experimentally [82]. The joining region of two dissimilar CNTs results in the formation of a junction. This junction acts as a nozzle or a diffuser, depending on the direction of the flow of the encapsulated material in the particular channel [31]. The junction in a CNT channel is therefore crucial in affecting the flow of the materials along a CNT channel [83].

The potential usage of metal filled CNTs is significant [84, 85]. Although variations in the types of materials used in filling CNTs are great, metal filled CNTs are one of the hybrids that show great potential in numerous applications. One of such examples is the filling of iron in CNTs demonstrated by Borowiak-Palen *et al.* [86]. The encapsulation of iron in CNTs is suitable to be used as magnetic field sensors due to the ferromagnetic behaviour of the system at room temperatures. Besides that, CNTs filled

with ferromagnetic fillers can also be used in controlling the heating of tumour tissues [87]. Studies have been conducted over the years involving the filling of materials in CNTs [88-91]. Many methods have been explored in filling metals into CNTs. These techniques include but are not limited to capillarity-induced filling, carbon arc discharge methods, wet chemical techniques and pyrolysis [36]. The investigations of the filling processes of metals in CNTs have been carried out in simulations and experimental studies [92, 93]. Zhang and Wang have used copper to fill CNTs by adopting a microwave plasma-assisted chemical vapour deposition (MPCVD) method [94]. The filling of copper in CNTs is mainly due to a sucking effect caused by capillary attraction. Similarly, the capillary effect of palladium in CNTs has been tested by Schebarchov and Hendy using MD simulations [35, 95].

Apart from filling CNTs, the transportation methods for the filled materials in CNTs are equally essential to ensure that delivery of the encapsulated substance is viable. Electromigration is an important mode of transport for metal atoms in nanotubes [96]. The forces in electromigration are dependent on the electric field and the scattering of electrons, known as the ‘direct’ and ‘wind’ forces respectively [97]. Through the manipulation of the electric field along the nanotubes, the migration of metal in CNTs can be accomplished due to the induction of electromigration forces. The electromigration process causes the metal atoms to move in the opposing direction to the electric field, i.e., in the direction of the electron flow. This transportation method has been observed in an experiment [98] and presented in atomistic simulations [99, 100].

The mass transport of various metals along CNTs has been demonstrated using a voltage gradient [101]. The transport system has demonstrated the achievement of atomic

scale mass transport along CNTs. The mass distribution is controlled since the direction and rate of the mass transport are affected only by the external electrical drive. The mass delivery of metal atoms in CNTs is also applicable in nanorobotic spot welding using electromigration processes. The use of nanorobotic manipulation to transport copper through inter-nanotubes has been demonstrated by Dong *et al.* [102]. The bias voltage required for the transportation of copper is between 1.5 and 2.5 V, with CNT diameters ranging from 40 to 80 nm. Uniform tubules have often been used to transport metal along CNTs [103]. The investigation involving the flow of metal in straight channels lacks the consideration of the effect of a channel junction on flow processes. By including a channel junction in the study of CNTs, the contributing factors of this feature can be addressed and a better understanding of the transportation of encapsulated metal in CNTs can be provided. Besides that, flow conditions such as the electromigration processes are equally important in resulting in the transportation of metal in CNTs.

1.2 Research motivation

The motivation behind the study of biomolecules in CNT channels is based on the possibility of the use of CNT channels as a delivery system for biomolecules in gene therapy and drug delivery etc. The flow velocity of any transported molecules in straight tubules remains relatively constant throughout the entire flow processes. However, the feature of a junction in CNT channels may act as a nozzle or diffuser for the flow, which alters the velocity of the transported molecules. Hanasaki *et al.* have shown that the velocities of water molecules increase as the molecules flow across a nanotube junction to a narrow nanochannel [31]. The role of CNT channels as a delivery system is therefore

worth investigating. The analyses for this study not only focus on the flow of the water molecules in the systems, but also on the changes in the shape of the delivered oligonucleotide in order to understand the effect of CNT junctions on the molecules flowing within the channels. The main attention given in this study is to understand the size effect of the CNT channels and the molecules within the channels, based on the interactive potentials between them.

An extension from this study is to investigate the flow of metal atoms within CNT channels due to electromigration processes. However, the preliminary stage of building the system requires a better understanding of the behaviour of metal atoms at temperatures lower than the melting point, and the reliability of the simulation programs required. Therefore, the study of premelting phenomena for aluminium serves these purposes. The program created for the study of premelting of aluminium is used at a later stage to simulate the flow of metal atoms in CNT channels.

The simulation of the premelting of aluminium uses the same ensemble as the simulation of biomolecules in CNT channels, which is based on the controlled amount of atoms/molecules, volume and temperature. By using an EAM potential for the system of molecules, we can understand the effect of the potential on atoms bonding strength and the effect of melting temperature achieved in a simulation environment. These results provide insights into the difference that could occur between simulation results and the real world phenomena. The transportation of metal atoms in a CNT channel is based on electromigration processes. It is therefore necessary to look into the method of rescaling the velocities of the metal atoms, such that the drift velocity of the moving metal atoms in CNT channels is not affected significantly.

The study of copper atoms transported in CNT channels is motivated based on the flow phenomena of metal atoms in CNTs. Since the interactions between molten metal atoms are much stronger as compared to liquid molecules, the transport processes of metal atoms along CNT channels are expected to differ significantly compared to the flow of organic or water molecules along CNT channels. Besides focusing on the change of the atomic configuration of the metal atoms along a CNT channel junction, the outcome of the flow parameters at different tube sizes are also important in understanding the nature of the flow between metal atoms in CNT channels. The detail reasoning for the interaction between the flowing encapsulated atoms and the CNT channel cannot be revealed through experiments. MD simulations are therefore crucial in attempting to provide insights into the working principles of these atoms, which results in the various flow phenomena in CNT channels. The analyses for this study highlights both the change in the structure of the metal atoms in CNT channel and the resulting flow phenomena of the metal atoms due to various conditions.

1.3 Objectives

The main objectives of this research are to study the flow phenomena of solvated oligonucleotide in CNT channels, develop a novel method of rescaling velocities for the MD simulations of electromigration of metal atoms in CNT channels, study the flow phenomena of metal atoms in CNT channels, and investigate the influences of CNT junctions on the flow of a solvated oligonucleotide and copper atoms. All these studies are conducted using the MD simulation methods.

1.4 Scope of the thesis

The scope of this thesis consists of:

- Examining the flow patterns of the fluid (water molecules) and oligonucleotide in CNT channels due to pressure.
- Investigating the effects of CNT junctions on the folding of an oligonucleotide.
- Analyzing the effects of the interactive potential on aluminium atoms at the (110) surface planes.
- Developing a novel method for rescaling the flow velocity of copper atoms along CNT channel due to electromigration.
- Investigating the effects of CNT junctions on the flow of copper atoms.
- Investigating the effects of the flow conditions of copper atoms along CNT channels.
- Investigating the flow phenomena of copper atoms along CNT channels.

1.5 Organization of the thesis

This section provides the information regarding the following chapters in this thesis. The thesis is organized as follows:

- Chapter 2 provides an overview of the existing studies of fluid and molecular flow in CNT channels.
- Chapter 3 explains the methodology undertaken for this research work and the proposed ideas for solving the limitations of existing studies.

- Chapter 4 presents the studies of fluid and an oligonucleotide flow in CNT channels.
- Chapter 5 highlights the effects of interactive potential on the premelting behaviour aluminium atoms.
- Chapter 6 presents the studies of copper atoms in CNT channels.
- Chapter 7 concludes the work that has been done and suggests future work for this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Molecular dynamics and CNTs

MD is an important method used in bionanotechnology. This is because it provides nanoscale images and also predicts the nanoscale interactions of unfamiliar combinations of biological and inorganic materials. Lu *et al.* describe the use of a SWCNT as a sensor and the use of nanopores for DNA sequencing [104]. The translocation of DNA through synthetic nanopores and the feature of nanodiscs can be examined using molecular modelling as the methodology. These studies give insight into the characteristics of biological molecules when interactions of biomolecules with nanotubes or nanopores are investigated using MD simulations and theories. The interactions involved may be van Der Waals interaction, ionic atomic charges, screening effect of nanotubes, etc.

The study of properties of biomolecules can also be achieved using MD to simulate the model of biological materials at different conditions. Pressure, for example, could induce denaturation on a biological macromolecule that resulted in a different effect compared to other influencing factors such as temperature or denaturants [105]. However, the disadvantage of MD is that the required simulation time is often longer than expected if accurate results are desired. Yet, MD is still desirable for many aspects of studies because in terms of cost and safety, MD still provides the better option than conventional experimental tests.

2.1.1 Properties of CNTs and connected CNTs

The study of CNTs and their applications has been shown to be essential for the advances in nanotechnology. Researchers have been studying various aspects of CNTs in order to fully understand and utilize their full potential. CNTs can be put into applications in the areas such as biomedical engineering, material science, nanoelectronics, etc. One of the important properties that determine the characteristics of CNTs is the chirality vector, C_h . This vector distinguishes the differences in the size and the chirality of the nanotubes.

The other property that is of interest is the electrical conductance of CNTs. R. Saito *et al.* have shown that the three-dimensional connection between two different diameters of CNTs can be calculated by the use of projection method and the method also determines the tunnelling conductance for metal-metal CNT junctions and metal-semiconducting CNT junctions [106].

According to the simulation study by Kowaki *et al.* [107], the melting temperature for an infinite graphite sheet, so-called graphene, is about 5800 K. However, Zhang *et al.* have shown that the premelting of SWCNTs is at 2600 K, and the melting temperature of perfect SWCNTs is about 4800 K [108].

2.1.2 Functionalization of CNTs

By understanding the properties of CNTs, many researchers are looking into various possibilities to functionalize CNTs to suit various applications. Thus, the system using bio-molecules to functionalize nanostructures has been a major interest for many

studies. Various aspects are suitable for such applications, such as in medical areas, electronic and other more. One of the most common and widely studied models involves the use of DNA and CNTs. The behaviour of DNA when being in contact with CNTs had been examined quite intensively especially to deepen the understanding of the characteristics of each of these molecules.

The studies of transportation, interaction, encapsulation, immobilization and functionalization of DNA in CNTs provide fundamental understanding of the advances in which DNA can be interacted with CNTs [13]. Most of these interactions involved the bonding of Van der Waals forces, π bonds and even electrostatic interactions. Besides interacting with CNTs, DNA can also disperse CNTs by the helical wrapping of DNA around the tubes [7]. However the molecules involved in the dispersion process were sequences of non-natural DNA strands.

2.1.3 Applications of CNTs

CNTs and carbon nanofibres are potential materials for biomedical applications. Quite often, organic materials such as proteins and DNA are used in altering or defining the response of CNTs with the biological environment. One of such example is the binding of antibodies with carbon nanofibres that was found to be successful using the treatment of poly (L-lysine) (PLL) [8]. Such modification of carbon materials is important in order for the binding of the two materials to be used for different applications. Other treatments of CNTs are also available such as oxidative acid treatment for aqueous dispersion or non-covalent stabilization [109]. These processes are available for the purification of as-produced materials.

Another aspect of CNTs that is worth understanding is the biocompatibility of CNTs. Lin *et al.* have discussed the solubilisation via chemical modification and functionalization for bioconjugated CNTs [109]. In recent advances, the use of CNTs had also developed into other applications such as nanocircuitry or act as a substance for neuronal growth. As CNTs come in semi-conductive and conductive forms, it is crucial that CNTs can be modified chemically or separated into segments of nanoscale building units for bioelectronic and nanobiotechnology applications [11]. Although the future of a biomolecules-CNTs hybrid system is promising, the fundamental results and practical applications that have been uncovered are still at the tip of the iceberg. Hence, more efforts are still required for the studies of the interdisciplinary system for biomolecules and CNTs.

The heterojunction of two CNTs can be determined using the indices (i,j) and the length of the tubules [110]. However, it is only applicable to symmetrical junctions. Calculations for surface tension and surface energy of LJ fluids from radial distribution function and density profile are achieved through the modification of Lekner and Henderson's statistical mechanics [111].

2.1.4 Advances of CNTs

The study of CNTs has been quite intensive over the past 10 years due to the variety of applications in various fields. Some of the potential areas in biomedical engineering are diagnostic tools and devices, biopharmaceutics, implantable materials and devices, surgical aids, etc [6]. In order to have a better understanding of the properties of CNTs, several bonding models have been come up with to explain the

interaction between the molecules. Some of the models that are available include the force field model, bond order model, semi-empirical model and the interlayer potential model [112]. These potential models are important for determining the mechanical, electrical and thermal properties of CNTs accurately.

Due to the size and structure of CNTs, the measurements of the properties of CNTs have become quite a challenge to many. Erik *et al.* [113] have explained that the few possible techniques of producing CNTs, which include arc-discharge, laser ablation, gas-phase catalytic growth from carbon monoxide and chemical vapour deposition (CVD), are able to characterize CNTs and the mechanics of CNTs. Another promising advancement for CNTs is the integration of CNTs with other materials to form nanotube-based composites. The composite materials have shown to improve in terms of structural strength and stiffness due to the presence of CNTs.

The production of CNTs with 0.5 nm diameters was achieved by Sun *et al.* [114]. However, the smallest CNT diameter was predicted by Sawada *et al.* to be around 4 Å [115]. Lortz *et al.* have fabricated nanocomposites with 4 Å of CNTs [116], whereas Zhao *et al.* have shown that the smallest CNT is 3 Å in diameter [117].

2.1.5 MWCNTs and protein nanotubes

Multi-walled carbon nanotubes (MWCNTs) are another form of nanotubes that exist apart from the SWCNTs. MWCNTs have great potential to be used as a building material in various fields, e.g. nanoelectromechanical system, because the nanotubes provide nanoscale mechanical and electrical properties that are suitable for constructing

nanodevices and nanomachines. Zhou *et al.* predicted in MD simulations that MWCNTs can be self-assembled from SWCNTs of various sizes using the “bottom-up” approach and can be separated into SWCNTs too [118]. The advantage of such a method is to provide the possibility of building various MWCNTs that have specific features and properties for the applications in nanotechnology.

Other options such as the organic nanostructures are also available for the use of the nanostructures as a building material for nano-components. The artificial self-assembled protein nanotubes are alternatives for the applications in molecular biomaterials. This material had been proven to be stable and relatively strong for practical applications [119]. Graveland-Bikker *et al.* found that α -lactalbumin nanotubes are stiffer than whole living cells after comparing with the Young’s moduli of other biological structures.

2.1.6 Diffusion of water through nanotubes

Dynamics of water molecules in CNTs play an important role in providing insight into the functionalization of CNTs. The transportation of water molecules through nanoscale channels, such as the SWCNTs, had been utilized to explore the on-off gate feature of CNTs [9]. This simulation study has shown that one of the various possibilities of developing CNTs into a nanoscale device, instead of only acting as a transporting channel for water molecules. However, the mechanism of water molecules travelling through CNTs is another aspect to be considered for the study of the transportation of nanomaterials.

The simulation of water diffusion through infinitely long narrow CNTs had shown that the concerted motion of water molecules depends not only on the interaction between water-water and water-carbon, but also on the number of water molecules and the temperature of the system [26], as shown in Figure 2.1.1. These conditions affect the speed of the diffusion and also the effectiveness of the diffusion.

Figure 2.1.1 Representative equilibrium simulation snapshots of water confined in (8,8) SWCNTs at 298 K. [Striolo, Nanoletters 6 (4) (2006) 633]

More studies can be done to verify the influence of various membrane thicknesses with the pore entrance/exit effect between water molecules and CNTs. The study of water molecules in CNTs has also suggested that CNTs might be exploited as unique molecular channels for the transportation of water molecules and protons [27]. This study focuses much on the hydrogen bonding between water molecules and also the attraction between the nanotube wall and water molecules. The hydrogen bonding between water molecules results in the chain like fashion of water flowing through the nanotubes. The tube size that is used for the study of such phenomena is 8.1 angstrom in diameter.

2.1.7 Nanochannels

The study of the CNT as a nanochannel was done to explore the mechanical properties of such channels and to understand the behaviour of fluid within these channels. Nanochannels can be built as a nozzle or diffuser, depending on the direction of flow in the channels. Dynamics of molecules within nanochannels has been investigated by many researchers in order to understand the effects of various interactive forces present between the nanochannels and the molecules within the nanochannels. For example, the behaviour of water molecules in various diameters of nanochannels was shown by Hanasaki *et al.*, using the method that they had developed, fluidized piston model [31]. Besides that, they also developed a new definition for internal radius of the CNT in order to reflect a much closer result for the streaming velocity ratio.

Although CNTs are hydrophobic in nature, the hydrophobicity is affected by the degree of flexibility of the nanotubes [120]. The radial collapse of CNTs on the other hand is affected by the presence of water molecules because of the interatomic interactions between water molecules and CNTs. These findings and calculations helped to explain the magnitude of the interactive forces that can exist within carbon nanochannels by comparing the original sizes of the nanochannels with the sizes of the nanochannels after the presence of water molecules. The size of the nanochannel can be affected by the presence of other molecules within the nanochannel. Thus, it is important to consider the factors that would affect the accuracy of the result for any simulation that requires the use of nanochannels with any other molecules within it.

2.2 Biomolecules

2.2.1 Conformations of DNA

Conformation of DNA is an important factor to be considered when DNA is used in nanotechnology and bioengineering. The change in the shape of DNA that occurs during simulation provides insightful information regarding the forces and interactions that are involved between DNA and the other molecules present. The orientation of DNA suggested that DNA is likely to be affected by factors such as charges, hydrophobicity and roughness of the surface that the DNA is attached to [19]. These conditions are necessary for setting up the parameters required for running simulation of DNA and other substances such as CNTs, graphite substrates and many more. By inducing forces, the conformational changes of DNA show more a detailed molecular mechanics principle behind such phenomena.

Different DNA bases are also another condition to be considered for the effect of conformational changes as the bases affect the overall ability of the DNA to interact with other molecules due to the different energy involved for each base. Gao *et al.* have shown that the adhesion of a single stranded DNA (ssDNA) segment with a graphite sheet can be overcome by a peeling force that depends on the peeling angle and the elasticity [20]. These results suggest that these conditions are essential for systems that incorporate mechanics of bio-nano-hybrid materials. However, the scope of the study did not include the contribution of entropy to the ssDNA. Besides that, statistical mechanics approach is not considered too.

2.2.2 DNA transportation

Transportation of DNA through CNTs is another part of the study of the functionalization of CNTs. The insertion of a DNA oligonucleotide into CNTs show the distribution of DNA and water molecules within the CNTs [32], as shown in Figure 2.2.1. It was shown that the encapsulation was dependent on the van der Waals force of nanotubes and DNA, whereas insertion of DNA into CNTs was influence by the tube size of nanotubes.

Figure 2.2.1 Simulation snapshots of a DNA oligonucleotide (8 adenine bases) interacting with a (10,10) CNT at 0, 30, 100 and 500 ps. Water molecules are not displayed for clarity. [Gao *et al.*, NanoLetters 3 (4) (2003) 471]

The study of the dynamics of DNA in CNTs is essential because the conformation of DNA explains the various ways DNA can be affected when being inserted into the nanotubes. External factor such as the concentration of ionic molecules inside the nanotubes was shown to have little effect on the structure of DNA [16]. Another point to be taken note of is when a double stranded DNA is used, a smaller CNT, e.g. 30 angstrom in diameter, would result in more pronounce effect of end fraying. The frayed ends of the

free base of DNA on the nanotube would cause the base to adhere to the side of the nanotube. Once the base is attached, it would not be detached from the nanotube.

On the other hand, the entry and exit of RNA through CNTs can be determined by the sequence of the oligonucleotide and hydrophobic interactions respectively [17]. Electrostatic effect was also considered in RNA translocation through CNTs in explicit solvent to prevent RNA molecules from being trapped hydrophobically in the membrane. An electric field that is applied to RNA molecules simulates the condition of an electrophoresis process. It is important for the studies of both DNA and RNA flowing through CNT membranes, or nanotubes made of other biological molecules in order to understand the difference in the dominant driving factor for the transportation through these channels.

2.2.3 Translocation of biomolecules

Translocation of biopolymers through nanopores was investigated in order to obtain information such as tunable pore sizes, stability, voltages of electric field and concentration of solution of the processes. By slowing down the translocation process of the DNA molecules [21], the bandwidth requirement for detecting the DNA molecules in a sensing system can be reduced. The reduction of the bandwidth provides a more efficient way of detecting molecules in the translocation process.

There was another group of study that explains the dynamic of oligonucleotides at nanopores using the theoretical model where hydrodynamic drag and electrical driving force were considered [121]. This resulted in fast translocations, where the translocation time was slower than the Zimm (non-free draining) time. The reason for the fastness was

because of the use of double stranded DNA. Double stranded DNA has a larger persistence length, and hence a longer relaxation time, as to compare to a single stranded DNA.

Besides nanopores, inorganic nanotubes were used for the study of nanofluidic devices for the single DNA molecule sensing. Fan *et al.* showed that there was a critical concentration that affects the ionic current during translocation of a single stranded DNA [91]. In that study, they found that the critical KCL concentration for the translocation of DNA through a nanotube using ionic current is $\sim 0.79\text{M}$. These findings have yield new insights into the translocation events of DNA.

2.2.4 Conditions affecting the transportation of biomolecules through CNTs

Molecular transport in CNTs is determined by many factors. Interfacial interaction between transported molecules and CNTs, the molecular interaction energy and entropy, chemical potentials inside and outside of CNTs, number of monomers involved in the transportation and molecular conformations are some of the areas that need to be considered for the processes of molecular diffusion and translocation [14]. Besides that, the pore size and hydrophobicity also play a part in the speed of molecular transportation and the ease of the molecules to enter the nanotubes [15]. The technique used by Storm *et al.* was known as DCV-GCMD, which is the combination of grand canonical Monte Carlo (GCMC) and MD simulations. They found out that for a hydrophobic nanotube, water and methanol molecules are harder to enter the tube, but

diffuse quickly once the molecules had entered the tube, and vice-versa. The resultant conclusion was that the transportation in a hydrophilic tube is faster than a hydrophobic tube.

The mechanisms for the transportation of molecules through nanopore/nanotubes are essential for understanding the functionality and design of nanosyringes. One of the studies has shown that hydrophobic cylindrical macromolecules are used to construct a nanosyringe and the nanosyringe is inserted into a biomembrane instead [122]. That study explained the two-step processes that have taken place on the membrane surface and the reorientation of the molecules. The results from this study suggested that the transport of hydrophilic groups across a membrane can be possible when the lipid-molecule interaction is established, such as the adhesion of the positive charged residue of antibiotic molecules with the negatively charged lipids. Water molecules however are vital for the spontaneous transport of the tube end across the membrane core.

2.3 Flow phenomena and molecular driving force

2.3.1 Insertion of peptides into CNTs

Besides using DNA, peptides are one of the substances that are often used in simulating the insertion of molecules in CNTs. One of the main purposes for such a simulation is to understand the driving forces that exist in the insertion of molecules into the CNTs. Liu *et al.* have shown that the dominant interactions resulting a self-insertion of peptides into nanotubes are the electrostatic interaction and the van der Waals interaction between the nanotubes and peptides [18]. The roles of the interaction forces

between different molecules often determine how successful can molecules being inserted into CNTs. Sometimes, other effects such as the hydrophobic effect, affect the chances of molecules to be inserted into CNTs. In such cases, applied forces in these systems would increase the possibility of having the molecules inserted and transported across the CNTs.

2.3.2 Fluid flow in CNTs

Bhatia *et al.* have recently developed a theory that is discussed of a single-component transport in nanopores [123]. The theory combines molecular oscillations with a viscous flow model. The kinetic molecular sieving between closely sized molecules is explained in the theory. The reflection in CNTs is nearly specular. At low densities where viscosity is negligible, the theory fits well to the observed phenomena.

In a steady-state flow, the flow velocity in a pipe is expressed as a function of the distance from the wall, z , [124]. The equation is shown as $U_y(z) = (\rho'g/2\eta)[(\delta + h)^2 - z^2]$, where the channel width is denoted as $2h$, the viscosity as η , slip length as δ , and the driven gravity as $\rho'g$ or pressure gradient as dP/dy in the y direction. The slip length is conventionally assumed to be zero. However, in nanopipes, the slip length is not negligible and hence affects the flow of the fluid. One of the applications of nanopipes is to be used as a transporting mode of biomolecules. Nonetheless, the feasibility of the mechanism for controlling the flow still requires a lot more investigation.

Based on the study by Majumder *et al.*, the flow in CNTs is four to five orders of magnitude faster than the fluid flow predicted from conventional theory [12]. This is

because ordered hydrogen bonds created between water molecules and the weak interaction between the wall of CNTs and the fluid molecules result in an almost frictionless flow.

The diffusion of methane, ethane and ethylene through CNTs was predicted by Mao *et al.* [125] using simulations. The results of the study show that the velocities of the molecules are greatly affected by the diameter of the tubules due to the interaction between the carbon atoms in the tubules and the molecules flowing within the tubules. As the diameter of the tubules increases, the flow of the molecules changes from single-file diffusion to normal mode diffusion.

Based on the study of helium and argon atoms flow in CNTs, the simulation of dynamic CNTs would result in a faster fluid flow than a static one [126].

2.3.3 Effects of forces and pressure on molecules

MD simulations are often performed with forces applied to a system of molecules. The purpose of applying various degrees of forces is to simulate a condition whereby gravity or pressure is induced to the molecules of the system that is studied. Ziarani *et al.* have shown that there are two methods of applying forces, namely the sinusoidal force and the pulse force [127]. These forces have different effects on the kinetic energy and the temperature of the moving molecules, distributed along the direction of the flow due to the applied force. However, effects on the atomistic solid walls due to the change in the kinetic energy and the temperature of the moving molecules have yet to be investigated. The difference is that the effects on the solid atoms are influenced by the moving molecules and not by the magnitude of the applied forces.

Besides inducing forces to a MD system, another method such as Fluidized Piston Model, FPM, [30] can also be employed. This method is used to drive the polyatomic fluid flow with a pressure gradient at a relatively lower computational cost. The limit of the fluidized piston model is that it could not produce the required streaming with the desired temperature for diameters of cylindrical channels that are of the order of about one or two fluid molecules. As compared to FPM, the disadvantage of an induced force is that the force could not result in a constant acceleration for a polyatomic fluid flow system. This is due to the fact that different molecules have different molecular weights and the application of the same magnitude of force would result in different accelerations for all the molecules/atoms present in the system.

2.4 Nanowires and metal atoms

2.4.1 Nanowire in CNTs

Since copper wire bonding has become increasingly important in wafer fabrication, the understanding of the mechanism of copper nanowire stretching is hence essential. The magnitude of force relaxation and period of yielding for copper nanowires at the high stretch velocity are lower compared to the low stretch velocity, whereas the first yield and rupture is relatively faster at the high stretch velocity [128].

In order to deepen the understanding of nanowires, the study of ultrathin wires using MD simulations is essential. Ultrathin copper nanowires encapsulated in CNTs are investigated by Choi *et al.* [129]. The copper nanowires in CNTs are formed as multishell packs composed of coaxial cylindrical shells, as shown in Figure 2.4.1. As the diameter

of CNT increases, copper nanowires have a face-centred-cubic structure similar to bulk. Their study found that at low temperatures, free standing copper nanowires are unstable whereas copper nanowires that are encapsulated inside CNTs are maintained well. This is because the walls of CNTs increase the stability of copper nanowires.

Figure 2.4.1 Four snapshots for Cu nanowires growth in a (10, 10) CNT. From the left side, the numbers of the inserted Cu atoms are 30, 100, 200 and 307, respectively. [Choi *et al.*, Physical Review B 68 (2003) 193405]

Another similar study that focuses on nanowires is the study of sodium nanowires. The MD simulations of the encapsulated sodium wire in a CNT are demonstrated by Kang [130]. As shown in Figure 2.4.2, it is found that linear chain of Na atoms is formed in a (4,4) CNT and zigzag structure and multi-shell structure is formed in a (5,5) CNT. The helical structure of sodium nanowires with atomic strands from 3 to 15 appears when the radius of CNTs increases further.

Figure 2.4.2 For (n, n) CNTs with $n = 4 - 18$. Na structures encapsulated in CNTs. [Kang *et al.*, Physica B 351 (2004) 144-150]

2.4.2 Surface diffusion and premelting of materials

The study of diffusion on surfaces has been an important field, especially since Langmuir and Taylor provided quantitative data for diffusion parameters on a clean metal surface [39]. Diffusion on the surface affects film growths, adsorption, catalyst reactions, evaporations, desorption, etc. According to Whitehouse, surface geometry plays an important role in surface function for nanotechnology [40]. Hove has also highlighted the essential relationship between surface science and nanotechnology [41].

The premelting for various metals is investigated intensively using MD simulations in recent years. The premelting phenomenon is assumed to be a surface-initiated process, or more generally an interface-initiated process [131]. Based on that assumption, the premelting effects can be expected on free surfaces or interfaces, which then propagate melting into the bulk. The surface premelting effects are associated with the formation of a liquid layer on the surface before melting. Local melting at the surface-vapour interface may occur when the following equality is satisfied: $\delta F + \Gamma_{sv} = \Gamma_{sl} + \Gamma_{lv}$,

whereby $\delta F < 0$, Γ_{sv} , Γ_{sl} and Γ_{lv} are the interfacial free energies and the subscripts s , l and v stand for solid, liquid, and vapour respectively [132]. Based on the relationship shown, it is clear that having a separating phase (liquid phase) in between the solid-vapour interface is thermodynamically more efficient for the system. Besides that, surface melting is also dependent on the orientation of the crystal-face of the metal [44]. For example, the Au surface with the (111) orientation does not favour the premelting phenomenon to occur [45]. Premelting was also not observed on the Al(001) surface [133].

The structure and dynamics of the premelting of the Al(110) and Pb(110) surfaces have been investigated [46, 134]. It was reported that the onset temperature for the surface melting of Al(110) surfaces is estimated to be at the temperature of 770 ± 25 K, with no lateral long-range order. Gobel *et al.* have established the properties of Al(110) surfaces through LEED experiments [47]. According to Polcik *et al.*, the Al(111) surface does not exhibit surface melting [135]. Besides that, they also found that Al atoms in the $[1\bar{1}0]$ rows have stayed intact up to the melting point. They have concluded that Al atoms possess the residual order of the quasiliquid, which is combined with liquidlike behaviour in the $[1\bar{1}0]$ segments.

MD simulations are often performed for the study of atomic behaviours of metals because experiments are often difficult to conduct and the results are sensitive to the external disturbances of the experimental equipment. In the study of surface structure of metals, the results obtained from MD simulations are compared with the experimental results obtained through low-energy electron-diffraction (LEED) measurements. Mikkelsen *et al.* have studied the temperature dependence of the surface structure and

vibrational amplitudes of the atoms on an Al(110) surface [136]. Based on their findings, they concluded that there are uncertainties in the determined values of the fourth and deeper layers of the Al(110) surface obtained through LEED measurements. This is because the readings for deeper layers have poorer sensitivity and the errors are due to the treatments of vibrations in the LEED analysis.

The premelting of Al(110) surfaces can be investigated using MD simulations. The interactions between the Al atoms can be described using various potential models. Up till now, the potential models that have been used in MD simulations are the pseudopotential model [53], the LJ potential model [54], the effective medium theory [42, 55], etc [137]. Conventionally, LJ potential is used to describe the interactions between organic molecules [56, 57]. However, experiments and theoretical studies have shown that LJ interactions can also be used to reasonably predict certain MD phenomena of the surface atoms of a metal [58, 59]. However, only two elastic constants can be prescribed to pair potentials for solids, rather than three. In the case of LJ interactions, only one elastic constants can be modelled [138]. Pair potentials are therefore unable to be used to model surface relaxations, reconstructions or defects properly [139]. Besides that, Pavlovska *et al.* have reported that the LJ potential model does not describe the interactions of Al atoms as realistic as the effective medium theory [140]. Since no study has yet reported the surface melting phenomenon of Al(110) surfaces using the EAM potential [61], it is appropriate and necessary to perform MD simulations of the Al(110) surface with this potential model describing the Al atoms.

2.4.3 Capillary adsorption in CNTs

CNTs have many applications, such as biomolecules transport, sensing, etc. One of the many interesting applications is the use of CNTs for making nanowires. There are several mechanisms for developing nanowires. Capillary action can be used to describe the filling of liquid into CNTs. Ajayan *et al.* have demonstrated the filling of Pb into CNTs through the opening of the tube ends [141]. The diameters of the filling lead in CNTs are able to change according to the size of the internal hollow structure of the tubules.

According to Dimitrov *et al.*, the rise of meniscus in nanotubes during a capillary action exhibits a $(\text{time})^{1/2}$ law [142]. The use of Lucas-Washburn law to describe the capillary phenomenon requires a modification of the law which includes the addition of the slip length term, δ , into the formula. The use of Langevin thermostat in simulations could slow down the rise of the meniscus in capillarity.

A study by Schebarchov *et al.* has found that the filling of metal nanoparticles in CNTs is carried out via capillary action, even with contact angles $>90^\circ$ [35]. If the liquid has a contact angle of more than 90° , the capillary force will depend not only on the pressure difference across the meniscus, but also on the Laplace pressure acting on the surface of the nanodroplet.

The opening of capped hollow CNTs is reported by Ajayan *et al.* [143]. The oxidation mechanism of the CNTs occurs layer by layer, which peels from the outer layer in order to initiate the opening of the tip. This phenomenon occurs at a reaction temperature higher than C_{60} but lower than the reaction temperature for graphite basal planes. According to their results, the filling of materials in CNTs is easier in a one-step

process from a closed tube than a two-step process which involves the opening of the cap first followed by the filling process.

The low surface tension material is found to wet CNT surfaces and even filling the tubes through capillary action. The study by Ajayan *et al.* has shown that the coating of CNTs by V_2O_5 is possible and that the use of CNTs as templates for thin-film ceramic structure is promising [144].

According to Hwang *et al.*, the capillary force on copper nanoclusters causes the filling of the material in CNTs, whereas the periodic barrier result in the directional movement of the particles [38].

Based on the study conducted by Marmur, the penetration of a droplet of a finite size into a capillary is dependent mainly on the drop size [145]. For a microgravity environment, a complete penetration of the droplet is possible for contact angles of up to 114° . The height and rate of penetration for a finite sized droplet are higher than that for the infinite liquid reservoir.

The capillary effect of palladium atoms in CNTs has been tested by Schebarchov *et al.* using MD simulations [146]. The capillary absorption of the palladium droplet was found to be in good agreement with Marmur's equation and that absorption of nonwetting liquids (such as metals) in CNTs is possible as long as the droplets are sufficiently small.

2.4.4 Filling of metal atoms in CNTs

Capillarity-induced filling, carbon arc discharge method, wet chemical techniques and pyrolysis are some of the techniques used in filling CNTs with metal atoms [36]. The filling of copper atoms in CNTs using laser vaporization techniques has been

demonstrated by Kokai *et al.* [147]. The advantage of this technique is that copper atoms are filled more efficiently into CNTs even at low copper content. The filling of copper in CNTs is demonstrated by Zhang *et al.* [148], using copper as the catalyst for the reaction. The feeding of hydrogen gas in the process inhibits the formation of carbon and thus facilitates the construction of nanowires with hollow structures in CNTs. Continuous growth of copper-carbon nanowires is driven by thermal driving forces. Besides copper, filling of CNTs can be achieved in CNTs with diameters of as small as 1.4 nm with carbon atoms [149].

Filling of iron in CNTs as small as 1.4 nm was achieved by Hatakeyama *et al.* [70], who use ferrocene as a starting material at 180 °C. On the other hand, the filling of iron atoms in CNT is also demonstrated experimentally by Borowiak-Palen *et al.* [86]. The resulting iron-filled SWCNTs show ferromagnetic behaviour even at room temperatures. Besides filling metal atoms, other interesting materials that have been explored in the filling of carbon nanotubes include fullerene [150].

The growth of palladium nanowires in MWCNTs is achieved using a microwave plasma-enhanced chemical vapour deposition system [151]. In this experiment, bamboo-like and Y-shaped CNTs can be observed, whereas the pentagonal and heptagonal defects would result in a positively curved surface and negatively curved surface respectively. The production of cobalt nanowires in CNTs can be achieved using a simple chemical process involving the catalytic synthesis of CNTs [152]. This process is able to produce Co nanowires of several micrometers long with a radius of 10 nm.

The formation of ultrathin copper nanowires and nanotubes at low temperatures is demonstrated by Kang *et al.* using classical MD simulations [153]. According to their

findings, helical multi-shell (HMS) copper nanotubes are unstable structures that can only be maintained at low temperatures. This is because the inner tube structure tends to collapse into the empty core of the inner shell. Kang *et al.* have found that cylindrical multishell (CMS) type copper nanowire has low vacancy formation energy in the core whereas that the maximum formation energy of an adhered atom exists in a 16-11-6-1 copper nanowire [154]. They concluded that due to the difference in the formation energy, vacancies that are found on the inner or outer shell tend to migrate to the core of the structure.

2.4.5 Potential usage of metal filled CNTs

One of the potential applications of metal filled CNTs is the use of such molecular hybrid in controlling the heating of tumour tissues, where CNTs are filled with ferromagnetic fillers [87]. Copper filled CNTs are important not only for the formation copper nanowires, but also for the usages in nanorobotic spot welding. The inter-nanotube mass transport of copper atoms along CNTs has been demonstrated by Dong *et al.* for the application in spot welding [102]. Due to the effective barrier of carbon atoms against oxidation, the copper core is ensured with long-term stability and favours the conservation of the filled material. Apart from that, copper-filled CNTs have also been observed to be used as nanoscale switches [155]. The electrical circuit along the copper filled CNTs is shorted when the electrical resistivity of the hybrid system drops.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Advantages and limitations of existing flow methodologies

in CNTs

To date, many studies of biomolecules using MD simulations have been carried out to show the dynamical behaviour and conformations of proteins. These studies are essential because the world of complex molecules is often too sophisticated for analyses based on experiments.

One of the studies that have attracted much attention is the investigation of DNA molecules and CNTs. This is because these elements play an important role in nanotechnology and biotechnology. Many efforts have thus been made to the development of DNA-CNTs experiments and DNA-CNTs simulations for analyses.

In recent years, the studies of combining DNA molecules and CNTs for various potential applications have been explored widely by researchers [156-161]. Most of the studies have explored the various possibilities of functionalizing CNTs using DNA molecules. However, these studies have focused much on the adsorption of biomolecules on the surfaces of CNTs, but not much on the adsorption of biomolecules in channels of CNTs. Liu *et al.* have predicted using simulations that the encapsulation of biomolecules in CNTs can be a potential form of delivery for drug, vaccine and even gene [162]. Hence the understanding of the encapsulation processes or even flow processes in CNTs is essential for building such systems.

The insertion of ssDNA into CNTs has been demonstrated by Okada *et al.* [25, 163]. In their study, the average diameter of the CNTs used is about 1.5 nm. The size of the tubule is suitable for the analyses to be performed in MD simulations. The success of ssDNA insertion in their study has proved that the size of CNTs used in MD simulation studies is rational and the flow of biomolecules in nano-size channels is possible. Nonetheless, the translocation of ssDNA in CNT channels with varying diameters has not been investigated yet. Therefore the simulation analyses for the flow along CNT junctions are essential, because the flow of oligonucleotides in CNT channels with junctions of varying diameters would soon be a reality. The investigation of CNT channels is important because the change in the diameter along the channel could act as a nozzle or diffuser for the transported materials, providing an alternative means of molecular transportation.

Another crucial aspect of the study of the flow of biomolecules in CNTs is the changes that occur in the shape of the biomolecules. This is because the structure of the biomolecules is not rigid and hence variation in external influences can result in the bending or rotation of the bonding between atoms and molecules. The conformations of the oligonucleotides are thus investigated in straight tubules of CNTs [23, 24]. However, these studies do not address the changes occurring in the oligonucleotide flowing through CNT channels with junctions of varying diameters. The interactions between the tubule, the oligonucleotide and the pressure flow in the solution result in the folding or stretching of the oligonucleotide.

Besides focusing on the importance of biomolecules, another focus is on the potential usage of nanowires in nanotechnology, and the delivery system for metal atoms.

In recent years, the growth of miniaturized components has been increasing greatly. Hence nano-components, such as copper nanowires, are becoming even more important for the construction of nanoelectronic components. The potentials of using CNTs as a template to grow nanowires are being focused on greatly these days [90]. The process in making nanowires requires copper particles to flow within CNT channels. Sometimes these channels may have different diameters along the tubules due to bending of the tubules or irregularities along the inner walls of the channels. Hence, the understanding of the flow phenomena of metal particles in CNT channels is important.

Experimental studies have shown that growth of copper wires in CNTs is possible [94, 164, 165]. Metal atoms can fill CNTs by capillary action, wet chemical processes or chemical vapour depositions. Due to weak solubility of copper with carbon, the surface of a CNT is not covered by copper atoms during an encapsulation process. During the encapsulation process, copper fills the inner tubule of a nanotube through capillary force or by thermal expansion of copper. The delivery process for copper atoms in CNTs however, is based on electromigration [166]. So far, the filling of copper into CNTs is conducted in straight tubules, and the diameters along the tubules are often assumed as constant. However, in reality, CNTs exist in many forms. CNTs may have kinks, junctions, branches of irregular diameters along the channels [94, 102, 166]. Due to changes that may occur in the diameter of a CNT, it is important that the study of metal filling in a CNT covers aspects such as nanotube junctions and the transportation method such as electromigration.

The study of the characteristic flow of metal atoms could show insights into how these atoms behave and flow in CNT channels with junctions. The change in the

diameters of the tubules could result in faster flow rates across the channels where cross sectional areas are relatively smaller, or it may result in slower flow rates due to repulsive forces by the carbon atoms at the junctions. To the best knowledge of the author of this thesis, no study has yet addressed the changes in the flow velocities of the metal atoms in CNT channels.

The use of MD simulation for the analyses of metal atom flow in nanotube channels is cost effective and fast. Compared to experiments, MD simulations of fluid flow are able to describe the phenomena on the atomic scale and provide simulation details such as molecular kinetic energy, molecular velocity, pressure, etc. The concept of the simulation of metal particles flowing along nanotube junctions is novel, thus providing valuable information in this study. The complexity of the experiments for capturing the behaviour of metal flow in CNTs is an important factor that encourages the use of MD simulations as a favourable method for investigating the flow phenomena. However, the time duration required for the completion of the simulation models is dependent on the speed of the computational system. In order to simplify the simulation processes, approximation of the CNT model is also considered in designing the simulation models.

The advantages and limitations of the existing MD simulations of fluid flow in CNT channels can be summarized as follows:

Advantages of existing flow methodologies in CNTs are:

1. Generating crucial information regarding the flow phenomenon in CNTs relevant to real life applications.

2. Providing descriptions on the flow behaviour of biomolecules and metal atoms in straight CNT channels.
3. Providing MD simulation results which are close to reality.
4. Addressing the flow conditions necessary for both biomolecules and metal atoms in CNTs.
5. Capturing the detail changes of the encapsulated materials in CNTs using MD simulations.

Limitations of existing flow methodologies in CNTs include the following:

1. The existing methodologies do not address the flow phenomena of molecules and atoms along nanotube junctions sufficiently.
2. The flow conditions affecting the transport of biomolecules and metal atoms along CNT channels are not explored.
3. The potential usages of CNT channels with junctions as a delivery system are not fully considered.
4. The transport of metal atoms along CNT channels using electromigration processes is not fully understood.
5. The experiments of metal and biomolecular flow in CNT are complex and difficult to conduct.

3.2 Proposed research

Figure 3.1.1 illustrates the proposed research that is carried out throughout the entire period of this study. The proposed research consists of performing MD simulations

using LJ and electrostatics potentials for biomolecular flow along CNT channels, developing a novel method of scaling velocities in MD simulation for the electromigration of metal atoms in CNT channels, and performing MD simulations for the electromigration of metal atoms along CNT channels. The plan is divided into 3 main stages.

The first stage involves performing MD simulations using LJ as the interaction between biomolecules. Nonequilibrium simulations are carried out to study the biomolecular flow behaviour. The results from these simulations are then used to analyze the fluid flow phenomena in CNT channels and the conformations of the oligonucleotide. The analyses are done mainly to find out the dynamical flow behaviour of water molecules and biomolecules in CNT channels. The molecules that were used in this research were water molecules, a 3-base ssDNA oligonucleotide and sodium ions. The simulations were carried out using applied forces on some water in order to induce a pressure difference. Sodium and oligonucleotides are then pushed forward by water molecules in order to study the effect of these molecules in CNT nanochannel systems under a pressure difference created by the piston like effect produced by water molecules. Another focus of this study is also to find out how folding of the oligonucleotide is affected by the diameter of the channels and by the strength of the fluid flow. In order to extend the understanding of the effect of the CNT junctions on atomic flow, the study of metal atoms flowing along CNT channels is devised. This study is carried out based on a simulation program written using MATLAB.

Before performing the simulation of metal flow using this program, the MD program is tested out using the study of Al surface diffusion at premelting temperatures

in stage two. The total number of atoms used in the system is less than 1000, which is sufficient for a stable system and requires less computational time. The MD method uses the EAM potential [61] to simulate the atoms under a NVT (controlled number of atom, volume and temperature) ensemble.

The result from this study is compared with Schommers premelting results [63] on an aluminium surface. The simulations on an Al surface are performed using EAM potential, whereas simulations by Schommers are based on general pseudopotentials. These two studies are compared based on the periodicity of the pair correlation function and the mean square displacement of the surface atoms. The strength of the interaction between atoms can be estimated using the periodic structure of the pair correlation function.

Stage two also focuses on improving the simulation program, by including additional algorithms into the program such as Steepest Descent Method and a velocity rescaling method for the simulation of metal atoms in CNT channels. The improved simulation program will enhance the accuracy of the simulation and generate more reliable data. The focus of this stage is to simulate electromigration of the metal atoms to flow along nanotube channels and observe the effect of the flow along the tube junctions. The electromigration process along CNT channels will be conducted using the proposed modified velocity rescaling method.

For the last stage of the study, the simulations for the flow of metal atoms will be further investigated by varying the parameters such as temperature, diameter of the channels, initial configuration of the metal atoms, magnitude of the biased voltage and the chirality of CNTs. These conditions are expected to affect the movement of the atoms,

which in turn influence the performance of the flow. The purpose of changing the parameters in the simulations is to compare the effects of the parameters in order to understand how a CNT junction influences the electromigration of metal atoms along the channel. Therefore, comparison of the effect of flow, molecular interactive strength, forces and velocities of flow phenomena are addressed.

Figure 3.1.1 Proposed research flow chart

3.3 Proposed methods

The research work for flow studies in CNT channels has been illustrated in Figure 3.1.1, with detailed descriptions of the work presented in three stages. In order to achieve the objectives of all stages, the following methods are proposed to examine the flow phenomena of various atoms in CNT channels.

1. To investigate the oligonucleotide flow in CNT channels

The investigation of biomolecular flow in CNT channels with water as solvent is performed using a program called CHARMM (Chemistry at Harvard Macromolecular Mechanics). This program provides good description of organic molecules based on CHARMM potentials. Since organic molecules are more complex in terms of the conformation of molecular arrangements, the combination of molecular mechanics, van der Waals and electrostatic interaction allows the results of the simulations to be more accurate. The detail studies of the flow of the oligonucleotide are discussed in Chapter 4.

2. To analyze the flow of metal atoms in CNT channels using a program written using MATLAB

Since van der Waals potential does not describe metal atoms well enough, there is a need to use a more reliable potential which gives a relatively better interactive description of the atoms. EAM has been chosen as the potential for metal atoms in this study due to the simplicity of the equation and accuracy of this potential as shown by Cai *et al.* [61]. As part of the research studies of flow phenomena in CNT channels, metal atoms are assumed to have filled into CNT channels in order to simulate the flow of these

atoms. In order to test out the feasibility of the simulation program written using MATLAB, the simulation of the premelting phenomena of the Al(110) surface has been performed. The study of premelting phenomena of the aluminium surface examines the effects of the EAM potential on surface atoms when temperatures vary. This stage of the study is important because the information of the surface activity of a metal slab provides the understanding of how metal atoms behave at temperatures lower than the bulk melting temperatures. The detailed description of the premelting surface study of aluminium is presented in chapter 5.

3. To investigate flow of metal atoms in CNT junctions

The objective of the final part of the study is to understand the effect of CNT junctions on the metal atoms flowing along CNT channels. By observing the flow phenomena of metal atoms, this study is focused on finding the factors in the flow which are affected by the junction of the channels. The novel rescaling method is also used in the simulation processes to calculate the adjusted velocities based on the thermal contribution to the velocities only. This study is described in chapter 6, which focuses on the simulation of metal atoms in CNT channels. A further investigation of varying flow conditions is also addressed in chapter 6 to show how the behaviour of copper atoms changes according to the magnitude of the affecting parameters. This stage of the study provides more insight to the role of the junction towards the flow of metal atoms in CNT channels. Although the geometrical aspect of the channel junctions holds a great emphasis in the simulations, the contributing factors of the carbon atoms are not neglected since interactions due to the carbon atoms are considered in this study as well.

3.4 Theories of MD simulations

3.4.1 Ensembles

MD simulations provide information at the microscopic level, which includes atomic positions and velocities. The conversion of this microscopic information to macroscopic phenomena such as pressure, energy, heat capacities, etc, requires statistical mechanics. MD simulations compute the behaviour of a system in terms of the function of time. The computation involves solving Newton's second law of motion, $\xi = ma$, where ξ is the force exerted on the atom, m is the mass of an atom and a is the acceleration of the atom. Integration of Newton's law of motion, using different integration algorithms, leads to atomic trajectories in space and time. The force on an atom is defined as the negative derivative of the potential energy function, $-\frac{dE}{dr}$, where E represents the energy function and r denotes the distance between two atoms [167].

An ensemble is a collection of points in phase space satisfying the conditions of a particular thermodynamics state. There are four types of ensembles [168]:

- Microcanonical ensemble: The thermodynamic state characterized by a fixed number of atoms, N , a fixed volume, V and a fixed energy, E . This corresponds to an isolated system. This ensemble is also commonly referred to as an NVE ensemble.
- Canonical ensemble: This is a collection of all systems whose thermodynamic state is characterized by a fixed number of atoms, N , a fixed volume, V and a fixed temperature, T . This ensemble is also commonly referred to as an NVT

ensemble.

- Isobaric-isothermal ensemble: This ensemble is characterized by a fixed number of atoms, N , a fixed pressure, P and a fixed temperature, T . This ensemble is also commonly referred to as an NPT ensemble.
- Grand canonical ensemble: The thermodynamic state for this ensemble is characterized by a fixed chemical potential, μ , a fixed volume, V and a fixed temperature, T . This ensemble is also commonly referred to as an μVT ensemble.

3.4.2 The velocity Verlet method

The potential energy is a function of the atomic positions ($3N$) of all the atoms in the system, which requires to be solved numerically. There are various numerical algorithms that can be used to integrate the equation of motion. However, the one that is used in the simulations of this thesis is known as the velocity Verlet method. The positions, velocities and accelerations can be approximated using Taylor series expansion [169]:

$$r_p(t + \delta t) = r_p(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 + \dots,$$

$$v(t + \delta t) = v(t) + a(t)\delta t + \frac{1}{2}b(t)\delta t^2 + \dots,$$

$$a(t + \delta t) = a(t) + b(t)\delta t + \dots,$$

where r_p represents the position, v represents the velocity (first derivative with respect to time) and a represents the acceleration (second derivative with respect to time). The acceleration can be expressed as,

$$a(t + \delta t) = \ddot{r}_p(t + \delta t) = \xi(r_p(t + \delta t))/m, \quad (3.1)$$

where m is the mass of the atom and ξ is the potential force between two atoms. The acceleration term can also be reduced from a second order equation to two first order equations, $\dot{r}_p(t) = v(t)$ and $\dot{v}(t) = \xi(r_p(t))/m$. The velocity Verlet method [169] can be achieved, starting by deriving the Taylor series expansions as such,

$$r_p(t + \delta t) = r_p(t) + \dot{r}_p(t)\delta t + \frac{1}{2}\ddot{r}_p(t)\delta t^2 + O(\delta t^3)$$

Next, using $v(t)$ to eliminate $\dot{r}_p(t)$, and $a(t)$ to eliminate $\ddot{r}_p(t)$, we get

$$r_p(t + \delta t) = r_p(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 + O(\delta t^3) \quad (3.2a)$$

Then, expanding the velocity function, $v(t + \delta t)$, we get

$$v(t + \delta t) = v(t) + \dot{v}(t)\delta t + \frac{1}{2}\ddot{v}(t)\delta t^2 + O(\delta t^3) \quad (3.2b)$$

The expression for $\dot{v}$ can therefore be replaced by ξ/m . However, the expression for $\ddot{v}$ requires a known quantity, and hence we expand the acceleration function, $\dot{v}(t + \delta t)$. The expansion of the acceleration term can be expressed as

$$\dot{v}(t + \delta t) = \dot{v}(t) + \ddot{v}(t)\delta t + O(\delta t^2) \quad (3.2c)$$

The expansion goes up to δt^2 for Eq. (3.2c) because we only require an approximation which is good to the order δt^3 . By multiplying Eq. (3.2c) by $\delta t/2$ and rearranging it, we get

$$\frac{\ddot{v}(t)\delta t^2}{2} = [\dot{v}(t + \delta t) - \dot{v}(t)]\frac{\delta t}{2} + O(\delta t^3)$$

The new expression for the velocity function is therefore,

$$v(t + \delta t) = v(t) + \dot{v}(t)\delta t + [\dot{v}(t + \delta t) - \dot{v}(t)]\frac{\delta t}{2} + O(\delta t^3),$$

$$v(t + \delta t) = v(t) + [\dot{v}(t + \delta t) + \dot{v}(t)]\frac{\delta t}{2} + O(\delta t^3),$$

$$v(t + \delta t) = v(t) + \frac{1}{2}(a(t) + a(t + \delta t))\delta t. \quad (3.2d)$$

Since

$$v\left(t + \frac{\delta t}{2}\right) = v(t) + a(t)\frac{\delta t}{2}, \quad (3.3)$$

Eq. (3.2d) can also be rearranged as

$$v(t + \delta t) = v\left(t + \frac{\delta t}{2}\right) + \frac{1}{2}(a(t + \delta t))\delta t, \quad (3.4)$$

whereas Eq. (3.2a) can be rearranged as

$$r_p(t + \delta t) = r_p(t) + v\left(t + \frac{\delta t}{2}\right)\delta t.$$

The Verlet method takes into the account of the positions, velocities and accelerations of the atoms involved. The velocity Verlet method has a velocity correction factor at half a time-step. This allows the velocity to take into account of the acceleration of the atom over the time-step to better predict the final velocity.

One of the advantages of using the velocity Verlet algorithm is that the velocity term appears directly in the equation of motion to be iterated, without extra effort or storage. Besides that, the equations also retain the superior numerical precision of the summed form [170]. The velocity Verlet method is the method of choice in MD simulations because it is more convenient for non-equilibrium MD calculations which require continuous or periodic rescaling of the velocities for atoms [171].

3.4.3 CHARMM potential

In the program named CHARMM, potential energy functions are usually expressed using Cartesian coordinates. The CHARMM potential energy is a sum of internal, or bonded, terms E_{bonded} , which includes the bond energy, $E_{bond-stretch}$, bond angle energy, $E_{bond-angle}$, and torsion angle energy, $E_{torsion-angle}$, of atoms, and external, or nonbonded terms, $E_{non-bonded}$. The E_{bonded} term is a sum of three terms [172]:

$$E_{bonded} = E_{bond-stretch} + E_{bond-angle} + E_{torsion-angle} \quad (3.5)$$

$$E_{bond-stretch} = \sum_{1,2 \text{ pairs}} K_b (b - b_0)^2, \quad (3.6)$$

where K_b = force constant and b = bond length. $E_{bond-stretch}$ is the energy of the bond between two atoms (described as 1,2 pairs).

$$E_{bond-angle} = \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2, \quad (3.7)$$

where K_θ = force constant and θ = bond angle. $E_{bond-angle}$ is the energy of bending a bond angle between atoms.

$$E_{torsion-angle} = \sum_{1,4 \text{ pairs}} K_\Phi (1 - \cos(\lambda\Phi)), \quad (3.8)$$

where K_Φ = force constant, Φ = dihedral angle and λ = coefficient of symmetry.

$E_{torsion-angle}$ is the energy barrier for the rotation of atoms around a single bond. The dihedral angle is angle of rotation between the first and fourth atom of a molecule (described as 1, 4 pairs). The non-bonded interaction,

$$E_{non-bonded} = E_{van-der-Waals} + E_{electrostatic}, \quad (3.9)$$

has two components:

$$E_{\text{van-der-Waals}} = \sum_{\text{nonbonded_pairs}} \left(\frac{A_{ik}}{r_{ik}^{12}} - \frac{C_{ik}}{r_{ik}^6} \right), \quad (3.10)$$

where r = distance between i^{th} and k^{th} atom and A, C = atom-type dependent constants, and

$$E_{\text{electrostatic}} = \sum_{\text{nonbonded_pairs}} \left(\frac{q_i q_k A_{ik}}{D r_{ik}} \right), \quad (3.11)$$

where D = effective dielectric function, q = charges of atom and r = distance between i^{th} and k^{th} atom.

The van der Waals interaction arises from a balance between repulsive and attractive forces of two atoms. It is often modelled using the LJ 6-12 potential. The term $\sim 1/r^{12}$, dominating at short distances, models the repulsion between atoms when two atoms are very close to one another. The term $\sim 1/r^6$, dominating at large distances, contributes to the attraction between two atoms [173].

3.4.4 Langevin dynamics

Langevin dynamics is a means of controlling the kinetic energy of the system, and thus, controlling the system temperature. Langevin dynamics function is used in NAMD (a parallel MD code) to control the system such that the system conforms to the constant temperature condition. The Langevin equation for a single atom i is as such [174]:

$$m_i \frac{d^2 r_i(t)}{dt^2} = \xi_i \{r_{p,i}(t)\} - (\gamma_f)_i \frac{dr_i(t)}{dt} + \psi_i(t). \quad (3.12)$$

The last two terms on the right side of the equation accompany the ordinary force, ξ , the particle experiences. The second term from the right, $(\gamma_f)_i \frac{dr_i(t)}{dt}$, represents the frictional damping force that is applied to the particle with a frictional coefficient, γ_f . The last term represents the random forces, ψ , that may be applied to the particle as a result of solvent interaction. m is the mass of the atom and r_p is the position of the atom in a system at time t .

The generalized Langevin dynamics unifies the first and second fluctuation-dissipation theorems [175], and was further discussed by Henery [176]. The fluctuation-dissipation theorem is an important fundamental for statistical mechanics that predicts the non-equilibrium states or irreversible processes in general. In a molecular motion, an external force or electric field can be applied to the system as a driving force. However, the forced motion experiences a friction or a resistive force as well in the system. The random impacts of surrounding molecules result in the random driving force on particles, and also the frictional force for a forced motion. Based on the internal relationship of these two types of forces, fluctuation-dissipation theorem can be manifested from it. When solute particles experience a driving force, this force is then translated to kinetic energy, and the medium acts as a dissipater of the kinetic energy, resulting in fluctuations among small molecules. The term representing the frictional force in the Langevin equation is exerted by the medium and basically works as a resistance towards the external work such that thermal energy is dissipated into the system. The random force is due to the random collisions of the surrounding molecules. The kinetic energy of the system is thus controlled in order to maintain the system's temperature. Likewise, an

isobaric-isothermal ensemble can also be generated by extending Langevin dynamics scheme to the Hoover ensemble [177, 178]. The potential and kinetic energy terms are adjusted by scaling the particle positions and momenta according to the cell volume. The process results in the expansion and contraction of the system to regulate pressure within the required fluctuations.

3.5 Potential energy and forces for metal atoms

3.5.1 Embedded atom method (EAM)

The modelling of metal particles using MD simulation requires careful consideration in the potential used. This is because metal particles are often modelled as solid materials and the bonding forces between atoms are much stronger. Compared to organic, liquid or gaseous materials, pair potentials are often insufficient to describe the interaction between metal atoms [179] since the bonding is based on atom pairs, neglecting the bonding capacity based on surrounding atoms.

EAM is a class of potential which combines pair potential and electron density embedded functions in its energy equation. As compared to the EAM, pair potentials do not properly account for local density variations. Although the total energy can be written as a sum of pair potentials, the total energy due to pair potentials will not consistently describe the forces in particular atomic configurations [180]. On the other hand, Daw and Baskes calculate the dominant energy of the metal by considering the energy required to embed an atom into the local electron density due to the surrounding atoms of the system for the EAM, in which the method results in many-body effects [181, 182]. The EAM

therefore combines the computational simplicity needed for defects and amorphous systems, and at the same time avoids the ambiguities of the pair potential schemes [183]. In this study, we use a more analytical form of EAM to describe the atoms in aluminium.

The total energy, which consists of the energy, F_i , needed for embedding the atoms into the homogeneous electron gas caused by the surrounding atoms and the energy for two-body interaction, ϕ_{ij} , is shown as [184]:

$$E_{tot} = \sum_i^N F_i(\zeta_i) + \frac{1}{2} \sum_{i,j}^N \phi(r_{ij}) \quad (3.13)$$

r_{ij} is the separation distance between atoms i and j . ζ_i denotes the host electron density at atom i due to all other atoms. $F_i(\zeta_i)$ is the embedded function in the universal form as suggested by Banerjea and Smith [185] and $\phi(r_{ij})$ is the two-body potential as an analytical form similar to the model function given by Rose *et al.* [186].

3.5.2 Forces on atom due to EAM potential

The force on an atom is calculated in this section to evaluate the magnitude of the acceleration of the atom. Due to the changes in the neighbouring atomic position, the overall effect of the homogeneous electron gas caused by the surrounding atoms and pair-potentials would result in changes of the force on the atoms. The force due to EAM potential at a point is the spatial gradient of the total system potential at that point. The force on the atom can be expressed as follows [187, 188]:

$$\xi_i = - \sum_{j=1, j \neq i}^N \left[\frac{d\phi(r_{ij})}{dr_{ij}} + \left(\frac{dF_i}{d\left(\sum_j \varsigma(r_{ij})\right)_i} + \frac{dF_j}{d\left(\sum_i \varsigma(r_{ji})\right)_j} \right) \left(\frac{d\varsigma(r_{ij})}{dr_{ij}} \right) \right] \frac{\vec{r}_{ij}}{|\vec{r}_{ij}|}, \quad (3.14)$$

where ξ_i represents the force at the i^{th} atom, N is the total number of atoms in the system and j is the number of neighbouring atoms to the i^{th} atom. r_{ij} is the distance between the i^{th} atom and the j^{th} atom. $\frac{d\phi(r_{ij})}{dr_{ij}}$ is the derivative of the pair-potential between the i^{th} atom and the j^{th} atom with respect to the distance between them. The next two terms, $\frac{dF_i}{d\varsigma(r_{ij})_i}$ and $\frac{dF_j}{d\varsigma(r_{ij})_j}$, are the derivatives of the ‘embedding function’ for the i^{th} atom and j^{th} atom respectively. $\varsigma(r_{ij})$ is the electron density provided to the embedded i^{th} atom by its surrounding j^{th} atoms and r_{ij} is the separation distance between atoms i and j .

In order to calculate the force on the i^{th} atom due to all the potentials, derivatives of the ‘embedded function’ for each of the i^{th} and j^{th} atoms can be computed simultaneously [189]. The host electron density is first calculated and stored in an array of matrix for all atoms. The derivatives of the ‘embedded function’ for the i^{th} and j^{th} atoms are computed using the stored host electron density values. The algorithm for this calculation is shown clearly at the section of the algorithm for the MD simulation in section 5.12 of chapter 5.

The following derivation of the function is related to the terms found in Eq. (3.14) for the force on an atom based on the EAM potential. The pair potential or two body potential is expressed as [61]:

$$\phi(r) = -\alpha \left[1 + \beta \left(\frac{r}{R_a} - 1 \right) \right] \exp \left[-\beta \left(\frac{r}{R_a} - 1 \right) \right], \quad (3.15)$$

where R_a , α and β are the parameters for pure element systems that has been predetermined, and r is the distance between two particles. If we let G be $\frac{r}{R_a} - 1$, the

derivative of G would be $\frac{dG}{dr} = \frac{1}{R_a}$. The pair potential in terms of G is then

$$\begin{aligned} \phi(G) &= -\alpha [1 + \beta G] \exp[-\beta G] \\ &= (-\alpha) \exp[-\beta G] - (\alpha \beta G) \exp[-\beta G]. \end{aligned} \quad (3.16)$$

The derivative of the pair potential in terms of the separation between the particles is as follows:

$$\begin{aligned} \frac{d\phi}{dr} &= \frac{d\phi}{dG} \times \frac{dG}{dr} \\ &= [\alpha \beta \exp(-\beta G) + (\alpha \beta^2 G - \alpha \beta) \exp(-\beta G)] \times \frac{1}{R_a} \\ &= \alpha \beta^2 G \exp[-\beta G] \times \frac{1}{R_a} \\ &= \frac{\alpha \beta^2}{R_a} \left(\frac{r}{R_a} - 1 \right) \exp \left[-\beta \left(\frac{r}{R_a} - 1 \right) \right]. \end{aligned} \quad (3.17)$$

The embedded function of the particles is made up of the embedded energy in relation to atomic electron density. The embedded function, $F(\zeta)$, is represented as [61]:

$$F(\zeta) = -F_0 \left[1 - \ln \left(\frac{\zeta}{\zeta_e} \right)^n \right] \left(\frac{\zeta}{\zeta_e} \right)^n + F_1 \left(\frac{\zeta}{\zeta_e} \right), \quad (3.18)$$

where ς is the host electron density and ς_e is the host electron density at equilibrium. n is equal to 0.5. F_0 and F_1 are constants for the embedded function where the latter is represented by $F_0 = E_c - E_v^f$. E_c and E_v^f are the cohesive energy and the vacancy formation energy respectively. The values for the constants can be obtained from Cai *et al.* [61].

The host electron density, ς , is written as the sum of electron density $\rho(r_{ij})$ contributed by the individual atom j surrounding atom i [61],

$$\varsigma_i = \sum_{j(\neq i)} \rho(r_{ij}). \quad (3.19)$$

r_{ij} represents the separation between the host atom i and the neighbour atom j . The electron density on the i^{th} atom due to each individual j^{th} atom is expressed as [61]:

$$\begin{aligned} \rho(r_{ij}) &= f_e \exp[-\chi(r_{ij} - r_e)] \\ \varsigma_i(r_{ij}) &= \sum_{j(\neq i)} \{f_e \exp[-\chi(r_{ij} - r_e)]\}, \end{aligned} \quad (3.20)$$

where χ is the parameter for a pure element system, f_e is the scaling constant that can be taken as unity for pure metals and r_e is the equilibrium nearest distance.

In order to include the electron density of each j^{th} atom into the force equation, Eq. (3.14), for the i^{th} atom, the derivative of the host electron density is calculated. The expression is represented as:

$$\frac{d\varsigma(r_{ij})}{dr_{ij}} = \sum_{j(\neq i)} \{-\chi f_e \exp[-\chi(r_{ij} - r_e)]\}. \quad (3.21)$$

The derivative of the embedded function is used in the force equation, Eq. (3.14), to represent the force at i^{th} atom due to the influence of electron density of the

surrounding the j^{th} atom. The gradient of the embedded function, $\frac{dF_i}{d\varsigma(r_{ij})}$, is described

below:

$$\begin{aligned}
 \frac{dF}{d(\varsigma_i)} &= \frac{d}{d\varsigma} \left\{ -F_0 \left[1 - \ln \left(\frac{\varsigma}{\varsigma_e} \right)^n \right] \left(\frac{\varsigma}{\varsigma_e} \right)^n + F_1 \left(\frac{\varsigma}{\varsigma_e} \right) \right\} \\
 &= \frac{d}{d\varsigma} \left\{ -F_0 \left(\frac{\varsigma}{\varsigma_e} \right)^n + F_0 \left(\frac{\varsigma}{\varsigma_e} \right)^n \ln \left(\frac{\varsigma}{\varsigma_e} \right)^n + F_1 \left(\frac{\varsigma}{\varsigma_e} \right) \right\} \\
 &= \frac{-F_0 n}{\varsigma_e^n} (\varsigma)^{n-1} + \frac{F_0 n}{\varsigma_e^n} (\varsigma)^{n-1} \ln \left(\frac{\varsigma}{\varsigma_e} \right)^n + \frac{F_0 n}{\varsigma_e^n} (\varsigma)^{n-1} + \frac{F_1}{\varsigma_e} \\
 &= \frac{1}{\varsigma_e} \left[F_0 n \left(\frac{\varsigma}{\varsigma_e} \right)^{n-1} \ln \left(\frac{\varsigma}{\varsigma_e} \right)^n + F_1 \right].
 \end{aligned} \tag{3.22}$$

$$\frac{dF_i}{d \left(\sum_j \varsigma(r_{ij}) \right)_i} = \frac{1}{\varsigma_e} \left[F_0 n \left(\frac{\left(\varsigma(r_{ij}) \right)_i}{\varsigma_e} \right)^{n-1} \ln \left(\frac{\left(\sum_j \varsigma(r_{ij}) \right)_i}{\varsigma_e} \right)^n + F_1 \right]. \tag{3.23}$$

3.5.3 Electromigration forces on metal atoms

The driving force for metal atoms to be transported from one end of the channel to another is described using the electromigration force. The two main components in the electromigration equation are the direct force and the wind force. The driving force (ξ_{em}) for the copper atom due to the electromigration process is expressed as [190]:

$$\xi_{em} = (Z_d + Z_w) eV_f = \left(Z_d + \frac{k_m}{\gamma(T)} \right) eV_f, \tag{3.24}$$

where Z_d and Z_w are the valence equivalents of the direct and wind forces respectively, e is the electron charge, and V_f is the electric field. The electric field is defined as the region in which a point charge experiences a force exerted by another charge particle. The unit of an electric field is voltage per meter, V/m (Vm^{-1}). T is the temperature in Kelvin and $\gamma(T)$ is the resistivity of the material. The resistivity is temperature dependent and can be described as $\gamma(T) = 2.96 + 0.00768(T - 473) \mu\Omega cm$ for copper [191]. The temperature independent quantity, K_m , for copper is given as $k_m = -33.3 \mu\Omega cm$ [97, 191].

Electromigration in metals is a forced atomic diffusion in which the driving force is due to an electric field and associated electric current in the metals [192]. The direct force in electromigration has been the subject of a long standing controversy [193] and has been discussed by many [194, 195]. Since the contribution of a direct force is understood to be small compared to the wind force according to Dekker *et al.*, the driving force for metal atoms is described using the wind force as a good measure for the main contribution to the driving force [191].

The wind force is one of the two components for the electromigration driving force. The wind force is a result of momentum exchange between the electron current and the moving atoms [192]. According to Ho and Kwok, the wind force was initially treated as electron-ion collision [196]. Huntington and Grone took into account the change of the electronic states caused by the collision [197]. The wind force was subsequently modified by Huntington and Ho, who considered the scattering of the holes as well, of which the effect is incorporated using a parameter known as the specific defect resistivity [196]. The electromigration of copper in CNTs is in fact a process which results a separation of

copper atoms from a bulk copper nanowire encapsulated in CNTs. The separated copper atoms due to electromigration are not only influenced by the scattering of electrons, but also influenced by the bulk resistivity of the bulk copper nanowire in CNTs. The translocation of copper atoms along CNT channels in our simulation studies only reflects the resulting transportation of the electromigrated copper atoms from the bulk copper nanowire along the channels. The driving force which leads to the translocation processes in the simulation studies should therefore be the electromigration force (we consider only the wind force for simplicity in this study), which includes the influences by the bulk resistivity from the host material, copper, as well.

3.5.4 Velocities of atoms

The velocity of atoms in a CNT channel can be described using Newton's equation of motion. We assume an N number of atoms being pushed by an electromigration force, ξ_{em} . The resulting equation of motion for the i^{th} atom travelling along the channel is written as:

$$m \frac{d}{dt} (v_i - u_i)_z = \xi_{em} + \sum_{j=1, j \neq i}^N (\nabla E_{ij})_z, \quad (3.25)$$

where m is the mass of the atom, v is the velocity of the atom at time $t+dt$, u is the velocity of the atom at time t and E is the potential energy between two atoms. The potential energy between two atoms can be defined as van der Waals interactions, CHARMM potential or EAM potential as mentioned in sections 3.4.3 and 3.5.1 respectively. The potential energy term in Eq. (3.25) is due to the combination of the

interaction of other flowing atoms with the i^{th} atom, and interaction of the carbon atoms of the channel with the i^{th} atom.

The relationship between average kinetic energy per axis and temperature is governed by the following equation [187]:

$$\sum_{i=1}^N \frac{1}{2} m_i (u_{x,i}^{old})^2 = \sum_{i=1}^N \frac{1}{2} m_i (u_{y,i}^{old})^2 = \sum_{i=1}^N \frac{1}{2} m_i (u_{z,i}^{old})^2 = \frac{1}{2} N k_B T, \quad (3.26)$$

where N is the total number of moving atoms, m is the mass of a moving atom, k_B is the Boltzmann constant and T is the temperature of the moving atoms. The initialization of the initial velocity of an atom, u^{old} , is achieved using the expression as followed (shown only in the z-direction):

$$\bar{u}_{z,i}^{old} = B \sqrt{\frac{k_B T}{m}}, \quad (3.27)$$

where B is an arbitrary value from 0 to 1 according to Gaussian distribution of velocity (is assigned only once for the initialization of the velocities). The velocity rescaling equation used for controlling the temperature of the system is expressed as [198]:

$$\frac{u_i}{u_i^{old}} = \sqrt{\frac{T_t}{T}}, \quad (3.28)$$

where u_i is the velocity of the i^{th} atom after rescaling, u_i^{old} is the velocity of the i^{th} atom before rescaling, T_t is the targeted temperature and T is the actual temperature of the system.

By substituting the rescaled value of the atomic velocity from Eq. (3.28) into Eq. (3.25), the final velocity of each atom along the CNT channel can be expressed as,

$$v_{z,i} = \left(u_{z,i}^{old} \sqrt{\frac{T_t}{T}} \right) + \frac{\Delta t}{m} \left\{ \xi_{em} + \sum_{j=1, j \neq i}^N (\nabla_r E_{z,ij}) \right\}. \quad (3.29)$$

From the equation above, it is obvious that the velocity of the atoms in CNT channels is dependent on the potential energy based on the interactions between atoms, and also the temperature of the atoms of the system. The purpose of deriving Eq. (3.29) is to show the relationship of various parameters with respect to the velocity of a moving atom.

However, in this study, we propose modified velocity and temperature terms to be used to calculate the rescaled velocity of the moving atoms in order to replace the second mathematical term shown in Eq. (3.29). This method improves the rescaling of the atomic velocities without significantly affecting the drift velocity of the moving atoms, and only the thermal contribution to the velocities are adjusted. In the new method, the rescaling of the velocities is performed by first removing the centre of mass velocity of the electromigrating atoms, and atoms are then rescaled using the temperature term that excludes the translational velocity caused by the electromigration processes. The additional velocity equation for an electromigrating atom in the z direction, before undergoing the rescaling process, is described as:

$$w_{z,i} = w_{z,i}^{old} + \frac{\Delta t}{m} \left\{ \sum_{j=1, j \neq i}^N (\nabla E_{ij})_z \right\}, \quad (3.30)$$

in which the driving force ξ_{em} is excluded from Eq. (3.29) and $w_{z,i}^{old}$ is an initial velocity term from that particular time step. The velocity of the i^{th} moving atom in the z direction, $w_{z,i}$, is then combined with $w_{x,i}$ and $w_{y,i}$ to derive the resultant velocity, w_i . The new

temperature, $T_{e,i}$, of the i^{th} moving atom, can be calculated as $T_{e,i} = \frac{m_i w_i^2}{3k_B}$. The new

velocity rescaling equation is then described as:

$$\frac{u_i^{new}}{u_i^{old}} = \sqrt{\frac{T_t}{T_{e,i}}}$$

$$u_i^{new} = u_i^{old} \sqrt{\frac{3k_B T_t}{m_i w_i^2}}, \quad (3.31)$$

where u_i^{new} is the velocity of the i^{th} atoms after rescaling, u_i^{old} is the velocity of the i^{th} atom with the inclusion of the electromigration force before rescaling, T_t is the targeted temperature and w_i is the velocity (the electromigration force is excluded) which contributes to the thermal effect of the i^{th} moving atoms. The final velocity in the z direction is then calculated as:

$$v_{z,i}^{new} = \left(u_i^{old} \sqrt{\frac{3k_B T_t}{m_i w_i^2}} \right) + \frac{\Delta t}{m} \left\{ \xi_{em} + \sum_{j=1, j \neq i}^N (\nabla_r E_{z,ij}) \right\}. \quad (3.32)$$

3.6 Summary

In this chapter, the advantages and limitations of the existing flow methodologies have been highlighted. The main advantage of the existing methods is that the scale of the simulation represents the reality quite closely. Nonetheless, the simulation duration is affected by the computational system. The proposed research is carried out in three main stages, mainly focusing on the simulation of the oligonucleotide flow in CNT channels, metal atoms flow in CNT channels and the comparison of these two flow phenomena in

order to understand the flow parameters that change with the size effect of the CNT nanotube junctions.

The potential and forces between the atoms are constructed based on the CHARMM potential, the van der Waals interaction and the EAM potential. The CHARMM potential and the van der Waals interaction are used to describe the interaction between the biomolecules, water molecules and CNT channels, whereas the van der Waals interaction and the EAM potential describe the interaction between metal atoms and CNT channels. Due to the complexity of the potentials exists in biomolecules, the CHARMM program has been chosen to handle the simulation of biomolecules in CNT channels. The simulation of the flow phenomenon of the metal atoms in CNT channels, on the other hand, is performed on a simulation program written using MATLAB.

In order to simulate the flow of metal atoms with the appropriate drift velocity, a new method for deriving the rescaled velocity is introduced using a modified velocity term. The modified velocity term is calculated by removing the centre of mass velocity of the electromigrating atoms and the electromigration force. The moving atoms are then rescaled using the temperature term that excludes of the translational velocity caused by the electromigration processes.

CHAPTER 4

SIMULATION OF BIOMOLECULES IN CNT CHANNELS

4.1 Experimental results for biomolecules filled CNTs

The investigation of the filling of CNT channels with a solvated oligonucleotide is an important study, which combines the knowledge of the transportation of water molecules and the oligonucleotide in CNTs. Most often, the investigations for the flow of water molecules in CNTs and the flow of oligonucleotide in CNTs are performed separately. The usage of the MD simulation for these studies is essential for addressing the flow behaviours of the transported molecules on the nanoscale. Nonetheless, the experimental evidences are equally as crucial. The information in this section is thus to highlight some of the phenomena related to the studies of the filled CNT channels with biomolecules and the translocation of biomolecules through nanopores, from both the experimental and simulation aspects.

By conducting simulation studies, Liu *et al.* have shown that the amount of water molecules entering a (15,15) CNT is affected by the pressure, which induces the infiltration of water molecules [199]. With the increase in pressure, the potential energy of water molecules increases, resulting in more water molecules being transported along the (15,15) CNT. However, when water molecules are provided with charges, the attraction between water molecules and carbon atoms in the CNTs leads to a blockage effect on the other water molecules flowing along the (15,15) CNT. The water molecules is then preferably to flow primarily through 3-5 Å from the centre in a (15,15) CNT, as shown in Figure 4.1.1. The region beyond the radius of 5 Å is occupied by stuck water

molecules. The distribution of water molecules in the CNT could be similar if the cross sectional area of the blockage of the tube is close to that in Figure 4.1.1.

Figure 4.1.1 Penetration of water molecules through the entry plane; (a) entry sites of the original NEAS and (b) entry sites of the charges enhanced NEAS. [Liu *et al.*, *Applied Physics Letters* 92 (2008) 101927]

According to the experimental work done by Okada *et al.*, the encapsulation of oligonucleotide in CNTs is more easily occurred when the bases of DNA are short (about 5 bases) [25]. This is because the DNA negative ion tends to maintain a random coiled conformation when the number of bases is too large. Figure 4.1.2 shows two examples of the encapsulation of ssDNA in CNTs. DNA with long bases is hence more prone to be adsorbed onto the outside wall of SWCNTs. Okada *et al.* also suggested that the insertion of the oligonucleotide can be achieved purely by van der Waals interactions [163]. This phenomenon is also verified by Cui *et al.* experimentally [200]. This means that the insertion occurred without an additional external force being applied directly to the oligonucleotide, such as the positive DNA irradiation. However, based on the study by Gao *et al.*, the critical size for inserting a ssDNA into a CNT is 1.08 nm, which is the (8,8)

CNT [32]. The insertion process is therefore hindered by the sizes of the opening which are smaller than the (8,8) CNT.

Figure 4.1.2 HR-TEM images of SWCNTs after ssDNA irradiation in the cases of using (a) 15A-DNA (about 5 nm lengths) and (b) 30A-DNA (about 10 nm lengths). The black lines in images indicate encapsulated materials. [Okada *et al.*, Chemical Physics Letters 417 (2006) 288-292]

The understanding of the translocation of oligonucleotides through small openings can be improved further through the investigation of the transport of biomolecules through nanopores. Storm *et al.* have conducted the transport of a DNA through a solid-state nanopores via a bias voltage experimentally [22]. The fast

translocation dynamics of the DNA through a narrow pore is based on the cumulative effect of the driving at the pore and the hydrodynamic friction outside. According to their findings, the fast polymer translocation is dominated by the hydrodynamic drag, counteracting the electrical driving force. Figure 4.1.3 shows the balance between the two dominating forces that determines the dynamics of the translocation of a DNA molecule through a nanopore.

Figure 4.1.3 The balance between the two dominating forces determines the dynamics of translocation of a DNA molecule through a nanopore: a driving force that pulls the DNA through the pore and a viscous drag force that acts on the entire DNA blob. At time t , the DNA on the left side of the pore has a radius of gyration of R_g , indicated by the dashed line. [Storm *et al.*, Nano Letters 5(7) (2005) 1193-1197]

The double stranded DNA (dsDNA) is transported through the nanopore at 120 mV bias (equivalent to a driving force of 110 pN), whereas the hydrodynamic drag is equal and opposite of the driving force. The viscous drag force on the DNA without specific DNA-pore interactions is about 0.3 pN, and hence the effect is negligible. As compared to the transport of a biomolecule in a tube, the effect of hydrodynamic drag for the transport of biomolecule in a tube channel is rather weak, since the amount of solvent molecules surrounding the biomolecule is relatively much lesser. On the other hand, the

driving force and the interaction between the biomolecule and the inner wall of the tube channel should instead be the main concerns for the translocation process in a tube channel.

Besides the work from Strom *et al.* [22], the same strength of the bias voltage is also used for the ion transport of DNA through nanopores, which is the experimental work conducted by Smeets *et al.* [201]. The experimental work has shown that the change in the salinity of the solution results in different folding conformations of the DNA molecule during transportation. The DNA molecule can either pass through the nanopore unfolded, or enter folded and exit with the tail of the DNA molecule unfolded. This phenomenon suggested that the change in the interaction with a DNA molecule during translocation results in the change of molecular conformations, which in the case of the DNA molecule may be in the state of folded or unfolded.

The translocation velocity of DNA through nanopores is investigated by Meller *et al.* experimentally [202]. Based on their report, the translocation speed of the DNA molecule depends linearly on the electrostatic potential drop for a restricted range of driving potentials. However, the data does not appear linear over a wider range. The electrical driving potentials that were set in their experiment are between 70 and 300 mV, in which the electrical driving forces are between 25 and 110 pN. If we consider the possibility of the screening effect of the DNA molecule that would reduce the strength of the driving force on the biomolecule, the final magnitude of the driving force may be reduced by 53%–85% [203, 204].

The use of carbon nanotubes as nanopores for the transport of ssDNA is made possible by Liu *et al.* [205]. Liu *et al.* have made a device in which one SWCNT spans a

barrier between two fluid reservoirs, for the purpose of detecting signals from the translocation of a single molecule through SWCNT. Figure 4.1.4 shows the single nanopore device that was fabricated by growing SWCNTs on an oxidized silicon wafer. Based on their findings, the translocation of a biomolecule along the CNT resulted in a detectable change of the flow of ionic current. The detection of the ionic conductance is the highest when metallic nanotubes, such as armchair nanotubes, are used. By considering the feasibility of detecting the flow of biomolecules along CNT channels through testing the ionic conductance, the use of metallic nanotube is a better option compared to semi-conducting nanotubes. The use of metallic SWCNTs for the transport of DNA oligomers is also recommended by He *et al.*, who carried out the experiment of DNA translocation in a SWCNT [206].

Figure 4.1.4 A single nanopore device was fabricated by growing SWCNTs at low densities on an oxidized Si wafer. [Liu *et al.*, Science 327 (2010) 64-67]

4.2 Translocation of biomolecules in CNT channels under pressure

4.2.1 Simulation conditions

MD simulations are performed in this study for the translocation of the oligonucleotide and water molecules. In the simulations, the oligonucleotide and water molecules are confined within a CNT channel modelled as a non-polarized, single-walled, armchair CNT. The structure of the CNT channel consists of two CNT junctions, each joined by two nanotubes of different diameters. The connecting joint of the CNT can be connected by a pentagon and a heptagon pair of carbons [78]. For this simulation study, two CNT channels are chosen for comparison: (8,8)-(12,12) and (10,10)-(14,14) CNT channels. The (8,8)-(12,12) CNT channel has 1688 carbon atoms, with a diameter of 10.8 Å for the (8,8) nanotube and a diameter of 16.2 Å for the (12,12) nanotube. The (10,10)-(14,14) CNT consists of 1980 carbon atoms, with diameters of 13.6 Å and 18.9 Å for the (10,10) and (14,14) nanotubes respectively. Both CNT channels are approximately 100 Å in length.

There are in total two systems that are set up for this study. The first system consists of a ssDNA oligonucleotide enclosed within a (8,8)-(12,12) CNT channel, with water molecules and sodium ions. The second system has the same ssDNA oligonucleotide enclosed in a (10,10)-(14,14) CNT channel. The ssDNA oligonucleotide has 3 nucleotides, cytosine, guanine and cytosine that form the biomolecules.

The TIP3 water model [207] is used with sodium counter ions to fill the CNT channels. There are a total of 257 water molecules in the (8,8)-(12,12) CNT channel,

whereas the (10,10)-(14,14) CNT channel is filled with 411 water molecules. Periodic boundary conditions are used with the periodic box being a rectangular shape of the sizes $102 \times 20 \times 20$ Å and $99 \times 20 \times 25$ Å for the (8,8)-(12,12) and the (10,10)-(14,14) CNTs respectively. The periodic boundary conditions mean that when an atom moves out of the box from the boundary, it is translated into the box from the opposite side, which is realized by using the commands “cellBasisVector”, “cellOrigin” and “wrapAll” in the NAMD configure file [208]. The centre of the periodic box is set as the origin of the coordinates.

The CNT channels are fixed in space. The carbon atoms of the CNT channels are modelled as uncharged LJ particles, with $\sigma_{cc} = 3.80$ Å and $\epsilon_{cc} = 0.105$ kcal/mol [32]. The carbon-carbon bond length is maintained at 1.42 Å and bond angles of 120° are maintained by a harmonic cosine angle. For simulating the translocation process in a solvent environment, the oligonucleotide is solvated in a water reservoir. The CHARMM force field is applied to the oligonucleotide and sodium ions. The oligonucleotide is initially placed within the CNT channels. Before the non-equilibrium MD simulations are performed, the energy minimization and equilibrium MD runs had been made. During the energy minimization and equilibrium runs, one of the atoms from the oligonucleotide is fixed to prevent the biomolecules from being pushed out of the CNT channels due to the hydrophobic effects of the water. The parallel MD code NAMD [209] is used for the simulation runs.

The Particle Mesh Ewald (PME) method is applied to the system to evaluate the electrostatic effects of all the molecules. The cutoff distance for the non-bond interactions among the oligonucleotide, water and CNTs is set at 12 Å. A pressure difference is

established in the systems to drive the oligonucleotide and water molecules translocating in the CNT channels. The simulations are performed at a constant temperature of 310 K in an NVT ensemble [210].

The analysis for this simulation is based on the effects of the pressure difference along the CNT channels. The simulation of the flow is conducted in a (8,8)-(12,12) CNT channel and a (10,10)-(14,14) CNT channel. The purpose of inducing a pressure difference in this simulation study is to create a virtual piston by applying a constant force to a layer of water molecules. These molecules would move along the direction of the force applied and subsequently push the rest of the molecules in the system. This initial pressure created by the groups of water molecules is similar to the pressure exerted by a piston. The length of the “piston” used is 20 Å (not shown here). There are in total three magnitudes of forces used to drive the water molecules: 0.1, 0.3 and 0.5 (kcal/mol Å), corresponding to 7, 21 and 35 (pN) respectively.

The magnitudes of the forces applied, 0.1, 0.3 and 0.5 (kcal/mol Å), are also equivalent to the pressure of 1.11×10^{-25} , 3.33×10^{-25} , 5.55×10^{-25} kcal/(mol Å³) respectively, whereas the pressure gradient is affected based on the change in the velocity of the flow from the wide to the narrow sections of the tube. The applied forces used in this simulation study are about the same level or weaker than the nonbonded intermolecular interactions, which range between 0.1 to 10 kcal/mol [211]. According to the experiment conducted by Storm *et al.*, the driving force for pushing DNA molecules through a nanopore with a diameter of about 100 Å requires around 110 pN, due to a bias voltage of 120mV [22]. Likewise, Smeets *et al.* have also conducted an experiment for the translocation of DNA through solid-state nanopores under similar conditions [201].

Based on the diameter of the nanochannel used in this simulation study, the magnitudes of the forces for inducing the pressure difference are therefore comparable to the electrical driving forces of <110 pN used in previous experimental study on the DNA translocation through a nanopore [202].

These forces are applied to the oxygen atoms of the water molecules. The applied forces on the hydrogen atoms are ignored in this simulation method. The oligonucleotide and some of the water molecules in this simulation are subjected to the effect of force indirectly. Besides that, permeation of water molecules along the centre of nanotube channels is conducted. The data is collected based on the permeation of water molecules along the centre of the nanotubes, which is approximately 3 nm in length.

The investigation of the simulations focuses on the conformational changes of the DNA oligonucleotide and the flow of water molecules in CNT channels due to pressures and size effects. The oligonucleotide is initially situated in the CNT channel and positioned with the tube axis aligned. The translocation of the oligonucleotide is based on the pressure difference created by the water molecules in the CNT channels.

Table 4.2.1 Simulation conditions

Cases	CNT channels	Applied forces (kcal/mol Å)	Length of simulations
1	(8,8)-(12,12)	0.1	10 ns
2	(8,8)-(12,12)	0.3	10 ns
3	(8,8)-(12,12)	0.5	10 ns
4	(10,10)-(14,14)	0.1	3 ns
5	(10,10)-(14,14)	0.3	3 ns
6	(10,10)-(14,14)	0.5	2 ns

The different magnitudes of forces used in different simulation cases are shown in Table 4.2.1. The simulation cases for the translocation of the oligonucleotide and water molecules through CNT channels are summarized in Table 4.2.1. Each case consists of a combination of different CNT channels with the applied forces used to drive the water molecules for the induction of a pressure difference. The simulation time step is set at 1 fs. Cases 1, 2 and 3 are conducted for 10,000,000 steps. Cases 4 and 5 are run in steps of 3,000,000. Lastly, case 6 is conducted for only 2,000,000 steps due to the highly repetitive translocating process that has occurred.

4.2.2 Analyses of the flow of water molecules and the oligonucleotide

The results presented in this section are in the ascending order, showing the smallest magnitude of force, 7 pN, to the biggest, 35 pN, for each of the nanochannels. For the (8,8)-(12,12) CNT channel, simulation frames are shown in three phases: the first phase, the middle phase and the last phase of the simulation.

Figure 4.2.1 shows the simulation processes in case 1. Since 1.08 nm is the critical diameter, the oligonucleotide did not pass through the centre of the tube of this diameter. From Figure 4.2.2, the main observable phenomenon is that the oligonucleotide did not come as close to the junction. The space available between the oligonucleotide and the inner wall of the CNT channel allowed more water molecules to pass through as shown in Figure 4.2.1. The following are the results for the permeation of the water molecules through the centre of the tube:

- The total number of permeation events after 2.68 ns in +x direction is: 64
- The total number of permeation events after 2.68 ns in -x direction is: 0

Figure 4.2.1 Overall views of the oligonucleotide in case 1. The frames show the processes at 0, 1.45 and 2.68 ns.

Figure 4.2.2 Enlarged views of the oligonucleotide in case 1. The views are processes at 0 and 2.68 ns.

Figure 4.2.3 shows the simulation of the oligonucleotide in case 2. The processes in Figure 4.2.3 have shown that the oligonucleotide was much closer to the junction of the tube diameter 1.08 nm than the oligonucleotide in case 1. A close up view in Figure 4.2.4 shows that a base (cytosine) from the oligonucleotide was situated near the junction.

The close contact of the oligonucleotide with the nanotube junction had resulted in the reduction of water molecules permeating through the centre portion of the tube with diameter 1.08 nm. As compared to case 1, there are in total 19 water molecules being reduced in the overall permeation process. The following are the results of the permeation of water molecules.

- The total number of permeation events after 2.68 ns in +x direction is: 45
- The total number of permeation events after 2.68 ns in -x direction is: 4

Figure 4.2.3 Overall views of the oligonucleotide in case 2. The frames show the processes at 0, 1.45 and 2.68 ns.

Figure 4.2.4 Enlarged views of the oligonucleotide in case 2. The views are processes at 0 and 2.68 ns.

Simulation processes for the flow of the oligonucleotide in case 3 are shown in Figure 4.2.5. The oligonucleotide is shown to position itself almost as similarly as the oligonucleotide found in case 2. However, comparing the detailed views in Figure 4.2.6 and Figure 4.2.4, the oligonucleotide in Figure 4.2.4 is found to be situated in an even closer position to the junction of the nanotube centre than in Figure 4.2.6. This resulted in even lesser water molecules permeating through the tube centre. Here are the amounts calculated:

- The total number of permeation events after 2.68 ns in +x direction is: 32
- The total number of permeation events after 2.68 ns in -x direction is: 2

The difference in the conformational change of the oligonucleotide in cases 2 and 3 is quite minimal as shown in Figure 4.2.6 and Figure 4.2.4. Both figures display a nearly compact form of the conformational folding of the oligonucleotide.

Figure 4.2.5 Overall views of the oligonucleotide in case 3. The frames show the processes at 0, 1.45 and 2.68 ns.

Figure 4.2.6 Enlarged views of the oligonucleotide in case 3. The views are processes at 0, 1.45 and 2.68 ns.

The simulation of biomolecules in a (10,10)-(14,14) CNT channel is presented in three frames showing the processes of the movement of the oligonucleotide in Figure 4.2.7. Three additional frames are also shown to illustrate the detailed descriptions of the oligonucleotide in an enlarged view in Figure 4.2.8.

Figure 4.2.7 shows the simulation processes in case 4. The oligonucleotide in Figure 4.2.7 is shown to be moving smoothly along the nanotube channel. Figure 4.2.8 focuses on the detailed view of the oligonucleotide. The second frame in Figure 4.2.8 shows that the oligonucleotide is conformed to an extended fashion when travelling along the centre of the tube. This could result in a change of the conformational energy of the oligonucleotide from the original state. The amount of water molecules permeating through the tube is as follows:

- The total number of permeation events after 2.7 ns in +x direction is: 591
- The total number of permeation events after 2.7 ns in -x direction is: 0

From the results of the permeation of water molecules in case 4, it is clear that no water molecules are flowing upstream. But the amount of water molecules flowing through the tube is much lesser than the simulation cases where the pressure difference is larger.

Figure 4.2.7 Overall views of the oligonucleotide in case 4. The frames show the process at 0, 0.68 and 2.7 ns.

Figure 4.2.8 Enlarged views of the oligonucleotide in case 4. The views are processes at 0, 0.68 and 2.7 ns.

Figure 4.2.9 shows the simulation of the oligonucleotide in case 5. The oligonucleotide in Figure 4.2.9 is travelling without any obstruction and that the water molecules are moving together with it. From Figure 4.2.10, the detailed views show that the oligonucleotide is in a much compact form than in case 4. Although the shape of the oligonucleotide is different from case 4, this did not cause a problem for the flow of water. Instead, the increase in the induced pressure resulted in an increase of the flow through the centre of the nanotube channel. Here are the results:

- The total number of permeation events after 0.59 ns in +x direction is: 1760
- The total number of permeation events after 0.59 ns in -x direction is: 0

Figure 4.2.9 Overall views of the oligonucleotide in case 5. The frames show the processes at 0, 0.23 and 0.59 ns.

Figure 4.2.10 Enlarged views of the oligonucleotide in case 5. The views are processes at 0, 0.23 and 0.59 ns.

The last case studied in Figure 4.2.11 is case 6. In Figure 4.2.11, the time interval taken for the snapshots is quite close to case 5, although there is an increase in the magnitude of the force applied. In Figure 4.2.12, the difference in conformation of the oligonucleotide is also quite minimal as compared to case 4. Hence, the change in the conformational energy of the oligonucleotide in cases 5 and 6 might be quite similar.

Despite so, the permeation of water through the tube centre is more dependent on the forces induced as the increase of the induced pressure difference does cause an increase in the amount of water molecules permeating through the tube centre. The results are as such:

- The total number of permeation events after 0.41 ns in +x direction is: 2075
- The total number of permeation events after 0.41 ns in -x direction is: 0

Figure 4.2.11 Overall views of the oligonucleotide in case 6. The frames show the processes at 0, 0.13 and 0.41 ns.

Figure 4.2.12 Enlarged views of the oligonucleotide in case 6. The views are processes at 0, 0.13 and 0.41 ns.

4.2.3 Analyses of effects of the induced pressure difference

Inducing a pressure difference into the simulation system is the condition set for the studies of the molecular flow in CNT channels. The figures shown in this section are results from the simulations that run under three magnitudes of forces: 7pN, 21pN and 35pN (equivalent to 0.1 (kcal/mol Å), 0.3 (kcal/mol Å) and 0.5 (kcal/mol Å) of the forces applied on a group of water molecules). These water molecules are located at the end of the channels, about 2 nm in distance starting from the positive end towards the centre of the nanotubes.

Figure 4.2.13 (a) shows the simulation snapshot of the oligonucleotide in case 1. As shown in Figure 4.2.13(a), the folded oligonucleotide is formed when the oligonucleotide is under the effect of lower pressure (case 1). On the other hand, the less folded oligonucleotide is found in case 3 (not shown here). According to the shape of the oligonucleotide, it is understood that the insertion of the biomolecules at the junction of the CNT channel is deeper for case 3 as compared to cases 1 and 2. This shows that the depth of the insertion is not only caused by the magnitude of the induced pressures in the system, but also dependent on the conformation of the oligonucleotide. The study on the translocation of the oligonucleotide suggested that different pressures in the system and sizes of nanotube channels could result in the change of the conformational shape of the oligonucleotide. In order to glean insight into the possible effect of the moving water molecules, the strength of the induced pressure within the same CNT channel is varied. The result shows that the conformation of the oligonucleotide at the junction would be affected by the translocation of water molecules. Ponnuswamy and Gromiha [212] have shown that there are two possible interactions involved in the unfolded chain of

oligonucleotides: the weakly formed hydrogen bonds between the nucleic acids chain and the solvent, and the steric interactions among parts of the chain. Hence, the possible reason for the above conformation difference is due to the interaction between the solvent molecules and the oligonucleotide. As the water molecules move at different speeds in different simulation cases, the interaction between the oligonucleotide and water molecules would also vary. Since the (8,8)-(12,12) CNT channel is too narrow for the oligonucleotide to pass through, the contributing factor would then be dependent on the water molecules instead. However, further studies would be needed to analyze the relationship between the oligonucleotide and the translocating solvent molecules.

Figure 4.2.13 Translocation of the oligonucleotide in the (8,8)-(12,12) nanotube. (a) A snapshot taken at 2.68 ns in case 1. (b) Position of COM of the oligonucleotide in the x-direction of the nanotube channel.

The position of the centre of mass (COM) of the oligonucleotide in the (8,8)-(12,12) CNT channel with respect to time is illustrated in Figure 4.2.13(b), where three different simulation cases are indicated based on the magnitude of the forces used. The position of the COM of the oligonucleotide was obtained using Visual Molecular Dynamics (VMD) [213]. The graph shows that the maximum position where the oligonucleotide has reached is $-24 \text{ \AA}$ of the CNT channel along the x-direction of the coordinate; this is achieved by the induction of the highest pressure among the simulation cases. The position at $-24 \text{ \AA}$ signifies the junction of the (8,8)-(12,12) CNT channel. The fairly constant COM position after about 300 ps indicates that the oligonucleotide has reached maximum insertion at the nanotube channel junction. It can also be seen in Figure 4.2.13(b) that the velocity of the oligonucleotide is dependent on the magnitude of the induced pressure, where the higher pressure causes a higher molecular flow.

Figure 4.2.14 shows the conformational energy of the oligonucleotide in the (8,8)-(12,12) CNT channel under three different induced pressures. The conformational energy is the potential energy incurred as a molecule moves between various conformations, which are the difference in the three-dimensional orientations of their atoms in space. The conformational energy is defined as the potential energy of the molecule, excluding the energy due to non-bonded interactions. The conformational energy at equilibrium state, in which no force is applied and the oligonucleotide is folded, is also plotted in the figure. It can be seen from Figure 4.2.14 that in each case the conformational energy of the oligonucleotide increases rapidly from a lower value to a relative higher value in about 200 ps after the force is applied at 0 ps. Then the oligonucleotide has reached to the CNT

junction region and stopped there for the rest of the simulation time. During this period, the conformational energy fluctuates around an average value for each case.

Figure 4.2.14 Conformational energy for the oligonucleotide in the (8,8)-(12,12) nanotube channel.

To show the effect of the pressure on the conformational energy more clearly, the time average of the conformational energy of the oligonucleotide for the different cases is shown in Figure 4.2.15. It can be seen that the induced pressure makes the conformational energy higher than the equilibrium state and the higher the pressure, the larger the conformational energy. At the lower pressure of case 1, the observation from the simulation snapshot in Figure 4.2.13(a) shows that the folded oligonucleotide forms lesser blockage at the channel junction. With a lower conformational energy, the oligonucleotide in case 1 is likely to be more stable than in case 2 (force of 0.3 (kcal/mol Å)) and case 3 (force of 0.5 (kcal/mol Å)). The lesser folding of the oligonucleotide in the

latter two cases has an arrangement of bases that are more linear. The linear arrangements of the bases possess higher conformational energies in them. The shape of the biomolecules due to this conformation resulted in more blockage at the nanotube junction due to the deeper insertion towards the (8, 8) centre region of the channels.

Figure 4.2.15 The average conformational energy of the oligonucleotide in the (8,8)-(12,12) and (10,10)-(14,14) nanotube channels for different forces applied. (force = 0 is for the equilibrium state).

The interactive force between the oligonucleotide and the (8,8)-(12,12) CNT channel is shown in Figure 4.2.16. When the oligonucleotide is subjected to a higher pressure, such as in cases 2 and 3, the interactive force between the oligonucleotide and the CNT channel becomes stronger. The increase in the interactive force is mainly due to the closer contact that had occurred between the oligonucleotide and the (8,8)-(12,12) CNT channel junction. The lesser folding of the oligonucleotide in cases 2 and 3 also contributes to a larger surface area for the interaction with the CNT channel junction. Since the CNT channel and the oligonucleotide are both hydrophobic, they would be

attracted to each other by van der Waals interaction. The change in the interactive force in the different cases suggests that the induced pressure acts as an additional force that shortens the distance between the oligonucleotide and the CNT channel junction, resulting in an increase in the van der Waals interaction. Since the interactive force between the oligonucleotide and the (8,8)-(12,12) CNT channel junction is higher in cases 2 and 3 relative to case 1, it is likely that the increment would lead to a greater repulsive effect between the oligonucleotide and the CNT channel.

Figure 4.2.16 Interactive force (in the x-direction) between the oligonucleotide and the wall of the (8,8)-(12,12) nanotube channel during the translocation process.

In order to have a better understanding of the tube size effect on the dynamics of the oligonucleotide in a CNT channel, the (10,10)-(14,14) CNT channel is used to repeat the MD simulations. The translocation of the oligonucleotide through the (10,10)-(14,14) CNT channel is shown in Figure 4.2.17(a), where three simulation snapshots are shown

for the various locations of the oligonucleotide along the CNT channel in case 4. The position of the COM of the oligonucleotide shown in Figure 4.2.17(b) indicates that the biomolecule moves faster when a higher pressure is induced. The cyclic process of the translocation in Figure 4.2.17(c) denotes a smooth flow of the oligonucleotide along the (10,10)-(14,14) CNT channel without any obstruction. As the channel diameter of the central tube is narrower than that of the two sides of the tubes, an increase in the velocity gradient is observed in Figure 4.2.17(b) along this central region, approximately from $-20 \text{ \AA}$ to $20 \text{ \AA}$ of the CNT channel. This means that tube sizes affect the velocity of molecules in the channels. The permeation calculation for water molecules along the centre region of the nanotube channel shows that the frequency of water molecules flowing has increased when the induced pressure is higher.

Figure 4.2.17 Translocation of the oligonucleotide in a (10,10)-(14,14) nanotube. (a) Snapshots of the translocation process in case 4 taken at 0, 0.68 and 2.28 ns respectively. (b) Position of the COM of the oligonucleotide in the x-direction of the nanotube channel. (c) Position of the COM of the oligonucleotide in the x-direction of the nanotube channel during the cyclic translocation processes.

The conformational energy of the oligonucleotide in the (10,10)-(14,14) CNT channel in one translocation cycle is shown in Figure 4.2.18, in which the conformational energy of the oligonucleotide is shown to increase from the equilibrium state as the pressure is induced into the system. Big fluctuation of the conformational energy is observed for the oligonucleotide in the (10,10)-(14,14) CNT channel. The fluctuation of the conformational energy is similar to that observed for the oligonucleotide in the (8,8)-(12,12) CNT channel. In order to have a better understanding of the tube size effect, the average conformational energy of the oligonucleotide in the (10,10)-(14,14) channel is also plotted in Figure 4.2.15. By comparing the conformational energy of the oligonucleotide, it is found that at a higher induced pressure (cases 2, 3, 5 and 6 with the applied forces of 0.3 (kcal/mol Å) and above), the oligonucleotide has a much larger conformational energy in the (8,8)-(12,12) channel than that in the (10,10)-(14,14) channel. The lower conformational energy (more folding) of the oligonucleotide in the (8,8)-(12,12) CNT channel occurs at a lower pressure (case 1 with the applied force of 0.1 (kcal/mol Å)); whereas a lower conformational energy (more folding) of the oligonucleotide occurs at a higher pressure (cases 5 and 6) in the (10,10)-(14,14) channel. The difference in the conformational energy between the two sizes of CNT channels suggests that the conformation of the oligonucleotide is affected not only by the moving solvent, but also by the blockage of the CNT channel junctions or tube sizes.

Figure 4.2.19 shows the variation of the interactive force between the oligonucleotide and the channel wall of the (10,10)-(14,14) CNT during the translocation processes. It can be seen that there is an increase in the interactive force between the -20 and 20 Å region of the CNT channel. This region represents the central region of

the (10,10)-(14,14) nanotube channel. A possible explanation for the force increment along the middle tract is that the distance between the oligonucleotide and the CNT channel is relatively smaller than it is at the two sides of the nanotube channel, thus resulting in a higher van der Waals interaction. The difference in the induced pressure does not contribute to the change in the magnitude of the interactive force between the oligonucleotide and the (10,10)-(14,14) nanotube channel. However, the different conformation of the oligonucleotide in different cases resulted in a slight shift in the magnitude of the interactive force along the middle tract (-20 to 20 Å), as compared between case 4, case 5 and case 6. This is because the lesser folding of the oligonucleotide in case 4 has a larger interactive area as compared to the latter two cases.

Figure 4.2.18 Variation of the conformational energy of the oligonucleotide during one cycle time in the (10,10)-(14,14) nanotube channel.

Figure 4.2.19 Interactive force (in the x-direction) between the oligonucleotide and the wall of the (10,10)-(14,14) nanotube channel in one translocation cycle.

4.3 Effects of fluid flow on the oligonucleotide folding in

SWCNTs

4.3.1 Simulation conditions

In this work, the folding of the ssDNA in CNT channels and the flow of water molecules in MD simulations using an induced pressure difference as the driving force is investigated. The induced pressure is achieved by applying forces on a layer of water molecules, acting as a piston to the entire system. The resulting movement of these water molecules will cause the oligonucleotide in the channels to flow in the direction of the forces applied. Two CNT channels are used for comparing their size effects on the

dynamical behaviour of the oligonucleotide. Besides addressing the conformation of the DNA molecule, the flow of water molecule is also investigated in this work in order to understand the effects of the induced pressure and the size of CNTs on the molecules. Because the pressure is applied on the water molecules and not on the oligonucleotide directly, the translocation of the oligonucleotide depends highly on the interaction between the water molecules and the oligonucleotide. The investigation of the interaction forces between the CNT channels and the oligonucleotide is thus necessary to understand the changes in forces that would occur between them. The detail explanations for the simulation parameters and conditions are given in section 4.2.1.

The shape of the oligonucleotide is compared using the radius of gyration of the molecule. The radius of gyration of the oligonucleotide is used as a reference for determining the changes that occur in the cross-sectional radius of the molecule. The radius of gyration is defined as [214]:

$$r_g^2 = \frac{\sum_i m_i (\bar{r}_i - \bar{r}_c)^2}{\sum_i m_i} \quad (4.1)$$

where m is the mass of the molecule and r_c is the COM.

The results from the MD simulations show that the radius of gyration of the oligonucleotide is affected not only by the strength of the pressure employed, but also by the diameter of the nanotube channels. The magnitude of the interactive force between the oligonucleotide and the CNT channels is affected by the distance between them due to the van der Waals interaction. However, the induced pressure can also act as an additional factor that influences this effect, depending on the size of the CNT channels that the molecule is in. By comparing the shape of the oligonucleotide based on the radius

of gyration, the cross-sectional diameter of the oligonucleotide affects the amount of the water molecules flowing through the nano-channels can be understood.

4.3.2 Analyses of the folding of the oligonucleotide

The investigation of the simulation focuses on the conformational changes of DNA oligonucleotide and water flow in CNT channels due to pressure and size effects of CNT junction. The oligonucleotide is initially situated in the CNT channel and positioned with the tube axis aligned. The translocation of the oligonucleotide is based on the pressure difference created by the water molecules in the CNT channel. The different magnitudes of applied forces used to induce pressure differences in various simulation cases are shown in Table 4.2.1.

Due to the presence of the oligonucleotide, the permeation of water molecules in the (8, 8)-(12, 12) CNT channel is affected by the size of the oligonucleotide and the magnitude of the induced pressure. Because the diameter 10.8 Å is the critical diameter for an oligonucleotide [32], the oligonucleotide does not pass through the centre of the (8, 8)-(12, 12) CNT channel. The oligonucleotide remains at the CNT channel junction and blocks off most of the water molecules flowing through the channel. Figure 4.3.1(a) shows a simulation snapshot of the oligonucleotide in case 3. The main observable phenomenon from the simulation snapshots from case 1 (not shown here) to case 3 (as shown in Figure 4.3.1(a)) is that the oligonucleotide is positioned much closer to the junction as the magnitude of the induced pressure is increased. The position of the oligonucleotide in the CNT channel is defined based on the placement of the COM of the oligonucleotide along the x axis of the channel. The blockage of the oligonucleotide at the

CNT junction affects the amount of water molecules flowing across the CNT channel. The detailed descriptions of the permeation of water molecules is described in Lim *et al.* [56]. Another factor affecting the flow of water molecules across the carbon nanotube junction is the change in the cross-sectional area of the oligonucleotide due to folding. The cross sectional area of the oligonucleotide becomes larger due to folding of the bases of the molecules. This creates a greater blockage to the water molecules entering the centre region of the nano-channel.

Figure 4.3.1(b) shows the van der Waals forces between the water molecules and the oligonucleotide along the x direction of the (8,8)-(12,12) CNT channel. The positive values in the forces mean that the water molecules and the oligonucleotide are experiencing an overall repulsive force, whereas negative values mean that there is an overall attractive force between the water molecules and the oligonucleotide. Figure 4.3.1(b) indicates that the van der Waals forces between cases 1, 2 and 3 are almost similar. However, the slight difference in the values of the forces indicates that as the induced pressure increases, the van der Waals forces between the water molecules and the oligonucleotide are inclined towards an attractive phenomenon. Although the repulsive effect exists at the ending of the oligonucleotide near the (12,12) nanotube, the flow of some water molecules into the (8,8) nanotube forms a more dominant attractive effect on the oligonucleotide at that narrow junction. This suggests that the folding of the oligonucleotide at high pressure is lesser, resulting in sufficient space between the oligonucleotide for the flow of water molecules.

As the pressure in the nanochannel increases, water molecules pass through the oligonucleotide much quickly. The repulsive forces induced by water molecules also

push the oligonucleotide to move closer toward the CNT junction. The decrease in the van der Waals forces could partly contribute to the change in the shape of the oligonucleotide, especially in the folding of the oligonucleotide. The higher attractive forces between the water molecules and the oligonucleotide would cause the oligonucleotide to fold lesser, due to the stretching of the oligonucleotide along the flow direction of the water molecules. The higher pressure results in a deeper insertion of the oligonucleotide into the narrower channel. Since the nanotube junction is too small for the oligonucleotide to flow through, the blockage by the junction resists the oligonucleotide from folding, forming a less folded shape of the oligonucleotide. The position of the oligonucleotide along the (8,8)-(12,12) CNT channel is also shown in Figure 4.3.1(a), where a higher pressure (case 3) shows a further displacement of the oligonucleotide towards the CNT junction at around $-24 \text{ \AA}$.

Figure 4.3.1 Translocation of the oligonucleotide in the (8,8)-(12,12) nanotube. (a) A snapshot taken at 2.68 ns in case 3. (b) Van der Waals forces between water molecules and the oligonucleotide in the (8,8)-(12,12) CNT channel.

In order to understand the effect of the van der Waals forces between the water molecules and the oligonucleotide, the van der Waals forces between the bases (guanine and cytosine) of the oligonucleotide from cases 1 to 3 are shown in Figure 4.3.2. Figure 4.3.2 shows the bases of the oligonucleotide are more repulsive to each other as the pressure of the system increases and the highest repulsive force occurs in case 2. Although the oligonucleotide is less folded at a higher pressure system (cases 2 and 3), the oligonucleotide is sandwiched between the nanotube junction and the pressurized water molecules. This is because the oligonucleotide is unable to flow through the centre region of (8,8) CNT channel any further as mentioned earlier. The pressure exerted by the water molecules forces the bases of the oligonucleotide to squeeze closer with each other toward the nanotube junction, hence increasing the van der Waals forces between the bases.

In case 2, the insertion of the oligonucleotide into the (8,8) nanotube region is lesser than that in case 3. Due to the built-up pressure at one end of the oligonucleotide, the distances between the bases are shortened in a linear fashion and thus cause greater interactions between them. As for case 3, the insertion of the oligonucleotide into the (8,8) nanotube region is deeper. When the pressure at one end of the oligonucleotide is built up, the “squeezing effect” between the bases is compensated by the forward insertion of the other end of the oligonucleotide. This reduces the repulsive effect between the bases. Since some water molecules are able to flow freely through the oligonucleotide and across the CNT junction, the increased pressure would not result in the increase in forces between water and the oligonucleotide that are of the same magnitude as that between the bases.

Figure 4.3.2 Van der Waals forces between the bases (guanine and cytosine) of the oligonucleotide in the (8, 8)-(12, 12) CNT channel.

Figure 4.3.3 shows the radius of gyration of the oligonucleotide in the (8, 8)-(12, 12) CNT channel under the influence of different pressures. When the radius of gyration of the oligonucleotide increases, the cross-sectional area of the oligonucleotide is decreased due to the linear arrangement of the bases of the oligonucleotide. The cross-sectional area is defined as the area parallel to the diameter of the nanotube. The radius of gyration of the oligonucleotide decreases when the oligonucleotide folds. Likewise, the radius of gyration of the oligonucleotide increases when the oligonucleotide unfolds. Figure 4.3.3 shows that the folded oligonucleotide is formed when the oligonucleotide is under the influence of a lower pressure. The result from the radius of gyration of the oligonucleotide has confirmed that folding of the oligonucleotide is less prominent as the pressure increases. The state of the oligonucleotide after equilibration at 0 ps is indicated as the “equilibrium” stage of the oligonucleotide and is used to compare with the other cases. The oligonucleotide in the (8, 8)-(12, 12) CNT channel has shown an overall increment in the unfolding of the oligonucleotide, compared to the initial equilibrium state. Because the radius of gyration of the oligonucleotide in case 3 is larger, the possibility of deeper insertion to the smaller nanochannel would be greater. This shows that the depth of insertion is mainly caused by the magnitude of the induced pressure in the system, the interaction of the oligonucleotide and the water molecules, and also the shape of the oligonucleotide. The radius of gyration has indicated the changes in the cross-sectional diameter of the oligonucleotide at different pressures, as shown in Figure 4.3.3. The result from the radius of gyration rectifies the uncertainty of the shape of the oligonucleotide in different simulation cases reported by Lim *et al.* [56].

Figure 4.3.3 Radius of gyration of the oligonucleotide in the (8,8)-(12,12) nanotube channel for different forces applied.

In order to further inspect the size effect of the CNT channel on the dynamics of the oligonucleotide, the (10,10)-(14,14) CNT channel is used to repeat the MD simulations. According to the findings of Wang *et al.*, the static properties of water confined in CNTs are mainly affected by the sizes of the tube diameter rather than the helicity effect of the tubes [215]. Since water properties are not affected by the helicity effect, the dynamics of the oligonucleotide due to water molecules is considered to be dependent on the effect of the tube diameter as well, instead of the helicity effect. The translocation of the oligonucleotide through the (10,10)-(14,14) CNT channel is shown in Figure 4.3.4(a), where three simulation snapshots show the oligonucleotide located at the centre of the CNT channel. The position of the oligonucleotide is presented in 3 simulation cases (cases 4, 5 and 6) to show the difference in the folding of the oligonucleotide. Figure 4.3.4(a) shows the oligonucleotide is less folded under a lower

pressure condition (case 4), as compared to the higher pressure conditions (cases 5 and 6). The phenomenon of the folding of the oligonucleotide can be further clarified using the explanation of the van der Waals forces between the water molecules and the oligonucleotide. As shown in Figure 4.3.4(b), the van der Waals forces between the water molecules and the oligonucleotide at the centre region of the (10,10)-(14,14) CNT channel (approximately between $-20 \text{ \AA}$ and $20 \text{ \AA}$) increase as the pressure increases in the system.

The increase in the van der Waals forces indicates a repulsive nature between the water molecules and the oligonucleotide as mentioned earlier. Since the van der Waals forces along the centre region of the CNT channel change significantly as compared to the forces at both ends of the tube (approximately $\leq -20 \text{ \AA}$ and $\geq 20 \text{ \AA}$), the conformation of the DNA is therefore affected more greatly by the water molecules while translocating along the centre tube. This possibility is reasonable since the diameter of the centre tube region is smaller than the diameters at the two ends of the CNT channel and, therefore, decreases the space for the distribution of molecules around the oligonucleotide. When cases 4, 5 and 6 are compared, it is obvious that the increase in the van der Waals forces at the centre region of the tube in case 4 is less significant than that in cases 5 and 6, as shown in Figure 4.3.4(b). The lower force has led to the lesser folding of the oligonucleotide in case 4. Due to the forces by the water molecules that are inclining more toward the attractive nature to the oligonucleotide, the oligonucleotide is less folded while translocating along the narrower tube region. The flow of the water molecules leads to a more linear arrangement of the bases of the oligonucleotide in case 4. This phenomenon is in fact different from the behaviour of the oligonucleotide in the (8,8)-

(12,12) CNT channel, where a higher pressure leads to a lesser folding of the oligonucleotide.

When comparing the van der Waals forces in the (8,8)–(12,12) CNT channel with the forces in the (10,10)–(14,14) CNT channel, it is evident that the forces in the (10,10)–(14,14) CNT channel are more repulsive. As more space is available between the oligonucleotide and the (10,10) tube region, more water molecules are able to form hydrogen bonding between water molecules around the oligonucleotide and the effect of hydrophobic forces on the oligonucleotide is more prominent. The surface contact between the oligonucleotide and water has also increased due to the spacing available in the (10,10) nanotube region. Water molecules are able to “wrap” around the oligonucleotide in the (10,10) nanotube region, whereas the interaction between water molecules and the oligonucleotide at the (8,8)–(12,12) CNT channel junction occurs only between water and the exposed oligonucleotide to the solvent.

Figure 4.3.4 Translocation of the oligonucleotide at the center of the (10,10)-(14,14) nanotube. (a) Snapshots of the oligonucleotide in Cases 4 (at 5.75 ns), 5 (at 5.22 ns) and 6 (at 5.13 ns) respectively. (b) Van der Waals forces between water molecules and the oligonucleotide in the (10,10)-(14,14) CNT channel.

At the (8,8)–(12,12) CNT channel junction, the amount of water molecules flowing toward the oligonucleotide and repelled by the oligonucleotide is minimal, whereas attraction between water and the oligonucleotide at the narrow junction is more dominant. Since the oligonucleotide in the (10,10) CNT interacts with more amount of water molecules, the number of water molecules repelled away from the oligonucleotide is also increased. The resulting van der Waals forces between the oligonucleotide and water would therefore incline to more repulsive nature.

The interaction between the bases of the oligonucleotide is further emphasized in Figure 4.3.5, showing the van der Waals forces between the bases (guanine and cytosine) of the oligonucleotide in the (10,10)-(14,14) CNT channel. Figure 4.3.5 shows that the less folded oligonucleotide in case 4 has led to a decrease in the van der Waals forces between the bases. The lower forces between bases of the oligonucleotide suggest that the

interactions between the bases are less repulsive, possibly due to the less folding of the oligonucleotide.

Figure 4.3.5 Van der Waals forces between the bases (guanine and cytosine) of the oligonucleotide in the (10,10)-(14,14) CNT channel.

Besides accounting the pressure as the contributing factor for the increasing amount of water molecules flowing along the (10,10)-(14,14) CNT channel, another possible factor is the blockage of the oligonucleotide. Figure 4.3.6 shows the radius of gyration of the oligonucleotide in the (10,10)-(14,14) CNT channel. Since the radius of gyration changes significantly along the entire channel, the main focus in Figure 4.3.6 is the comparison of the radius of gyration along the centre region of the (10,10)–(14,14) CNT channel only, between -20 Å and 20 Å. The radius of gyration of the oligonucleotide in the centre region of the (10,10)–(14,14) CNT channel suggests that lesser folding occurs when the lowest pressure is induced to the system (case 4), as shown in Figure 4.3.6. The decrease in radius of gyration of the oligonucleotide in Figure 4.3.6 signifies a greater folding of the oligonucleotide as the pressure increases. The

difference in the shape of the oligonucleotide influences the degree of blockage towards the number of water molecules flowing along the (10,10)-(14,14) CNT channel.

Figure 4.3.6 Radius of gyration of the oligonucleotide in the (10,10)-(14,14) nanotube channel in one translocation cycle.

Based on the findings, it is concluded that the folding of the oligonucleotide in the (8,8)-(12,12) CNT channel is due to the external force from the pressure applied, the effect of the nanotube junction and the interactions between water molecules and the oligonucleotide. As for the oligonucleotide in the (10,10)-(14,14) CNT channel, the main effect of the folding is dependent on the water molecules and the pressure. When the cross-sectional area of the junction is sufficiently large, the folding of the oligonucleotide is more dependent on the pressure of the flow and the van der Waals forces between the water molecules and the oligonucleotide. Ponnuswamy and Gromiha [212] showed that there are two possible interactions involved in the unfolded chain of the oligonucleotide: the weakly formed hydrogen bonds between the nucleic acids chain and the solvent and

the steric interactions among parts of the chain. Since the effect of electrostatic forces on the conformation of the oligonucleotide is very minimal, the electrostatic factor is therefore neglected in this study.

According to Rathore *et al.*, when the conformational space is limited, the unfolded state of the protein is destabilized by reducing the entropy of the protein [216]. However, the stabilization of the protein is dependent upon the relative magnitude of the change in enthalpy and entropy. The relationship of the energies can be expressed as $\Delta E = \Delta H - T\Delta S$, where E is the free energy, H is the enthalpy, and S is the entropy. In this study, the encapsulation of the oligonucleotide tends to decrease the entropy of the oligonucleotide [32]. In the case of the translocation of the oligonucleotide in the (8,8)–(12,12) nanotube channel, the increase in pressure results in a greater change in the van der Waals forces between water and the oligonucleotide. The decrease in van der Waals forces means that the total potential energy (enthalpy) is reduced and the net free energy is lower. Muthukumar showed that the escape of a polymer through a hole is achieved only when the polymer is able to overcome the free-energy barrier at the hole [217]. Since the net free energy at the nanotube junction is lower in the case of the oligonucleotide in the (8,8)–(12,12) nanotube channel at a high pressure, the insertion of the oligonucleotide into the narrow region of the channel has indeed deepened.

In the case of the translocation of the oligonucleotide in the (10,10)–(14,14) nanotube channel, the van der Waals forces between water and the oligonucleotide have shown to increase as the pressure is increased. The increase in van der Waals forces means that the total potential energy is increased and the net free energy should be higher. However, in order to maintain a lower free-energy barrier across the wider (10,10)

nanotube, the change in the entropy of the oligonucleotide is increased instead and forms a more folded state of the oligonucleotide.

Lastly, the radial distribution of the water molecules around the oligonucleotide at the centre region of the (10,10)-(14-14) nanotube channel is shown in Figure 4.3.7. The flow of the solvent around the oligonucleotide is affected greatly by the shape of the oligonucleotide present in the narrow region of the CNT channel. Figure 4.3.7 shows that the distribution of the water molecules is concentrated more at the radius of 3 Å away from the centre of the oligonucleotide when a high pressure is induced in the system (case 6). The centre of the oligonucleotide is defined at the joining atom between guanine and cytosine. Since the folding of the oligonucleotide in case 4 is lesser, the distribution of water molecules is also less concentrated and varies at a wider range of the radius from the centre of the oligonucleotide, between 3 Å and 6 Å, away from the centre of the oligonucleotide.

Figure 4.3.7 The radial distribution of water molecules around the oligonucleotide at the center region of the (10,10)-(14-14) nanotube channel for different forces applied.

Oligonucleotides and oligopeptides are two different types of biomolecules that can be inserted into CNT channels. According to the results generated from the studies in this thesis, it is clear that some of the characteristics involving the insertion of oligonucleotides into CNTs are quite similar to the insertion of oligopeptides into CNTs. One of the similarities between these two types of biomolecules is that both are encapsulated into CNTs mainly through van der Waals interactions [218]. During insertion, the conformation of these two biomolecules takes place. The conformations of oligonucleotides and oligopeptides will both result in the strengthening of the van der Waals and hydrophobic interactions with CNTs [219]. However, oligonucleotides and CNTs hydrophobic interactions occur through the affinity between nucleic bases of the oligonucleotide and the carbon rings of the CNTs; whereas oligopeptides and CNTs hydrophobic interactions is established through the affinity between aromatic ring structures, or hydrophobic side chains, in oligopeptides and the carbon rings of the CNTs [219]. Another similarity between the encapsulation of oligonucleotides and oligopeptides in CNTs is that both types of biomolecules show a decrease in the enthalpy energy during the insertion process, resulting in an overall lower free energy for the system.

4.4 Summary

This chapter reviews the novel studies of the solvated oligonucleotide flow in CNT channels. The flow phenomena in CNT channels and the folding of the oligonucleotide have been addressed. The simulations set up are based on the pressure

difference as the driving force to move the molecules in CNT channels. Two sizes of the nanotube channels have been examined and compared.

The results from the MD simulations have shown that the amount water molecules flowing along the CNT channels is not only influenced by the magnitude of the induced pressure, but also based on the diameter of the channel and the shape of the oligonucleotide that forms at the junction or along the flow. As pressure increases, the folding of the oligonucleotide forms a more linear configuration (higher conformational energy) in the (8,8)-(12,12) CNT channel whereas the folding becomes more prominent (lower conformational energy) in the (10,10)-(14,14) CNT channel. Due to the size of the nanotube junctions, the effect on the conformation of the oligonucleotide is also different. Although the repulsive forces from the water molecules cause the oligonucleotide to fold, the size of the (8,8)-(12,12) nanotube junction can in fact resist such folding and result in a more linear arrangement of the bases of the oligonucleotide. The gradient of the position of the COM of the oligonucleotide in the (10,10)-(14,14) CNT channels with respect to time indicates the velocity of the oligonucleotide, as depicted in Figure 4.2.17(b). The change in the gradient suggests that the velocity of the oligonucleotide across the junctions of the (10,10)-(14,14) CNT channels is more significant when the pressure applied is smaller.

CHAPTER 5

EXTENSION OF STUDY: PREMELTING OF THE ALUMINUM (110) SURFACE

5.1 Experimental results for the premelting of the aluminum surface

The study of the premelting of the aluminium surface is conducted in this thesis for two main purposes: to understand the behaviour of the atomic activities at the premelting temperature and to verify the reliability of the simulation program based on the results generated from this study. In this section, the experimental results of the premelting of aluminium surfaces are presented. The results from various experiments provide the essential references for the verifications of the temperatures at which the surface atoms on the Al (110) surface change their state. The results from the experiments therefore verify the reliability of the simulation program created for the study of the premelting of the aluminium surface. The same simulation will be used in chapter 6 for the simulation of copper flow in CNT channels.

Based on the experimental results by Blanckenhagen *et al.*, the anomalous increase of the mean-square vibrational amplitudes of Al (110) occurs at temperatures above 620 K [46]. The increase in the mean-square vibrational amplitudes is reflected as a decrease in intensity of a (02)-LEED as shown figure 5.1.1. However, in terms of the graph of the mean-square vibrational amplitudes versus temperature, the anomalous increase in the atomic vibrations would be reflected in the graph as a decrease in the

gradient. On the other hand, the results from Dosch *et al.* using X-ray scattering have shown that the surface disordering of Al (110) occurs at 690 K [220].

Pavlovska *et al.* have shown that at low temperatures (< 420 K), the surface state of Al (110) is destroyed by thermal disordering [140]. The phenomenon is reflected as an increase in work function. At temperatures between 750 and 800 K, anharmonic vibrations occur both parallel and normal to the Al (110) surface, attributing to surface roughening.

Figure 5.1.1 Temperature dependence of the integrated intensity of the (02)-LEED spot. [Blanckenhagen *et al.*, Journal of Vacuum Science & Technology A 5 (1987) 649]

The simulation results of the premelting of Al (110) surface by Stoltze *et al.* have suggested that the melting temperature to be closed to 770 K [42, 52], whereas results from ion shadowing measurements show that the surface melting to be closed to 815 K [221]. The slight difference in the surface melting temperature is expected between simulation results and the experiment results, since the strength of the atomic potential affects the interaction between the atoms.

Surface premelting is an important phenomenon for us to understand the melting process of an open surface. The quasiliquid layer that occurs at premelting is an evident that shows that the overheating of solid does not occur, since the quasiliquid layer is a nucleation centre for the melting process. According to Theis and Horn, the top layer of the Al(110) surface is detected to be close to liquid aluminium at 931 K, by using the photoemission spectra [222]. Besides that, they have also found that the increase in the thickness of the quasiliquid layer is linearly dependent on the logarithm of $(T_M - T)$ as shown in Figure 5.1.2, where T_M is the melting temperature of the solid and T is the assigned temperature. The formation of the quasiliquid layer occurs at (150 ± 20) K below T_M .

Figure 5.1.2 Thickness of the quasiliquid layer on Al(110) as a function of temperature derived from Al 2*p* line-shape analysis. [Theis and Horn, Physical Review B 51 (11) (1995) 7157-7159]

Since the quasiliquid layer starts from the surface of a solid, it is important that the changes to the surface atoms are investigated to show how the physical changes on

the surface of a solid is associated with premelting processes. The analysis of the atomic arrangement helps to provide further insights to the premelting transition. By understanding the atomic disorder at the surface, the surface premelting phenomenon of Al can therefore be explained using thermal disordering of atoms on the top layers of the Al surface. According to Pedemonte *et al.*, a strong enhancement of thermal vibration amplitudes of top layer Al atoms, and the increase of the vacancy percentage are observed at temperatures above 650 K [223]. They have suggested that the segments of $\langle 1\bar{1}0 \rangle$ atomic chains moving against each other are present within the molten layer at the surface through their experimental results. The surface channelling peak is shown to remain up till 800 K, as depicted in Figure 5.1.3.

Figure 5.1.3 Evolution of the $\langle 1\bar{1}0 \rangle$ surface channelling peak in the temperature range between 305 and 890 K. [Pedemonte *et al.*, Nuclear Instruments and Methods in Physical Research B 193 (2002) 563-567]

Besides that, the channelling pattern for the Al(110) surface at 890 K is also not completely flat [224]. Based on the results of the experiment conducted by Pedemonte and Bracco, the channelling pattern suggested that there is still residual order along the

$\langle 1\bar{1}0 \rangle$ azimuth within the quasiliquid layer. They have also observed that there is an increase of the vacancy percentage up to 24% at 650 K, which suggests adatom-vacancy proliferation is the precursor to surface melting at temperatures above 600 K.

Apart from the premelting phenomenon of Al(110), Al(100) surface premelting is investigated by Jezequel *et al.* [225]. According to their experimental results, no evidence of molten or fully disordered layers is observed for the top layers of Al(100) below the bulk melting temperature. As for the case of the Al(110) surface, a strong deviation from a linear behaviour in their photoemission experiments is found at temperatures above 450 K. Jezequel *et al.* suggested that the anharmonicity could be larger at the surface.

5.2 Simulation details for bulk Al slab and Al(110) surface

5.2.1 Computational methods

MD simulations are performed to study an Al(110) surface. The MD code is written using MATLAB. The system consists of a slab of an Al fcc crystal, where the two free surfaces are (110) planes. The slab has a total of 432 atoms, divided into 12 layers. Each layer consists of 36 atoms. The slab has dimensions of $22.28 \times 15.75 \times 15.75 \text{ \AA}^3$ in the x , y and z directions respectively. There are two types of analysis carried out in this study: the bulk analysis for the Al slab and the surface analysis for the Al(110) surface. Periodic boundary conditions are applied in all three directions for the bulk analysis. However, periodic boundary conditions for the surface analysis are imposed parallel to the surface (x and y directions) of the slab in order to allow diffusion of atoms along the z direction at high temperatures.

The atoms in the system are modelled as EAM atoms with the cutoff distance between two atoms as $r_{cut} = 1.65a_0$ ($a_0 = 4.05 \text{ \AA}$). The simulations for the aluminium slab are run at a controlled temperature. The temperature of the system is maintained constant throughout the simulation process using velocity rescaling [198]:

$$\frac{v^{new}}{v^{old}} = \sqrt{\frac{T_t}{T}}, \quad (5.1)$$

where v^{new} is the velocity of the atoms after rescaling, T_t is the targeted temperature and T is the actual temperature of the system. Based on the work presented by Bussi *et al.*, the modification to the velocity rescaling method proposed by them gives a good sampling to the canonical ensemble in MD simulations [226]. Although the simple velocity rescaling method is insufficient in producing a correct Boltzmann distribution, Bussi *et al.* have mentioned that the simple velocity rescaling algorithm can still be used to produce useful results, as long as the systems are not small. The simple velocity rescaling method used in this chapter is mainly for the simulation of the Al bulk material, in which the system is more like an infinite one since periodic boundary conditions are used in the simulation studies of this chapter. The limitation of the simple velocity rescaling method is thus less significant.

The temperature of the system is calculated based on the average kinetic energy as described in the following [187]:

$$\sum_{i=1}^N \frac{1}{2} m_i \sum_{\beta=x,y,z} \bar{v}_{\beta,i}^2 = \frac{3}{2} N k_b T, \quad (5.2)$$

where N is the number of atoms in the system and k_b is the Boltzmann constant. The Verlet method is used in the algorithm of the simulations and the neighbour list is

constructed in order to improve the efficiency of the program. Visual Molecular Dynamics (VMD) is used for the visualization of the system [213].

The simulation cases for the aluminium slab consist of bulk and surface analyses. There are in total 9 simulation cases in this study. Temperatures for the aluminium bulk analysis are assigned as 240, 584, and 708 K; temperatures for the Al(110) surface analysis are assigned as 240, 400, 500, 579, 710 and 810 K. The time simulated for each case is 12 ps at the assigned temperature. The simulation time steps are set at 2 fs.

5.2.2 Potential and force

Figure 5.2.1 highlights the algorithm of controlling the metal atoms using the EAM potential and the algorithm of the force induced on the atoms due to the potential. In order to initialize the program, the parameters of the EAM potential model are first defined by the user. The atom pairs are then selected based on the information stored in the neighbour list. The use of the neighbour list is to reduce the part of the computational effort required for calculating the EAM potential. The energy required to embed the i^{th} atom into the system depends on the neighbouring contribution of the electron density and the pair potential by the neighbouring atoms.

The force on the atom, Eq. (3.14), is dependent on the derivative of the pair potential and the embedded function. However, besides taking the derivative of the function based on the i^{th} atom, the derivative of the embedded function based on each of the j^{th} atom is also required. In order to generate the terms for the force equation, Eq. (3.14), the force induced on the i^{th} atom has to be calculated simultaneously with the force induced on the neighbouring j^{th} atom of the i^{th} atom. The energy of the system is

calculated by summing up the pair potential term and the embedded function for all the atoms in the system.

Figure 5.2.1 Algorithm for the EAM potential and induced force

5.2.3 Simulation algorithm

Figure 5.2.2 shows the algorithm of the MD simulation of the Al(110) surface. The numbers indicated at each section of the algorithm represent the steps of the simulation process. Step 1 indicates the initiation of the program. The variables and constants required for the simulation are defined at this step. Step 2 involves the setting of the coordinates, velocities and accelerations of the atoms in the system. The neighbour list and the host electron density at equilibrium are also created at this stage. A neighbour list is a table which consists of the list of atom pairs that lie within the distance of the interaction range [227]. The simulation loop for the MD study starts at step 3. Within the loop, temperature control mechanism, the Verlet method, periodic boundary conditions, the EAM potential model and the force on atoms are all executed for every time steps. The mechanism controlling the temperature in step 4 is the velocity rescaling method.

At step 5, the positions of the atoms are first updated using the Verlet algorithm, followed by checking the new positions of the atoms with respect to the original positions of the atoms in the original computational box, which is simply known as the primary cell. Image cells are replicas of the primary cell which surround the primary cell. When atoms are diffused away from one side of the primary cell into the surrounding image cells, the atoms are then translated back into the primary cell by allowing the atoms to re-enter to the opposite side of the primary cell. Next, the neighbour list, the EAM potential and the Verlet algorithm are executed in step 5 to recalculate the velocity of the atoms based on the accelerations due to the resultant forces. The mean square displacement, pair correlation function, layer structure factor and mean square vibrational amplitude are calculated at step 6, together with the tabulation of energies and temperatures of the

system. The final consolidation of the data and the analysis are carried out after the completion of the simulation at step 8.

Figure 5.2.2 Simulation algorithm

5.3 The atomic behavior of bulk Al slab and Al(110) surface

5.3.1 Analyses of bulk Al slab and Al(110) surface

In this section, the results from MD simulations of the Al(110) surface premelting using the EAM potential is reported and the differences between the results of this study and those of Schommers are addressed. The following findings relate two results between the two different simulation studies.

1. We found that using the EAM potential proposed by Cai *et al.*, the premelting phenomenon for the outer layer of the aluminium slab occurs at an even lower temperature than that reported by Schommers.
2. The diffusion coefficient calculated through mean square displacements is greater at 710 K than that reported by Schommers.

The pseudopotential model used by Schommers is expressed as [228]:

$$\sigma(r) = \sigma_{ind}(r) + \sigma_d(r), \quad (5.3)$$

where $\sigma_{ind}(r)$ represents the ion-electron-ion interaction (indirect ion-ion interaction) and $\sigma_d(r)$ represents the direct interaction between ions. The indirect ion-ion interaction takes the following form [229]:

$$\sigma_{ind}(r) = \frac{\Omega_0}{\pi^2} \int_0^\infty \frac{G(q)(\sin(q_w r))}{q_w r} q_w^2 dq_w. \quad (5.4)$$

Ω_0 represents the specific volume, $G(q_w)$ is the energy-wave-number characteristic, r is the distance between two atoms and q_w is the wave number [230]. The direct interaction between the ions is approximated based on the Coulomb potential, $Z^{*2}e^2/r$, of the point charges, Z^*e . The equation for the direct interaction between the ions is shown as follows [228]:

$$\sigma_d(r) = \frac{Z^{*2}e^2}{r} + \varphi_v(r), \quad (5.5)$$

where $\varphi_v(r)$ represents the additional van der Waals-type interaction from the finite extension of ions due to the core electrons. Based on the model developed by Schommers, the interactions between the atoms are determined according to the point charges of the ions and the conduction electrons, Eqs. (5.4) and (5.5), whereas the EAM potential used in this study is described as the total energy, Eq. (3.13), required to embed atoms into the homogeneous electron gas plus the energy from two-body interactions. The main difference between these two models is that the latter describes the potential energy by approximating the electron density of the embedding function while the model developed by Schommers describes the interactions by taking account of the point charges of the ions and electrons. The strength of the interactions between aluminium atoms using the EAM potential may be slightly weaker than the pseudopotential used by Schommers.

The weaker interactions between the atoms caused by the EAM potential in this study is likely to result in the disordered arrangements of the atoms on the Al(110) surface with low thermal energy. The diffusion processes by jumps and exchanges are

also easier to occur due to weaker energy barrier. Therefore, the premelting temperature for the Al(110) surface is expected to be lower than that reported by Schommers.

In order to have a clearer understanding of the effects of the EAM potential on the premelting of the Al(110) surface, the structure and dynamics of the atoms on the aluminium slab have been verified using the pair correlation function and the mean square displacement of the atoms in the z direction of the slab surface. The pair correlation function, i.e., the probability distribution for the distances between two atoms, for the Al(110) surface is compared with the pair correlation function for the bulk Al.

Figure 5.3.1 shows the surface dynamic behaviour of aluminium atoms at various temperatures. The darker shaded atoms represent the positions of atoms after simulation at the specified temperature. The surfaces of the slab are positioned to the left and right sides of each slab, where the z direction is represented horizontally. According to Figure 5.3.1, the close packing of aluminium atoms is in the perfect lattice position at temperatures up to 579 K. As the temperature is increased further, disordered aluminium atoms become more prominent, especially at 710 K. This phenomenon occurs at a lower temperature than the expected premelting temperature of 810 K. In order to confirm these findings, pair correlation functions are plotted based on bulk and surface atoms. Figures 5.3.2, 5.3.3 and 5.3.4 show the pair correlation results for the bulk aluminium at 240 K, the Al(110) surface at 240 K and the bulk aluminium at 584 K, respectively. According to Figures 5.3.2, 5.3.3 and 5.3.4, the periodic structure of the pair correlation function fits well to Schommers' result. However, the peak value for the pair correlation function in this study is slightly higher. The difference between the peaks in this study and that reported by Schommers is about 0.5 orders apart. Figures 5.3.5, 5.3.6 and 5.3.7 show the

pair correlation function at the Al(110) surface at 579 K, the bulk aluminium at 708 K and the Al(110) surface at 710 K respectively. The anharmonicities in Figure 5.3.7 suggest that the premelting phenomenon might occur near 710 K, similar to that reported in Schommers' result.

Figure 5.3.1 Surface dynamic behaviours of aluminum atoms at various temperatures. The darker shaded atoms represent the positions of atoms after simulation at the specified temperature.

Figure 5.3.2 Pair correlation function for bulk Al at 240 K.

Figure 5.3.3 Pair correlation function for the Al(110) surface at 240 K.

Figure 5.3.4 Pair correlation function for bulk Al at 584 K.

Figure 5.3.5 Pair correlation function for the Al(110) surface at 579 K.

In Figure 5.3.6, the periodic structure of the pair correlation function describing the bulk Al at 708 K is quite reasonable. Figure 5.3.7 shows the pair correlation function for the Al(110) surface at 710 K. The difference between the highest and lowest peaks for the pair correlation function of surface atoms at 710 K is about 1.5. Based on Schommers' result, the difference between the highest and lowest peaks in the pair correlation function of the outermost Al(110) surface at 710 K is about 1.5. Compared to Schommers' result, the periodic structure of the pair correlation function (Figure 5.3.7) is similar to the premelting condition at 710 K reported by Schommers.

Figure 5.3.6 Pair correlation function for bulk Al at 708 K.

Figure 5.3.7 Pair correlation function for the Al(110) surface at 710 K.

The temperature dependence of the layer structure factors, $S_x(K)$, for the outermost four layers of the Al(110) surface is shown in Figure 5.3.8. The layer structure factor is given as [65]:

$$S_{l,x}(K) = \left\langle \frac{1}{n_l} \sum_{i \in l} e^{iKr_{v,i}} \right\rangle, \quad (5.9)$$

where $K = (2\pi/a_0)(0,0,2)$ is the reciprocal lattice vibration vector along the rows in the [001] direction, a_0 is the lattice parameter, $r_{v,i}$ is the radius vector of the i^{th} atom and n_l is the number of atoms in the l^{th} atomic layer. The angular bracket indicates an averaging over the simulated trajectories. For a perfectly ordered fcc structure at 0 K, $S_x(K)$ is equal to 1 whereas for a disordered structure such as liquid, $S_x(K)$ is equal to 0. The layer structure factors for the four outermost layers decrease with temperature almost

linearly until around 710 K (Figure 5.3.8). The vibrational amplitudes of the atoms at these layers increase and the phenomenon becomes more significant at around 710 K. The decrease in the slope of the layer structure factors at temperatures between 600 K and 710 K suggests a loss of order in the atomic arrangement for the outermost four layers, which is associated with the melting phenomenon. As reported by Stoltze *et al.*, the phenomena of the disordering and melting of an Al(110) surface occur layer by layer [42]. The first three layers melted at a temperature approximately less than 100 K below the bulk melting temperature ($= 800$ K). The melting temperature for the Al(110) surface in the model is thus quite close to the melting temperature of the Al(110) surface region described by Stoltze *et al.* They have used the effective-medium theory for the description of the interatomic interactions in their simulation models. Based on the report of Frolov *et al.* [231], the change in the trend of the linearly decreasing layer structure factor for the Cu(110) surface indicates that the surface atoms begin to leave their regular positions and become adatoms. This phenomenon results in the formation of vacancies. Therefore, the disorder of the surface atoms at around 710 K in Figure 5.3.8 represents the occurrence of the complex diffusion events on the Al(110) surface, which eventually leads to the melting phenomenon of the surface as temperature increases.

In order to confirm the results of the layer structure factors, we examined the study of the surface melting of the V(110) plane performed by Yang *et al.* They reported the behaviour of the V(110) plane based on layer structure factors [64]. According to them, the layer structure factors that are lower than 0.5 indicate that a partly disordered state exists in the layer configuration, and layer structure factors that are lower than 0.1 mean that the plane is fully out of the ordered state. Figure 5.3.8 shows that the layer of

the first two layers of the Al(110) surface decrease to nearly 0.5 at around 710 K. This result suggests that the layer configurations of the first two layers are partly disturbed while the inner layers are still close to perfectly ordered configurations.

Figure 5.3.8 The temperature dependence of the layer structure factors for the outermost four layers of the Al(110) surface.

Shu *et al.* have studied the anisotropic surface melting of Al(110) by MD simulations, using glue potential as the interactions between the atoms in the metal [65]. According to their results, the density change in the first layer of the crystal occurs at 600 K. The change in density is assumed to have resulted in the formation of adatoms and vacancies. In this study, the pair correlation function for the Al(110) surface has implied that a surface premelting phenomenon had occurred at around 710 K due to the anharmonicities of the periodic structure in the pair correlation function. The comparison between results of this study and the results reported by Shu *et al.* has verified that the outermost surface melting temperatures reported by these two studies are almost similar.

The results from Shu *et al.* showed that the top four layers of the Al(110) surface became liquid-like at 945 K, which was modelled as the melting point of the crystal. By comparison, the melting temperature of the outermost four layers of the Al(110) surface in this study is lower than the melting point reported by Shu *et al.*. This is because the disorder of the four layers of the Al(110) surface begins to occur at around 710 K (Figure 5.3.8), and premelting is prominent at a temperature of 710 K due to the reduction in periodicity of the pair correlation function (Figure 5.3.7).

The mean square vibrational amplitudes of the atoms on the Al(110) surface are plotted as a function of temperature in Figure 5.3.9 along the x , y and z directions, corresponding to the $[001]$, $[1\bar{1}0]$ and the $[110]$ directions respectively. The results show that the mean square vibrational amplitudes of the surface atoms along the x and y directions increase greatly at 710 K, showing an anharmonic increment. The easiest diffusion path for the atoms on the Al(110) surface is along the y direction. The anharmonic behaviour of the vibrations along the x direction indicates that jump-exchange processes might start to occur on the Al(110) surface at temperatures between 650 K and 710 K, with the help of the occurrence of strong lateral vibrations of the row atoms along the $[001]$ direction. Ferrando had explained that the vibrational amplitudes in the $[001]$ direction on (110) surfaces increase at high temperatures and thus facilitate the occurrence of jump-exchange processes [66, 67]. Montalenti *et al.* have also suggested that strong lateral vibrations along the $[001]$ direction cause the adatom to be pushed or pulled by row atoms in the perpendicular direction, which eventually leads to correlated jump-exchange processes rather than long jumps along the channel [67]. Long jumps and simple exchange processes are possibly the only processes to have occurred on the

Al(110) surface above 600 K, which is close to the experimental result reported by Pedemonte *et al.* [224].

Figure 5.3.9 The mean square vibrational amplitudes of the atoms on the Al(110) surface along the x , y and z directions a function of temperature.

Chen *et al.* have performed the simulations of the oscillatory surface relaxations in Al using the EAM developed by Daw and Baskes to describe the interactions between atoms [68]. The period of the oscillation of Al atoms along the [110] direction on the Al(110) surface was found to be close to the nearest-neighbour distance ($=2^{-1/2}a$, where a is the lattice constant). Figure 5.3.9 shows that the vibrational amplitudes of the atoms perpendicular to the Al(110) surface are maintained within the range of the nearest-neighbour distance. These findings suggest that the EAM potential resulted in ordered oscillation of the atoms in the direction perpendicular to the Al(110) surface at temperatures lower than the bulk melting temperature.

The layer diffusion coefficient of the surface atoms parallel to the surface is given by [232],

$$\lim_{t \rightarrow \infty} \langle r^2(t) \rangle = 4D_c t, \quad (5.10)$$

where

$$r^2(t) = \left\langle \frac{1}{n_l} \sum_{i \in l} r_i(t + \Delta t) - r_i(t) \right\rangle, \quad (5.11)$$

in which the angular bracket, $\langle \rangle$, represents the averaging over time origins (Δt), n_l is the number of atoms on the surface, D_c is the diffusion coefficient and $r^2(t)$ is the mean square displacement. The diffusion coefficient affects the diffusion rate of the surface atoms, whereas the mean square vibrational amplitudes vary according to the temperature of the system.

According to the calculation of the diffusion coefficient, Eq. (5.10), the diffusion constant for the outermost layer at 810 K is about 11.76×10^{-5} cm²/sec, whereas Schommers reported a diffusion constant of 9.6×10^{-5} cm²/sec at 810 K. Hence, it is clear that premelting has indeed occurred at a temperature lower than 810 K, based on the potential applied in this study. As the premelting has been determined to occur at a temperature lower than 810 K using the assigned potential, the results obtained from the simulation at a temperature of 810 K are not be reported here.

The equilibrium melting temperature of the Al material, which is modelled using the EAM, is determined using the Lindemann index. The Lindemann index has been widely used to determine the melting temperatures of bulk solids [108]. According to the Lindemann criterion, the bulk matter is considered melted when the root mean square (rms) bond length for the thermal fluctuation of the solid increases more than 10-15% of the original value or when the Lindemann index value abruptly increases at a particular temperature [233, 234]. The Lindemann index is equal to the rms distance of a particle

from its equilibrium position, divided by the averaged nearest neighbour distance [235]. As shown in Figure 5.3.10, the equilibrium melting temperature for the Al material (modelled using the EAM) is around 810 K. According to Song *et al.*, the premelted layer width of a material depends on the degree of the undercooling [236]. The decrease in the undercooling results in the increase of the layer width. The critical undercooling temperature for aluminium is about 0.16 percent below the melting temperature, T_m , as reported by Lu and Li [237]. Based on the equilibrium melting temperature (810 K) found in this study, the critical undercooling temperature would then be about 680 K.

Figure 5.3.10 Lindemann index from MD simulations of the model EAM Al material.

5.4 Summary

The initial set up for the extension of the study on metal atoms flow in CNT channels has been demonstrated in this chapter. The algorithm describing the EAM potential between metal atoms and the simulation algorithm written using MATLAB are shown in Figures 5.2.1 and 5.2.2 respectively. These approaches are the primary steps to

generate metal atoms before the simulation of the metal atoms flowing within a CNT channel can be achieved. As an effort to understand the effect of EAM potential on metal atoms, the study of surface premelting on an aluminium slab has been performed and discussed in this chapter.

There are in total two main systems that are examined for the premelting study, the bulk aluminium and the aluminium surface at different temperatures. The simulations were performed at temperatures from 240 K to 810 K. The surface of the aluminium is orientated along the [110] direction. The results show that the pair correlation function has a good relation to the Schommers model for bulk aluminium at 584 K and for the surface layer at 240 K. However, the MD analyses using the EAM potential revealed that the premelting of the Al(110) surface occurred at a lower temperature than that reported by Schommers. The pair correlation function for the surface layer at 710 K indicates the anharmonicity in the periodic structure. The diffusion constant at 810 K is calculated to be much larger than that at 810 K reported by Schommers. Hence, premelting of the Al(110) surface in this study has indeed occurred at a temperature lower than 810 K. The disordered layer configurations of the first two layers of the Al(110) surface have been verified using the layer structure factor as a function of temperature and the premelting phenomenon occurs at 710 K. The mean square vibrational amplitudes suggested that the correlated jump-exchange processes are likely to occur at temperatures higher than 650 K and the vertical vibrational amplitude is maintained within the range of the nearest-neighbour distance at temperatures lower than the bulk melting temperature. The results from this simulation study also show satisfactory correlation with the experimental results generated by various sources.

CHAPTER 6

SIMULATION OF COPPER ATOMS IN CNT CHANNELS

6.1 Experimental results for copper filled CNT

The binding of copper atoms is different from the binding of water molecules and the oligonucleotide, because the basis of interactions between the atoms is not the same. Due to the differences in the interaction potentials, the dynamics of the metal atoms in CNT channel and the dynamics of the solvated oligonucleotide thus vary. The investigations of copper filled CNTs are studies that mainly address the formation of copper nanowires in CNTs and the delivery of copper using CNTs. In this chapter, studies of copper filled CNTs mainly focus on the changes that occur to the filled material in CNTs, establishing a better understanding of the flow phenomena in CNT channels and the conditions affecting them.

The flow of copper in CNT channels is driven by the electromigration forces. The experiment on the electromigration of the copper nanowire that was done by Fujisawa *et al.* has shown that the crystal growth energy of the copper nanowire, involving about 70 moving atoms, is about 9 aJ [98]. During electromigration, the stress in the copper is in a tensile state. As a result of relaxing the tensile stress, compressive stress is generated in the copper nanowire. On the other hand, Hwang *et al.* have reported that the potential energy of copper cluster in the (5,5) CNTs is about 1.5 eV [38].

The experiment conducted by Golberg *et al.* has shown that copper may fill CNTs fully or discretely [155], as shown in Figure 6.1.1. The copper fills CNTs with electromigration processes. Based on the authors' estimation, the temperature of the

copper inside CNTs can be as high as 1500°C, surpassing the melting point of the filled material.

Figure 6.1.1 Structural and crystallographic characteristics of the starting copper-filled CNT cables. [Golberg *et al.*, *Advanced Materials* 19 (2007) 1937]

The transportation of copper atoms along CNTs using electromigration is also shown by Dong *et al.* experimentally [102]. According to their experimental results, the melting of copper core in CNTs, with inner diameter of 39 to 22 nm, occurs at 700° C. As the size of the copper material decreases, the melting point would decrease even further due to the effect of the surface-to-volume ratio. Figure 6.1.2 shows the time-resolved TEM images of the flowing process of a copper filled CNT. Based on the flow direction and the behaviour of the copper flow in CNTs, Dong *et al.* have concluded that other

flow mechanisms, such as capillary and thermal expansion, are excluded from their experiment.

Figure 6.1.2 Time-resolved TEM images from video frames showing the flowing processes of a copper filled CNT. [Dong *et al.*, Nano Letters 7 (2007) 58-63]

Fan *et al.* have shown experimentally that the deposition of copper on a surface can be achieved through the electromigration of copper in copper filled CNTs [238], a process known as electromigration-based deposition (EMBD). The EMBD can be carried out on the object surface which is either conductive or insulate, as shown in Figure 6.1.3. If the object surface is thermal and electric resistive, reheating and reshaping of the deposits are possible. This is because if the probe has a larger thermal energy capacitance than the CNT, the interface between the probe and CNT will have the lowest temperature. The cooled-down deposit will therefore unable to be reheated for reshaping. According to the experimental work conducted by Fan *et al.* [238], the flow of the copper in the CNT is confirmed to be due to electromigration. The inner copper core flows out of the tip of the CNT when the bias voltage is reached to 2.0 V. For the simulations of copper flow in CNTs, it is thus appropriate to assume 2.0 V to be the minimum bias voltage for the electromigration of copper to occur in CNT channels. Besides exploring on the transport of copper-filled CNTs, Fan *et al.* have also found that the copper filled between the

neighbour CNTs and the CNT injector can be sucked into the injector, most probably due to the electromigration-induced inter-tube mass transport [239].

Figure 6.1.3 Schematic of electromigration-based deposition (EMBD). (a) A metal layer on the object surface is necessary to form the electric circuit for EMBD. (b) If a probe is attaching to the sidewall of the metal-filled CNT (m@CNT), the object surface can either be conductive or insulate. [Fan *et al.*, IEEE International Conference on Robotics and Automation, Shanghai, China (2011) 2686-2691]

Electromigration often plays a role in driving the metal out of CNTs. One such example is the release of copper iodide from copper iodide encapsulated in CNTs [240]. Costa *et al.* have experimentally found that the electrical conductivity calculated for encapsulated copper iodide is closer to copper than the copper iodide bulk figures. One of the possibilities is that the elevated current densities and the Joule heating effects of copper iodide lead to localized phase transformations, or the iodine depletion, at the crystallites closer to the biased tip where higher electric fields are expected to be found. The discharge of copper ions results in the deposition of copper crystals, as reported by Dong *et al.* [102].

There are various methods of producing copper filled CNTs. Haase *et al.* have demonstrated the synthesis of carbon coated copper nanowires using copper(II)-acetylacetonate as a precursor [241]. As part of the investigation of copper-filled CNTs, Haase *et al.* have also conducted the experiment for the removal of the copper filling from the carbon wrapping. According to their findings, the copper filling melts and leaves the carbon sheath under heating conditions down to 800 °C. For copper nanowires of even smaller scales, the copper would melt at an even lower temperature due to the surface effect. Figure 6.1.4 shows the copper nanowires reheated at different temperatures.

Figure 6.1.4 Copper nanowires reheated at different temperatures: (a) at 1000 °C – tubes totally empty, (b) at 840 °C – at least 50% empty. [Haase *et al.*, Surface & Coating Technology 201 (2007) 9184-9188]

The extrusion of the metal from metal-filled CNTs can lead to the production of metallic nanospheres on the tip of nanotubes. The fabrication process is also known as nanobubbling. Fan *et al.* have shown that among the two methods, electron-beam-induced bubbling (EBIB) and electromigration-based bubbling (EMBB), EBIB does not result in bubbling for copper-filled CNTs [242]. At first, a copper polyhedral nanoparticle

is formed on the tip of the nanotube. As the bias voltage increases, a spherical particle forms on the tip of the nanotube. The process of nanobubbling for a copper-filled CNT is shown in Figure 6.1.5. For the flow of copper to occur, a bias voltage is applied to the two ends of the CNT up to 2.0 V to 2.5 V. Based on this evidence, the minimum amount of a bias voltage for copper flow through the CNT is thus 2.0 V.

Figure 6.1.5 EMBB processes. (a) EMBB using a copper filled CNT. (b) Sphere on the tip by EMBB. (c) A sphere formed on a nanotube. [Fan *et al.*, Proceedings of 10th IEEE International Conference on Nanotechnology Joint Symposium with Nano Korea, Korea (2010) 649-654]

6.2 Transportation of copper atoms along a (5,5)–(4,4) CNT channel

6.2.1 Simulation conditions

MD simulations are performed in this study for the transportation of copper along a CNT channel. The MD code is written using MATLAB [243]. In the simulations, the copper atoms are confined within a CNT channel modelled as a nonpolarized, single-walled, and armchair CNT channel. The structure of the CNT channel consists of one CNT junction, joined by two nanotubes of different diameters. The connecting joint of the CNTs can be connected by a pentagon and heptagon pair of carbons [78]. The CNT channel is generated using CoNTub [110]. For this simulation study, a (5,5)–(4,4) CNT channel is constructed. The (5,5)–(4,4) CNT channel has 596 carbon atoms, with a diameter of 6.8 Å for the (5,5) nanotube and a diameter of 5.4 Å for the (4,4) nanotube. The CNT channel is approximately 82 Å in length, spanning the z coordinate between –41 and 41. The CNT channel is fixed in space.

There are a total of 20 copper atoms in the (5,5)–(4,4) CNT channel. Metal atoms were initially placed within the CNT channel. Before the nonequilibrium MD simulations were performed, energy minimization and equilibrium MD runs had been made.

The copper atoms in the system are modelled using the EAM [61] with the cutoff distance between two atoms as $r_{cut} = 1.65a_0$ ($a_0 = 3.615$ Å).

The interaction between copper and carbon can be expressed in the form [244],

$$E_{Cu-C}(r) = \sum_{i < j} \left[\frac{C_{12}(i, j)}{r_{ij}^{12}} - \frac{C_6(i, j)}{r_{ij}^6} \right], \quad (6.1)$$

where r is the distance between two atom pairs, $C_6 = 41.548$ (eVÅ⁶) and $C_{12} = 2989.105$ (eVÅ¹²). The cutoff distance is set at 10 Å [245]. A bias voltage is applied to the system to drive the copper atoms along the CNT channel. The driving forces (ξ_{em}) exerted on the transported atoms by the electromigration process can be expressed in the following equation [190]:

$$\xi_{em} = (Z_d + Z_w)eE = \left(Z_d + \frac{K_m}{\gamma(T)} \right) eE, \quad (6.2)$$

where Z_d and Z_w are the valence equivalents of the direct and wind forces respectively, e is the electron charge, and E is the electric field. T is the temperature in Kelvin and $\gamma(T)$ is the resistivity of the material. The resistivity is temperature dependent and can be described as $\gamma(T) = 2.96 + 0.00768(T - 473)$ μΩcm for copper [191]. The parameters for copper are given as $K_m = -33.3$ μΩcm and $Z_w = -11.3$ [97, 191].

The driving force for metal atoms is described using the wind force as a good measure for the main contribution to the driving force. During the MD simulations, copper atoms would move along the opposite direction of the force applied and therefore the electromigration force is induced towards the $-z$ direction. In the experiment conducted by Golberg *et al.*, the copper mass is transported using 6–10 V of potential [155], whereas Dong *et al.* used a bias voltage of 2.1 V for transporting copper in CNTs

[246]. In this simulation study, the voltages are set at 2, 4, 6, 8 and 10 V. The positive values of energies or forces are used to indicate the repulsive effect between atoms, whereas the negative values are indications of the attractive effect between atoms.

The calculated electromigration force is added to the interatomic force of copper atoms. Due to the added electromigration force, the temperature of copper is increased because an electromigration process results in the resistive heating of the filling material in CNTs. The temperature of copper is adjusted throughout the simulation process using the modified velocity rescaling method, which is developed in this thesis as:

$$\frac{u_i^{new}}{w_i^{old}} = \sqrt{\frac{T_t}{T_{e,i}}}, \quad (6.3)$$

where u_i^{new} is the velocity of the i^{th} atom after rescaling, w_i^{old} is the velocity of the i^{th} atom with the inclusion of the electromigration force before rescaling, T_t is the targeted temperature and $T_{e,i}$ is the temperature (the electromigration force is excluded) which contributes to the thermal effect of the i^{th} moving atom. The Verlet method is used in the algorithm of the simulations and the neighbour list is constructed in order to improve the efficiency of the program. Visual Molecular Dynamics (VMD) [247] is used for the visualization of the system.

The simulation cases are set up based on the combinations of different magnitudes of bias voltages and different temperatures. Dong *et al.* have investigated the flow of copper in CNTs at temperatures ranging between 700 and 1800 K using MD simulations [246]. However, the study conducted by Alper and Politzer. [188] has shown that the

temperature-dependent behaviour of copper is found to be in good qualitative agreement using the potential due to Cai and Ye. [61] at temperatures between 300 and 1100 K. To maintain good accuracy of the description of copper atoms at different temperatures, the initial temperatures of copper atoms for the simulation study are set at 373, 673, 873, 1073 and 1273 K. The analyses for the simulations at 1273 K are reasonably acceptable because the bulk material of copper is maintained as solid at this temperature. The simulation time step is set at 1 fs. The maximum simulation duration for this study is set at 20 ps, which is sufficient for the transportation of copper atoms along the entire CNT channel.

6.2.2 Analyses of the dynamical behaviour of copper atoms in a (5,5)–(4,4) CNT channel

The investigation of the simulations focuses on the transport of copper along a CNT channel under the influence of electromigration processes. Copper atoms are initially situated in the wider end of the channel and aligned parallel with the tube axis. A bias voltage is applied along the channel to induce a driving force for the copper atoms to propel toward the narrow end of the channel. The magnitude of the flow is affected according to the variation in temperatures and magnitude of the voltage applied. According to this simulations study, the threshold voltage value for the electromigration of the entire copper mass in a (5,5)–(4,4) CNT channel to occur is 0.25 V. The investigation of the simulations also focuses on the role of the CNT junction acting mainly as a geometric barrier to the flow.

Since the transportation of metal atoms along CNTs is often demonstrated in tubes which are uniform in diameters [103], the effect of varying CNT diameters such as a junction shows an interesting outcome to the transportation of metal atoms. Figure 6.2.1 shows the transportation of copper atoms along a CNT channel at 873 K, with a bias voltage of 2 V. According to the figure, the copper mass is transported as an entire entity along the channel, with no separation of any copper atom from the group of copper mass. When the copper mass reaches the junction, the distances between copper atoms are shortened and the atoms are “pushed” towards the junction as depicted in Figure 6.2.1(b). The “squeezing” effect on the copper mass is caused mainly by the electromigration force and the blockage of the CNT junction. As the applied electromigration force continues to work against the junction of the channel, the copper atoms are realigned due to the repulsive energy from the CNT junction and eventually flow into the narrower region of the channel, which is shown in Figure 6.2.1(c).

Figure 6.2.1(d) illustrates that the junction of the channel causes the copper mass to increase in length after exiting from the channel junction. However, a slight difference between the spacing of the copper atoms at the front and rear ends of the copper mass exists at the (4,4) CNT. The copper atoms at the front end have narrower spacing compared to the copper atoms which are closer to the CNT channel junction, as shown in Figure 6.2.1(e). When copper mass is blocked by the channel junction during the transportation process, no copper atoms are observed to be detached from the copper mass to move into the (4,4) CNT. This is because the magnitude of the electromigration force is strong enough to overcome the energy barrier presented by the CNT junction to

push the entire copper mass it, and also the diameter ratio of the two joined CNTs is closed to 1.

Figure 6.2.1 Transportation of copper along a (5,5)–(4,4) CNT channel with a 2 V bias voltage at 873 K. Snapshots were taken at (a) 1.6 ps, (b) 3.4 ps, (c) 4.4 ps, (d) 6.7 ps and (e) 9.0 ps respectively.

While the copper mass is delivered along the channel, the electromigration force that contributes to the flow phenomena would result in the temperature increase among the copper atoms due to effect of Joule heating [155]. The change in the temperature of the copper mass shows how an electromigration process would result in the temperature

increase of copper in relation to that of the initial temperature of the copper mass. Figure 6.2.2 shows the temperature change of copper atoms under the influence of electromigration processes, with the initial copper temperatures set between 373 and 1273 K. At 373 K, the increase in the voltage causes the temperature of copper atoms to change the most. An applied voltage of 10 V resulted in the change of about 800 K in copper atoms as shown in Figure 6.2.2(a).

When the initial temperature of copper atoms is set at 1273 K, the applied voltage of 2 V causes the temperature to increase by about 25 K, whereas an applied voltage of 10 V results in only an increase of about 230 K among the copper atoms as illustrated in Figure 6.2.2 (e). The increase in bias voltages has mainly altered the kinetic energy of the copper atoms, therefore causing the temperature of the copper mass to elevate. When the copper mass is blocked by the channel junction (at about 4 ps as shown in Figure 6.2.2), the kinetic energy of the copper atoms is reduced, hence effectively lowering the change in temperature. For systems with initial temperatures of 673 K and above, the maximum increase caused by an applied voltage of 10 V is less than 270 K, whereas an applied voltage of 2 V results in temperature differences of less than 100 K. The total temperature achieved in the simulations of the flow of copper atoms in the (5,5)–(4,4) CNT channel is ranged between 1200 and 1500 K, for the bias voltage of 10 V. The high bias voltage applied onto copper atoms has in fact resulted in an increase in the temperature which is closed to that reported by Golberg *et al.* at 1500 K, as the bias voltage increases to 10 V [155]. Since the temperature of copper atoms is linked to the velocities of the copper atoms, this means that the temperature adjustment based on the new rescaling velocity method is fairly reliable.

Figure 6.2.2 Temperature change of copper atoms during transportation processes. The CNT channel temperature enveloping copper atoms is initially set at (a) 373 K, (b) 673 K, (c) 873 K, (d) 1073 K and (e) 1273 K respectively.

As mentioned earlier, the atomic arrangement of copper atoms during transport processes changes due to the effect of the channel junction and the electromigration forces. To have a better understanding of the relationship between the copper mass and the CNT channel during the flow, the investigation of the change in the interactive forces between the copper mass and the CNT channel is conducted. The position of the copper

mass in the CNT channel is defined based on the placement of the COM of copper along the z axis of the channel. The interactive forces between the copper mass and the CNT channel are shown in Figure 6.2.3. The CNT channel is divided into three main segments for the analyses of the interactive forces between copper and the CNT channel. The three main segments of the CNT channel are: the (5,5) CNT region (between -40 and -11 Å), the channel junction (between -11 and 2 Å) and the (4,4) CNT region (between 2 and 40 Å).

When copper is transported in the (5,5) CNT region, the interactive forces between copper and the CNT channel are generally low. The interaction forces are less than 0.5 aJ/Å when the copper mass is transported along the CNT channel between -30 and -11 Å. However, as the copper mass approaches the CNT junction region, the interactive forces between the channel and copper increases. The increasing interactive forces at the junction are indications of strong repulsive forces being developed in order for the separation of copper atoms and the CNT channel junction to occur.

By comparing the figures (a)–(e) in Figure 6.2.3, it is noted that the highest interactive force occurs when copper is near the junction at a surrounding temperature of 373 K, with an applied bias voltage of 10 V. The maximum interactive force between copper and the CNT channel junction at a temperature of 373 K, with an applied voltage of 10 V is about 6.5 aJ/Å, as shown in Figure 6.2.3(a). When the initial temperature of the copper mass is set at 1273 K, the dynamics of the copper atoms are close to that of the liquid state since the melting temperature of copper is around 1358 K [188] and therefore the thermal vibration of copper atoms at 1272 K is large compared to the state of copper at other lower temperatures. During the flow process at 1273 K, the copper mass which is

blocked by a CNT channel junction is able to reconfigure the arrangement of the copper atoms more easily owing to the large thermal vibration, hence resulting in lesser repulsive forces between copper and the CNT junction.

Compared to the copper mass at higher temperatures, the atomic arrangements of copper atoms at lower temperatures are much more organized and compact due to smaller thermal vibrations. When the electromigration forces (driving forces) are strong, the repulsive forces between the CNT channel junction and the copper mass at lower temperatures would be higher too. The interactive forces at the (4,4) CNT region are almost similar to the interactive forces at the (5,5) CNT region. The interaction between copper atoms and the straight portions of the channel ((4,4) CNT and (5,5) CNT) is quite low. The interaction forces that occurred in the straight portions of the channel are also not affected by the difference in temperature and electromigration forces.

To have a clearer understanding of the atomic arrangement of the copper mass at different temperatures and under the influences of different electromigration forces, the potential energy of copper is presented in Figure 6.2.4 for a better illustration. The potential energy of copper atoms plays an important role in causing the changes to the atomic configuration. This is reflected as the change in the interaction between copper atoms. According to Figure 6.2.4, the significant change to the atomic configuration of copper atoms occurs only at the CNT junction due to the large variation of the potential energy, whereas the potential energy of copper at the (5,5) CNT region is almost similar at all the temperatures and the potential energy of copper at the (4,4) CNT region is almost similar at all the temperatures too.

Figure 6.2.3 Interactive forces of copper atoms and the CNT channel. The CNT channel temperature enveloping copper atoms is set at (a) 373 K, (b) 673 K, (c) 873 K, (d) 1073 K and (e) 1273 K respectively.

Figure 6.2.4 also shows that the potential energy of the copper mass at the junction is higher when the initial temperature of the copper mass is lower and when the electromigration forces are higher. At lower initial temperatures, the thermal vibration of copper atoms is small; hence the movement of copper atoms is less. As the copper mass

is transported towards the CNT junction, the combination of the electromigration force and the blockage of the junction cause the potential energy of copper atoms to increase. As the reorganization of the copper atoms at lower temperatures is more difficult, the resulting potential energy is thus higher. The copper atoms with high potential energies are likely to repulse one another due to the “squeezing” effect of the electromigration force and the blockage of the junction.

Based on the observation of the potential energy of copper in Figure 6.2.4, the potential energy at the z coordinate between -30 and -12 Å is negative. This indicates that the copper atoms are in a compact state and the attractive energy dominates among them. As copper atoms pass through a CNT junction, the potential energy would increase, showing that atomic distances between copper atoms are closer than the initial atomic separation of copper atoms at the (5,5) CNT. The reduction in atomic distances of copper atoms at the CNT junction results in the overall repulsive effect among the copper atoms.

Since the space in the (4,4) CNT region is narrower than that in the (5,5) CNT region, the mobility of copper atoms in the (4,4) CNT region is confined. As such, the interaction between copper atoms is more frequent, resulting in more repulsion between copper atoms. The outcome of this phenomenon is reflected as a relatively higher potential energy of copper atoms in the (4,4) CNT region as compared to copper atoms in the (5,5) CNT region. In addition, the differences can be explained as the change in the atomic arrangement of copper, whereby a CNT junction acts as a buffer region for the change to occur.

Figure 6.2.4 Potential energy change of copper atoms along the CNT channel. The CNT channel temperature enveloping copper atoms is set at (a) 373 K, (b) 673 K, (c) 873 K, (d) 1073 K and (e) 1273 K respectively.

Figure 6.2.5 focuses on the resistive force acted on the copper mass by the CNT channel. By comparing all the figures in Figure 6.2.5, Figure 6.2.5(e) shows the resistive forces on the copper mass with least fluctuations. The main reason for the minimal fluctuation in Figure 6.2.5(e) may be the randomness of copper atoms at the junction at 1273 K. When the temperature is 373 K, the maximum resistive force acting on the copper mass by the CNT channel junction is about $6 \text{ aJ}/\text{\AA}$, which is larger than the

maximum resistive force at the temperature of 1273 K under the same applied voltage of 10 V. For the transportation of the copper mass along the (5,5) CNT and (4,4) CNT regions, the resistive forces indicated in Figure 6.2.5(a)–(e) are close to 0 aJ/Å. Since the resistive forces are low along the (5,5) CNT and (4,4) CNT regions, the difference in the resistive effect of the CNT channel on the flow between these two regions would be quite insignificant.

Figure 6.2.5 Resistive forces on the transportation of copper atoms along the CNT channel. The CNT channel temperature enveloping copper atoms is set at (a) 373 K, (b) 673 K, (c) 873 K, (d) 1073 K and (e) 1273 K respectively.

6.2.3 Analyses of the atomic arrangement of copper atoms under electromigration conditions

The simulations in this study focus on the outcome of the atomic arrangement of the copper mass along a CNT channel due to electromigration conditions. When copper atoms are transported along the junction, the positions of the copper atoms undergo rearrangement in order to change the energy of the copper mass. The CNT junction forms a barrier to the flow of copper. Figure 6.2.6(a) shows the transportation of copper atoms along a (5,5)–(4,4) CNT channel. According to the results of the simulations (not shown here), the copper mass is transported as an entire entity along the channel, with no separation of any copper atom from the group of copper mass regardless of the change in the applied bias voltages. This is because the magnitude of the electromigration force is strong enough to overcome the energy barrier presented by the CNT junction, thus driving the entire copper mass across it.

In this simulation study, the energy of copper atoms is changed as the copper atoms undergo rearrangement of the atomic positions. There are two colours specifically highlighted in Figure. 6.2.6 for two copper atoms, in which they are in red and yellow. The red and yellow colours represent the positions of copper atoms number 1 and 2 respectively. The positions of red and yellow copper atoms in Fig. 6.2.6 (b) indicate the orientation of the copper mass in the channel initially. The change in the positions of the coloured copper atoms represent the change in the orientation of the entire copper mass as shown in Figs. 6.2.6 (b) and (c). The change in the orientation of the copper mass is the result of the copper mass translocating along the CNT channel junction. While the copper atoms are propelled towards the (4,4) CNT channel during transportation, the

combination of the channel junction and the driving force causes the copper atoms to move away from the original state. Figures 6.2.6(b) and (c) show the difference in the atomic positioning of the copper atoms in the (5,5) CNT and the (4,4) CNT respectively. At a low bias voltage (2 V), the energy of the copper mass is changed when the entire copper mass is rotated by an angle of approximately 45 degrees with respect to the y coordinate during the transportation process along the CNT junction by the electromigration force.

When copper atoms are transported along the CNT junction by the electromigration force, the rotating phenomenon causes the potential energy of copper atoms to increase. This process results in a higher total energy of the copper mass, which improves the ability of the flowing copper atoms to overcome the energy barrier of the junction. In general, the change in temperature poses minimal influence to the rotating phenomenon of the copper mass during the transportation process along the CNT junction.

Figure 6.2.6 Transportation of copper along a (5,5)–(4,4) CNT channel. (a) Side view of copper transport along a CNT channel. (b) Copper transport along the (5,5) CNT. (c) Copper transport along the CNT junction.

Based on further investigations, the rotation of the copper mass is found not to be an artefact of the initial condition of the copper atoms. The main procedure and initial conditions that are considered in this study include the minimization process, temperature, velocity and the positioning of the copper atoms in the CNT channel. The minimization process is performed before every simulation study is conducted. This procedure ensures that the atoms are placed in the positions where the atomic energies of copper atoms are at the lowest. The application of this simulation procedure does not affect the rotation phenomenon. The effect of temperature on the rotation of copper atoms is negligible and is mentioned in the earlier paragraph. The difference in the initial temperature is therefore not responsible for resulting in the rotation phenomenon of the copper atoms.

The initial velocity is assigned randomly amongst the copper atoms in accordance to Boltzmann distribution. Repeated simulation results show that a slight difference between the velocities of copper atoms, which is less than $1 \text{ \AA/fs}$, does not cause the rotating phenomenon of the transported copper atoms to be of any difference. However, it should be noted that when the copper atoms are initially positioned similar to Figure 6.2.6 (c), the transported copper atoms will not rotate in a similar fashion. The reason for this is not due to the artefact of the positioning of the copper atoms, but is due to the geometry of the CNT junction, in which the central axis of the (4, 4) CNT is positioned asymmetrically against the central axis of the (5, 5) CNT along the y-axis, affecting the interaction of the junction and the copper mass.

When the copper mass is delivered along the channel, the electromigration force that contributes to the flow phenomenon would result in the increase in the temperature of the copper mass due to the effect of Joule heating [155]. By assuming a constant

temperature ensemble for the copper mass initially, the ratio of the temperature for the copper mass shows how the effect of an electromigration process would result in the increase in temperature of copper in relation to that of the initial temperature of the copper mass. Figure 6.2.7 shows the temperature ratio of copper during an electromigration process versus the initial temperature of copper. The temperature ratio is defined as the ratio of the temperature of copper during the flow to the temperature of copper at the initial state. A high temperature ratio suggests that a large proportion of the energy contributed by the electromigration process is used to increase the thermal vibration of copper, whereas a low temperature ratio suggests that a large proportion of the energy contributed by the electromigration process is used to propel the copper mass towards the narrow ending of the channel. At a low bias voltage, the temperature ratio of the copper mass is quite small. Although electromigration processes contribute to the increase in the temperature of the copper mass, the data in Figure 6.2.7 suggest that a low bias voltage can in fact affect the temperature ratio of copper quite minimally. Since the temperature ratio is small, the thermal vibration of the copper mass would also not change significantly compared to the initial state.

As the bias voltage increases, the temperature ratio of the copper mass would increase accordingly. For a bias voltage of 10 V, the maximum temperature ratio at 673 K is about 1.7, which is about 54% more than the effect of 2 V on the temperature ratio at 673 K. The temperature ratio of the copper mass reduces gradually as the initial temperature of the copper mass increases. The reduction in the temperature ratio suggests that as the initial temperature of the copper mass becomes higher, the thermal vibration of the copper mass would be large enough so that any further increase in the bias voltage

would result in small contributions to the overall thermal vibration of the copper atoms. This phenomenon is valid provided that there is no abrupt increase in the temperature of copper atoms within a few picoseconds due to the electromigration processes.

Figure 6.2.7 Temperature ratio of copper during an electromigration process versus the initial temperature of copper.

Figure 6.2.8 shows the total interactive forces between copper and a (5,5)-(4,4) CNT channel junction under the influence of different bias voltages. The interactive force between copper and the (5, 5)–(4, 4) CNT channel junction is defined using the derivative of Eq. (6.1) with respect to r ,

$$\xi_{Cu-C}(r) = -\sum_{i < j} \left[\frac{12C_{12}(i, j)}{r_{ij}^{13}} - \frac{6C_6(i, j)}{r_{ij}^7} \right] \left| \vec{r} \right|, \quad (6.4)$$

where r is the distance between two atom pairs, $C_6 = 41.548 \text{ (eV}\text{\AA}^6)$ and $C_{12} = 2989.105 \text{ (eV}\text{\AA}^{12})$. The flow of copper along the CNT channel is achieved by applying a driving force on all copper atoms. When the driving forces (bias voltages) are high, the interactive forces between copper and the CNT channel junction are high too. As

mentioned earlier, the copper atoms at a lower bias voltage tend to adopt a rotating phenomenon while being transported along the channel junction. By comparing the phenomenon with Figure 6.2.8, it can be understood that the rotating phenomenon leads to less repulsive interaction between copper atoms and the CNT channel junction at a lower bias voltage because lower interactive forces tend to favour a more attractive effect.

When the applied bias voltage is increased to drive the copper atoms, the interaction between copper atoms and the CNT channel junction becomes stronger because copper atoms at high bias voltages are more repulsive to the CNT junction. The copper mass is hence working against the blockage of the junction. According to Figure 6.2.8, the highest interactive forces occur when the initial temperature of the copper atoms is 673 K. For initial temperatures that are higher, the increase in the interactive forces is not as significant as that which occurs at 673 K. The higher interactive forces at high bias voltages are reflected as having a more repulsive effect on the copper atoms by the CNT channel junction.

Figure 6.2.8 Total interactive forces between copper and a (5,5)-(4,4) CNT channel junction under the influence of different bias voltages.

In order to understand the effect of the temperature on the changes in the interactive forces between copper and the CNT channel junction, the investigation of the change in the interactive forces using various temperatures is conducted, as shown in Figure 6.2.9. At low initial temperatures, the interactive forces between copper and the CNT junction are higher compared to that at higher temperatures. The increase in the bias voltage leads to even higher interactive forces between copper and the CNT junction. As the initial temperature increases, the interactive forces decrease and fall between the range of 50 and 70 aJ/Å. The change in the interactive forces can be explained based on the thermal vibration of copper atoms. As temperature rises, the thermal vibration of copper atoms becomes larger. The large vibration level allows copper atoms to interact more frequently with the channel junction, resulting in an overall more attractive effect between copper and the CNT junction, which is reflected as lower interactive forces compared to cases at lower temperatures. At a low temperature, copper atoms are less mobile and more compact; hence the repulsive energy from the CNT channel works against the entire copper mass.

Figure 6.2.9 Total interactive forces between copper and a (5,5)-(4,4) CNT channel junction under the influence of different initial temperatures.

Figure 6.2.10 shows the radial forces on the transportation of copper along a (5,5)-(4,4) CNT channel. The radial forces are defined along the plane that is parallel to the cross sectional area of the CNT channel. The position of the COM of copper shows the location at which the copper mass is situated along the CNT channel. The location of the CNT channel junction is represented between -11 and 2 Å in Figure 6.2.10. According to Figure 6.2.10, the changes in the radial forces are significant when copper is transported along the channel junction, as shown between -13 and 0 Å. Apart from that, the radial forces in the (5,5) CNT are relatively lower, whereas the radial forces in the (4,4) CNT show the oscillating behaviour of copper atoms moving towards the tube end.

When the initial temperature of the copper mass is low, the radial forces experienced by the channel junction are high. The high radial forces are due to the resistance acting on the copper mass by the channel junction, in which the copper atoms consist of small thermal vibrations. At a high temperature, copper atoms with large thermal vibrations have higher mobility. This results in lower radial forces between copper atoms and the channel junction, which indicates the overall lesser repulsion between them.

Apart from that, Figure 6.2.10 also shows that low bias voltages result in lower radial forces between copper atoms and the channel junction. At a low bias voltage, the magnitude of the oscillation of the copper atoms in the (4,4) CNT is smaller. When the bias voltage is increased, the radial force between copper and the CNT channel is stronger and the strength of the oscillation is also greater. The difference in the radial forces is more significant for different bias voltages at a low temperature than that at a higher temperature. This is because the compensation for the energy to transport copper

along the channel junction against the energy barrier is overcome by the rise in the temperatures.

Figure 6.2.10 Radial forces on the transportation of copper along a (5,5)-(4,4) CNT channel. The temperature of the CNT channel is set at (a) 673 K, (b) 873 K, (c) 1073 K respectively.

6.3 Effects of junctions sizes on the flow of copper atoms along CNT channels

6.3.1 Simulation conditions

In the MD simulations of this study, the CNT channels are modelled as nonpolarized, single-walled, and armchair CNT channels. A CNT channel consists of one CNT junction, joined by two nanotubes of different diameters. The connecting joint of the CNTs is connected by a pentagon and heptagon pair of carbons [78]. The CNT channel is generated using CoNTub [110]. Four CNT channels are constructed for this simulation study: the (12,12)–(5,5) CNT channel, the (12,12)–(7,7) CNT channel, the (12,12)–(9,9) CNT channel and the (12,12)–(10,10) CNT channel. The diameters of the (5,5) nanotube, the (7,7) nanotube, the (9,9) nanotube, the (10,10) nanotube and the (12,12) nanotube are 6.77 Å, 9.48 Å, 12.2 Å, 13.5 Å and 16.2 Å respectively. The length of the CNT channels is between 110 and 170 Å, spanning the z coordinate between –65 and 105 Å. The CNT channels are fixed in space. The MD code is written using MATLAB [243]. Before the nonequilibrium MD simulations were performed, energy minimization and equilibrium MD runs had been made.

The CNT channel in this study acts mainly as a geometrical constraint for the flow of copper atoms. The MD methods are not applied to carbon atoms. However, the role of carbon atoms in the simulation of copper flow is necessary as the interaction between copper and carbon atoms affects the flow processes of the copper atoms along the channel. The purpose of assuming a fixed channel is to simplify the cases in order to

understand the effect of the CNT junction geometry on the transport behaviour of copper atoms.

The results obtained by assuming fixed carbon atoms reflect how the energy of copper atoms changes along the junction of the channel when the number of unknown factors affecting the flow, such as the movement of carbon atoms, the velocity of carbon atoms and the momentum of carbon atoms against the flow materials, is reduced. The change in the interaction forces between copper and carbon atoms along the junction also shows how the junction acts as a barrier to the flow of copper atoms with the gradual narrowing of the channel diameters. Since the premelting temperature of CNTs is high (about 2600 K) and the length of the CNT structure in this study is short, the assumption of a rigid structure is reasonable as long as the temperature of the system is lower than the suggested premelting temperature of CNTs [108].

Copper atoms are initially situated near the opening of the (12,12) CNT for all the nanochannels and the copper mass is aligned parallel with the tube axis. There are 100 copper atoms in the each of the CNT channels. The copper atoms are modelled using the EAM [61] with the cutoff distance between two atoms as $r_{cut} = 1.65a_0$ ($a_0 = 3.615 \text{ \AA}$). The total internal energy of a metal system of N atoms can be described using Eq. (3.13). The van der Waals interaction between copper and carbon can be expressed as Eq. (6.1).

A bias voltage is applied along the channel to induce a driving force for the copper atoms to flow along the CNT channels. The driving force (ξ_{em}) exerted on the transported atoms by the electromigration process is similar to Eq. (6.2). The positive values of energies or forces from the results are used to indicate the repulsive effect

between atoms, whereas the negative values are indications of the attractive effect between atoms.

The temperature of the copper atoms is controlled by the modified velocity rescaling method, shown in Eq. (6.3). The Verlet method is used in the algorithm of the simulations and the neighbour list is constructed in order to improve the efficiency of the program. VMD [247] is used for the visualization of the system.

The temperature setting for this simulations study is based on the analyses done under section 6.2.1. In order to prevent any discrepancy to the quality of the results based on the potential used for copper atoms, the temperature of copper for this simulation study is set at 1073 K, which is lower than 1100 K. The simulation time step is 1 fs. The maximum simulation duration for this study is set at 20 ps, which is sufficient for the transportation of copper atoms along the entire CNT channel.

6.3.2 Analyses of copper due to different junction sizes

The transportation of copper in various CNT channels is illustrated in Figure 6.3.1. The simulations of this study consist of four different cases, where each case focuses on one type of CNT channel. The (12,12)-(5,5) CNT channel, (12,12)-(7,7) CNT channel, (12,12)-(9,9) CNT channel and the (12,12)-(10,10) CNT channel are each referred to as cases 1, 2, 3 and 4 respectively. The (12,12)-(5,5) CNT channel has a total of 2048 carbon atoms, whereas the (12,12)-(7,7) CNT channel, the (12,12)-(9,9) CNT channel and the (12,12)-(10,10) CNT channel contain 1854, 1956 and 1998 carbon atoms respectively. The length of the (12,12) CNT is set at 45 Å for all the cases, whereas the

length of the (5,5) CNT is set at 100 Å, and the (7,7) CNT, the (9,9) CNT and the (10,10) CNT are set at 60 Å for all the cases.

For this study, the (12,12) CNT is defined as the upstream section, and the (5,5) CNT, the (7,7) CNT, the (9,9) CNT and the (10,10) CNT as the downstream sections. Due to the variation in the diameter of the narrow section of the CNT channels in different cases, the lengths and sizes of the CNT junctions for all the four cases are different, therefore resulting in different lengths of the channels. The entrance of the channel junction refers to the position between the CNT junction and the (12,12) CNT, whereas the exit of the channel junction refers to the position between the CNT junction and the downstream sections. The diameter ratio used in this study is defined as the ratio of the cross-sectional diameter of the upstream CNT to that of the downstream CNT, which is also the same as the ratio of the cross-sectional diameter of the entrance to that of the exit of the channel junction. The diameter ratios for cases 1, 2, 3 and 4 are 2.4, 1.7, 1.3 and 1.2 respectively. In order to maintain a relevant comparison between the simulation cases, the number of copper atoms and the initial positions of copper in the upstream CNT are constructed similarly for all cases. The MD simulation results for the size effect of CNT channel on copper flow are illustrated in Figures 6.3.2–6.3.6.

The atomic configuration of copper along the CNT channel undergoes a significant change when copper is obstructed by the CNT channel junction. In order to observe the changing trend of the atomic structure of copper due to different CNT channel junctions, the potential energy of copper at different simulation times as copper flows from one end of the channel to the other is plotted. Figure 6.3.2 illustrates the potential energy of copper during the flow along CNT channels. As copper approaches

the junction in cases 1 and 2, the obstruction from the junction halts the approaching copper atoms. The electromigration force continues to drive the remaining copper atoms forward, leading to the shortening of the distances between the copper atoms in the copper mass. This phenomenon leads to an increase in the potential energy of copper atoms, where copper atoms are most likely to repel one another and reconfiguration of atoms occurs.

Cases 3 and 4 show low increase in the potential energy compared to cases 1 and 2 because the diameter ratios of the channel junctions are relatively smaller than the latters. When the copper mass reaches the exit of the channel junction, the potential energy of copper atoms rises to the maximum. Although the kinetic energy of copper atoms is reduced at the channel junction, an increase in the potential energy of copper atoms and the forces provided by the electromigration process are sufficient enough to overcome the potential energy barrier caused by the carbon atoms of the CNT channel junction.

The strength of the potential energy barrier is closely related to the diameter ratio of the channel junction. Since the diameter ratio of the channel junction in cases 1 and 2 is larger, increase in the potential energy of copper in cases 1 and 2 is much more significant than that in other cases. According to the simulation results, it is found that a difference of 16.67 % in the cross-sectional diameter of the upstream and the downstream CNT, as in case 4, results in a nearly insignificant increase in the potential energy of copper atoms at the junction. On the other hand, a difference of 58 % in the cross-sectional diameter of the upstream and the downstream CNT, as in case 1, causes an increase of 18 % in the potential energy of copper atoms at the channel junction.

Figure 6.3.1 Copper flow in CNT channels. Cases 1, 2 3 and 4 refer to copper in the (12,12)-(5,5) CNT channel, the (12,12)-(7,7) CNT channel, the (12,12)-(9,9) CNT channel and the (12,12)-(10,10) CNT channel respectively.

The Van der Waals forces between copper and the CNT channel in the z direction is shown in Figure 6.3.3. The position of the copper is determined based on the position of the COM of the copper mass. We compare the interactive forces in the 4 cases to distinguish the effect of the junction size on the impedance of the copper flow. The junction of the CNT channel is tapered along the length of the channel (z direction), giving direct obstruction to the flow of copper. As shown in Figure 6.3.3, the van der Waals force between copper and the CNT channel is the strongest in case 1. The van der Waals forces in cases 2, 3 and 4 have shown a smaller increases between -20 and 20 Å. This suggests that the channel junction is mainly responsible of increasing the van der Waals forces between copper and the CNT channel, whereas sections of straight channels

have a nearly negligible effect on the interactive forces between copper and the CNT channel in the z direction.

Figure 6.3.2 The potential energy of copper along CNT channels during the electromigration transport.

The van der Waals interactions between the downstream CNT (at the position between 20 and 50 Å) and copper (from cases 1 to 4) show nearly similar interactions. The interactive force in case 1 shows a gradual reduction trend over a distance of 20 Å. The explanation for this phenomenon is that the flow of copper atoms into the downstream CNT as depicted in case 1 is slow and incomplete, thus the remnants of copper atoms leaving in the channel junction are reflected as a gradual reduction of the van der Waals forces. Ease of clearance at the channel junctions, such as in cases 3 and 4, is essential in assuring small interaction between copper and the channel junction.

Figure 6.3.3 Van der Waals forces between copper and the CNT channels during the electromigration transport.

After expressing the interactive forces associated with copper and the CNT channel, the relationship of the average forces (between copper and the channel junction) with respect to the diameter ratio is plotted in Figure 6.3.4 to illustrate the magnitude of the interaction due to different sizes of the junction. The size of the junction is represented using the diameter ratio. According to Figure 6.3.4, the gradient of the average van der Waals force between copper and the channel junction decreases as the diameter ratio increases. For the case where the diameter ratio is smaller than 1.3, the rate of increase in van der Waals force is relatively greater. The higher gradient in the van der Waals force at diameter ratio lower than 1.3 can be explained based on the area of contact between the copper mass and the CNT junction.

When the diameter ratio is lower than 1.3, the copper mass that flows along the CNT channel junction does not undergo significant changes in the droplet size and the surface area due to the less narrowing of the junction. Instead, the contact between the junction and the copper mass occurs only at the surfaces, and the magnitude of the

contact is dependent on the slope of the channel junction that tapers to the downstream CNT. As the ratio increases, the increase in contact between the inner surface of the junction and the surface of the copper mass is even greater and hence is reflected as a high gradient in van der Waals force at diameter ratios lower than 1.3. However, as the diameter ratio continues to increase, the total reaction by the driving force and the blockage of the junction eventually forces the copper atoms to rearrange its atomic structure in order to accommodate to the shape of the channel junction, in which the surface area of the copper mass also changes.

The atomic rearrangement of the copper atoms that results in the increase in the surface area of copper is due to the change in the volume of the copper mass. Increase in the inner surface area of the junction and the increase in the surface area of the copper mass result in a proportional increase in the van der Waals interaction that is steady and less steep. The low gradient of the van der Waals force is reflected at diameter ratios higher than 1.3 as shown in Figure 6.3.4.

Figure 6.3.4 Average forces between copper and the channel junction in CNT channels of different diameter ratios.

The illustration of the flow phenomenon for this study is presented in Figure 6.3.5, showing the change in the velocity of the copper mass along the CNT channel with respect to the positioning of the COM of the copper atoms along the channel in the z direction. Initially, the copper mass is situated in the (12,12) CNT for all the simulation cases. The flow is then induced using the same bias voltage for all the cases. Based on the results in Figure 6.3.5, the velocity of the copper flow along the channel junction has reduced compared to the velocity at straight sections. This illustrates the effect of the junction on the flow impedance of the copper mass. The reduction in the velocity is mainly due to the blockage of the junction, which significantly hinders the copper mass from propelling forward. The most distinct change in the velocity of the flow observed from Figure 6.3.5 is the velocity of copper in case 1. Besides attributing the flow characteristic of copper to the influence of the junction, the resulting velocity of copper at the narrow channel is also closely related to the interaction between copper atoms at the downstream CNT and the copper atoms at the junction.

The length of the CNT channel junction in case 1 spans the z coordinate between -21 and 5 Å. As shown in Figure 6.3.5, the velocity of copper does not stabilize at the position near 5 Å, but continues to increase further beyond the 20 Å position. The stabilization of the velocity occurs only when copper atoms have completely passed through the junction, and thus the increase in the velocity signifies the existing interaction between the copper atoms at the junction and the copper atoms at the downstream CNT. As the cross-sectional diameter of the downstream CNT increases, the copper atoms are able to flow through the junction much easily and hence the variation in the velocity for cases 2, 3 and 4 is smaller.

Another interesting characteristic in relation to the flow of copper along the channel is the difference between the velocity of copper flow in the upstream CNT and the velocity of copper flow in the downstream CNT. Figure 6.3.6 shows velocity ratio of copper with respect to the diameter ratio of the channel. The velocity ratio is defined as the ratio of the velocity of copper at the upstream CNT to the velocity of copper at the downstream CNT. Similarly, the diameter ratio is defined as the ratio of the cross-sectional diameter of the upstream CNT to the cross-sectional diameter at the downstream CNT as mentioned earlier. We find that as copper flows from the upstream CNT to the downstream CNT, the resulting velocity of copper in the (12,12)–(5,5) CNT channel does not increase, but rather decreases slightly. This is reflected as the velocity ratio of more than 1.

Figure 6.3.5 Velocities of copper along the CNT channel during the electromigration transport.

The reduction in the velocity of copper along the downstream CNT is due to the resistance by the inner surface of the downstream CNT. Referring to Figure 6.3.3, the van

der Waals interaction between copper and the CNT junction has shown to be higher for cases 1 and 2 as reconfiguration of the atomic structure of copper atoms occurs at the channel junction, which leads to the elongation of the copper mass structure in the narrow downstream CNT. Since the copper mass in cases 1 and 2 has a larger contact area with the downstream CNT compared to that in the upstream CNT, the resistive forces acting on the surface of the copper mass by the downstream CNT is expected to be slightly higher, especially for case 1.

The flow of the incompressible liquid along a pipe of varying diameters is often described using Bernoulli's principle or the continuity equation of the volumetric flow rate. The cross-sectional area of the flow is inversely proportional to the average flow velocity as shown in the volumetric flow rate equation, $Q/A=v$, where Q is the volumetric flow rate, A the cross-sectional area of the flow and v is the average flow velocity. Based on this relationship, the flow velocity increases as the area of the channel becomes narrower.

The phenomenon of an increase in the flow velocity along a narrower tube along a channel occurs in cases 2, 3 and 4, except in case 1. Nonetheless, the increase in the magnitude of the velocity along a narrower tube is still quite minimal. One of the major differences between the classical theory and the atomic simulation model is that in the latter model, the movements of each atom in the flow and the interaction of every atom in the flow with the atoms of the channel have been taken into significant considerations. The results obtained are therefore reflected as a time average of the flow behaviour of the flowing atoms, rather than the general behaviour of the flow material as a whole.

Figure 6.3.6 Velocity ratios of copper in CNT channels of different diameter ratios.

The velocity distribution of copper atoms in CNT channels is shown in Figure 6.3.7. The main difference between Figures 6.3.5 and 6.3.7 are that the former depicts the average velocity of the copper mass as a whole, whereas the latter shows the translocating velocity of each of the copper atoms with respect to time along the CNT channels in the z direction. The velocity scale is shown in both positive and negative values. The positive velocity value means that the copper atom is moving downstream, whereas the negative velocity value means that the copper is moving upstream.

According to Figure 6.3.7, the velocities of copper atoms vary widely at the junction of (12,12)-(5,5) and (12,12)-(7,7) CNT channels (Cases 1 and 2 respectively), at 10000 ± 500 (fs). Due to the blockage of the junction, the jamming of some copper atoms becomes significant. The blockage results in the decrease of the velocities of the trailing atoms. The accumulation of copper atoms at the junction results in the leading copper atoms being forced out from the junction into the downstream. The increases in the velocities of the leading copper atoms at 10000 ± 500 (fs) in Figure 6.3.7 indicate the phenomenon of which the leading copper atoms are being forced out from the junction.

However, such wide variation in the velocities of copper atoms is less significant in both the (12,12)-(9,9) and (12,12)-(10,10) CNT channels (Cases 3 and 4 respectively).

Figure 6.3.7 Velocity distributions of copper atoms in different sizes of CNT channels with respect to time.

6.4 Effects of electromigration on copper in CNT channels

6.4.1 Simulation conditions

The CNT channels in this simulation study are modelled as nonpolarized, single-walled, and armchair CNT channels. One CNT junction for a CNT channel, which is joined by two nanotubes of different diameters, is constructed. The connecting joint of the CNTs is connected by a pentagon and heptagon pair of carbons [78]. The CNT channel is generated using CoNTub [110]. The (12,12)-(6,6) CNT channel, the (12,12)-

(8,8) CNT channel and the (12,12)–(10,10) CNT channel are constructed for this simulation study. The diameters of the (6,6) nanotube, the (8,8) nanotube, the (10,10) nanotube and the (12,12) nanotube are 8.12 Å, 10.83 Å, 13.54 Å and 16.25 Å respectively. The lengths of the CNT channels are between 110 and 130 Å, spanning the z coordinate between -65 and 65 Å. The MD code is written using MATLAB [243]. Before the non-equilibrium MD simulations were performed, energy minimization and equilibrium MD runs had been made. Carbon atoms are fixed in space. The EAM potential for copper atoms, the van der Waals interaction between copper and carbon atoms, and the temperature adjustment for copper atoms are given in detail in section 7.1.1. There are 100 copper atoms in each of the CNT channels.

Eq. (6.2) is used here to describe the driving force (ξ_{em}) exerted on the transported atoms by the electromigration process. In this study, the bias voltage is set at 2, 6 and 10 V. The positive values of energies or forces from the results indicate the repulsive effect between atoms, whereas the negative values are indications of the attractive effect between atoms. VMD [247] is also used for the visualization of the system.

The temperature of copper for the simulations is therefore set at 1100 K. Based on the potential used for copper atoms, higher temperatures are not considered in this study to avoid any discrepancy to the quality of the results. The simulation time step is 1 fs. The maximum simulation duration for this study is set at 20 ps, which is sufficient for the transportation of copper atoms along the entire CNT channel.

6.4.2 Analyses of copper due to electromigration processes

Table 6.4.1 Simulation cases

CNTs	Bias voltage		
	2 V	6 V	10 V
(12,12)–(6,6)	Case 1	Case 4	Case 7
(12,12)–(8,8)	Case 2	Case 5	Case 8
(12,12)–(10,10)	Case 3	Case 6	Case 9

The simulation cases for the flow of copper in various CNT channels are illustrated in Table 6.4.1. The simulations consist of nine different cases, where each case adopts a combination of different CNT channels with a bias voltage used for driving the copper atoms during electromigration. The (12,12)–(6,6) CNT channel has a total of 1894 carbon atoms, whereas the (12,12)–(8,8) CNT channel and the (12,12)–(10,10) CNT channel contain 2008 and 2098 carbon atoms respectively. The length of the (12,12) CNT is set at 60 Å for all the cases, whereas the length of the (6,6) CNT, the (8,8) CNT and the (10,10) CNT are set at 45 Å for all the cases.

For this study, the (12,12) CNT is defined as the upstream section of the channel, and the (6,6) CNT, the (8,8) CNT or the (10,10) CNT as the downstream section of the channel. The CNT junction refers to the section of the channel where the diameter of the upstream CNT reduces gradually to the diameter of the downstream CNT. Since the size of the CNT junction varies according to the diameter difference between the upstream and the downstream CNTs, the overall lengths of the three CNT channels are thus unequal. The diameter ratio used in this study is defined as the ratio of the cross-sectional

diameter of the upstream CNT to that of the downstream CNT, which is also the same as the ratio of the cross-sectional diameter of the entrance to that of the exit of the CNT junction. The diameter ratios for the (12,12)–(6,6) CNT channel, the (12,12)–(8,8) CNT channel and the (12,12)–(10,10) CNT channel are 2.0, 1.5 and 1.2 respectively. A large diameter ratio indicates a relatively higher gradient of slope along the channel junction. In order to maintain a relevant comparison between the simulation cases, the number of copper atoms and the initial positions of copper in the upstream CNT are constructed similarly for all cases. The flow of copper in three variations of CNT channels is shown in Figure 6.4.1. The flow direction is determined by the application of the electromigration force, which is along the CNT channels in the z direction.

Figure 6.4.1 Copper flow along three different CNT channels.

The flow of copper along the CNT channels is achieved through the driving forces provided by the bias voltages. Since the bonding between the copper atoms are stronger compared to gaseous or weakly bonded liquid molecules, the copper droplet in CNT channels is moving as a bulk mass, instead of loosely arranged atoms. This can be seen

clearly in Figure 6.4.1. Regardless of the change in the diameter of the CNTs along the channels, the copper atoms do not diffuse separately, which indicates the minimal size effects of the CNT channels on the bonding of copper atoms. Although the geometrical effect on the bonding of copper is low, the temperature and the driving forces play important roles in affecting the energy of the copper mass. In this study, the effect of bias voltages is focused upon. The relationships of the applied bias voltage and the geometrical structure of CNT channels are plotted in Figure 6.4.2 to indicate the effect of these two conditions on the potential energy of the copper mass.

During the flow of the copper mass along the CNT channels, the main factor affecting the change in the potential energy of the copper mass is the CNT junction. As shown in Figure 6.4.2, the changes in the potential energy occur between 6 and 10 ps, the duration at which copper is passing through the CNT junctions. The potential energy of the copper mass is quite stable when the mass is flowing outside of the CNT junctions range. The magnitude of the potential energy changed in copper indicates the variation in the stability of the copper structure. By comparing the potential energy, a qualitative understanding of the effects of bias voltages on the structure of copper along CNT channels can be provided. Figure 6.4.2 shows that a bias voltage of 2 V causes the lowest variation in the potential energy of copper along the CNT junction region, as compared to 6 and 10 V. The change is also more significant in the (12,12)–(6,6) CNT channel than in the other CNT channels. It is clear that the low bias voltage of 2 V results in a lower structural change in copper than that at higher bias voltage, but the duration required for the copper mass to resume a stable structure after passing through a (12,12)–(6,6) CNT

junction is similar to that at higher bias voltages. On the other hand, such phenomenon is not obvious in the (12,12)–(10,10) CNT channel that has relatively smaller diameter ratio.

Figure 6.4.3 presents the density ratio of the copper mass, which is defined as the ratio of the copper density at the downstream to the copper density at the upstream, due to different bias voltages. Although the copper mass undergoes a structural change due to the reduced diameter along the CNT channels, the density change of copper is analyzed to observe the possible change in the properties of the bulk mass. The effect of electromigration on the change of copper density is highlighted using the density ratio of copper.

According to Figure 6.4.3, the overall copper density in the downstream of the three CNT channels has the tendency to increase when the applied bias voltages are increased. The density ratios of copper in the (12,12)–(6,6) CNT and (12,12)–(8,8) CNT channels show a nonlinear behaviour as compared to the density ratio of copper in the (12,12)–(10,10) CNT channel. This nonlinear behaviour of the density ratio may be due to the additional effect caused by the obstruction of the CNT channel junctions on the flow of copper. The bias voltage of 6 V is possibly the ideal voltage for the copper density to increase the most as the copper mass flows along a CNT channel with a junction feature.

To understand the magnitude of the “friction” on the transport of copper mass along the CNT channels, the interactive forces (van der Waals interaction) between the CNT channel and copper are analyzed and shown in Figure 6.4.4. The interactive force on the copper mass is acting parallel to the flow direction of the copper mass, which is along the CNT channel. When copper is flowing along the channel, the main obstruction

from the CNT junction causes an increase in the van der Waals interaction between copper and the CNT channels between -20 and 20 Å, as shown in Figure 6.4.4.

Figure 6.4.2 The potential energy of copper along CNT channels in cases 1 to 9.

Figure 6.4.3 Density ratio of copper due to different bias voltages.

Apart from the CNT junction region, the resistance caused by the CNTs on the copper mass at the upstream and downstream region is quite minimal. The obstruction of the CNT channel is mainly responsible for resulting in the structural changes in the copper mass by resisting the flow. This is because the potential barrier of the channel junction leads to the built up in the potential energy of the copper mass, resulting in the structure transition before copper flows downstream.

The geometrical shape of the CNT junction is the main factor that causes the highest resistive forces on the copper. However, the variation in bias voltages also plays a significant role in affecting the resistance of copper flow at the CNT junction, due to the change in the driving forces on copper atoms. Figure 6.4.4 shows that the van der Waals interaction between copper and the CNT channel increases as the bias voltage increases. The strength of the resistance is strongest in the (12,12)–(6,6) CNT channel, followed by the (12,12)–(8,8) CNT channel and the (12,12)–(10,10) CNT channel. Comparing cases 3,

6 and 9, the highest resistive forces in the region between -20 and 20 Å are almost similar.

Figure 6.4.4 Interactive forces between copper and CNT channels along the flow direction.

Figure 6.4.5 shows the change in the transport velocities of the copper mass along CNT channels with variations in the bias voltage. When copper is transported along the CNT junction, the velocity of the copper mass reduces for a short duration due to the restructuring of the copper atoms at the CNT junction. The velocities of copper atoms eventually resume to constant after all copper atoms leave the junction region. The reduction of copper velocity relies strongly on the geometrical structure of the channel junction. As the diameter ratio of the channel increases, the obstruction to the flow of copper becomes greater.

To understand the impact of the bias voltage on the reduction of copper flow velocities, a comparison is made between different magnitudes of bias voltages. As shown in Figure 6.4.5, the increase in bias voltage leads to less reduction in the velocity of copper at the CNT junction. Although the increase in the bias voltage leads to higher driving forces on copper atoms, it should be noted that the copper mass does not stabilize any faster after leaving the CNT junction. The copper velocity in the downstream only stabilizes when all copper atoms leave the junction completely, which means the diameter ratio of the channel is the dominant factor.

As copper flows along the CNT channel, the velocity of copper in the downstream varies compared to that in the upstream. Figure 6.4.6 shows the velocity ratios of copper in CNT channels due to different bias voltages. The velocity ratio is defined as the ratio of the copper velocity in the downstream CNT to that in the upstream CNT. According to Figure 6.4.6, the low bias voltage results in the increase of the copper velocity in the downstream of the (12,12)-(6,6) CNT channel, the (12,12)-(8,8) CNT channel and the (12,12)-(10,10) CNT channel, showing as a velocity ratio of more than 1.

Figure 6.4.5 Velocities of copper along the CNT channels in cases 1 to 9.

The velocity ratio of copper in CNT channels reduces gradually when bias voltages are higher than 2 V. The velocity ratio for copper remains significantly lower as the bias voltage continues to increase. At bias voltages higher than 6 V, the velocity ratio of copper in the (12,12)-(10,10) CNT channel is close to 1.00, and thus the variation is quite minimal. It is noted that the velocities of copper in the downstream CNTs are generally lower than that in the upstream CNT when the bias voltage is high. This suggests that the velocity eventually becomes slightly lower when copper is transported into the narrow CNT region of the channel, instead of increasing in speed.

In this study, the CNT junction in the (12, 12)–(10, 10) CNT channel has shown minimal effect on the interaction with the copper mass. The main reason is incomplete filling of copper in the (12, 12) CNT, and hence the transition from the (12, 12) CNT to the (10, 10) CNT does not significantly affect the flow of the copper mass.

Based on the studies done by Zhang *et al.* [248, 249], it is clear that transport behaviours along a CNT channel are indeed affected by the structure of the CNT channel with junctions. Zhang *et al.* have shown that the conductance G is length dependent along a (12, 0)/(n,m)/(12, 0) heterostructures, whereas the conductance spectra are dependent on the dihedral angles of the ($n1,m1$)/($n0,m0$)/($n1,m1$), single wall CNT double intramolecular junctions. Comparing with the studies of Zhang *et al.*, the flow behaviour along the CNT channel in the case of a copper mass is instead dependent on the gradient of the slope along the channel junctions due to the variation in the cross-sectional diameters of the channel, in which the additional influence of the magnitude of the driving forces (the electromigration forces) plays an equally important role.

Figure 6.4.6 Velocity ratios of copper in CNT channels due to different bias voltages.

Figure 6.4.7 shows the velocity distribution of copper atoms in CNT channels. The difference between Figures 6.4.5 and 6.4.7 are that the former depicts the average velocity of the copper mass as a whole, whereas the latter shows the translocating velocity of each of the copper atoms with respect to time along the CNT channels in the z direction. The velocity scale is shown in both positive and negative values. The positive velocity value means that the copper atom is moving downstream, whereas the negative velocity value means that the copper is moving upstream, or the existence of backflow.

According to Figure 6.4.7, the backflow of copper atoms at the junction occurs in all three cases of different bias voltages at 10000 ± 300 (fs). However, no backflow is found in the (12,12)-(10,10) channel. By comparing the case studies with three different bias voltages, it is clear that the backflow phenomenon at the lowest bias voltage (2 V) tends to last the longest. Since the lowest bias voltage (2 V) results in a lower driving force for copper atoms, the exit of copper atoms through the junction towards the downstream is much slower. The trailing atoms are hence easily trapped, and therefore circulate much longer within the junction.

Figure 6.4.7 Velocity distribution of copper atoms along the CNT channels at different time.

6.5 Effect of CNT chirality on the spiral flow of copper atoms in their cores

6.5.1 Simulation conditions

The simulations of copper flow are performed in this study using copper atoms as the transported particles in different CNT channels. The MD code is written using MATLAB [243]. In the simulations, the copper atoms are confined within two CNT channels that are modelled as nonpolarized, single-walled, armchair and zigzag CNT channels. The CNT channels are generated using CoNTub [110]. Each of the CNT channel consists of one CNT junction, joined by two nanotubes of different diameters. For the purpose of comparing the effect of the CNT chirality on the flow of copper atoms, a (5,5)–(4,4) CNT channel with a metal–metal junction and a (8,0)–(7,0) CNT channel with a semiconductor–semiconductor junction are constructed. The (5,5) and the (4,4) CNTs are known to be metallic, whereas the (8,0) and the (7,0) CNTs are known to be semiconductors [77].

The CNT channels are chosen such that the difference in the diameters between the two channels is minimal. This ensures that the study is not affected by the geometrical differences between the two CNT channels. The (5,5)–(4,4) CNT channel has 828 carbon atoms, with a diameter of 6.8 Å for the (5,5) nanotube and a diameter of 5.4 Å for the (4,4) nanotube. The (8,0)–(7,0) CNT channel has 795 carbon atoms, with a diameter of 6.3 Å for the (8,0) nanotube and a diameter of 5.5 Å for the (7,0) nanotube. Both of the CNT channels are approximately 112 Å in length, spanning the z coordinate between –53 and 59 Å. The CNT channels are fixed in space.

There are a total of 28 copper atoms in each of the CNT channels. The copper atoms are placed close to the wider opening of the channel end initially. Before the nonequilibrium MD simulations were performed, energy minimization and equilibrium MD runs had been made.

The copper atoms in the system are modelled using the EAM as described in Eqs. (3.13) and (3.14). The interaction between copper and carbon can be expressed in the form similar to Eq. (6.1). Eq. (6.2) is used to describe the electromigration force on the copper atoms. Since the temperature of copper is increased during the simulations, the temperature of copper is adjusted throughout the simulation process using the modified velocity rescaling mentioned in Eq. (6.3).

For this simulation study, the voltages are set at 2 V and 4 V. Low bias voltages are chosen for this simulation study so that the erratic behaviour of copper atoms due to the strong driving forces can be less significant. The reason for using these voltage values are explained under section 6.1.1. The positive values of energies or forces are used to indicate the repulsive effect between atoms, whereas the negative values are indications of the attractive effect between atoms. VMD [247] is used for the visualization of the system.

The simulation cases are set up based on the combinations of different magnitudes of bias voltages, temperatures, different CNT channels and the positioning of the cross-sectional configuration of the copper atoms. Based on the explanation provided under section 6.1.1, the initial temperatures of copper atoms for this simulation study are set at 673 K and 1073 K. The simulation time step is set at 1 fs. The maximum simulation

duration for this study is set at 20 ps, which is sufficient for the transportation of copper atoms along the entire CNT channel.

In this study, the force field parameters for the CNT channels are not established. In order to simplify the cases, the different CNT chirality is distinguished according to the difference in the spatial distribution of carbon atoms along the channels. The electronic properties of CNTs with different chirality and the effect of the electronic properties of metallic and semiconducting nanotubes on the flow of copper atoms will not be considered at this stage. Since the different force field parameters are not set for carbon atoms, the effect of the spatial distribution of carbon atoms is thus the main consideration for the interactions between copper atoms and carbon atoms, in which only the Lennard Jones interactions between CNT channels and copper atoms are considered.

6.5.2 Analyses of the spiral flow phenomenon of copper atoms

The simulations of the flow of copper atoms in CNT channels are performed to investigate the spiral flow of copper atoms along the channels due to the different chirality of CNTs. A bias voltage is applied along the channel to induce a driving force for the copper atoms to propel from the wider end of the channel (upstream) towards the narrow end of the channel (downstream). The magnitude of the flow is affected according to the variation in temperatures and the magnitude of the voltage applied. According to an earlier report [250], the threshold voltage value for the electromigration of the entire copper mass in a (5,5)–(4,4) CNT channel to occur is 0.25 V.

Since the distributions of carbon atoms along a metal–metal CNT channel and a semiconductor–semiconductor CNT channel are different [78], it is of great interest to

understand how the flow phenomenon varies according to the type of CNT channel used. Figure 6.5.1(a) shows the transportation of copper atoms along a (5,5)–(4,4) CNT channel at 673 K, with a bias voltage of 4 V. The copper atoms are initially positioned in the (5,5) CNT as depicted in Figure 6.5.1(b). The atoms shown in Figures 6.5.1(b)–(d) represent the first four atoms of the copper mass. The first four copper atoms are used as a representation of the flow behaviour in this study because the copper mass in the straight CNT are mainly made up of the repetition of the first four copper atoms.

As the electromigration force is applied to the copper atoms, the copper mass flows along the upstream channel, goes through the channel junction, and undergoes an atomic restructuring process. Due to the narrowing of the diameter along the channel, the copper atoms are rearranged through the combined effect of the driving force, and the interactive forces between carbon and copper. The resultant configuration of the copper atoms in the (4,4) CNT is shown in Figure 6.5.1(c). As more copper atoms are being pushed into the narrow channel and the copper mass continues to flow, the copper atoms that have left the junction tend to shift slightly, which is shown as a spiral flow behaviour at a very small angle in Figure 6.5.1(d). Lim and Zhong have previously addressed the spiral flow phenomenon of copper atoms at a channel junction [251]. However, a more intensive investigation shows that the copper atoms not only undergo considerable changes in the junction, but also form a restructured copper mass with two copper atoms visible through the cross-sectional view of the (4,4) CNT.

Figure 6.5.2(a) shows the flow of copper atoms in a semiconductor–semiconductor CNT channel. It is observed that while the initial arrangement of the copper atoms in the (8,0) CNT, shown in Figure 6.5.2(b), is similar to the arrangement of

the copper atoms in the (5,5) CNT, the resulting restructuring of the carbon atoms in the narrow section of the (7,0) CNT has turned out to be slightly different compared to the arrangement in the (4,4) CNT. The atoms shown in Figures 6.5.2(b)–(d) represent the first four atoms of the copper mass. Figure 6.5.2(c) shows the configuration of the first four copper atoms in the (7,0) CNT when the copper mass has just entered into the narrow channel.

Figure 6.5.1 (a) Transportation of copper along a (5,5)–(4,4) CNT channel with a 4 V bias voltage at 673 K. Snapshots were taken at (b) 5.4 ps, (c) 8.1 ps, (d) 15.1 ps respectively.

Figure 6.5.2 (a) Transportation of copper along a (8,0)–(7,0) CNT channel with a 4 V bias voltage at 673 K. Snapshots were taken at (b) 5.4 ps, (c) 8.1 ps, (d) 15.1 ps respectively.

Copper atoms in the (7,0) CNT have a similar distribution as that shown in Figure 6.5.1(c). However, as the flow proceeds farther, the first four copper atoms are observed to have rotated in an angle of about 90° , which is much more than that in the (4,4) CNT. The larger rotational angle is likely to be caused by the arrangement of copper atoms at the junction when the copper mass first enters into the narrow section of the channel, and also the magnitude of the interactive forces between copper and carbon due to the difference in the spatial distribution of carbon atoms. The difference in the degree of the rotational angle in the spiral flow highlights the influence of the CNT chirality on the flow of encapsulated metal atoms.

In order to understand the effect of the initial position of copper atoms on the flow behaviour, two cases of different atomic placement of the encapsulated copper mass are addressed in this study. Based on the result obtained from the energy minimization procedure mentioned under section 2, the copper mass is constructed based on the repetition of four copper atoms. The first four atoms are shown in Figure 6.5.3(a). This arrangement as the 0° configuration of copper atoms is assigned in this study. Since the CNT junctions of the channels are asymmetrical, the copper mass is rotated at an angle of 45° such that the interaction between the CNT junctions and the copper mass is different from that of the 0° configuration. The rotated configuration at an angle of 45° is shown in Figure 6.5.3(b).

The factors affecting the spiral flow of copper mass along the CNT channel include temperatures, the initial position of the copper atoms, the magnitude of the bias voltages and the interaction of carbon atoms in CNT channels with the encapsulated

metal atoms. In Figures 6.5.4 to 6.5.7, each of the possible parameters which affect the flow behaviour of the copper atoms along different CNT channels is investigated.

Figure 6.5.3 Initial arrangement of the first four copper atoms with (a) 0° of rotation, and (b) 45° of rotation.

Figure 6.5.4 shows the spatial distribution of the first four copper atoms along the cross-sectional plane with a 2 V bias voltage at 673 K. When the first four copper atoms flow into the narrow section of the channel, the atoms converge to the central position as they move downstream. The atoms are realigned from four positions into two positions, as shown in the cross-sectional view of the channels in Figure 6.5.4. A similar change in the positions of the copper atoms can also be observed in Figures 6.5.1(b) and 6.5.1(c). The copper atoms converge towards the central position, which is between 0 Å and -1 Å for the y axis and 0 Å for the x axis, as they move downstream. This phenomenon is obvious in the channels regardless of the initial position of the copper atoms. However, it is noted that since three out of the four copper atoms in the 45° configuration is closer to the central axis of the narrow channel (between 0 Å and -1 Å for the y axis), the cross-sectional path taken by the copper atoms is shorter, and hence the spiral flow is quite insignificant. By comparing Figures (a)–(d) in Figure 6.5.4, it is clear that the spiral flow phenomenon in the (8,0)–(7,0) CNT channel is more obvious than that in the (5,5)–(4,4)

CNT channel at the 0° configuration. It is also noted that since the bias voltage is low (2 V), the weak driving force does not result in strong repulsion by the junction of the channel. The convergence of the copper atoms therefore undergoes a smoother transition.

Figure 6.5.4 The spatial distribution of the first four copper atoms along the cross-sectional plane with a 2 V bias voltage at 673 K. The first four copper atoms are arranged at (a) 0° in the (5,5)–(4,4) CNT channel, (b) 45° in the (5,5)–(4,4) CNT channel, (c) 0° in the (8,0)–(7,0) CNT channel, (d) 45° in the (8,0)–(7,0) CNT channel. The values indicated beside the data points represent the z positions of the copper atoms along the CNT channel.

Figure 6.5.5 shows the flow of copper mass along the channels with a 2 V bias voltage at 1073 K. The increase in temperature highlights the change in the dynamics of the copper atoms, compared to the dynamics of copper atoms in Figure 6.5.4. According

to Figure 6.5.5, the copper atoms fluctuate much stronger at 1073 K than that at 673 K. Due to the increase in thermal vibration, the random motions of the copper atoms do not form a significant spiral flow behaviour when they travel along the CNT channel.

Figure 6.5.5 The spatial distribution of the first four copper atoms along the cross-sectional plane with a 2 V bias voltage at 1073 K. The first four copper atoms are arranged at (a) 0° in the (5,5)–(4,4) CNT channel, (b) 45° in the (5,5)–(4,4) CNT channel, (c) 0° in the (8,0)–(7,0) CNT channel, (d) 45° in the (8,0)–(7,0) CNT channel. The values indicated beside the data points represent the z positions of the copper atoms along the CNT channel.

The cross-sectional views in Figure 6.5.5 also show that the movements of the copper atoms are more constrained within the downstream channel when the copper atoms are in the (8,0)–(7,0) CNT channel than that in the (5,5)–(4,4) CNT channel. The

difference in the dynamic of copper atoms not only depends on the change in the temperature, but is also affected by the distribution of the carbon atoms in the different channels, in which the distribution of the interactive forces between carbon and copper atoms varies between the two channels. The resulting configuration of copper atoms in the downstream section of the channel at a higher temperature is similar to a single thread, connected by a series of a single copper atom. This phenomenon is observable in both the (8,0)–(7,0) and (5,5)–(4,4) CNT channels.

For cases where a higher bias voltage is necessary for driving the copper mass along the CNT channels, the flow phenomenon of copper atoms at a bias voltage of 4 V is investigated instead. Figure 6.5.6 shows the spatial distribution of the first four copper atoms along the cross-sectional plane with a 4 V bias voltage at 673 K. As the driving force increases, the collision of the copper mass and the CNT channel junction becomes stronger. The flow of the copper mass to overcome the blockage and to proceed farther into the narrow channel is hence more significant than that at a lower bias voltage. Figure 6.5.6 shows the cross-sectional flow path of the copper atoms along the (5,5)–(4,4) CNT channel and the (8,0)–(7,0) CNT channel. The spiral flow phenomenon of the first four copper atoms is more significant at the (8,0)–(7,0) CNT channel than that at the (5,5)–(4,4) CNT channel.

As mentioned earlier, the copper atoms at the 45° configuration is closer to the central axis of the downstream channel. The path taken by the copper atoms is thus shorter and the spiral flow phenomenon is lesser. Besides that, the (8,0)–(7,0) CNT channel also favours the spiral flow path taken by the copper atoms more as compared to the (5,5)–(4,4) CNT channel. The spiral flow of copper atoms is most significant at the 0°

configuration in the (8,0)–(7,0) CNT channel as shown in Figure 6.5.6(c). Based on the previous study, the reconfiguration of the copper atoms along the CNT channel is necessary for the increase in potential energy of the copper mass, so that the potential barrier of the channel junction can be overcome [250].

Figure 6.5.6 The spatial distribution of the first four copper atoms along the cross-sectional plane with a 4 V bias voltage at 673 K. The first four copper atoms are arranged at (a) 0° in the (5,5)–(4,4) CNT channel, (b) 45° in the (5,5)–(4,4) CNT channel, (c) 0° in the (8,0)–(7,0) CNT channel, (d) 45° in the (8,0)–(7,0) CNT channel. The values indicated beside the data points represent the z positions of the copper atoms along the CNT channel.

The increase in temperature results in a greater fluctuation in the flow of the copper atoms. Figure 6.5.7 illustrates the behaviour of the copper atoms with a 4 V bias

voltage at 1073 K. As compared to Figure 6.5.6, the spiral flow behaviour of the copper atoms is significantly reduced and the flow path along the x and y axes is much shorter. Instead of fluctuating about in the x and y plane, the combination of a stronger driving force and a higher temperature leads to a flow behaviour that favours the forwards movement in the z axis along the CNT channels much quickly. The combined energies on the copper atoms allow the copper mass to overcome the potential barrier much easily and hence the copper atoms flow along the channel junction without much fluctuation, compared to Figure 6.5.5 at the same temperature. The resulting reconfiguration process also is shorter. Nonetheless, the spiral flow phenomenon is still evident in Figure 6.5.7(c).

Although the sizes of the CNT channels are similar, the outcomes in the flow motion are quite different. At a 4 V bias voltage, the spiral flow phenomenon of copper atoms along the (8,0)–(7,0) CNT channel is clearer, as shown in Figures 6.5.6 and 6.5.7. These results suggest that the junction due to different chirality of the CNT channel does affect the way copper atoms move in the channel. By having a different distribution of carbon atoms around the CNT channel, the (8,0)–(7,0) CNT channel tends to interact with the copper atoms more strongly around the wall of the channel, creating a rotational pattern in the flow path in the downstream section.

The spiral flow phenomenon of copper atoms in CNT channel reflects the formation of the helical structure of the copper mass in the downstream CNT channel. Choi *et al.* have shown that copper nanowires in CNTs are multishell packs composed of coaxial cylindrical shells, with some having a single-atom chain at their centre [129]. These shells are formed by rows of atoms wound helically. The investigation of the effect of the CNT chirality on the formation of the copper atoms in the downstream CNT

channel is thus important because the degree of rotation suggests the amount of copper which can be formed into a more compact helical structure.

Figure 6.5.7 The spatial distribution of the first four copper atoms along the cross-sectional plane with a 4 V bias voltage at 1073 K. The first four copper atoms are arranged at (a) 0° in the (5,5)–(4,4) CNT channel, (b) 45° in the (5,5)–(4,4) CNT channel, (c) 0° in the (8,0)–(7,0) CNT channel, (d) 45° in the (8,0)–(7,0) CNT channel. The values indicated beside the data points represent the z positions of the copper atoms along the CNT channel.

A good coverage of the filling of copper in the cross-sectional area of the CNT channel is essential for improving the stability of the hybrid structure consisting of the CNT and metallic atoms. The resistance of copper filled CNTs to compression [252] and torsion [253] has shown to increase with the number of the copper atoms in the CNTs.

According to the results, the most compact copper structure in a CNT channel occurred at 673 K with a 4 V bias voltage in the downstream section of the (8,0)–(7,0) CNT channel. This is also the condition under which the spiral flow phenomenon is most evident. The results of this study suggest that the CNT channel with a semiconductor-semiconductor junction is a more favourable carbon material to be used for the transport of copper atoms and to form a better hybrid system of copper filled CNT.

6.6 Summary

This chapter reviews the novel studies of copper flow along CNT channels. The flow phenomena of copper atoms in the (5,5)–(4,4) CNT channel, the effects of the junction size and magnitudes of bias voltages on the electromigration of copper atoms along CNT channels, and the investigation of copper flow along CNT channels of different chirality have all been addressed. These studies are conducted using MD simulations, which are written using MATLAB. The flow of the copper atoms is driven by electromigration processes.

Overall, the simulations have shown that the transportation of copper through a (5,5)–(4,4) CNT channel using electromigration forces results in the flow of copper as an entire entity and “squeezing” effect occurs at the channel junction. The “squeezing” effect on the copper mass is mainly caused by the blockage of the CNT junction and the electromigration force that is pushing the copper mass towards the junction. When the initial temperature is high, the change of the temperature of copper due to the applied bias voltage is low. Nonetheless, the effect of the bias voltage on the temperature of copper is still significant. As copper atoms flow towards the (5,5)–(4,4) CNT junction, the junction

acts as a barrier and affects the atomic configuration of the copper. The change in the atomic configuration is dependent on the initial temperature of the copper mass and the magnitude of the electromigration forces involved.

At high temperatures, the thermal vibration of copper atoms is large too, hence resulting in greater separation between the copper atoms. Such separation reduces the interactive forces between copper atoms and the CNT channel at the junction. The “loosening” of copper atoms at the junction is further proven based on the weakened potential energy of the copper as the initial temperature of the system increases. The change in the potential energy of copper in the (5,5) CNT and the (4,4) CNT regions also highlights the buffer effect of a CNT junction for the changing atomic arrangement of the copper mass. The resistive forces of the CNT channel on copper flow are quite insignificant throughout the entire transportation process, except at the region where copper is blocked by the CNT channel junction. As the applied bias voltage increases, the total interactive forces between copper and a (5,5)-(4,4) CNT channel junction become higher. The maximum interactive force occurs at the initial temperature of 673 K. The radial forces acting on the copper mass by the channel junction at low initial temperatures are relatively higher than that at higher initial temperatures.

The junction sizes of the CNT channels are described using the ratios of the upstream and downstream diameters of the channel. As the copper mass moves along the channel junction, the distances between copper atoms become shorter, and result in the reconfiguration of the atomic structure of the copper mass.

The change in the potential energy of copper atoms has suggested that the repulsive effect between the copper atoms is more significant along junctions with larger

diameter ratios. One of the factors resulting in the high potential energy in copper atoms is due to the fact that junctions with large diameter ratios interact more with copper atoms as the surface area of the junction is larger. The van der Waals repulsion from the channel junction causes the velocity of copper atoms to slow down along the junction region, but subsequent flow into the narrow tubule does not result in the increase in the flow velocity. This is because the velocity of the copper mass in the downstream CNT is affected by the inner surface of the downstream CNT and the copper atoms are less mobile compared to fluid molecules. These factors result in a different flow characteristic compared to fluid flow along a convergence nozzle.

The main factor that affects the potential energy of the copper mass is the CNT junction, but addition in the bias voltage enhances the potential energy of the copper mass, which alters the stability of the copper structure. The increase in the bias voltage (up to 6 V) also results in the increase in the copper density in the downstream of the three CNT channels. As copper is transported along the CNT channels, the resistance on the flow is most significant at the CNT junction, and the increase in the bias voltage elevates the resistance towards the flow. However, the diameter ratio of the channel is the dominant factor for considering the magnitude of the resistive forces on the flow of copper.

The velocity of copper reduces significantly when the copper mass is transported along the channel junction. The increase in bias voltage however reduces the resistive effect of the junction on the velocity of copper. The velocity in the upstream CNT is relatively higher than that in the downstream CNT, but the increase in the bias voltage dampens this effect.

Apart from the occurrence of the rearrangement of copper atoms at the junction during the flow, copper atoms are also observed to undergo a rotation of 45 degrees about the axis of the tube when the applied bias voltage is low (2 V). However, this phenomenon is not observed at higher voltages (8 V and 10 V) for the (5,5)–(4,4) CNT channel. The studies have also shown that the copper atoms in the (8,0)–(7,0) CNT channel have a larger rotational angle as compared to that of the copper atoms in the (5,5)–(4,4) CNT channel.

The initial positioning of the copper atoms affects the way copper atoms converge towards the downstream of the channel. The 0° configuration has a longer curvature path compared to the 45° configuration because the positions of the copper atoms at 0° configuration are farther from the central axis of the downstream channel. When the temperature increases, the movement of the copper atoms along the channel is more erratic and the spiral flow phenomenon is significantly reduced. This is due to the increase in thermal vibration. The most significant spiral flow phenomenon of the copper atoms is observed when the bias voltage is 4 V at 673 K, with a 0° configuration in a (8,0)–(7,0) CNT channel.

Since the distributions of carbon atoms are different in the metal–metal and the semiconductor–semiconductor CNT channels, the results show that the spiral flow phenomenon of copper atoms in the downstream section of the semiconductor–semiconductor CNT channel is more evident compared to that in the metal–metal CNT channel.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

According to the results in this thesis, the changes that occur in the flow of biomolecules and metal atoms along the CNT junctions have shown to be dependent on the applied forces to the system, the size of the CNT junctions and also the interactions between molecules and atoms. Since the flow of the biomolecules in a CNT channel is influenced greatly by the strength of the interactions between the molecules, the change in the velocity of the flow and the shape of the oligonucleotide along the junction is therefore significantly affected by the size of a CNT channel junction. The interactions between metal atoms are different from the interactions between biomolecules. The flow properties of the metal atoms in a CNT channel is therefore expected to be different. The difference in the velocity of copper atoms along the upstream and the downstream sections of carbon nanotube channels is shown to be minimal. However, significant changes in the atomic configurations of copper atoms and the interactions between copper and CNT channel junctions are observed. In order to minimize the drift velocity of copper atoms from being affected significantly during the electromigration process, a modified velocity rescaling method has been proposed for the simulation of copper flow in CNT channels. The following three sections highlight the results obtained from the simulations of the oligonucleotide flow, the simulations of a surface structure consisting of aluminium atoms and the transport of copper atoms along CNT channels by electromigration.

7.1.1 Conclusions of translocation of biomolecules in CNT channels under pressure

The novel studies of the biomolecular flow in CNT channels have been reviewed and the objective of understanding the flow phenomena has also been achieved. The progress of the work is summarized as two journal papers [56, 83].

A novel study of a solvated oligonucleotide translocating in CNT channels with an induced pressure difference is carried out using MD simulations. Three magnitudes of forces are applied to water molecules to induce different pressures into the system. Two CNTs of (8,8)-(12,12) and (10,10)-(14,14) are used as nanochannels for the study of the flow behaviour of the oligonucleotide and water molecules. According to the results, the critical size of the nanotube for the oligonucleotide to flow through is about 1.36 nm in diameter. Another significant phenomenon that can be observed from the (8, 8)-(12, 12) CNT is that the amount of water molecules flowing through the small CNT is affected by the conformational shape of the oligonucleotide, which causes blockage at the junction of the nanochannel. The CNT junction of the (8, 8)-(12, 12) CNT channel can thus act as a filter for the solvated oligonucleotide. However, the amount of water molecules flowing through the (10, 10)-(14, 14) CNT is more dependent on the strength of the pressure.

The conformational energy of the oligonucleotide is affected more significantly by the strength of the pressure when the oligonucleotide is in the (8, 8)-(12, 12) CNT, rather than in the (10, 10)-(14, 14) CNT. The increase in the conformational energy of the oligonucleotide would result in a more linear arrangement of the bases in the oligonucleotide.

The interactive force between the oligonucleotide and the CNT is dependent on two factors: the diameter of the nanotube and the strength of the induced pressure. The junction of the nanotube channel also plays a part in the interactive forces because in a narrower nanotube, the closer contact between the oligonucleotide and the CNT channel inner wall would result in an increase in the interactive force between them.

The change in the position of the COM of the oligonucleotide in the (10, 10)-(14, 14) CNT with respect to time has suggested that the velocity of the oligonucleotide is dependent on the influence of the induced pressure. The increase in the induced pressure resulted in a higher gradient of the change in COM when the oligonucleotide is travelling along the tube centre of the (10, 10)-(14, 14) CNT. The insertion of the oligonucleotide at the junction of the (8, 8)-(12, 12) CNT is deeper when a higher pressure is applied.

The gradient of the position of the COM of the oligonucleotide with respect to time has shown that the oligonucleotide moves more quickly along the centre tube of the (10, 10)-(14, 14) channel than that along the two ends of the channel. This means that the delivery process at the centre of the tube is sped up. The initial gradient of the COM is found to ascend slightly when the oligonucleotide starts to move into the region where the diameter of the tube becomes smaller. However, the gradient of the COM is eventually decreased after leaving the tube region that is narrower.

In order to further elaborate the effect of the shape of the oligonucleotide on the flow of water molecules in the carbon nanotube channel, the shape of the oligonucleotide is described using the radius of gyration. The finding of the folding of the oligonucleotide along the CNT channel is novel. The results show that the folding of the bases of the oligonucleotide depends on the magnitude of the pressure and the blockage due to the

(8,8)-(12,12) CNT channel junction. The folding of the oligonucleotide is mainly dependent on the interactive forces (van der Waals forces) between the oligonucleotide and the water molecules. A higher induced pressure results in a deeper insertion of the oligonucleotide in the (8,8)-(12,12) CNT channel due to lesser folding of the oligonucleotide and a higher attractive force is present between the water molecules and the oligonucleotide.

However, the oligonucleotide translocating through the (10,10)-(14,14) CNT channel under the induced pressures applied has shown signs of lesser folding at a lower pressure. The repulsive forces between the oligonucleotide and the water molecules are higher when the system is at a higher pressure. The van der Waals forces between the bases of the oligonucleotide are affected by the folding of the oligonucleotide. The higher repulsive forces between the bases of the oligonucleotide signify the resistance of the bases against the folding of the oligonucleotide caused by the effect of the water molecules. The radial distribution of the water molecules in the (10,10)-(14,14) CNT channel has shown that flow of water is concentrated more at a radius of 3 Å away from the centre of the oligonucleotide when the oligonucleotide is folded. However, the distribution of water varies at a wider range when the oligonucleotide is less folded in the (10,10)-(14,14) CNT channel. Based on the results and analyses of the flow of an oligonucleotide in CNT channels, the function of CNT channels as a delivery system for the transport of an oligonucleotide and the flow phenomena of the biomolecules are better understood.

7.1.2 Conclusions of premelting of the aluminium surface

For the extension of the study for the molecular and atomic flow in CNT channels, metal atoms are chosen as the flowing particles instead of biomolecules. In order to perform the simulations of the flow of metal atoms, a simulation program is developed using MATLAB. The simulation program is tested out by performing MD simulations of the aluminium slab in order to investigate the premelting phenomena of the Al(110) surface. This work is summarized in a journal paper [243]. This approach highlights the effects of the EAM potential on metal atoms such that a deeper understanding of the potential used can be established. The application of this potential model to metal atoms will then be established in future for the study of metal atoms flow in the CNT channels. Based on the results collected, the simulation program written using MATLAB has shown to be reliable.

The simulation of the premelting of the aluminium surface is run at 9 different temperatures for the bulk analyses and surface analyses. The results show that the pair correlation function has a good relation to the Schommers model for bulk aluminium at 584 K and for the surface layer at 240 K. However, the MD analyses using the EAM potential revealed that the premelting of the Al(110) surface occurred at a similar temperature as that reported by Schommers. The pair correlation function for the surface layer at 710 K indicates the anharmonicity in the periodic structure. The result for the diffusion constant at 810 K is shown to be much larger than that at 810 K reported by Schommers. Hence, premelting of the Al(110) surface in this study has indeed occurred at a temperature lower than 810 K. The disordered layer configurations of the first two layers of the Al(110) surface have been verified using the layer structure factor as a

function of temperature and the premelting phenomenon occurs at 710 K. The mean square vibrational amplitudes suggest that the correlated jump-exchange processes are likely to occur at temperatures higher than 650 K and the vertical vibrational amplitude is maintained within the range of the nearest-neighbour distance at temperatures lower than the bulk melting temperature.

7.1.3 Conclusions of transport of copper atoms along CNT channels using electromigration processes

Another novel study in this thesis involves the transport of copper atoms along CNT channels with junctions. The investigation for the flow of copper atoms has been reviewed. The objectives of exploring the role of the channel junction on the flow of copper atoms and the flow phenomena of copper atoms in CNT channels have been achieved. The newly developed method for the rescaling of velocities for the electromigrating copper atoms is implemented successfully as well. The progress of the work is summarized as four journal papers [250, 251, 254, 255].

The first part of the investigation of copper flow focuses on the electromigration process along a (5,5)–(4,4) CNT channel. As copper atoms flow along the junction of the (5,5)–(4,4) CNT channel, the narrowing of the channel at the junction causes the copper mass to be “squeezed”. This effect is the result of the combination of the electromigration force (driving force) and the blockage of the channel junction. In order to overcome the energy barrier of the junction, reconfiguration of the positioning of the copper atoms is required, and thus the rotation of the copper mass is observed. The rotational angle is

about 45° about the axis of the tube. As copper flows towards the CNT junction, the junction acts as a barrier and affects the atomic configuration of the copper mass. The change in the atomic configuration is dependent on the potential energy of the copper mass, the magnitude of the electromigration forces involved and the blockage of the channel junction. When the temperature is high, the thermal vibration of copper atoms is large too, hence resulting in greater separation between the copper atoms. Such separation reduces the interactive forces between copper atoms and the CNT channel at the junction. The “loosening” of copper atoms at the junction is further proven based on the weakened potential energy of the copper as the temperature of the copper mass increases.

The interactive forces between copper and the CNT junction increase as the bias voltage increases. This is due to the strong repulsive forces being developed in order for the separation of copper atoms and the CNT channel junction to occur. Higher repulsion between copper and the CNT channel is also observed at a lower temperature of copper atoms. The radial forces acting on copper atoms by the channel junction are high when the temperature of the copper mass is low. However, the resistive forces of the CNT channel on copper flow are quite small throughout the entire transportation process, except at the region where copper is blocked by the CNT channel junction.

In order to further understand the various conditions that affect the flow phenomena of copper along CNT channels, the junction sizes of the CNT channel and the magnitude of the electromigration force have been addressed. Diameter ratio is a ratio that describes the difference in the diameter between the upstream and the downstream of the CNT channel. When the diameter ratio is large, the inner surface area of the CNT

junction becomes large as well. The greater narrowing of the junction with large diameter ratio also means that more interactions between the carbon atoms at the junction and the copper atoms occur during the flow, due to the increase in the inner surface area of the channel junction. This results in greater resistance to the flow of copper atoms, and the repulsive effect is stronger. With this, the reconfiguration of the copper atoms is reflected as an increase in the potential energy at the junction of the channel. An interesting phenomenon involving the flow of copper atoms is that the velocities of copper atoms in the downstream do not increase significantly even though the diameter of the flow channels changes.

Since electromigration forces drives the copper atoms to move along the CNT channels, the change in the electromigration would result in the change in the flow behaviour of the copper mass as well. The change in the electromigration force is mainly due to the change in the bias voltage. When the flow of copper atoms is blocked by the channel junction, the electromigration force increases the ability of the copper mass to work against the resistance. The diameter ratio of the channel is the dominant factor for considering the magnitude of the resistive forces on the flow of copper along the junction. The electromigration force enhances the potential energy of the copper mass at the junction, leading to greater instability in its structure and increases the interaction between copper atoms and the carbon atoms at the channel junction. The difference in the velocity of the copper mass in the upstream and downstream CNT channels is significantly reduced when the bias voltage is increased.

The change in the potential energy of the copper atoms in the (5,5)–(4,4) CNT channel is different from the change of the potential energy of the copper atoms in CNT

channels of other sizes. Through observations, the decrease in the potential energy in the downstream of the (5,5)–(4,4) CNT channel is most likely due to the spiral flow phenomenon that has taken place after the copper atoms flow out of the channel junction in the (5,5)–(4,4) CNT channel. With this understanding, the investigation of the spiral flow phenomenon of copper atoms in CNT channels is thus carried out. This study mainly focuses on the dynamical movements of the copper atoms along CNT channels of different chirality.

The initial positioning of the copper atoms in the upstream section of the CNT channels affects the way copper atoms converge towards the downstream of the channel. The 0° configuration has a longer curvature path compared to the 45° configuration because the positions of the copper atoms at 0° configuration are farther from the central axis of the downstream channel. The difference in the bias voltage affects the strength of the copper atoms to propel along the channel, in which a lower bias voltage leads to a flow that has less curvature along the downstream of the channel. The increase in the temperature causes the movement of the copper atoms to be more erratic and therefore the spiral flow phenomenon along the channel is significantly reduced. The spiral flow phenomenon is most significant when the bias voltage is increased up to 4 V at 673 K.

The results have shown that the spiral flow phenomenon of copper atoms in the downstream section of the semiconductor–semiconductor CNT channel is more evident compared to that in the metal–metal CNT channel. Based on the study in this thesis, it is understood that flow of copper atoms in CNT channels can be improved or altered through the changes in the magnitude of bias voltages, temperature and channel sizes of the channel, particular the diameter ratio of the channel junctions. The ease of

electromigrating copper atoms along CNT channels can thus be optimized based on the various flow conditions that are investigated.

7.2 Major contributions

In this research, the MD simulations of the flow of biomolecules and metal atoms along CNT channels with junctions have been conducted mainly to investigate the flow phenomena of these two filling materials and the effects of the channel junctions on these flows. Due to the scale of the studied materials, MD methods have been chosen so that analyses on the atomic scale are possible. The major contributions of these studies include:

- Providing a new idea of translocating the DNA oligonucleotide in CNT channels using the induced pressure difference.
- Revealing how the amount of water molecules changes along CNT channels with junctions, with the combined blocking effect of the oligonucleotide and the channel junctions.
- Revealing new insights to the folding phenomenon of the oligonucleotide while the biomolecules translocate along CNT channels with junctions.
- Explaining the mechanism behind the changes in the flow phenomena of the solvated oligonucleotide in CNT channels, including the role of the channel junctions.
- Explaining the difference in the effect of the MD potentials used on the diffusion of aluminium atoms.

- Developing a novel rescaling method for the electromigration of metal atoms in CNT channels.
- Providing a new idea of using CNT channels with junctions for the transportation of copper atoms.
- Providing novel insights to the changes that occurred in the configuration of copper atoms along CNT channels.
- Explaining the changes of the distribution of copper atoms along CNT channels due to different flow conditions.
- Revealing the effect of electromigration on the transportation of copper atoms along CNT channels with junctions.
- Providing novel insights to the changes in the flow phenomena of the copper atoms in CNT channels due to the size of the channel junctions.
- Highlighting the effect of the chirality of CNT channels on the electromigration of copper atoms.
- Explaining the spiral flow phenomenon of copper atoms due to the channel junctions.

7.3 Recommendations for future work

The studies on the flow of biomolecules and metal atoms along CNT channels are important research contributions towards the advancement of nanotechnology. Flow of biomolecules and metal atoms along CNTs is a fundamental process which occurs in applications involving the delivery of drugs and metal. In spite of the amount of work

that has been carried out over the years, the understanding of nanoflow is still quite limited and there are many challenges ahead. With regards to these issues, the future work for the studies of nanoflow is promising and many areas can be explored further. The recommended future works includes the following.

1. The analysis of biomolecules and metal atoms flowing along CNT channels with unrestrained carbon atoms

The proposed novel study of flowing biomolecules and metal atoms along CNT channels with unrestrained carbon atoms will provide important information regarding the effects of the expansion and compression of the CNT channel junctions on the encapsulated materials. Since carbon atoms are not fixed in space, the cavity along the channel will no longer remain as a fixed volume during simulation. This model improves the analyses of the current studies, which address the mobility of carbon atoms and the resulting flowing phenomena due to the movement of carbon atoms. The limit of the CNT junctions to withstand the flowing pressure can also be investigated based on the design of this model.

2. The analysis of the thermal distribution of the CNT channels during electromigration processes

The thermal analysis of the CNT channels due to the electromigration processes is essential for the understanding of the heat distribution of the channels during the flow of the metal atoms. In order to prevent overheating of the CNT channels during the

electromigration processes, thermal analyses of the channels target the possible critical areas along the channel, especially the junction of the channel. This work is recommended to investigate the heat distribution profile along the channel, which has thus far unexplored.

3. The analysis of the MWCNT channels for the flow of biomolecules and metal atoms

Currently, the studies of CNT channels have been focused on SWCNT channels with junctions. The theoretical studies via simulations for the narrowing of MWCNTs have thus far been neglected, especially for the filling of various materials. The narrowing of MWCNTs may exist in the form of a junction, or a gradual reduction of the carbon layering. A thorough investigation involving the profile of the narrowed MWCNT channels and the flow phenomena involved is very insightful and the suitability of MWCNT channels for various applications may be determined.

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