MOLECULAR SIMULATION OF NANO SCALE
TRANSPORT PHENOMENA

Soumik Banerjee

Dissertation submitted to the Faculty of Virginia Polytechnic Institute and State
University in partial fulfillment of the requirements of the degree of

Doctor of Philosophy

in

Engineering Mechanics

Dr. Ishwar K. Puri, Chair
Dr. Romesh C. Batra
Dr. Muhammad Hajj
Dr. Michael W. Hyer
Dr. Kyungwha Park

June 16, 2008
Blacksburg, Virginia

Keywords: Nanotechnology, Molecular Dynamics, Carbon Nanotube
MOLECULAR SIMULATION OF NANOSCALE
TRANSPORT PHENOMENA
Soumik Banerjee

ABSTRACT

Interest in nanoscale heat and mass transport has been augmented through current trends in nanotechnology research. The theme of this dissertation is to characterize electric charge, mass and thermal transport at the nanoscale using a fundamental molecular simulation method, namely molecular dynamics. This dissertation reports simulations of (1) ion intake by carbon nanotubes, (2) hydrogen storage in carbon nanotubes, (3) carbon nanotube growth and (4) nanoscale heat transfer. Ion transport is investigated in the context of desalination of a polar solution using charged carbon nanotubes. Simulations demonstrate that when either a spatially or temporally alternating charge distribution is applied, ion intake into the nanotubes is minimal. Thus, the charge distribution can either be maintained constant (for ion encapsulation) or varied (for water intake) in order to achieve different effects. Next, as an application of mass transport, the hydrogen storage characteristics of carbon nanotubes under modified conditions is reported. The findings presented in this dissertation suggest a significant increment in storage in the presence of alkali metals. The dependence of storage on the external thermodynamic conditions is analyzed and the optimal range of operating conditions is identified. Another application of mass transport is the growth mode of carbon nanostructures (viz. tip growth and base growth). A correct prediction of the dominant growth mode depends on the energy gain due to the addition of C-atoms from the carbon-metal catalyst solution to the graphene sheets forming the carbon nanostructures. This energy gain is evaluated through
molecular dynamics simulations. The results suggest tip growth for Ni and base growth for Fe catalysts. Finally, unsteady nanoscale thermal transport at solid-fluid interfaces is simulated using non-equilibrium molecular dynamics simulations. It is found that the simulated temperature evolution deviates from an analytical continuum solution due to the overall system heterogeneity. Temperature discontinuities are observed between the solid-like interfaces and their neighboring fluid molecules. With an increase in the temperature of the solid wall the interfacial thermal resistance decreases.
This thesis is dedicated to my fiancée Sudeshna without whose continuous support, encouragement and inspiration it would never have been accomplished.
ACKNOWLEDGEMENTS

I extend my gratitude and sincere thanks to my advisor Prof. Ishwar K. Puri for his constant help and guidance that contributed to the completion of this dissertation. Professor Puri not only inspired me through myriad interesting discussions and brainstorming sessions, but also made sure that I worked on a research topic that was both intellectually stimulating and useful to the scientific community. I would also like to thank my co-advisor Prof. Sohail Murad for his continuous guidance. Without his invaluable input this dissertation would not be completed. Gratitude is expressed to my dissertation committee – Professors Romesh C. Batra, Muhammad Hajj, Michael W. Hyer, and Kyungwha Park – for their unwavering support and encouragement.

I express my sincere thanks to my colleagues Sayangdev Naha and Ganesh Balasubramanian with whom I collaborated on various research projects. I would specially like to thank my colleagues Anindya De, Sayangdev Naha, and Ashok Sinha for their continuous support and for the numerous debates and discussions that I have had with them, both academic and non-academic. Without their presence the whole experience of working in the lab over the past four years would not be as much enjoyable and intellectually stimulating as it has been. I express sincere gratitude to Prof. Ranjan Ganguly for all the motivating discussions that I have had with him. Gratitude is expressed to Prof. Swarnendu Sen for his help and guidance in numerous aspects.

Finally, I thank my parents Mrs. Jolly Banerjee and Mr. Swapan Banerjee for their unwavering support. The confidence in my abilities and encouragement that they have continuously provided me with has led to the culmination of my PhD.
CONTENTS

Abstract ............................................................................................................................... ii
Acknowledgements ........................................................................................................... v
Contents ............................................................................................................................. vi
List of Figures .................................................................................................................. viii
List of Tables .................................................................................................................... xii
Chapter 1: Introduction ....................................................................................................... 1
  1.1. Motivation ............................................................................................................ 1
  1.2. Objective .............................................................................................................. 4
  1.3. Contributions ........................................................................................................ 5
  1.4. Outline of the dissertation .................................................................................... 6
Chapter 2: Background ....................................................................................................... 7
  2.1. Carbon Nanostructures ......................................................................................... 7
  2.2. Molecular Simulation Methods ............................................................................ 9
      2.2.1. Molecular Dynamics ................................................................................... 11
  2.3. Ion Adsorption in Carbon Nanotubes .................................................................. 13
  2.4. Hydrogen Storage in Carbon Nanotubes .............................................................. 14
      2.4.1. Storage Mechanism ..................................................................................... 14
      2.4.2. Review of Previous Hydrogen Storage Investigations ............................... 16
      2.4.3. Means of Enhanced Storage ...................................................................... 22
  2.5. Carbon Nanotube Growth Mode .......................................................................... 27
  2.6. Nanoscale Heat Transfer at Solid-Fluid Interfaces ............................................. 28
Chapter 3: Ion Adsorption in Carbon Nanotubes ............................................................. 30
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>30</td>
</tr>
<tr>
<td>3.2</td>
<td>Methodology</td>
<td>31</td>
</tr>
<tr>
<td>3.3</td>
<td>Results and Discussion</td>
<td>35</td>
</tr>
<tr>
<td>Chapter 4: Hydrogen Storage in Carbon Nanotubes</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>44</td>
</tr>
<tr>
<td>4.2</td>
<td>Methodology</td>
<td>45</td>
</tr>
<tr>
<td>4.3</td>
<td>Results and Discussion</td>
<td>49</td>
</tr>
<tr>
<td>Chapter 5: Carbon Nanotube Growth Mode</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>60</td>
</tr>
<tr>
<td>5.2</td>
<td>Methodology</td>
<td>62</td>
</tr>
<tr>
<td>5.3</td>
<td>Results and Discussion</td>
<td>65</td>
</tr>
<tr>
<td>Chapter 6: Nanoscale Heat Transfer at Solid-Fluid Interfaces</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>69</td>
</tr>
<tr>
<td>6.2</td>
<td>Methodology</td>
<td>70</td>
</tr>
<tr>
<td>6.3</td>
<td>Results and Discussion</td>
<td>73</td>
</tr>
<tr>
<td>Chapter 7: Conclusions</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>Ion Adsorption in Carbon Nanotubes</td>
<td>81</td>
</tr>
<tr>
<td>7.2</td>
<td>Hydrogen Storage in Carbon Nanotubes</td>
<td>81</td>
</tr>
<tr>
<td>7.3</td>
<td>Carbon Nanotube Growth Mode</td>
<td>82</td>
</tr>
<tr>
<td>7.4</td>
<td>Nanoscale Heat Transfer at Solid-Fluid Interfaces</td>
<td>82</td>
</tr>
<tr>
<td>Bibliography</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Appendix A</td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Figure 2.1:</strong></td>
<td>Various types of carbon nanotubes are characterized by their respective chiral angles.</td>
</tr>
<tr>
<td><strong>Figure 3.1:</strong></td>
<td>Schematic diagrams of the simulated charge distributions. (The deeper shade corresponds to a negative charge on a carbon atom while the lighter shade is for a positive charge.)</td>
</tr>
<tr>
<td><strong>Figure 3.2:</strong></td>
<td>Schematic diagram of the simulated system.</td>
</tr>
<tr>
<td><strong>Figure 3.3:</strong></td>
<td>Water molecule intake by the nanotubes for different charge distributions. Initially, a 13.96% sodium chloride solution surrounds the carbon nanotube and the system is at ambient temperature and pressure. The surface charge density in each case (except for the uncharged nanotube) is 0.825 C/m².</td>
</tr>
<tr>
<td><strong>Figure 3.4:</strong></td>
<td>Water molecule intake by carbon nanotubes used as conventional electrodes for different charge densities, also for a 13.96% initial sodium chloride solution. The surface charge densities on the electrodes are zero (uncharged nanotube), 0.825 C/m², 1.65 C/m² and 3.3 C/m².</td>
</tr>
<tr>
<td><strong>Figure 3.5:</strong> (a) Sodium and (b) chloride ion intake by the nanotubes for different charge distributions and for conditions that are used to obtain the results in Fig. 3.3.</td>
<td>41</td>
</tr>
<tr>
<td><strong>Figure 4.1:</strong></td>
<td>Comparison of result from Prof. Murad's Code with that of LAMMPS.</td>
</tr>
<tr>
<td><strong>Figure 4.2:</strong></td>
<td>Schematic diagram of the simulated system. Interconnects made of Li-, Pd- and Ti-ions, and C atoms (purple) are used to join adjacent carbon nanotubes (green), surrounded by hydrogen molecules (blue).</td>
</tr>
</tbody>
</table>
Figure 4.3: Variation of hydrogen storage with pressure at 273 K for various interconnect materials joining the carbon nanotubes.

Figure 4.4: (a) Variation of hydrogen storage with pressure at 273 K in the presence of Li ion interconnects for various charge patterns on the carbon nanotubes. The plot in the inset presents similar results at 100 K. (b) Schematic of the circumferential ring type charge distribution (Banerjee et al, 2007). The dark lines represent sites with negative charges, while lighter ones represent positive charges.

Figure 4.5: Hydrogen storage isobars for uncharged nanotubes in the presence of Li ion interconnects. The inset presents the slope of these isobars at various temperatures. Here, 

\[ f(T_r) = \frac{\partial \rho_r}{\partial T_r} \bigg|_{p_r} / 1.2k_p^{0.8} \]

Figure 4.6: Hydrogen storage isotherms for uncharged nanotubes in presence of Li ion interconnects. The inset presents the slope of these isotherms at various pressures. Here, 

\[ g(p_r) = \frac{\partial \rho_r}{\partial p_r} \bigg|_{T_r} / 0.8kT_0^{-1.2} \]

Figure 4.7: Hydrogen storage isobars for uncharged nanotubes in the presence of C interconnects. The inset presents the slope of these isobars at various temperatures. Here, 

\[ h(T_r) = \frac{\partial \rho_r}{\partial T_r} \bigg|_{p_r} / 1.1k_p^{0.35} \]

Figure 4.8: Hydrogen storage isotherms for uncharged nanotubes in presence of C interconnects. The inset presents the slope of these isotherms at various pressures. Here, 

\[ q(p_r) = \frac{\partial \rho_r}{\partial p_r} \bigg|_{T_r} / 0.35kT_0^{-1.1} \]
Figure 4.9: Variation of hydrogen storage with pressure in open and closed-ended carbon nanotube electrodes in the presence of Li ion interconnects. ........................................... 59

Figure 5.1: Schematic illustrating the growth modes of carbon nanotubes. ...................... 61

Figure 5.2: A two-dimensional orthographic view of the molecular dynamics simulation domain with the carbon nanotube (green), which is surrounded by ambient Ar (gray), growing on top of the metal catalyst particle (blue) that has dissolved carbon (red). ...... 64

Figure 5.3: Variation of the total system energy with time. ............................................ 66

Figure 5.4: Variation of the energy change with respect to temperature for Ni and Fe. . 67

Figure 6.1: A 3-dimensional view of the molecular dynamics simulation domain in which Ar (cyan) fills a space of 28 nm between two 1 nm thick blocks of solid Fe. Fluid atoms on both sides of the walls indicate periodicity. A close-up orthographic view shows the observed Ar–atom layering at the solid-fluid interface. ................................................. 72

Figure 6.2: The temperature (dotted line) and density (solid line) distributions across the x-wise direction after the system nears its steady state. The solid Fe walls are located between 14-15 nm and 43-44 nm. The fluid domain is divided into several 4 Å thick slabs along the x-direction for the purpose of spatial characterization, and the density and temperature distributions within them are sampled at uniform time intervals. ............... 74

Figure 6.3: Temporal evolution of the fluid temperature obtained explicitly from the simulations and empirically from an analytical solution to Fourier’s law of heat conduction (assuming homogenous and constant properties). .................................................. 76

Figure 6.4: Schematic of the system solved using Fourier’s Equation. ......................... 77

Figure 6.5: Temporal evolution of the interfacial thermal resistances for wall temperature of 125 K (based on heat fluxes calculated using a first principles and a quasi-continuum
approach). The interfacial temperature drop is calculated as a time average over 100 ps.
........................................................................................................................................... 79

Figure 6.6: Change in the Kapitza resistance (based on heat fluxes calculated using a first principles approach) with respect to varying wall temperature. The fluxes and temperature drops are averaged over 2000-4000 ps. .......................................................... 80
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Table 2.1:</strong></td>
<td></td>
</tr>
<tr>
<td>Comparative table of the hydrogen storage capacities of various carbon nanostructures.</td>
<td>20</td>
</tr>
<tr>
<td><strong>Table 3.1:</strong></td>
<td></td>
</tr>
<tr>
<td>Values of parameters used in the simulations for preferential ion intake</td>
<td>35</td>
</tr>
<tr>
<td><strong>Table 3.2</strong></td>
<td></td>
</tr>
<tr>
<td>Number of ions, water molecules, and encapsulated solution strength for various surface charge patterns. The surface charge density is 0.825 C/m²</td>
<td>43</td>
</tr>
<tr>
<td><strong>Table 4.1:</strong></td>
<td></td>
</tr>
<tr>
<td>Values of parameters used in the simulations for hydrogen storage.</td>
<td>47</td>
</tr>
<tr>
<td><strong>Table 5.1:</strong></td>
<td></td>
</tr>
<tr>
<td>Lennard Jones interaction parameters for Fe, Ni, C and Ar.</td>
<td>63</td>
</tr>
<tr>
<td><strong>Table 5.2:</strong></td>
<td></td>
</tr>
<tr>
<td>A chart showing representative energy values for a temperature of 700 K.</td>
<td>68</td>
</tr>
<tr>
<td><strong>Table 6.1:</strong></td>
<td></td>
</tr>
<tr>
<td>Lennard Jones interaction parameters for Fe and Ar.</td>
<td>71</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

Recent developments in nanotechnology pay an increasing importance on transport phenomena at the nanoscale. The bulk of the work so far has been either experimental or a theoretical approach modeled after continuum scale phenomena. There is a lack of agreement between the results of various groups. It is therefore important to understand these phenomena from a fundamental perspective. Molecular modeling can provide a basis for understanding nanoscale transport phenomena. Nanoscale transport can be of several kinds, such as charge, mass and thermal transport. The aim of this dissertation is to characterize these three forms of nanoscale transport using molecular dynamics (MD).

1.1. Motivation

Charge transport at the nanoscale is an area of immense interest to the scientific community. Charge separation is of interest to the field of bioanalysis, where desalination is of great importance. A fundamental understanding of ion separation processes is also pertinent to environmental science because they present a means for water purification based on nanofluidics. Electrostatic phenomena can be implemented at the nanoscale with a smaller absolute charge than at larger scales. For instance, due to a large surface area to volume ratio, nanotubes have a larger surface charge density than their mesoscale counterparts for similar local charge values. Thus, electrostatically charged carbon nanotubes (CNTs) can be used effectively as nanopumps for ion separation from a solution, as demonstrated later in the dissertation. Ion encapsulated nanotubes can also be used as nanoreactors for possible chemical reactions.
Mass transport at the nanoscale is pertinent to adsorption by nanomaterials as well as flow through and across nanostructures. It has important applications in hydrogen storage at the nanoscale. The US Department of Energy (DOE) benchmark for hydrogen storage is 6.5 weight percent and a volumetric density of 62 kg H₂/m³ (Wang and Johnson, 1999b) in a storing material. The use of hydrogen as a fuel is limited in large part because of lack of progress in developing suitable storage and delivery systems. Materials that adsorb significant quantities of hydrogen are therefore urgently needed. The special hydrogen adsorbing characteristics of carbon nanomaterials make them rather suited as hydrogen storage devices. Due to their high surface area and capillarity, CNTs have high hydrogen storage capacity. In this dissertation, the feasibility of CNT as a hydrogen storage device is investigated.

Mass transport at the nanoscale is also pertinent to species diffusion and growth due to bond formation. Catalyzed growth of carbon nanostructures occurs mainly through two modes, i.e., base growth when the metal nanoparticle remains at the bottom of the nanotube, or when it is lifted by the growing carbon nanostructure due to tip growth. A correct prediction of the dominant growth mode can be very useful for applications that involve metal-encapsulated CNTs. For instance, ferromagnetic metal particles at the end of CNTs can be used to align them. The dominant growth mode depends on the energy gain due to the addition of C-atoms from the carbon-metal catalyst solution to the graphene sheets forming the carbon nanostructures. Such growth modes are characterized in the dissertation through molecular simulations.

Thermal transport at the nanoscale is a topic of growing interest for researchers. The most significant question surrounding nanoscale thermal transport is the evaluation
of boundary resistances between nanoscale interfaces (Swartz and Pohl, 1989). Quantification of the interfacial thermal resistance (also known as Kapitza resistance (Kapitza, 1941)) has several applications. Thermal management of electronic packaging (thermo-electrics) (Darabi, 2002), nanofabrication techniques (Chen, 2000) as well as efficient nanoscale energy transfer are some of the pertinent applications of nanoscale thermal transport. Molecular dynamics has been one of the tools used to comprehend the physics of thermal conductivity in liquids (Heyes and March, 1996) and to study different modes of thermal transport in nanofluids (Eastman et al., 2004). This dissertation presents results that related to characterization of interfacial thermal transport.

Molecular dynamics simulations have contributed significantly to enhance the fundamental understanding of physical mechanisms at the nanoscale. Molecular simulations can be used to study many important unanswered questions relating to the permeation, adsorption, and selectivity of gases in nanoporous materials (Sourirajan and Matsuura, 1985) that primarily involve molecular forces and, thus, cannot be directly addressed by continuum approaches. A fundamental molecular level approach (such as MD) can address these issues directly and unambiguously. The MD method (Allen, 1987, Haile, 1992, Evans and Morris, 1990, Murad et al., 1993) has been used to investigate a variety of static and dynamic properties of fluids in nanopores (Murad et al., 1993, Lin and Murad, 2001, Murad et al., 1998, Murad et al., 2003) and shown that osmosis, reverse osmosis, ion-exchange and gas separations can be observed for nonpolar, polar and electrolyte solutions. The bulk of the concluded work presented here is related to nanoscale transport. Hence, MD has been chosen as the preferred method.
1.2. Objective

The aim of the research presented is to characterize the transport of mass, charge and heat at the nanoscale through molecular simulations. With regards to charge transport, preferential ion adsorption in CNTs is characterized. The effect of charge pattern on CNT surfaces on the intake of either water or ions is determined. The aim of this project is to come up with an effective strategy by which the intake of either ion or water inside CNT can be controlled. Molecular dynamics is used to investigate the charge transport phenomenon.

Next, mass transport at the nanoscale is characterized. Two relevant problems are presented. The first research project involves hydrogen storage in CNTs. Molecular simulation is used to study the effect of temperature, pressure, configuration, presence of metal interconnects, surface charge on the enhancement of hydrogen storage in CNTs. The objective is to come up with optimal conditions for storage. The second project aims at prediction of the growth mode during catalytic synthesis of CNTs. A variety growth conditions relevant to the CVD synthesis of CNTs, including a range of temperature (700 – 1100 K) and two different catalysts (iron and nickel) are simulated.

Finally, nanoscale thermal transport at solid-fluid interfaces is characterized using non-equilibrium molecular dynamics (NEMD) simulations. The results thus obtained are compared with those obtained using continuum scale approximations. The thermal resistance at the interface is evaluated for various solid temperatures and its time evolution is quantified.
1.3. Contributions

The key contributions highlighted in the dissertation are listed below:

1. The dissertation demonstrates that CNTs with varied charge distributions can be used as devices for the controlled intake of either ions or polar solvents. For a spatially or temporally alternating charge distribution, a nanotube preferentially encapsulates polar solvents (such as water) from a solution, while a uniform charge distribution promotes the intake and encapsulation of ions.

2. The optimal conditions for hydrogen storage in CNTs are identified. While the literature suggests that metallic contaminants enhance storage, the findings presented in this dissertation suggest that this is significant for alkali and not transition metals. Charging the CNT surfaces does not significantly enhance hydrogen storage. It is found that the bulk of the hydrogen storage occurs inside CNTs due to their nanocapillarity effect. However, hydrogen storage is much more dependent on external thermodynamic conditions such as the temperature and the pressure than on these facets of the CNT structure. The dependence of storage on the external thermodynamic conditions is analyzed and the optimal range of operating conditions is identified.

3. The energy gain due to the addition of carbon atoms from the nanoparticle to the CNT is evaluated through atomistic scale MD simulations. The results suggest that while in case of Fe nanoparticle, the surface interaction energy is greater than the energy gain; the converse is true for Ni. Hence, the presence of Ni catalyst promotes tip growth while Fe catalyst promotes base growth.
4. The MD simulation results suggest that thermal transport at the nanoscale is remarkably different from that at the continuum scale. It is observed from the results that the nanoscale system has a discrete temperature drop at the solid-fluid interface due to phase segregation of the fluid. The thermal resistance at the interface is a function of the solid temperature and decreases as the temperature of the solid increases.

1.4. Outline of the dissertation

An introduction to the research presented in the dissertation is provided in Chapter 1. Chapter 2 provides a background to the research and the terminology discussed in the dissertation. It also cites the literature pertinent to the results presented in the chapters that follow. The results and discussion in the dissertation can be essentially divided into four parts, as discussed in Chapters 3 through 6. Chapter 3 presents results related to nanoscale charge transport. It typically deals with the application of nanoscale charge transport to preferential ion intake in CNTs. Chapters 4 and 5 are related to mass transport and talk about two different applications. While Chapter 4 discusses hydrogen storage in CNTs and scopes of enhancement, Chapter 5 presents a molecular model that predicts the growth mode of CNTs. The results presented in the former chapter suggest means to improve hydrogen storage in carbon nanostructures while those presented in the latter chapter are pertinent to several methods used in CNT synthesis such as the Chemical Vapor Deposition (CVD). Simulation results for unsteady nanoscale thermal transport is provided in Chapter 6. Finally, Chapter 7 presents the salient conclusions related to the results discussed in Chapters 3 through 6.
Chapter 2: Background

2.1. Carbon Nanostructures

Carbon nanostructures, such as CNTs and carbon nanofibers (CNFs), are graphitic ($sp^2$-hybridized) structures made of carbon that have characteristic dimensions of the order of nanometers. In recent times, carbon nanostructures have attracted wide attention due to their wide range of applications. Carbon nanotubes are graphene sheets rolled into seamless tubes with diameters that are of the order of nanometers. In addition to the ability to store hydrogen, they also possess other outstanding properties such as mechanical strength, metallic or semiconducting behavior and metal particle encapsulation (Yu et al., 1999, Kong et al., 2000, Yu et al., 2000, Collins et al., 2000, Rueckes et al., 2000, Ren and Price, 2001, Akita et al., 2001). Carbon nanofibers basically consist of an intercalation of these graphitic planes at a fixed distance (0.355 nm) from each other to form a variety of structures. Carbon nanotubes and nanofibers are usually grown on metallic surfaces by the catalytic action of one or more transition metals. The nanofibers have enhanced strength, and thermal and electrical properties as compared to nanotubes (Louchev et al., 2003, Heremans and Beetz, 1985, Heremans, 1985, Endo et al., 2001). Activated carbon is an amorphous variety of carbon with high surface area due to the presence of carbon nanoparticles. All these allotropes of carbon exhibit hydrogen adsorption capabilities.

A CNT can be one of three types; (1) armchair, (2) zigzag and (3) chiral depending on the orientation along which the graphitic planes are folded. Figure 2.1 describes the chiral vector $\vec{c} = m\vec{a}_1 + n\vec{a}_2$ and the chiral angle $\theta$. When the value of $\theta$ is,
respectively, 30°, 0° or anywhere in between, a nanotube is respectively called zigzag, armchair or chiral. The chiral vector \( \vec{c} \) is expressed in terms of the unit vectors \( \vec{a}_1 \) and \( \vec{a}_2 \)

\[
\vec{c} = m\vec{a}_1 + n\vec{a}_2
\]

- For armchair, \( m = n \)
- For zigzag, either \( m = 0 \) or \( n = 0 \)
- For chiral, both \( m \) and \( n \) are non-zero

Here, \( \theta \) is the chiral angle.

**Figure 2.1:** Various types of carbon nanotubes are characterized by their respective chiral angles.

that are oriented along two particular directions along the unit hexagonal cell. The constants \( m \) and \( n \) determine whether the nanotube is of the armchair, zigzag, or chiral type. The nanotube is of the armchair type if \( m = n \), zigzag if either \( m \) or \( n \) are zero, and chiral for all other cases. Similarly, a nanofiber can also be of three types, namely, platelet, tubular or herringbone, based on the orientation of its graphitic planes. If the
planes are perpendicular or parallel to the axis of the fiber, the nanofiber is of a platelet or tubular type, respectively. If the graphitic planes are inclined with respect to the axis, it is referred to as a herringbone nanofiber. The various adsorption, storage and conducting properties of CNTs depend on its chirality.

2.2. Molecular Simulation Methods

Molecular simulation refers to theoretical methods and computational techniques to model or mimic the behavior of molecules. These techniques are frequently used in the fields of computational chemistry, computational biology and materials science for studying molecular systems ranging from a few atoms to a system of millions of molecules. By definition, molecular simulation methods have a lowest level resolution of individual atoms.

Molecular simulations can be used to study many important unanswered questions relating to the permeation, adsorption, and selectivity of gases in nanoporous materials (Sourirajan and Matsuura, 1985) that primarily involve molecular forces and, thus, cannot be directly addressed by continuum approaches. A fundamental molecular level approach (such as MD) can address these issues directly and unambiguously. The MD method (Allen, 1987, Haile, 1992, Evans and Morris, 1990) has been used to investigate a variety of static and dynamic properties of fluids in nanopores (Murad et al., 1993, Lin and Murad, 2001, Murad et al., 1998, Murad et al., 2003) and shown that osmosis, reverse osmosis, ion-exchange and gas separations can be observed for nonpolar, polar and electrolyte solutions.

Molecular dynamics and Monte Carlo methods have relative advantages and disadvantages depending on the system and properties being simulated. While MD is a
deterministic method that solves for the equation of motion of individual molecules and looks at the time evolution of the system, conventional Monte Carlo is stochastic and samples a given set of random movements of atoms/molecules, selecting or rejecting it on the basis of the configurational energy. Monte Carlo is usually time-independent. Computationally too these methods have relative merits and demerits based on the system at hand. In MD the position of each atom/molecule is determined by solving the equation of motion, while in case of Monte Carlo the motion is stochastically sampled and hence generally involves less computational time. However, if there are a large number of rejections in stochastic motions (e.g. dense fluids), the computational time increases. Monte Carlo is better suited to simulation of moderate-density fluids while MD is advantageous in case of higher density fluids such as gases under high pressure or liquids. Further, MD can be used to calculate dynamic properties while conventional Monte Carlo cannot determine these properties. Grand Canonical Monte Carlo can handle a variable number of particles while MD is usually implemented with a constant number of particles. One central similarity in both these methods is the use of a potential function. The accuracy of the results predicted by Monte Carlo or MD depends on the accuracy of the potential function. One therefore needs to be careful in selecting the potential function.

The density functional theory is a quantum mechanistic approach for solving atomic scale systems and is hence more fundamental than MD or Monte Carlo. One of the drawbacks of this method is that the exact form of the universal energy density functional is unknown and approximation is involved. Also, since quantum mechanistic calculations typically involve length scales of the order of Angstroms, it is
computationally expensive to characterize systems with dimensions of several nanometers. Hence, molecular simulations provide an optimal approach to model nanoscale systems.

2.2.1. Molecular Dynamics

Molecular dynamics simulations compute the motions of individual molecules in models of solids, liquids and gases. It provides a technique to compute trajectories and velocities of atoms and molecules in a nanoscale system. Molecular dynamics method can be used effectively to investigate a variety of nanoscale transport processes. For instance, various physical properties of carbon nanostructures depend primarily on the intermolecular forces between the atoms constituting the membrane pores (or surface) and the atoms (or molecules) that surround them. Similarly, the adsorption/absorption of gases on the surface and in the pores of a nanostructure also depend on these forces, as does the ability of certain molecules to diffuse faster in nanopores as compared to other molecules. Only a fundamental molecular level approach (such as MD) can address these issues directly and unambiguously. A typical MD simulation methodology can be implemented using the following steps:

1. Establishing the initial configuration (geometry) of a suitable nanostructure to be used during the molecular simulation:

The initial configuration depends on the system that is characterized. For all the simulations presented in this dissertation, the initial configuration comprises of essentially two different kinds of structures, (1) a complex molecule/membrane, the structure of which is obtained experimentally and is available from the literature (e.g. (Li et al., 2003b)), (2) metal or gaseous atoms. The initially assigned structure for the metal
or gaseous atoms usually comprises of a face centered cubic (fcc) or a body centered cubic lattice. This initial configuration can be far removed from the realistic minimum-energy equilibrium structure. The simulated system is given a random initial velocity distribution that scales with the required temperature and allowed to evolve temporally and the total energy is monitored. The system is said to relax as it evolves from its initial configuration and velocity distribution (that may be arbitrary) towards equilibrium. When the total energy reaches a minimal value, the system is said to have equilibrated. This signifies that the system is independent of its initial state (since it has reached thermodynamic equilibrium) and can be characterized. The active sites or surfaces correspond to simple atoms (such as monatomic gases like Ar) or complicated molecular structures (such as CNTs).

2. Prescribing the intermolecular interactions:

The interactions between the various molecules in the simulated system can be modeled using a suitable empirical potential which is typically a function of the distance between the atoms. A common example of a potential function is the LJ potential with the Coulombic interaction term, represented by the following functional form

\[ u_{ij} = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{r_{ij}}. \]  

(2.1)

In Eq. (2.1), \( u_{ij} \) denotes the interaction potential between sites i and j, \( r_{ij} \) the scalar distance between sites i and j, \( \sigma_{ij} \) and \( \varepsilon_{ij} \) are the LJ interaction parameters, and \( q_i \) and \( q_j \) represent the charges on sites i and j (although not all sites have charges). The potential parameters \( \sigma \) and \( \varepsilon \), and charges \( q \) are usually obtained from the literature.
The gradient of the potential function provides the force. At any instant, the total force on an atom due to all other atoms in the system can be evaluated. The acceleration of each atom at each time step can be thus obtained. A suitable numerical integration scheme can then evaluate the velocities and positions of each atom at any instant. This temporal evolution of the system can be then used to evaluate useful properties of the nanoscale system.

An MD simulation can either be based on a system at thermal equilibrium or non-equilibrium. For example, if a nanoscale system has an imposed temperature gradient the system is not at thermal equilibrium. In such situation the dynamics of the molecules can be computed using NEMD.

2.3. Ion Adsorption in Carbon Nanotubes

Interest in nanofluidic fundamentals stems from possible applications of nanoreactors (Tessonni et al., 2005) and nanodevices for fluid transport, bioanalysis (Fan et al., 2005, He et al., 2006, Khandurina and Guttman, 2002) and drug delivery (Martin et al., 2005). For instance, the selectivity in biological ion transport (Bell, 1998) through nanochannels (Duax et al., 2003) is of great importance in bioanalysis. The controlled encapsulation of specific ions within CNTs or their ability to selectively transport various substances is of significance in this regard (Hoos et al., 2006). With the development of fabrication methods for nanochannels (Datta et al., 2006), electro-osmotic flow (Qiao and Aluru, 2005), (Petsev and Lopez, 2006) through them has become a recent focus of research, and novel devices such as nanofluidic transistors (Karnik et al., 2005) and nanofluidic pumps (Chen et al., 2005) have been developed.
Due to their desirable chemical stability and electrical conductivity, the nanoscale dimensions of CNTs produce a relatively large surface area-to-volume ratio, making their use attractive in charge separation devices and as electrodes (Chen et al., 2004a, Dai et al., 2005). The mass transport (Duren et al., 2002), ion concentration (Duax et al., 2003), velocity distribution (Nagayama and Cheng, 2004, Kang et al., 2004, Hanasaki et al., 2004) and slip length (Kotsalis et al., 2004) have been investigated for flow inside CNTs. It is also important to characterize the ion-channel interaction (Duax et al., 2003, Arista, 2001) to properly understand electro-osmotic flows in electrically charged nanochannels. While techniques for the encapsulation of particular species have been proposed (Jeong et al., 2003, Jeong et al., 2002) none seem to be based on a generic controlled intake method. In this dissertation MD simulations have been used to demonstrate the utility of CNTs for water and ion separation (and subsequent encapsulation) from a salt solution.

2.4. Hydrogen Storage in Carbon Nanotubes

2.4.1. Storage Mechanism

The hydrogen adsorbing characteristics of carbon nanomaterials make them attractive candidates for storage devices. The nanosize adds another degree of freedom for fine-tuning the material properties, since the CNT length and its curvature also influence the thermodynamics of storage. In this dissertation methods to systematically evaluate the hydrogen adsorption limitations of various carbon nanostructures using MD simulations have been described. Strategies to overcome these limitations with structural modifications, such as metal encapsulation (Sen and Puri, 2004) have also been suggested. For instance, alkali metal-doped carbon nanostructures have been found to be even better adsorbents than carbon nanostructures (Chen et al., 1999).
Elemental carbon is known to adsorb significant quantities of hydrogen (Wang and Johnson, 1999c, Dillon et al., 1997) due to the strong intermolecular attractive forces between the molecules of the two species. This, in conjunction with exceptional capillarity and high surface area, leads to hydrogen adsorption in CNTs (Pederson and Broughton, 1992, Schmidt, 1993). Hydrogen is adsorbed both on the surface of the nanotubes as well as in the interstitial sites in triangular arrays of nanotubes called nanoropes. In addition, hydrogen is absorbed within the volume described by the nanotubes. The curvature inside the nanotubes subjects hydrogen atoms to stronger attraction than offered by a graphitic plane. This causes the nanotubes to be more efficient in hydrogen adsorption than planar structures. The hydrogen adsorption in a nanotube essentially occurs through two mechanisms (Li et al., 2003a):

1. Physisorption:

Through this process hydrogen molecules are adsorbed inside of a nanotube or in the interstice of a nanotube mesh due to a van der Waals attractive force between the carbon and hydrogen. There is no theoretical limit to the percentage of hydrogen that can be stored by this means because hydrogen is adsorbed in multiple layers. However, at room temperature and atmospheric pressure, only a monolayer of hydrogen is formed on the surface of the tube (Cabria et al., 2006), which limits the adsorption to 3.3% by weight (Zuttel et al., 2002). The effective surface area available for adsorption is an important parameter (Zhou et al., 2004b). The Brunauer-Emmet-Teller (BET) surface area characterization is widely used to estimate the physisorption capacity of CNTs (Ye et al., 1999).
2. **Chemisorption:**

   Here, the hydrogen molecules are covalently bonded to the carbon atoms of the nanotube. Each carbon atom in the nanotube is sp\(^2\) hybridized, bonded with three other carbon atoms and has a dangling π-bond. Therefore, there can be at most one hydrogen atom stored (chemisorbed) per carbon atom. Theoretical calculations based on density functional theory show that this limits the maximum storage limit to 7.7% (Li et al., 2003a) by weight. Desorption of the hydrogen atoms thus adsorbed is more difficult than in the case of physisorption and requires a higher temperature for hydrogen release.

2.4.2. *Review of Previous Hydrogen Storage Investigations*

1. **Carbon Nanotubes:**

   There is wide disparity in the experimental results reported by researchers for the maximum hydrogen storage in single-walled nanotubes (SWNTs) (Zhou et al., 2004b, Hirscher et al., 2003, Dillon et al., 2000, Liu et al., 1999, Yang, 2000). In addition, as mentioned above, various experimentally obtained high storage capacity results (Dillon et al., 1997, Chambers et al., 1998) have not yet been corroborated (Hirscher et al., 2003, Pinkerton et al., 2000), even theoretically by using MD simulations, Monte Carlo methods or the density functional approach. The hydrogen weight percentage is generally measured by volumetric or gravimetric methods, both of which are prone to errors, causing discrepancies in the results. The impurity and limited quantity of the various nanotube samples might also account for a relatively large scatter in the experimental data (Hirscher et al., 2003). Thermal desorption spectrometry (TDS) is an effective method for the measurement of hydrogen adsorption but calibration using unstable hygroscopic materials like calcium hydride can produce erroneous results. Some of the
more efficient methods to measure the hydrogen adsorption are by the use of sensitive high-pressure microbalances (Pan et al., 2005), the tangent-mass method (Li et al., 2003c), and the elastic recoil detection method (Naab et al., 2006). Hirscher et al. (2003) claim that some of the experiments reported a higher adsorption rate than realistically possible.

Some experiments have implied that in SWNTs hydrogen storage is possible at moderate temperatures and ambient pressures at levels above the minimum volumetric storage prescribed by DOE (Wang and Johnson, 1999b, Dillon et al., 2000). However, other investigators have reported that a useful amount of hydrogen can only be stored at cryogenic temperatures and/or very high pressures (Ye et al., 1999, Liu et al., 1999). In addition, the experimentally obtained high storage capacity results of Chambers et al. (1998) and Dillon et al. (1997) have not yet been corroborated by theoretical or numerical simulations. Table 2.1 compares the various experimental results for hydrogen storage in nanotubes (Hirscher et al., 2003). It is clear from the data that it is important to more fully understand the hydrogen storage mechanism in carbon nanostructures to resolve the discrepancies.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Material</th>
<th>Temperature (K)</th>
<th>Pressure (Mpa)</th>
<th>Maximum Storage (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Callejas et al., 2004</td>
<td>Reduced CNT</td>
<td>77</td>
<td>0.04</td>
<td>3</td>
</tr>
<tr>
<td>Chambers et al., 1998</td>
<td>GNF</td>
<td>300</td>
<td>12</td>
<td>65</td>
</tr>
<tr>
<td>Chambers et al., 1998</td>
<td>GNF (tubular)</td>
<td>298</td>
<td>11.35</td>
<td>11.26</td>
</tr>
<tr>
<td>Authors, Year</td>
<td>Type</td>
<td>Property</td>
<td>Temperature</td>
<td>Value 1</td>
</tr>
<tr>
<td>--------------</td>
<td>------</td>
<td>----------</td>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>Chambers et al., 1998</td>
<td>GNF (herringbone)</td>
<td>298</td>
<td>11.35</td>
<td>67.55</td>
</tr>
<tr>
<td>Chambers et al., 1998</td>
<td>GNF (platelet)</td>
<td>298</td>
<td>11.35</td>
<td>53.68</td>
</tr>
<tr>
<td>Chen et al., 1999</td>
<td>Li-CNT</td>
<td>473-673</td>
<td>0.1</td>
<td>20</td>
</tr>
<tr>
<td>Chen et al., 1999</td>
<td>Li-CNT</td>
<td>&lt;313</td>
<td>0.1</td>
<td>14</td>
</tr>
<tr>
<td>Chen et al., 2004</td>
<td>CNT</td>
<td>298</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Darkrim et al., 2000</td>
<td>SWNT</td>
<td>80</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>Dillon et al., 1997</td>
<td>SWNT (low purity)</td>
<td>273</td>
<td>0.04</td>
<td>5-10</td>
</tr>
<tr>
<td>Dillon et al., 2000</td>
<td>SWNT (high purity)</td>
<td>298</td>
<td>0.04</td>
<td>3.5-4.5</td>
</tr>
<tr>
<td>Fan et al., 1999</td>
<td>CNF</td>
<td>300</td>
<td>10.1</td>
<td>~10</td>
</tr>
<tr>
<td>Guay et al., 2004</td>
<td>CNT</td>
<td>293</td>
<td>10</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Gupta et al., 2000</td>
<td>GNF</td>
<td>300</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>Haluska et al., 2004</td>
<td>SWNT</td>
<td>77</td>
<td>0.1</td>
<td>&lt;0.46</td>
</tr>
<tr>
<td>Hirscher et al., 2001</td>
<td>SWNT-Fe</td>
<td>Ambient</td>
<td>0.08</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Hirscher et al., 2002</td>
<td>SWNT (ball-milled in Ar)</td>
<td>Ambient</td>
<td>0.08</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Hirscher et al., 2002</td>
<td>SWNT (ball-milled in D₂)</td>
<td>Ambient</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Author</td>
<td>Type</td>
<td>Temperature</td>
<td>Capacity</td>
<td>Current</td>
</tr>
<tr>
<td>-----------------</td>
<td>--------------------</td>
<td>-------------</td>
<td>----------</td>
<td>---------</td>
</tr>
<tr>
<td>Liu et al., 1999</td>
<td>SWNT (50% purity)</td>
<td>300</td>
<td>10.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Lueking, 2004</td>
<td>CNT</td>
<td>300</td>
<td>0.1</td>
<td>~0.1</td>
</tr>
<tr>
<td>Nishimiya et al., 2002</td>
<td>SWNT</td>
<td>295</td>
<td>0.1</td>
<td>0.86</td>
</tr>
<tr>
<td>Nützenadel et al., 1999</td>
<td>SWNT (50-70% pure, electrochemical)</td>
<td>-</td>
<td>-</td>
<td>~2</td>
</tr>
<tr>
<td>Orimo et al., 1999</td>
<td>Nanostructured graphite</td>
<td>300</td>
<td>1</td>
<td>7.4</td>
</tr>
<tr>
<td>Panella et al., 2005</td>
<td>CNT</td>
<td>300</td>
<td>~6</td>
<td>~0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>77</td>
<td>~6</td>
<td>~2.5</td>
</tr>
<tr>
<td>Pinkerton et al., 2000</td>
<td>Li-CNT</td>
<td>473-663</td>
<td>0.1</td>
<td>0.72-4.2</td>
</tr>
<tr>
<td>Rajalakshmi et al., 2000</td>
<td>SWNT (80% pure, electrochemical)</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td>Shen et al., 2004</td>
<td>CNT</td>
<td>300</td>
<td>&lt;1.5</td>
<td>1</td>
</tr>
<tr>
<td>Tibbetts et al., 2001</td>
<td>MWNT</td>
<td>296</td>
<td>3.59</td>
<td>0.04</td>
</tr>
<tr>
<td>Wang et al., 1999</td>
<td>SWNT</td>
<td>80</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Yang et al., 2000</td>
<td>Li-MWNT</td>
<td>~473-673</td>
<td>0.1</td>
<td>~2.5</td>
</tr>
<tr>
<td>Authors</td>
<td>Nanomaterial</td>
<td>Temperature</td>
<td>Pressure</td>
<td>Capacity</td>
</tr>
<tr>
<td>--------------------</td>
<td>--------------------</td>
<td>-------------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>Yang et al., 2000</td>
<td>K-MWNT</td>
<td>&lt;313</td>
<td>0.1</td>
<td>~1.8</td>
</tr>
<tr>
<td>Ye et al., 1999</td>
<td>SWNT (high purity)</td>
<td>80</td>
<td>7.18</td>
<td>8.25</td>
</tr>
<tr>
<td>Yin et al., 2000</td>
<td>SWNT</td>
<td>300</td>
<td>16</td>
<td>6.5</td>
</tr>
<tr>
<td>Yoo et al., 2005</td>
<td>CNT</td>
<td>573</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Zacharia et al., 2005</td>
<td>CNT (Pd doped)</td>
<td>300</td>
<td>2</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>CNT (V doped)</td>
<td>300</td>
<td>2</td>
<td>0.69</td>
</tr>
<tr>
<td>Zhou et al., 2006</td>
<td>Activated Carbon</td>
<td>77</td>
<td>6</td>
<td>10.8</td>
</tr>
<tr>
<td>Zhu et al., 2001</td>
<td>MWNT</td>
<td>~290</td>
<td>~10</td>
<td>&gt;3</td>
</tr>
<tr>
<td>Züttel et al., 2002</td>
<td>SWNT</td>
<td>~293</td>
<td>~0.1</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

**Table 2.1:** Comparative table of the hydrogen storage capacities of various carbon nanostructures.

Numerical simulations of hydrogen storage have been mostly performed using molecular modeling. The three widely used techniques are the Monte Carlo (Guay et al., 2004), MD (Dodziuk and Dolgonos, 2002) and density functional theory approach. In the first two of these methods the interaction between the carbonaceous material and hydrogen is usually represented by a classical empirical potential function (Wang and Johnson, 1999b, Wang and Johnson, 1999a, Gordon and Saeger, 1999, Williams and Eklund, 2000, Bernholc et al., 1997, Rzepka et al., 1998, Darkrim and Levesque, 1998). Another frequently used approach accounts for the chemisorption process in CNTs. This
type of modeling requires that the electronic states be explicitly simulated. Examples of such simulations are available in the work by Lee et al. (2000) and Lee and Lee (2000).

Molecular simulations have contributed significantly to enhance fundamental understanding of the physical mechanisms and intermolecular forces that account for the considerable hydrogen adsorption/storage in carbon nanopores (Wang and Johnson, 1999c, Bernholc et al., 1997, Rzepka et al., 1998, Darkrim and Levesque, 1998, Wang and Johnson, 1999a). However, there are disparities in the results obtained by these methods that are mainly due to the potential function used and the geometry and chirality of the nanotube that are considered. These numerical approaches have not yet addressed some important issues that will be described in this dissertation. The most important of these is an investigation of the enhancement of the hydrogen storage capacity of a carbon nanopore/nanorope by making structural changes in the pore as well as in the overall nanostructure composition (for instance, by encapsulating selected metals within the nanostructure).

2. Carbon Nanofibers and Active Carbon:

Apart from single and multi-walled CNTs, there are other carbon nanostructures such as CNFs and activated carbon that can adsorb large quantities of hydrogen (Chambers et al., 1998, Fan et al., 1999, Gupta et al., 2000, Zhou et al., 2006, Panella et al., 2005). This is due to the large surface area of these nanostructures as well as the inherent strong attractive intermolecular force between carbon and hydrogen. Carbon nanofibers or graphitic nanofibers (GNF) are usually formed by the catalytic action of metals (like Ni, Co, Fe) on certain gas phase fullerenic species or carbon derivatives. A form of graphite called beta-graphite saturates out of the metal catalyst surface to form
the nanofibers. Carbon nanofibers are of three types, tubular, herringbone and platelet and have an interlayer distance of 0.355 nm just as in CNTs. (Chambers et al., 1998) have reported an unusually large amount of hydrogen uptake in nanofibers. They claimed that the material is able to adsorb 20 L of hydrogen per gram of carbon at 120 atmospheres and 25 °C, which is equivalent to more that 60% by weight. That claim has not been corroborated through experiments by other groups, which have produced different results (Ahn et al., 1998, Tibbetts et al., 2001, Orimo et al., 1999). The theoretical calculations of Li et al. (2003a) show that at room temperature the adsorption cannot exceed 7.7% by weight.

Activated carbon, such as AX-21, is a form of carbon with a high surface area and pore volume. Several experiments performed to measure the hydrogen adsorption in activated carbon have concluded that this form of carbon has a better adsorption capacity than even CNTs (Zhou et al., 2004a, Schimmel et al., 2004). While the surface area of the nanotubes is the highest at normal temperatures and pressures, at high pressures and/or low temperature, the surface area of activated carbon is much greater than that of the SWNTs. This is because of the bundling of the nanotubes at such conditions. Hence, at high pressures, activated carbon adsorbs more hydrogen than CNTs (Schimmel et al., 2004).

2.4.3. Means of Enhanced Storage

The goal of current research is to further explore additional ideas, since most experimental and theoretical investigations show that while carbon nanostructures are advantageous in comparison to other materials used for hydrogen storage, they are still unable to attain storage greater than desired limits, such as one set by DOE. Various
means have been proposed to increase the hydrogen storage capacity of carbon nanostructures. For instance, nanotube characterization has revealed that the ends of the nanotubes are covered with hemispherical fullerene caps (Hirscher et al., 2001). Thus, in order to enable the access of hydrogen into the interior of the tube, the end of the nanotube must be cut or opened (Liu et al., 1999, Stepanek et al., 2000, Hirscher et al., 2002, Darkrim and Levesque, 2000). While nanotubes with open ends can be synthesized, those with closed ends can be cut open by either exposing a nanotube to ultrasonic treatment (Dillon et al., 1997) or by ball milling. The closed ends of the nanotubes are also susceptible to being opened by oxidation because of the strained nature of the rings (Thess et al., 1996, Tsang et al., 1993, Ajayan et al., 1993). A dilute solution of an acid can be used to sonicate the nanotube sample and open its ends by oxidation. Some reports on high hydrogen adsorption properties of sonicated nanotubes by Dillon et al. (1997) have been put in doubt by Hirscher et al. (2001) who claimed that the high adsorption was due to the Ti particles that were trapped in the nanotubes during the sonication process in the titanium sonicator.

Ball milling is another method to remove the fullerene caps at the ends of nanotubes so as to enhance the hydrogen storage. Reactive ball milling has shown that this strategy is effective. It is also an effective means to enhance storage in other carbon nanomaterials (Awasthi et al., 2002). The process of ball milling destroys the crystalline structure at places and opens up traps for hydrogen storage. This is an interesting issue that can be resolved by careful simulations of carbon nanostructures that have purposefully inserted defects. The geometry of the nanotubes also plays an important role in the storage capacity. The adsorption characteristic changes with variation of chirality
and diameter (Gu et al., 2001, Shen et al., 2004). The diameter of a nanotube changes the packing geometry and hence influences the hydrogen take-up.

Carbon nanoropes and nanofibers, which are two-dimensional triangular lattices of SWNTs, have been found to have a larger storage capacity than simple SWNTs (Cao et al., 2001, Stan and Cole, 1998a, Zhu et al., 2001, Yin et al., 2000). This is due to a larger effective surface area that can be exposed to adsorption, since the interstitial space is also utilized for enhanced hydrogen storage. Careful modeling of these arrays of nanotubes requires a suitable choice of van der Waal’s gap between the tubes. The van der Waal’s gap changes with changing pressure and temperature conditions and so it is important to assume a realistic value.

Density functional theory investigations have shown that hydrogen storage is enhanced when the hydrogen molecules are dissociated into atoms (Han and Lee, 2004). Atoms can easily penetrate the CNT pores and get chemisorbed as well (Haluska et al., 2004). This can be achieved either at low temperature and high-pressure conditions or through catalysis by metals (Yoo et al., 2005). Thus hydrogen storage capacity of carbon nanostructures increases at high pressures (Tarasov et al., 2003, Volpe and Cleri, 2003) and low temperatures (Nishimiya et al., 2002). Experiments as well as molecular modeling studies have shown that at pressures much larger than atmospheric pressure, CNTs exhibit a higher hydrogen storage capacity, since at higher pressures hydrogen molecules are physisorbed in the interstices of the nanotubes as well as in the interior. While temperatures near cryogenic (77K) enhance hydrogen storage (Wang and Johnson, 1999b, Williams and Eklund, 2000, Meregalli and Parrinello, 2001), such low temperatures are not acceptable as practical operating temperatures.
Ci et al. (2003) have reported an enhancement in the storage capacity by annealing CNTs in the temperature range 1700-2200 °C. This is attributed to the modification of the grain structures for the as-synthesized nanotubes that use a floating catalyst. In addition, since as-synthesized CNTs have a variety of functional groups attached to their surfaces that can retard the process of hydrogen adsorption by reducing the available surface area, heat treatment removes these groups and thus increases hydrogen adsorption.

Carbon nanotubes also have enhanced storage capacities when they carry a charge (Simonyan et al., 1999) or have encapsulated metal nanoparticles (Endo et al., 2003). This is due to the increased electrostatic interaction between the fluid and solid phases as well as due to dissociation of hydrogen molecule into atoms. Insertion of Pt, Li, Rb (Che et al., 1999), Cs, K (Gao et al., 1998), and Ni (Shaijumon et al., 2005) induces a charge on the nanotubes. The insertion of K or Cs leads to an excess negative charge of about \(-1e\) per 8 C atoms (Grigorian et al., 1998) that leads to increased hydrogen adsorption. Alkali metals (such as Li) doped CNTs also display a marked increase in hydrogen storage at room temperature (Chen et al., 1999).

Experiments have shown that CNTs can electrochemically store relatively large amounts of hydrogen (Heremans, 1985, Nutzenadel et al., 1999, Rajalakshmi et al., 2000, Chen et al., 2004b). As-synthesized CNTs have been used as electrodes that can be charged and discharged in cycles. Rajalakshmi et al. (2000) have used an 80% pure nanotube sample and reported hydrogen storage of up to 2.9 weight %. They observed that the maximum storage was reached after about 20 cycles of charge and discharge. Lee
et al. (2000) further identified adsorption sites on the exterior, interior of the nanotubes, as well as in the interstices of bundles of nanotubes.

Hydrogen spillover is an important phenomenon where hydrogen molecules are first adsorbed by metal atoms and later desorbed and physisorbed by carbon atoms (Zacharia et al., 2005). The experimental results have shown that multi-walled nanotubes (MWNTs) synthesized by metal oxide catalysts have a large hydrogen adsorption capacity. The active temperature range for adsorption is 25 to 100 degrees C, which is useful for practical applications. Callejas et al. (2004) have investigated an effect similar to spillover and reported the enhanced storage of around 3% by weight at 77K and 0.04 MPa.

Recently, Yildirim and Ciraci (2005) have reported enhanced hydrogen storage by coating a SWNT with Ti atoms. They claimed that each Ti atom binds with up to four hydrogen molecules. The first hydrogen molecule is adsorbed by way of dissociation but the later adsorptions involve intact hydrogen molecules. They claimed hydrogen storage of up to 8%. Previous results have demonstrated an enhancement of storage in alkali-metal doped nanotubes (Chen et al., 1999) due to the catalytic action of alkali-metal ions in hydrogen dissociative adsorption. These findings support future investigations of hydrogen adsorption in nanotubes that contain encapsulated metal ions.

To summarize the results from the literature review presented in this section (and Table 2.1), current experimental results for hydrogen storage do not agree with each other. Thus, an accurate and reliable theoretical or numerical approach is required to understand these discrepancies.
2.5. Carbon Nanotube Growth Mode

The first detailed observation of the synthesis and growth of graphitic CNFs (“filamentary carbon”) was made by Baker et al. by decomposing acetylene in the presence of a nickel catalyst (Baker, 1989). A catalytically active transition metal nanoparticle (i.e., of Fe, Ni and their alloys, such as stainless steel) can be created through the initial formation of a carbon deposit. This deposit develops in a reducing environment that has high gas-phase carbon activity at elevated temperatures (Sacco et al., 1984), (Kock et al., 1985). The deposited carbon diffuses into the catalyst nanoparticle, nucleates within it, and emerges in the form of CNTs or nanofibers (CNFs). The subsequent catalyzed growth of CNTs and CNFs occurs mainly through two modes. The base growth mode arises when the metal nanoparticle catalyzing the growing carbon nanostructure remains at the bottom of the nanotube. For this type of growth the adhesive forces between the substrate and the catalyst nanoparticle are typically too large for the particle to be lifted as the CNT/CNF grows. Alternately, the catalyst nanoparticle is lifted by the growing carbon nanostructure during tip growth, and remains at the tip of the CNT/CNF after its growth ceases.

The experimentally observed base growth mode by Wu et al. was facilitated by an Fe catalyst immersed in C₂H₄ with a ~162.86 torr partial pressure and 1048 K temperature (Wu et al., 2008). The other gaseous species were H₂ (carrier gas) and Ar (inert). The experimental results of Ducati et al. revealed a predominance of vertically aligned CNTs grown through a tip-growth mode with Ni as catalyst and C₂H₂ as the carbon source gas at a temperature of 823 K and 1.5 torr partial pressure (Ducati et al., 2004). However, experimental results related to growth mode of CNTs show wide
variation. Hence, it is important to develop a simulation tool to successfully predict the growth mode of CNT at various conditions. Molecular dynamics simulation results that predict the growth mode of CNTs is presented in this dissertation.

2.6. Nanoscale Heat Transfer at Solid-Fluid Interfaces

The application of MD and NEMD has found wide usage in the determination of thermal properties of Silicon (Keblinski et al., 2002) and the effects of grain size (Bodapati et al., 2006, Tang and Yao, 2006) and phonon scattering (Schelling et al., 2004) on thermal resistance across grain boundaries have also been explored. The interest in studying interfacial thermal transport using NEMD has received considerable attention for solid-solid interfaces (Stevens et al., 2007) as well as for interfaces between liquids (Patel et al., 2005) and thin films (Twu and Ho, 2003, Angadi et al., 2006, Hegedus and Abramson, 2006, Chiritescu et al., 2007).

There is, however, limited literature that have addressed a basic understanding of thermal transport phenomenon between simple solid-fluid interfaces and the bonding between liquid and solid atoms (Xue et al., 2003, Xue et al., 2004) using a simple model of alternate liquid and solid blocks. Recent study of heat transfer through a solid trapped between liquid region shows that the structural details exercise an effect on the thermal properties of solid (Chaudhuri et al., 2007a). Non-equilibrium MD is the simulation technique applied for the study of simple solid-fluid interfacial heat transfer phenomena. Also, the dependence of thermal slip on interaction at the interface has been discussed in literature (Khare et al., 2006).

Since the length scales associated with nanostructures are comparable with those of the energy carriers that facilitate thermal transport, the corresponding nanoscale
properties are different from those at the continuum. The role of the interfacial resistance (Swartz and Pohl, 1989) during nanoscale thermal transport thus also differs from its characteristics at larger scales (Cahill et al., 2003). Moreover, the structural details of a nanoscale interface have a significant influence on the local thermal properties. The attraction of liquid molecules to hydrophilic surfaces promotes structural ordering at interfaces, which enhances the local thermal conductivity (Murad and Puri, 2008, Henderson and Vanswol, 1984). There is also evidence that the local intermolecular interactions can introduce temperature discontinuities across these interfaces (Khare et al., 2006). Kapitza first discussed the existence of an interfacial contact resistance during heat transfer between liquid helium and heated metal surfaces such as copper and lead (Kapitza, 1941). The interfacial (Kapitza) resistance,

$$R_k = \frac{\Delta T}{\dot{q}}, \quad (2.2)$$

represents the ratio of the temperature drop at the interface to the normal heat flux across it (Barrat and Chiaruttini, 2003, Pollack, 1969). Thermal transport across nanoscale solid-fluid interfaces, e.g., those formed when nanoparticles and nanostructures are immersed in fluids, is also influenced by the locally large surface area to volume ratio (Eastman et al., 2004).

In summary, the literature provides some information and results on nanoscale heat transfer at solid-fluid interfaces. However, a lot of the research on nanoscale thermal transport makes implicit assumptions of the validity of continuum scale relations. Also, not much research data is available on transient heat transfer. This dissertation presents comparison of heat transfer evaluated from MD simulations with that obtained from continuum scale assumptions.
Chapter 3: Ion Adsorption in Carbon Nanotubes

3.1. Introduction

It is important to characterize the ion-channel interaction (Akita et al., 2001, Qiao and Aluru, 2005) to properly understand electro-osmotic flows in electrically charged nanochannels. While techniques for the encapsulation of particular species have been proposed (Petsev and Lopez, 2006, Karnik et al., 2005) none seem to be based on a generic controlled intake method. Molecular dynamics simulations have been used to demonstrate the utility of CNTs for water and ion separation (and subsequent encapsulation) from a salt solution.

The magnitude of the charge placed on each atom of a CNT provides a finite overall surface charge density. Three different electrostatic charge distributions on the nanotube (that can be implemented in applications (Chen et al., 2005, Zhao et al., 2002)), as shown schematically in Figure 3.1, have been considered:

1. First, the CNTs are assumed to behave as conventional electrodes for which one half of the nanotube atoms have a positive charge (on the positive electrode) with negative charges on the other half (that acts as the negative electrode).

2. Next, the CNTs are assumed to contain alternate axial bands of positive and negative charges along the length of each CNT in the form of lengthwise arrays of charged carbon atoms.

3. Finally, rings of alternate positive and negative charges arrayed along the circumferences of the CNTs are considered. (The conventional electrode discussed above is a special case of this configuration. As a consequence of the
imposed periodic boundary conditions with regards to the position of the atoms, such an electrode is essentially a single nanotube divided into two halves, one charged positive and the other negative.)

**Figure 3.1:** Schematic diagrams of the simulated charge distributions. (The deeper shade corresponds to a negative charge on a carbon atom while the lighter shade is for a positive charge.)

### 3.2. Methodology

The MD method that has been used is based on an extension of a technique developed to investigate confined fluids. This method has been used to investigate a variety of static and dynamic properties of fluids in nanopores (Murad et al., 1993, Lin and Murad, 2001, Murad et al., 1998, Murad et al., 2003) and it has been demonstrated that osmosis, reverse osmosis, ion-exchange and gas separations can be observed in a simulation that uses this technique for both nonpolar, polar and electrolyte solutions.
These studies have clarified many issues related to the separation of ionic solutions using reverse osmosis, ion exchange, and gases using zeolite membranes.

Molecular dynamics simulations are widely used in nanofluidics (Qiao and Aluru, 2005, Duren et al., 2002, Hanasaki et al., 2004) because usual continuum scale simulations do not accurately predict the flow characteristics (Qiao and Aluru, 2005). The MD simulations are based on a method used to investigate osmosis (Murad and Lin, 1999, Murad and Lin, 2002). Two (10,10) single-walled armchair CNTs of 1.375 nm diameter, 1.122 nm length, and 2.49 Å pore size are considered. In the simulation, the nanotubes are placed in a $2.75 \times 2.75 \times 3.366$ nm box. The carbon atoms of each nanotube are placed at their known equilibrium positions using a simple harmonic-type tethering potential that approximately corresponds to the atoms’ vibrational frequency. The CNTs in the cuboid domain are initially surrounded by a uniform (13.96% or 8.03% by weight) aqueous sodium chloride solution. Periodic boundary conditions on the position of the atoms are used in all directions to eliminate surface effects. Hence, the system is effectively infinite in all directions as shown in Figure 3.2. Due to these periodic boundary conditions, the nanotubes on the two opposite sides of the cuboid shaped domain are essentially joined end to end in the form of a single CNT.

A typical simulation considers 1302 molecules/atoms in a cyclically replicated cuboid, of which 400 atoms constitute the CNTs. There are 41 ions each of sodium and chloride with an additional 820 water molecules. A Gaussian thermostat maintains constant temperature (Allen, 1987) and the molecules initially have a Gaussian velocity distribution corresponding to the system temperature, which is 300 K. The timestep for all the simulations is constant throughout and has a value of 1 fs.
The solution density determines the length of the solution compartment in the direction that is parallel to the axis of the CNTs. The 8.03% and 13.96% solutions have densities of 1054.42 kg/m$^3$ and 1097.9 kg/m$^3$, respectively. The other two dimensions are fixed at 2.75 nm in order to ensure that the CNTs are completely immersed in the solution. A fifth-order Gear predictor–corrector algorithm is used to numerically model translational motion and a fourth-order predictor–corrector algorithm for rotational motion using the quaternion method (Allen, 1987, Evans and Murad, 1977). The size independence of the simulations is verified by considering a larger domain that had double the volume of a smaller test domain. It consisted of 1700 water molecules, 85 ions each of sodium and chlorine, and 400 carbon atoms (that made up the CNTs). The nanotube size, fluid density, temperature and sodium chloride solution concentration

Figure 3.2: Schematic diagram of the simulated system.
were identical to the typical simulations in the smaller domain. The results of both simulations agreed closely and there was at most a difference in water intake of 9 molecules.

Established models for water, ions and carbon pores (Berendsen et al., 1981, Chandrasekhar et al., 1984, Turner et al., 2002) have been chosen to simulate the nanoscale system under consideration (described in Figure 3.2). Water was modeled using the simple point charge (SPC) model (Berendsen et al., 1981), ions with the so-called primitive intermolecular potential model (Chandrasekhar et al., 1984, Turner et al., 2002, Jorgensen et al., 1982) and CNTs using the parameters provided in Ref. (Turner et al., 2002). All site-site interactions in the present study were thus modeled using the LJ potential model with the Coulombic potential term, as described earlier in Eq. (2.1). The potential parameters $\sigma$ and $\varepsilon$, and charges $q$ were obtained from the literature. These models have been shown to closely represent experimental geometries, energies of ion–water complexes, and energies of solvation, etc. (Chandrasekhar et al., 1984). Lorentz-Berthelot mixing rules were used for cross interactions (Allen, 1987) and the reaction field method, with a cut-off radius of 9.5 Å, was used to model long range interactions (Watts, 1974, Tironi et al., 1995). It has been verified that the transport processes taking place in the simulations are insensitive to cut-off radii greater than the one used here. The parameters $\sigma_{ii}$ and $\varepsilon_{ii}$ used in the present study are given in Table 3.1. The cross interaction parameters $\sigma_{ij}$ and $\varepsilon_{ij}$ are obtained from Lorentz-Berthelot mixing rules, $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$, $\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}}$.  


<table>
<thead>
<tr>
<th>Molecule</th>
<th>Interacting sites</th>
<th>$\sigma$ (Å)</th>
<th>$\varepsilon$ (kJ/mole)</th>
<th>$q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H</td>
<td>3.17</td>
<td>0.65</td>
<td>-0.82</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0</td>
<td>0</td>
<td>+0.41</td>
</tr>
<tr>
<td>Ions</td>
<td>Na</td>
<td>1.9</td>
<td>6.7</td>
<td>+1</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>4.42</td>
<td>0.49</td>
<td>-1</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>3.4</td>
<td>4.94</td>
<td>+/- 0.25</td>
</tr>
</tbody>
</table>

**Table 3.1:** Values of parameters used in the simulations for preferential ion intake.

### 3.3. Results and Discussion

The various charge patterns on the CNTs induce dissimilar effects on water (Qiao and Aluru, 2005) and ion separation, and change their intake effectiveness. The first observation from the results is that the alternate charge distributions (using the lengthwise axial band and round circumferential ring patterns) almost entirely inhibit ion intake into the nanotubes while allowing for water transport. In contrast, the conventional electrodes promote ion separation and both water and preferential ion transport. For all cases, charged CNTs behave as reservoirs for the intake of water and/or ions.
The number of water molecules inside a CNT reaches a saturation limit, as shown in Figure 3.3. (There, the charge magnitude on each CNT electrode is 0.125 times the electronic charge, i.e., $2 \times 10^{-20}$ C, resulting in a surface charge density of 0.825 C/m$^2$.)

The number of water molecules inside a CNT reaches a saturation limit, as shown in Figure 3.3. (There, the charge magnitude on each CNT electrode is 0.125 times the electronic charge, i.e., $2 \times 10^{-20}$ C, resulting in a surface charge density of 0.825 C/m$^2$.)

It is evident from Figure 3.3 that the maximum number of water molecules inside a nanotube occurs when it is used as a conventional electrode. The minimum intake takes place when an axial band charge pattern is applied. An uncharged nanotube contains more water molecules at equilibrium than when the CNTs are charged with either
alternate axial band or circumferential ring patterns due to the polar behavior of water molecules that act as dipoles due to small charges on the H (positive) and O (negative) atoms. As a result, water is both attracted and repelled by charged electrodes, whether positive or negative, while an uncharged CNT behaves neutrally. An uncharged nanotube surface has a graphitic structure and is thus hydrophobic. When charged, water molecules are attracted to the nanotube wall due to Coulombic interaction that can thus be made hydrophilic as suggested by experimental results (Valentini et al., 2005). In the case of an electrode, the nanotube wall is homogenously charged. Hence, depending on the local charge, either a hydrogen or oxygen atom in water orients itself towards the wall (Qiao and Aluru, 2005, Valentini et al., 2005), which makes the nanotube surface less hydrophobic and more hydrophilic thereby increasing the water intake. When the carbon atoms are charged in the form of alternate bands or rings, the charge distribution does not assist the geometric structure of a water molecule. Consequently, partially positive hydrogen or partially negative oxygen atoms do not become oriented end-to-end efficiently, which decreases water intake.

The conventional electrodes have a larger intake of water molecules than uncharged CNTs, since the negative electrode and positive electrode, respectively, attract the sodium and chloride ions. As these ions move into the negative electrode and positive electrode CNTs, they drag the polar water molecules with them. Thus, two types of nanotube configurations are possible (which are differentiated by the change pattern), one for separating ions using conventional electrodes and another to separate water from a salt solution (or conversely enrich the ion concentration within a solution by removing water molecules).
Figure 3.4 shows results for conventional electrodes with surface charge densities of 0.825 C/m², 1.65 C/m² and 3.3 C/m². (In comparison, the surface charge density of a sodium ion is 0.353 C/m².) The number of water molecules inside a CNT increases with an increase in the surface charge density. The fractions of water molecules encapsulated inside the CNTs from the surrounding bath for the three cases are, respectively, 10.12%, 12.07%, and 12.68% (as compared to an 8.05% intake for an uncharged nanotube). For a 0.825 C/m² charge density, the encapsulated solution strength is 15.27%, which is more...
concentrated than the residual solution external to the nanotube. Further, as the electrode surface charge density increases to 1.65 C/m² and 3.3 C/m², this encapsulated solution strength also increases.

Due to its smaller size, the surface charge density of a sodium ion is about 5.4 times larger than of a chloride ion (0.065 C/m²). Sodium has a higher absolute hydration enthalpy of -406 kJ/mol than chlorine (-363 kJ/mol) because of this larger charge density. Both sodium and chloride ions become hydrated and associate with water molecules in the simulations. However, a sodium ion-water cluster is structurally more rigid (due to the higher Na⁺ surface charge density) than a corresponding chloride ion-water cluster so that the latter is the more flexible of the two. A sodium ion-water cluster has a size of ~10 Å (Murad and Lin, 2002) while a typical chloride ion-water cluster is ~13 Å. While the diameter of a simulated CNT is 13.75 Å, the available diameter for ion and water transport is smaller (~10 Å) once the dimensions of the carbon atoms on the two opposite sides of the circular cross section are accounted for. Thus, a hydrated chloride ion-water cluster that is more flexible has a better chance of entering a nanotube since it can squeeze into it more readily. The higher surface charge density of the sodium ion and the relatively greater flexibility of the chloride ion-water cluster are therefore two competing factors that determine the relative uptake of these ions by the CNT. This hypothesis is in agreement with the simulation results.

Figure 3.5(a) and (b) show that, for all the different charge patterns on the CNT, the number of chloride ions absorbed inside the nanotube is greater than or equal to the number of sodium ions absorbed for lower surface charge densities (uncharged or 0.825 C/m²). Thus, the relatively higher flexibility of the chloride ion-water cluster is the
dominant factor in case of lower surface charge density on the CNTs. The concentrations of sodium ions in mass percent in the negative CNT electrodes are 5.79%, 10.40% and 26.24%, respectively, for surface charge densities of 0.825 C/m², 1.65 C/m² and 3.3 C/m². For the same surface charge densities, the chloride anion concentrations in the CNTs are 10.60%, 12.21% and 18.50%, respectively. Clearly, as compared to sodium ions, the number of chloride ions is larger, for a surface charge density of 0.825 C/m² and lower when there are higher surface charge densities on the CNT electrodes. Thus, in case of electrodes with higher surface charge densities, such as 1.65 C/m² and 3.3 C/m², the larger surface charge density of the sodium ion is a dominating factor due to the presence of a relatively stronger electrostatic field due to the presence of the charge on the surface of the CNTs. Consequently, the number of sodium ions entrapped in the CNT is larger. These results show that a charged nanotube can be utilized to separate and encapsulate water and/or ions from a surrounding solution. Further, the ion adsorption can be modified quantitatively by varying the CNT surface charge density.

The numbers of sodium and chloride ions entering the CNTs for different charge distributions are shown in Figure 3.5(a) and (b), respectively. Figure 3.5(a) shows that the number of sodium cations encapsulated inside a CNT is highest when a conventional electrode is used. This is due to the electrostatic attraction force between the negatively charged nanotube wall and the sodium ions (Arista, 2001).
Figure 3.5: (a) Sodium and (b) chloride ion intake by the nanotubes for different charge distributions and for conditions that are used to obtain the results in Fig. 3.3.
In case of uncharged nanotubes, some sodium ions do enter the nanotube along with water molecules due to the attractive force between the negatively charged oxygen at the center of a water molecule and a positively charged sodium ion. In case of the alternate band or ring pattern charges on the nanotube, the entry of sodium ions is restricted. Chloride ions behave similarly, as shown in Figure 3.5(b).

The selective intake of the ions by the nanotubes for three different charge patterns is shown in Figure 3.5(a) and (b) for a CNT surface charge density of 0.825 C/m². With an alternate axial band pattern, at equilibrium only 2.44% each of sodium and chloride ions are found to enter the CNTs from the surrounding bath. With the alternate circumferential ring pattern no sodium ions and 2.44% chloride ions are encapsulated. The water intake for the two alternate patterns is 5.73% (band) and 6.83% (ring) of the initial surrounding solution. For the alternate bands, the encapsulated solution strength inside the nanotube is 6.9% as compared to the initial 13.96% NaCl solution outside it. The circumferential ring pattern is more effective at precluding ions. It completely disallows transport of chloride ions into the nanotubes and only a single sodium ion enters the nanotube, thus encapsulating a dilute 2.23% sodium ion solution in water.

When the external solution strength is lowered to 8.03% for a CNT surface charge density of 0.825 C/m², both the alternate band and ring charge patterns are more efficient at purifying water. In this case, there is an intake of only a single sodium ion and no chloride ions into the CNT for the axial band distribution, while there is no ion intake at all for the circumferential ring pattern.

Table 3.2 summarizes the results for various surface charge patterns. The results suggest that spatially alternating charge patterns placed on CNTs favor water intake but
significantly inhibit ion encapsulation. In order to verify whether these effects also occur if the charges alternate temporally, the surface charge density (0.825 C/m²) on a conventional electrode was alternated every 0.2 picoseconds, i.e. the negative electrode periodically became a positive electrode and vice versa. Then, the electrode acted solely as a water intake device (with a 61 water molecule intake) and no ions were encapsulated.

<table>
<thead>
<tr>
<th>Species</th>
<th>Ambient</th>
<th>Alternate band</th>
<th>Alternate ring</th>
<th>Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>820</td>
<td>47</td>
<td>56</td>
<td>83</td>
</tr>
<tr>
<td>Sodium</td>
<td>41</td>
<td>1</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Chlorine</td>
<td>41</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Solution</td>
<td>13.96</td>
<td>6.47</td>
<td>~3.4</td>
<td>~15.28</td>
</tr>
</tbody>
</table>

Table 3.2: Number of ions, water molecules, and encapsulated solution strength for various surface charge patterns. The surface charge density is 0.825 C/m².
Chapter 4: Hydrogen Storage in Carbon Nanotubes

4.1. Introduction

Carbon nanotube is considered a prospective material for hydrogen storage. However, there is a wide disparity in the hydrogen storage measurements for SWNTs (Liu et al., 1999, Zhou et al., 2004a, Hirscher et al., 2003, Dillon et al., 2000). Reports of high storage capacities (Dillon et al., 1997, Chambers et al., 1998) remain uncorroborated (Hirscher et al., 2003, Pinkerton et al., 2000).

As described earlier in Section 2.4, some experiments imply that storage in CNTs is possible at levels above the minimum volumetric storage prescribed by DOE at moderate temperatures and ambient pressure (Wang and Johnson, 1999b, Dillon et al., 2000) but other investigations have found that a useful amount of hydrogen can only be stored at cryogenic temperatures and/or very high pressures (Liu et al., 1999). It has been suggested that some measurements erroneously provide a higher adsorption rate than is realistically possible (Hirscher et al., 2003), since the CNT storage capacity at normal temperature and pressure is limited (Becher et al., 2003).

The intent of the research presented here is to resolve this conflicting information using a fundamental molecular approach based on MD simulations, which are used to evaluate hypothetically possibilities that could enhance hydrogen storage in CNTs through changes in the ambient conditions and structural or surface modifications. The latter include formulating a linear CNT ensemble of closed- or open-ended CNTs joined with metal or carbonaceous interconnects (Chen et al., 1999, Sen and Puri, 2004) (as shown in Figure 4.2), or providing surface charges to the CNTs.
4.2. Methodology

To validate the results obtained from LAMMPS hydrogen storage in (10,10) armchair SWNT (diameter 1.375 nm) has been simulated using MD at 10 K for pressure ranging between 10 atmospheres (1.01 MPa) to 75 atmospheres (7.6 MPa). The same system has been simulated with the well-established MD code of Professor Murad. Figure 4.1 shows the storage isotherm. It can be seen that storage of more than 4% can be achieved at an extremely low temperature and high pressure although in reality such low temperatures (cryogenic) cannot be generally implemented.

![Figure 4.1: Comparison of result from Prof. Murad's Code with that of LAMMPS.](image-url)
Figure 4.1 compares the results from Dr. Murad’s code (Murad et al., 2003) to that obtained from LAMMPS. The external conditions of temperature and pressure were the same. The dimensions of the nanotubes were the same. Reasonable agreement is seen at pressures lower than 50 atmospheres. This pressure range (1 -50 atm) has been used for the hydrogen storage simulation using LAMMPS.

Various simulation techniques have been used for the molecular modeling of nanoscale adsorption, such as MD (Dodziuk and Dolgonos, 2002), Monte Carlo (Guay et al., 2004) and density functional theory (Tarasov et al., 2003). These can all illuminate the physical mechanisms and intermolecular forces that promote hydrogen adsorption/storage in carbon nanopores (Wang and Johnson, 1999c, Rzepka et al., 1998, Darkrim and Levesque, 1998). The interaction between a carbonaceous material and hydrogen is usually represented in MD simulations through an empirical potential function (Wang and Johnson, 1999c, Tarasov et al., 2003). The results presented here are from simulations that are based on the massively parallel LAMMPS code in which these interactions are modeled using a LJ potential that considers Coulombic interactions, as described earlier in Eq. (2.1). The parameters $\sigma_{ij}$ and $\varepsilon_{ij}$, are obtained from the literature (Turner et al., 2002, Egorov et al., 2000, Mitchell et al., 2004) and are listed in Table 4.1 for various cases. The cross interaction parameters $\sigma_{ij}$ and $\varepsilon_{ij}$ are obtained from Lorentz-Berthelot mixing rules, $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$, $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$. A typical input file and a data file used for the simulations are included in Appendix A.
The simulation configuration is described in Figure 4.2. The cuboid 25.967 nm × 6.875 nm × 6.875 nm domain consists of two (10,10) single-walled armchair CNTs of 1.375 nm diameter, 1.122 nm length, and 2.49 Å pore size that are surrounded by hydrogen. The system temperature is varied between 25 K and 470 K and the pressure varied between 10 and 50 atmospheres (or 1.01 MPa-5.05 MPa). A hollow nanowafer consisting either of metal ions or carbon connects the interiors of the two CNTs but it is not chemically bonded to them.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Interacting sites</th>
<th>σ (Å)</th>
<th>ε (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>2.915</td>
<td>0.3158</td>
</tr>
<tr>
<td>Ions</td>
<td>Li</td>
<td>2.27</td>
<td>0.016</td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td>1.13</td>
<td>1608.0</td>
</tr>
<tr>
<td>Pd</td>
<td></td>
<td>2.45</td>
<td>33.08</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>C</td>
<td>3.40</td>
<td>0.2327</td>
</tr>
</tbody>
</table>

Table 4.1: Values of parameters used in the simulations for hydrogen storage.
When the nanowafer has metal ions, these are provided with alternate positive and negative charges that maintain overall charge neutrality. The carbon atoms in the CNTs are either uncharged, or carry positive (anode) or negative (cathode) charges. A circumferential pattern has been considered that consists of rings of alternate positive and negative charges that are arrayed along the circumference of the CNTs as described in Figure 4.4a. Periodic boundary conditions apply in all directions to eliminate wall effects so that the system is effectively infinite in all directions. The number of hydrogen

**Figure 4.2**: Schematic diagram of the simulated system. Interconnects made of Li-, Pd- and Ti-ions, and C atoms (purple) are used to join adjacent carbon nanotubes (green), surrounded by hydrogen molecules (blue).
molecules depends on the external pressure and temperature, which at 10 atm and 273 K is 330. These molecules initially form an fcc lattice that equilibrates through the simulations. A Gaussian thermostat maintains constant temperature (Darkrim and Levesque, 1998) and the molecules have an initial velocity distribution corresponding to the system temperature. A cutoff distance of $9\ \text{Å}$ is used for both LJ and Coulombic forces. Results obtained by implementing the Ewald sum in selected cases are compared with those obtained with long-range cut-offs and no appreciable changes are detected.

Based on the equilibrium configuration, the number (hence mass) of hydrogen molecules that are either stored inside the CNTs or physisorbed on their surfaces has been calculated. Each data point in the plots presented in the next section represents results obtained from a single run of the MD simulation. One of the objectives of this research is to investigate the enhancement of storage inside and on the surface of the CNTs due to spillover of hydrogen (Zacharia et al., 2005, Lueking and Yang, 2002) in presence of metal ions. Hence, physisorbed hydrogen on the surface of the metal interconnect is not considered.

4.3. Results and Discussion

Figure 4.3 presents results for hydrogen storage in open-ended CNTs at 273 K and pressures in the range from 1 to 55 atm. The CNTs are uncharged and connected to a hollow nanowafcr consisting of Li, Pd or Ti ions, or electrostatically inert C atoms. While the presence of Li ions is found to increase $\text{H}_2$ storage, in contrast with some earlier findings (Guay et al., 2004, Zacharia et al., 2005, Yoo et al., 2005) it is found that the heavier transition metals Ti and Pd do not enhance it. At 54.75 atm, Li ions augment storage by 12.33% (as compared to storage with a carbon interconnect). At that pressure,
a nanowafer containing Li ions also induces 57.48% and 49.11% more storage than the corresponding configurations containing Ti and Pd ions, respectively. The experimental finding that alkali metal ions have a positive influence on hydrogen storage in carbon nanostructures (Haluska et al., 2004) has been corroborated but it has been found that this enhancement is significant only at higher pressures (it is 1% by weight at 273 K). Surprisingly, however, it is found that a transition ion nanowafer interconnect placed between two CNTs diminishes H₂ storage.

Figure 4.4 presents the influence of electrostatic charges placed on CNT surfaces on hydrogen storage at 273 K when the nanotubes are joined by a Li ion interconnect or nanowafer.
Figure 4.4: (a) Variation of hydrogen storage with pressure at 273 K in the presence of Li ion interconnects for various charge patterns on the carbon nanotubes. The plot in the inset presents similar results at 100 K. (b): Schematic of the circumferential ring type charge distribution (Banerjee et al, 2007). The dark lines represent sites with negative charges, while lighter ones represent positive charges.
The details for CNT electrodes and circumferential ring-type alternating charges (Banerjee et al., 2007) is described in the previous chapter and schematically described in the Figure 4.4a. At lower pressures, CNT electrodes store more hydrogen (resulting in a 20.27% enhancement at 9.94 atm) but at higher pressures, uncharged CNTs are more effective. At all pressures, the alternating circumferential ring charge induces the lowest storage.

The hydrogen molecule is charge neutral but has a dipole moment in the presence of charged surfaces (Toffolo et al., 2005). Hence, at lower pressures this molecule orients itself according to the electrostatic field (that is created due to the presence of charges on the surface of the CNTs), thereby increasing storage. In contrast, at pressures exceeding 35 atm (i.e., at higher densities) the average hydrogen-hydrogen and hydrogen-CNT intermolecular distance decreases so that the repulsion due to the Coulombic potential becomes more significant than the electrostatic attraction. Thus, hydrogen molecules are no longer able to orient themselves as they do at lower pressures. Additionally, the adsorbate-adsorbate (i.e., H$_2$-H$_2$) repulsion dominates in the presence of a charged surface when a hydrogen monolayer is present on the CNT surface (Yun and Gyeong, 2005). Hence, CNT electrodes exhibit lower storage at higher pressures.

The effect of increasing pressure on hydrogen storage at 100 K in the presence of a Li ion nanowafar interconnect is presented in the inset of Figure 4.4. It shows that higher pressures promote storage for both uncharged CNTs and CNT electrodes. Consistent with the results for 273 K, storage at higher pressures (> 22 atm) is greater for uncharged nanotubes than for electrodes. At lower pressures, storage is higher for CNT electrodes, e.g., at 20.06 atm storage is 6.94% greater with electrodes as compared to
uncharged CNTs. These results indicate that storage in the presence of Li ions depends upon both the pressure and the charge on the CNT surfaces.

Figure 4.5 and Figure 4.6 present the effects of temperature and pressure on hydrogen storage for three isobars (at 1, 5 and 10 atm) and two isotherms (at 273K and 100K) for uncharged CNTs connected by a Li ion nanowafer. Lower system temperatures promote storage as previously reported (Han and Lee, 2004). At 100K, the storage is almost 8.5 times greater at a 10 atm pressure as compared to that at 1 atm.

The volumetric storage density $\rho$ is the storage per unit volume at a given temperature and pressure. A regression analysis to fit a curve through the data in Figure 4.5 and Figure 4.6 provides the relation

$$\rho_r \sim \left(\frac{p_r}{T_r}\right)^{0.8}$$

where $\rho_r = \frac{\rho}{\rho_0}$, $p_r = \frac{p}{p_0}$, and $T_r = \frac{T}{T_0}$,

(4.1)

which differs from the ideal gas law. This variation can be attributed to the van der Waals forces between the CNTs, metal ions and hydrogen molecules. In Eq. (4.1) $\rho_0$, $p_0$, and $T_0$ denote a reference density (at STP), pressure (1 atm) and temperature (273 K). In comparison with the ideal gas relation, the dependence of $\rho$ on the temperature in Eq. (4.1) is stronger than on the pressure. The slope of the isotherms $\left|\frac{\partial \rho_r}{\partial p_r}\right|_{T_r} = 0.8kT_r^{-1.2} p_r^{-0.2}$ varies as $\sim p_r^{-0.2}$ and, as seen in the inset in Figure 4.6, increases most rapidly in the range 0–40. When $p_r > 40$, the increase in slope tapers and becomes virtually linear, denoting diminishing returns for hydrogen storage with increasing pressure. The ideal value in this context for $p_r \approx 40$ (or $p = 40$ atm). The slope of the isobars $\left|\frac{\partial \rho_r}{\partial T_r}\right|_{p_r} / 1.2k p_r^{0.8}$ varies as
~\(T_r^{-2.2}\), and decreases rapidly for \(T_r > 0.6\) as demonstrated in the inset in Figure 4.6. This implies that storage increases most when \(T_r < 0.6\) (or \(T < 165\) K). This behavior can be utilized for the sequential adsorption (increasing \(p\), decreasing \(T\)) and desorption (increasing \(T\), decreasing \(p\)) of hydrogen. Decreasing the temperature however involves an additional energy input into the system, although it is one which could be harvested when the temperature is increased to desorb hydrogen.

![Graph of reduced volumetric storage vs. reduced temperature](image)

**Figure 4.5:** Hydrogen storage isobars for uncharged nanotubes in the presence of Li ion interconnects. The inset presents the slope of these isobars at various temperatures.

Here, \(f(T_r) = \left. \frac{\partial \rho_r}{\partial T_r} \right|_{p_r} \cdot 1.2kp_r^{0.8}\).
Figure 4.6 shows that CNTs store significantly more hydrogen than can be compressed in an equivalent volume. For instance, at 273 K and 10 atm, volumetric storage in CNTs connected by a Li-ion nanowafer is 183% greater than for simply compressed hydrogen. While the mass density of compressed hydrogen increases linearly with pressure in accord with the ideal gas relation, the corresponding storage in CNTs is nonlinear.

![Graph showing hydrogen storage isotherms for uncharged nanotubes in presence of Li ion interconnects.](image)

**Figure 4.6:** Hydrogen storage isotherms for uncharged nanotubes in presence of Li ion interconnects. The inset presents the slope of these isotherms at various pressures. Here,

\[
g(p_r) = \left. \frac{\partial \rho}{\partial p_r} \right|_{T_r} / 0.8kT_r^{-1.2}.
\]
A similar analysis is presented in Figure 4.7 and Figure 4.8 for uncharged CNTs connected by an uncharged C interconnect. A regression analysis suggests that

\[ \rho_r \sim \left( \frac{p_r}{T_r} \right)^{0.35}, \]

which again differs from the ideal gas relation. Moreover, the exponents on the reduced pressure and temperature are different from those for Li ion interconnects under otherwise identical conditions. This suggests that hydrogen storage in the presence of Li ion interconnects is more sensitive to variations in the pressure and temperature.

Figure 4.7: Hydrogen storage isobars for uncharged nanotubes in the presence of C interconnects. The inset presents the slope of these isobars at various temperatures. Here, \( h(T_r) = \left. \frac{\partial \rho_r}{\partial T_r} \right|_{p_r} / 1.1 k p_r^{0.35} \).
This is attributed to the higher physisorption binding energies in Li-doped CNTs as compared to pristine CNTs (Cabria et al., 2005).

Figure 4.7 and Figure 4.8 again show that hydrogen storage increases at higher pressures and lower temperatures. The correlation coefficients for the fitted curves in Figure 4.7 are 0.988, 0.995 and 0.9605 for the 1 atm, 5 atm and 10 atm isotherms respectively. The inset of Figure 4.7 shows the variation of the slopes of the isobars

\[
\left( \frac{\partial \rho_r}{\partial T_r} \right)_{p_r} = -1.1 k p_r^{0.35} T_r^{-2.1}
\]

with temperature. Here, a transition to a near linear regime occurs when \(T_r > 0.65\) (\(T < 180\ K\)).

**Figure 4.8:** Hydrogen storage isotherms for uncharged nanotubes in presence of C interconnects. The inset presents the slope of these isotherms at various pressures. Here,

\[
q(p_r) = \left. \frac{\partial \rho_r}{\partial p_r} \right|_{T_r} / 0.35 k T_r^{-1.1}.
\]
The dependence of storage on pressure with a C interconnect differs from one in which Li ions are present, as shown in Figure 4.8. Since the exponent on the pressure term is small (0.35), the slope of the isotherm \( \left( \frac{\partial \rho_r}{\partial p_r} \right) = 0.35 k T_r^{-1.1} p_r^{-0.65} \) is almost linear (inset of Figure 4.8) when \( p_r > 25 \) (or \( p > 25 \) atm). The chemical stability of Li-doped CNTs produces a wider pressure range over which H\(_2\) storage increases appreciably (Chen et al., 1999). Despite the qualitative similarities in storage when the two interconnects are used, the optimal storage conditions when C interconnect are employed are different from those containing Li ions.

Whether a CNT is open or closed also plays a role in storage. Figure 4.9 compares storage at two temperatures (100 K and 273 K) in CNT electrodes with either open or closed ends joined by a Li ion nanowafer interconnect. At 273K and \(~20\) atm, storage in open CNTs is 294\% higher than in the closed nanotubes, since in the former case the CNT interiors are also available for hydrogen physisorption through a capillary effect. The effective volume inside each CNT is 87\% of the volume of the layer of hydrogen molecules physisorbed on its exterior surface. However, at 273 K and 20 atm the storage inside CNTs accounts for about 75\% of the total storage. Thus, hydrogen molecules are more densely stored inside a CNT than outside it. (The behavior at 100 K is similar.) The dense storage inside CNTs as compared to their exteriors is due to the smaller short-range hydrogen-hydrogen repulsive force inside the nanotubes, as described by (Zheng et al., 2005).
In spite of the van der Waals forces between the hydrogen molecules and the carbon atoms of the CNTs, storage is limited by the repulsive forces between the hydrogen molecules. (Stan and Cole, 1998b) have demonstrated through theoretical calculations that there is a stronger adsorbate-adsorbate binding inside such nanotubes. This results in greater storage inside the CNTs.

**Figure 4.9:** Variation of hydrogen storage with pressure in open and closed-ended carbon nanotube electrodes in the presence of Li ion interconnects.
Chapter 5: Carbon Nanotube Growth Mode

5.1. Introduction

A carbon deposit can be created at elevated temperatures on catalytically active transition metal nanoparticles that are placed in a reducing environment with high gas-phase carbon activity (Sacco et al., 1984), (Kock et al., 1985). The deposited carbon diffuses into the catalyst nanoparticle, nucleates within it, and emerges in the form of CNTs or CNFs. The subsequent catalyzed growth of CNTs and CNFs occurs mainly through two modes. The base growth mode arises when the metal nanoparticle catalyzing the growing carbon nanostructure remains at the bottom of the nanotube. For this type of growth the adhesive forces between the substrate and the catalyst nanoparticle are typically too large for the particle to be lifted as the CNT/CNF grows. Alternately, the catalyst nanoparticle is lifted by the growing carbon nanostructure during tip growth, and remains at the tip of the CNT/CNF after its growth ceases.

The nature of the growth mode, whether tip or base, is important for various applications. For instance, the nucleation of metal particles on the end caps of CNTs can assist in the alignment of these nanostructures in the presence of external electric or magnetic fields, thus imparting directional properties to materials in which these are embedded (Park et al., 2008), (Camponeschi et al., 2007). Such functionalized tips can also be used to attract other molecules for various applications, e.g., for functionalization with protonated amines (–NH₃⁺Cl⁻) that add positive charges to CNTs, which allows binding to negatively charged RNA molecules (Krajcik et al., 2008). Continuum scale
CNT growth models that typically assume a certain growth mode (Zhang and Smith, 2005) can also benefit from these predictions.

Illustrations of the two growth modes are presented in Figure 5.1. The likely growth (tip or base) mode depends on the energy gain \( \Delta E_{np\rightarrow CNT} \) due to the addition of C-atoms from the carbon-metal catalyst solution to the graphene sheets forming the CNTs and CNFs. For tip growth to occur, the catalyst particle is lifted from a substrate only if the energy gain is sufficient to overcome the surface binding or interface energy between the nanoparticle and the substrate, i.e., \( \Delta E_{np\rightarrow CNT} \geq \gamma R_p^2 \), where \( \gamma \) and \( R_p \) respectively denote the surface energy per unit area and the diameter of the metal catalyst particle. Smaller energy gains lead to base growth. The prediction of the dominant growth mode for a specific condition requires that \( \Delta E_{np\rightarrow CNT} \) be determined using MD.

Figure 5.1: Schematic illustrating the growth modes of carbon nanotubes.
simulations. One can justify either growth mode on the predicted energy gain, an analysis that is found to be more robust than one based on characteristic time scale considerations.

The experimentally observed base growth mode by Wu et al. was facilitated by an Fe catalyst immersed in C₂H₄ with a ≈162.86 torr partial pressure and 1048 K temperature (Wu et al., 2008). The other gaseous species were H₂ (carrier gas) and Ar (inert). The experimental results of Ducati et al. revealed a predominance of vertically aligned CNTs grown through a tip-growth mode with Ni as catalyst and C₂H₂ as the carbon source gas at a temperature of 823 K and 1.5 torr partial pressure (Ducati et al., 2004). The simulations correspond to conditions for these two representative cases.

5.2. Methodology

The MD simulations are based on the massively parallel LAMMPS code. (Plimpton, 1995) The interaction between the carbon atoms in the metal and the nanotube are modeled using the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential

\[
E = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \left[ E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i} \sum_{j \neq i} \sum_{l \neq i} E_{ijkl}^{TORSION} \right].
\] (5.1)

The \(E^{REBO}\) term has the same functional form as the hydrocarbon REBO potential (Brenner et al., 2002). The \(E^{LJ}\) term adds longer-range interactions (2 Å < \(r < r_{cutoff}\)) using a form similar to the standard LJ potential. The \(E^{TORSION}\) term is an explicit four-body potential that describes various dihedral angle preferences in hydrocarbon configurations. The Ni-Ni and Fe-Fe interactions are modeled using the Embedded Atom Model (EAM) potential,
\[ E_i = F_a \left( \sum_{j \neq i} N_{ij} \rho_j (r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{ij} (r_{ij}), \quad (5.2) \]

where \( F \) denotes the embedding energy, which is a function of the atomic electron density \( \rho \), \( \phi \) a pair potential interaction, and \( \alpha \) and \( \beta \) the element types of atoms \( i \) and \( j \).

The multibody nature of the EAM potential is a result of the embedding energy term. Both summations in the formula are over all neighbors \( j \) of atom \( i \) within the cutoff distance \( r_{\text{cutoff}} \). The interactions between Ar-Ar, Ar-Ni/Fe, Ar-C and Ni-C are modeled using a LJ potential, as described earlier in Eq. (2.1). The LJ interaction parameters \( \sigma_{ij} \) and \( \varepsilon_{ij} \) are obtained from the literature (Nigra et al., 2004, Turner et al., 2002) and are listed in Table 5.1 for various cases.

<table>
<thead>
<tr>
<th>Interaction parameters</th>
<th>( \varepsilon ) (eV)</th>
<th>( \sigma ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Ar</td>
<td>0.0103</td>
<td>3.4</td>
</tr>
<tr>
<td>Ar-Ni</td>
<td>0.1426</td>
<td>3.57</td>
</tr>
<tr>
<td>Ar-Fe</td>
<td>0.0516</td>
<td>3.7</td>
</tr>
<tr>
<td>C-Ar</td>
<td>0.00497</td>
<td>3.4</td>
</tr>
<tr>
<td>C-Ni</td>
<td>0.0688</td>
<td>3.57</td>
</tr>
<tr>
<td>C-Fe</td>
<td>0.02495</td>
<td>3.7</td>
</tr>
</tbody>
</table>

**Table 5.1:** Lennard Jones interaction parameters for Fe, Ni, C and Ar.
The simulation configuration is schematically described in Figure 5.2. The 13.75 nm × 2.75 nm × 54.8 nm cuboid domain consists of a (10, 10) single-walled armchair CNT of 1.375 nm diameter, 2.74 nm length, and 2.49 Å pore size. The CNT, placed on top of a Ni or Fe nanoparticle with dissolved C atoms, is surrounded with an Ar ambient. Thus, the simulations model experimental conditions following carbon diffusion into the metal catalyst and its subsequent nucleation. The C-atom concentration in the metal is 6.67% for both cases. The system temperature is varied between 700K and 1100K, and the pressure is maintained at 760 torr (1 atm). Periodic conditions apply to the boundaries in order to eliminate wall effects so that the system is effectively infinite in all directions.

Figure 5.2: A two-dimensional orthographic view of the molecular dynamics simulation domain with the carbon nanotube (green), which is surrounded by ambient Ar (gray), growing on top of the metal catalyst particle (blue) that has dissolved carbon (red).
A typical simulation for a Fe nanoparticle consists of 6825 Fe atoms, 2748 C atoms, 44 Ar atoms and the CNT. A similar simulation for Ni consists of 8253 Ni atoms, 2275 C-atoms, 44 Ar atoms and the CNT. Initially, all molecules that are not part of the CNT form an fcc lattice that equilibrates through the simulations. A thermostat maintains constant temperature so that the molecules have an initial velocity distribution corresponding to the system temperature. A cutoff distance of 3 Å for the AIREBO and 6 Å for the LJ potential is used. Once the configuration equilibrates, the total energy of the carbon atoms that have attached to the CNT is calculated, since the difference between the initial and final energies of these atoms equal $\Delta E_{np\rightarrow CNT}$. A typical input file for LAMMPS and the data file specifying the initial configuration are provided in Appendix A.

5.3. Results and Discussion

The time evolution of the total system energy at 800K is presented in Figure 5.3. The system under consideration is the one with the Fe nanoparticle. The system energy reaches a minimum value and remains constant after 75 fs. The data is sampled between 8,500 fs and 18,500 fs, which is well beyond this equilibration time, to obtain the equilibrium energy values for the various cases. The initial energy of the carbon atoms dissolved in the catalyst particle is likewise sampled between 100 fs and 2,500 fs, and the corresponding average values are reported.
Figure 5.4 presents the temperature dependence of $\Delta E_{np\rightarrow CNT}$ for both Fe and Ni catalysts. In the case of Fe, the magnitude of the energy change decreases with an increase in temperature between 700 and 900K, but is thereafter constant at higher temperatures. The specific surface energy for Fe $\gamma = 0.17$ eV/Å$^2$ (Vitos et al., 1998) so that the surface interaction energy for a typical 10 nm Fe catalyst particle $\gamma R^2_p \approx 1700$ eV. For temperatures between 700-1100K, $\Delta E_{np\rightarrow CNT} < 600$ eV, Since $\Delta E_{np\rightarrow CNT} < \gamma R^2_p$, this indicates a base growth mode. There is a weak temperature dependence of the energy change in the case of Ni and $\Delta E_{np\rightarrow CNT} > 125$ eV over the entire temperature range. For Ni, $\gamma = 0.125$ eV/Å$^2$, i.e., for a typical 3 nm Ni catalyst particle, $\gamma R^2_p \approx 113$ eV, which is
smaller in value than $\Delta E_{np\rightarrow CNT}$. Hence, the energy change due to bond formation is large enough to induce tip growth. Table 5.2 provides representative energy values for a simulation at 700K. It demonstrates that while $\Delta E_{np\rightarrow CNT} > \gamma R_p^2$ for Ni, the converse is true for Fe catalyst.

**Figure 5.4:** Variation of the energy change with respect to temperature for Ni and Fe.
### Table 5.2: A chart showing representative energy values for a temperature of 700 K.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\Delta E$ (eV)</th>
<th>$\gamma$ (eV/A$^2$)</th>
<th>$\gamma R^2_p$ (eV)</th>
<th>Growth Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>598.46</td>
<td>0.170</td>
<td>1700.0</td>
<td>Base</td>
</tr>
<tr>
<td>Ni</td>
<td>207.43</td>
<td>0.125</td>
<td>112.5</td>
<td>Tip</td>
</tr>
</tbody>
</table>
Chapter 6: Nanoscale Heat Transfer at Solid-Fluid Interfaces

6.1. Introduction

Recent interest in nanoscale cooling has lead to increasing research on thermal transport at the nanoscale. This in turn provides key inputs into the mechanisms involved in heat conduction. As particle size is decreased the surface area to volume ratio increases, thereby making the heat transfer at the solid-fluid (nanoparticle-fluid) interface more important (Eastman et al., 2004). The physics of interfacial heat transfer, especially for simple solid-fluid interfaces, is thus an important area of concern for researchers, and the complete understanding of the temperature jump at interfaces due to thermal resistance (Kapitza resistance) for different combination of materials and at different temperatures is an area waiting to be explored. The temporal variation of Kapitza length is also an interesting problem to be aware of.

One of the exciting areas of research that is drawing huge attention is multi-scale analysis and the attempt to construct the necessary bridge between the same physical phenomena occurring at two different scales; heat transfer at interfaces in the continuum level and at the nanoscale need to shake hands (Xiao and Belytschko, 2004), and the ability to suitably incorporate the boundary conditions for such problems remains a hurdle to be overcome (Xu and Li, 2007).

In the nanoscale, heat transfer at solid-fluid interfaces involves a thermal slip that characterizes the resistance at the interface. It is very important to measure the slip values in order to fully understand this phenomenon. It is extremely difficult to design experiments at the nanoscale. Hence, molecular simulations are used to model heat
transfer at the nanoscale. The results from these simulations can provide useful information. The literature in this field is scanty and only characterizes the resistance at steady state. However, keeping in mind the inherent transient nature of the phenomena, it is important to characterize the time evolution of the temperature profile at the interface. This Chapter presents results related to heat transfer at solid-fluid interfaces. Nanoscale thermal transport has been simulated at a solid-fluid interface by placing cooler liquid-vapor Ar mixtures adjacent to warmer Fe walls. The equilibration of the system towards a uniform overall temperature is investigated using NEMD simulations from which the heat flux is also determined explicitly.

6.2. Methodology

Atomistic simulations, such as those based on MD which is a fundamental technique rooted in the principles of classical mechanics (Poulakakos et al., 2003), can help explain interfacial effects (Murad and Puri, 2007b, Murad and Puri, 2007a) during nanoscale thermal transport (Heyes and March, 1996). Examples of such MD studies (Xue et al., 2003) include investigations of heat transfer between simple solid-fluid interfaces (Wang et al., 2007, Murad and Puri, 2008) and of the bonding between liquid and solid atoms (Xue et al., 2004). These simulations have been limited to steady state investigations of nanoscale thermal transport across interfaces (Chaudhuri et al., 2007b, Khare et al., 2006, Wang et al., 2007, Maruyama, 1999, Chaudhuri et al., 2007a). Another limitation is that the heat flux is not typically determined explicitly in these simulations, but rather \textit{a posteriori} using the Fourier heat conduction law (Maruyama, 1999). In order to address these two issues, a NEMD approach is employed to investigate
the transient thermal transport across a nanoscale interface in which the values of $\dot{q}$ are explicitly determined.

<table>
<thead>
<tr>
<th>Interaction Parameters</th>
<th>$\epsilon$ (eV)</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Ar</td>
<td>0.0103</td>
<td>3.4</td>
</tr>
<tr>
<td>Ar-Fe</td>
<td>0.0516</td>
<td>3.7</td>
</tr>
</tbody>
</table>

**Table 6.1:** Lennard Jones interaction parameters for Fe and Ar.

The Fe-Ar and Ar-Ar interactions have been modeled using the LJ potential as described in Eq. (2.1). The values of the LJ interaction parameters $\sigma_{ij}$ and $\epsilon_{ij}$ are listed in Table 6.1 (Lummen and Kraska, 2004).

Molecular dynamics simulations have also been able to reproduce the temperature discontinuities across solid-fluid interfaces by modeling the solid atoms with a harmonic potential function (Ohara and Suzuki, 2000, Maruyama, 1999). While this is a better representation than the LJ model which tethers solid atoms to their respective equilibrium positions, we employ the even more realistic EAM potential which incorporates many-atom interactions (Mendelev et al., 2003, Daw et al., 1993) that are otherwise neglected in a pair-potential scheme (Johnson, 1989). It has been demonstrated in the literature that EAM potentials are very accurate in modeling properties involving metal (such as Fe) surfaces (Daw and Baskes, 1984). The EAM model has been explained in details in Eq. (5.2) in Chapter 5. The relevant parameters for the EAM model are obtained from the literature (Mendelev et al., 2003).

The simulation configuration is described in Figure 6.1. The 3 nm × 3 nm × 58 nm cuboid contains two 3 nm × 3 nm × 1 nm Fe blocks that restrain a liquid-vapor Ar
mixture (with an initial 33% vapor volume fraction) between them. These solid Fe blocks extend from 14-15 nm and 43-44 nm along the x-direction. The Ar liquid-vapor mixture consists of 3402 atoms that initially form an fcc lattice which equilibrates through the simulations. Periodic boundary conditions apply in all directions to eliminate wall effects so that the system is essentially infinite. The cut-off distance for the LJ interactions between both the metal-fluid and the fluid-fluid atoms is 10 Å, or roughly 3 atomic diameters. Linear momentum is conserved throughout the entire simulation. In the simulation, the linear momentum is rescaled to the initial value every 10 timesteps.

**Figure 6.1:** A 3-dimensional view of the molecular dynamics simulation domain in which Ar (cyan) fills a space of 28 nm between two 1 nm thick blocks of solid Fe. Fluid atoms on both sides of the walls indicate periodicity. A close-up orthographic view shows the observed Ar–atom layering at the solid-fluid interface.
The system is initialized at a temperature of 100K. During the first 300 picoseconds (ps), a velocity-rescaling temperature control is applied for all atoms. This ensures an initial equilibrium state for which the entire system is at uniform temperature. Subsequently, for the next 700 ps, the temperature of the solid atoms is controlled while fluid atoms are allowed to behave freely and equilibrate. At 1000 ps, the Fe blocks are provided with a step increase to a higher temperature (by increasing the kinetic energy of the atoms), which is thereafter maintained with constant velocity rescaling for the remainder of the simulation. The simulations are based on the massively parallel LAMMPS code (Steve, 1995, Plimpton, 1993) and are advanced through successive 0.1 fs time steps. A typical input file for LAMMPS and the data file specifying the initial configuration are provided in Appendix A.

6.3. Results and Discussion

Figure 6.2 presents the averaged number density distribution of the Fe and Ar atoms when both Fe blocks are maintained at 120 K. The figure shows that the fluid atoms adjacent to the solid walls migrate closer towards them due to the Fe-Ar intermolecular interactions to form discrete interfacial layers in agreement with previous investigations (Murad and Puri, 2008, Xue et al., 2004, Xue et al., 2003, Ohara and Suzuki, 2000, Maruyama, 1999).

The consequent higher Ar atom density at the interface causes a local increase in the interfacial pressure so that the packed fluid layers are quasi solid-like. Since the fluid is initially a liquid-vapor mixture, this inhomogeneous density distribution occurs due to phase segregation. Ar atoms that are further removed from the walls do not experience the wall-vapor intermolecular attraction and thus remain homogeneously distributed. In
contrast, the migration of the fluid Ar atoms towards the walls to form the quasi-crystalline layers from proximal vapor-containing regions that are a few atomic diameters removed from the interfaces creates local vacancies. Essentially, Ar atoms closest to the walls exhibit a denser and more packed quasi-crystalline behavior, those further removed from the interfaces behave as fluid, with vacancies separating these two regions.

**Figure 6.2:** The temperature (dotted line) and density (solid line) distributions across the x-wise direction after the system nears its steady state. The solid Fe walls are located between 14-15 nm and 43-44 nm. The fluid domain is divided into several 4 Å thick slabs along the x-direction for the purpose of spatial characterization, and the density and temperature distributions within them are sampled at uniform time intervals.
Figure 6.2 also presents the average temperature (based on a local equilibrium approximation) of each 4 Å thick slab in the domain. The temperature of each slab is calculated from the velocities of the atoms in the lab using the equi-partition assumption, i.e. \( T = \frac{m v_{\text{rms}}^2}{k_b} \). Here, \( m \) is the mass of the Ar atom, \( k_b \) is the Boltzmann constant, and \( v_{\text{rms}} \) is the root mean square velocity of the atoms in the slab. The Ar atom layers adjacent to each wall have a temperature nearly equal to that of the solid. This is followed by a sharp temperature drop in the fluid extending from approximately four molecular layers away from each wall (Murad and Puri, 2008, Freund, 2005). The Ar atoms in the four molecule thick interfacial regions show little tendency towards significant translational motion since, being attracted to the Fe atoms, they are held relatively immobile. These quasi-crystalline Ar layers have a higher effective thermal conductivity than atoms in the corresponding fluid phase (Freund, 2005). In contrast to fluid behavior at the continuum scale, a significant temperature discontinuity occurs in the vacancies that follow the interfacial Ar atom layers, since energy transfer through these sparsely populated regions is hindered.

Figure 6.3 presents the temporal evolution of the characteristic fluid temperature, which is averaged over all slabs, as the simulation proceeds from its initial thermodynamic nonequilibrium state to a steady state. An analogous average temperature can also be obtained from the analytical solution of the continuum Fourier heat equation

\[
\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial X^2},
\]

where \( \theta \) denotes a dimensionless temperature \((T(x,t)-T_w)/(T_f-T_w)\), \( \tau \) a dimensionless time \( \alpha t/L^2 \) (\( \alpha = 1.12 \times 10^{-7} \) m\(^2\)/s denotes the bulk Ar thermal diffusivity at the initial system temperature of 100 K, \( L \) the length of the domain in x-direction), \( X \) a dimensionless length \( x/L \). The boundary conditions correspond to fixed
wall temperatures of $T_w$. The solution follows the expression $\theta(X, \tau) = \sum_{n=1}^{\infty} \frac{2}{n \pi} (1 - \cos(n \pi)) \sin(n \pi X) e^{-n^2 \pi^2 \tau}$. The geometry along with initial and boundary conditions for this solution are shown in Figure 6.4.

**Figure 6.3:** Temporal evolution of the fluid temperature obtained explicitly from the simulations and empirically from an analytical solution to Fourier’s law of heat conduction (assuming homogenous and constant properties).
The response of the MD simulations to thermodynamic non-equilibrium differs from that of the analytical continuum solution. The simulation provides evidence of nonequilibrium effects even after 5000 ps whereas the analytical solution reaches steady state by 3000 ps. Moreover, Figure 6.3 also shows that the bulk temperature temporarily stabilizes after $\approx 2500$ ps. This occurs due to a temporary departure from the quasi-crystalline interfacial layering of Ar atoms as the system equilibrates. This reordering impedes heat transfer for $\approx 200$-400 ps so that the fluid temperature remains virtually constant. Thermal transport resumes following the molecular rearrangement, but at a slower rate. In contrast, the continuum analysis assumes homogenous system properties for all times, although the simulation results presented in Figure 6.2 contain evidence to the contrary. The source for the discrepancy between the continuum analytical solution and the MD simulations is attributed to the heterogeneous system characteristics due to the interfacial layering of Ar atoms. This provides emphasis for the assertion that for values of the heat flux to be accurate, these must be determined explicitly from nanoscale simulations rather than implicitly using continuum relations.

This issue is investigated further. It is typical to determine the heat flux across nanoscale interfacial layers using a bulk thermal conductivity, i.e., by essentially making

**Figure 6.4:** Schematic of the system solved using Fourier’s Equation.
a quasi-continuum approximation. Instead the net energy flux $\dot{q}_{sf}$ is calculated from the solid molecules $s$ to the fluid molecules $l$, i.e., $\dot{q}_{sf} = (\dot{E}_{fs} - \dot{E}_{sf}) / 2$, where $\dot{E}_{fs}$ and $\dot{E}_{sf}$ denote the energy fluxes from a fluid to solid and solid to fluid molecules, respectively (Ohara, 1999). Here, the intermolecular energy transfer $\dot{E}_{fs}$ is computed from the scalar product of the relative force $\vec{f}_{fs}$ and the velocity $\vec{v}_{fs}$. With this approach, the total thermal energy transferred from a high temperature wall to the low temperature fluid adjacent to it is $\dot{q} = \sum_s \sum_l \dot{q}_{sf}$, which can also be used to determine $R_k$ (Eq. 2.2) explicitly from the simulation. Further, assuming for a specified mass $m = N_{Ar}M_{Ar}$ that the approximate energy flux $\dot{q}_{ap} = (mc/A)(dT_{av}/dt)$, where $N_{Ar}$ and $M_{Ar}$ denote the number of Ar atoms in the system and their molecular mass, $A$ the interfacial area through which heat flows, $c$ the constant volume specific heat of Ar, and $T_{av}$ the average fluid temperature, an expression is obtained for the approximate Kapitza resistance $R_{k,ap} = (A/mc)\Delta T/(dT_{av}/dt)$. Figure 6.5 presents the temporal variation of $R_k$ and $R_{k,ap}$ when the temporal values of $\Delta T$ are identical. Again, there is almost an order of magnitude difference in the values of these two interfacial resistances. The thermal resistance values obtained from the molecular simulations are consistently higher in magnitude when compared to the values obtained using the continuum approximation. The presence of the temperature jump at the interface restricts the thermal transport causing an increase of the thermal resistance at the interface. Such discontinuity in the temperature profile is neglected in the corresponding continuum model and hence it provides a lower value of the thermal resistance. Their behaviors are similar although their rates of increases are different. The interfacial thermal resistance increases over time.
The influence of wall temperature on the thermal resistance is examined next. For each simulated case, the value of $\Delta T$ is averaged over the period from 2000-4000 ps, and the heat flux $\dot{q}_{av} = (1/2000) \sum_{i=2000ps}^{4000ps} \dot{q}_i$ to determine the average interfacial resistance $R_{k,av}$, which is presented in Figure 6.6 with respect to increasing wall temperature $T_w$.

**Figure 6.5:** Temporal evolution of the interfacial thermal resistances for wall temperature of 125 K (based on heat fluxes calculated using a first principles and a quasi-continuum approach). The interfacial temperature drop is calculated as a time average over 100 ps.
Figure 6.6: Change in the Kapitza resistance (based on heat fluxes calculated using a first principles approach) with respect to varying wall temperature. The fluxes and temperature drops are averaged over 2000-4000 ps.

As \( T_w \) increases, the pressure within the fluid and hence on the quasi-crystalline layers rises. Consequently, the interfacial molecular layers become more closely packed and the local intermolecular interactions are enhanced. Consequently, thermal transport through these layers also increases, leading to a decrease in the interfacial thermal resistance according to the relation \( R_{k,av} \propto T_w^{-4.8} \).
Chapter 7: Conclusions

7.1. Ion Adsorption in Carbon Nanotubes

The results presented in this dissertation demonstrate that when spatially or temporally alternate charge patterns are applied to CNTs, ion intake into them is minimal. While ion flow through charged nanochannels has been previously investigated (Qiao and Aluru, 2005, Kang et al., 2004), the role of alternating spatial or temporal charge patterns to accomplish the controlled intake of either ions or polar solvents such as water has not been described. The interesting consequence of the results presented here is that nanotubes can be used for the preferential intake of only water molecules. They can thus be used as water-purifying devices (or conversely as ion concentrators for the solution external to CNTs). These CNTs can also be used as water or ion encapsulation devices, depending on the applied charge pattern.

7.2. Hydrogen Storage in Carbon Nanotubes

The results indicate that while alkali metal nanowaf er interconnects increase storage, albeit by a relatively small amount, the inclusion of unassociated transition metal ions such as Pd and Ti do not. Carbon nanotube electrodes store only slightly higher amounts of hydrogen in the presence of Li ions at pressures lower than 25 atm. Results from the simulations also show that nanotubes with open ends store significantly more hydrogen than those with closed ends. In general, the simulated data imply that CNTs do not store more than 1% hydrogen by weight at 273 K. Thus a high pressure and low temperature operating condition is necessary for reasonable storage. The dependence of storage on the ambient temperature and pressure is influenced by the interconnect
material. In presence of an interconnect made of Li ions, increasing the ambient pressure above 40 atm and decreasing the temperature below 165 K leads to the largest incremental enhancement in hydrogen storage. However, in presence of a C atom interconnect pressures greater than 25 atm and temperatures less than 180 K produce similar results.

7.3. Carbon Nanotube Growth Mode

The growth modes of CNTs using atomistic MD simulations are investigated and the results are qualitatively validated against experimental evidence. The MD results suggest different growth modes for Ni and Fe catalysts. While the magnitude of energy gain for a wide range of temperatures typically encountered in catalyzed CNT growth is smaller than the surface interaction energy for Fe, the converse is true for Ni. The MD simulation results suggest that Ni catalyst nanoparticles are conducive for tip growth while Fe nanoparticles promote base growth. Use of Ni produces a local minimum energy at approximately 900K while for Fe-catalyzed growth, the energy gain decreases to a constant minimum value at temperatures exceeding 900K. A phenomenological time scale is insufficient to definitively characterize the nature of the growth mode. Thus, it is imperative to quantify the energy gain due to the addition of carbon atoms to a CNT based on more fundamental considerations such as MD simulations.

7.4. Nanoscale Heat Transfer at Solid-Fluid Interfaces

It is concluded that unsteady nanoscale thermal transport differs from that at the continuum scale. It takes longer for a nanoscale system to respond to an imposed temperature difference (applied through velocity rescaling) than predicted by an analytical continuum solution. The steady state temperature distribution between the
quasi-crystalline fluid interfacial layers adjacent to a solid wall and the rarified fluid–side vacancy-containing region following these layers exhibits a discontinuity due to phase segregation in the fluid. As the average temperature difference between the warmer interface and cooler fluid equilibrates over time, the heat flux also decreases. Overall, the interfacial thermal resistance decreases with increasing wall temperatures as $R_{k,av} \propto T_w^{-4.8}$. 
BIBLIOGRAPHY


Stevens, R.J., Zhigilei, L.V. & Norris, P.M. (2007). Effects of temperature and disorder on thermal boundary conductance at solid-solid interfaces: Nonequilibrium


APPENDIX A

Typical LAMMPS input file to compute hydrogen storage:

# 3-d LJ hydrogen storage

dimension 3
boundary p p p
atom_style full
neighbor 0.5 bin
neigh_modify delay 3
read_data INPUT_LMP_570.dat

#kspace_style ewald 1.0e-2
bond_style harmonic
bond_coeff 1 1201.1 0.254

# LJ potentials
pair_style lj/cut/coul/cut 3.0
pair_coeff 1 1 1.0 1.0
pair_coeff 2 2 0.737 1.166
pair_coeff 1 2 0.858 1.083
pair_coeff 3 3 0.0493 0.7787
pair_coeff 1 3 0.222 0.88935
pair_coeff 2 3 0.1906 0.97235

# Define groups

group cnt type 2
group hyd type 1
group li type 3

# Initial velocities

temperature mobile hyd full
velocity hyd create 0.26316 482748 temp mobile
fix 1 all nve
fix 2 hyd temp/rescale 100 0.26316 0.26316 0.02 1.0
fix_modify 2 temp mobile
# Static nanotube and metal

velocity cnt set 0.0 0.0 0.0 units box
fix 3 cnt setforce 0.0 0.0 0.0
fix 4 cnt aveforce 0.0 0.0 0.0
velocity li set 0.0 0.0 0.0 units box
fix 5 li setforce 0.0 0.0 0.0
fix 6 li aveforce 0.0 0.0 0.0

# Run

timestep 0.0003
thermo 10000
thermo_style custom step atoms temp pe ke eng evdwl
thermo_modify temp mobile
thermo_modify lost ignore
dump 1 all custom 100000 dump.position.* type mol x y z
dump 2 all xyz 100000 dump.xyz.*
run 1000000
Typical LAMMPS data file to specify initial configuration for the computation of hydrogen storage:

# Lammps input file for carbon nanotube

2088   atoms
22   bonds
0   angles
0   dihedrals
0   impropers

3   atom types
1   bond types

0.0 89.083   xlo xhi
0.0 23.585   ylo yhi
0.0 23.585   zlo zhi

Masses

1   1.0
2  12.0
3  12.0

Atoms

1     1  1  1.0   9.969015121   9.969015121   9.969015121
2     1  1 -1.0  10.223014832   9.969015121   9.969015121

………………………………………………………………

43    22  1  1.0  79.752120972  19.938030243  19.938030243
44    22  1 -1.0  80.006118774  19.938030243  19.938030243
45    23  2  0.0  20.960548401  11.546074867   9.446883202
46    23  2  0.0  20.960548401  11.063755989   9.549403191

………………………………………………………………

2043    23  2  0.0  68.124099731  13.179007530   9.884426117
2044    23  2  0.0  68.124099731  12.283014297   9.485504150

………………………………………………………………

2087    66  3  0.0  42.500000000  12.500000000  20.000000000
2088    67  3  0.0  45.000000000  10.000000000  20.000000000

Bonds

1     1   1  2
2     1   3  4
21 1 41 42
22 1 43 44
Typical LAMMPS input file to predict growth of carbon nanotubes:

```
# 3-d Carbon Nanotube Growth
dimension        3
boundary         p p p
units           metal
atom_style       atomic
newton           on
read_data        INPUT_LMP_13.5.dat

# Hybrid Potentials

pair_style       hybrid lj/cut 6.0 eam/fs airebo 3.0
pair_coeff       ** airebo CH.airebo NULL C C NULL
pair_coeff       ** eam/fs Fe_mm.eam.fs Fe NULL NULL NULL
#pair_coeff      3 3 lj/cut 0.0024  3.4
pair_coeff       1 2 lj/cut 0.02495 3.7
pair_coeff       1 3 lj/cut 0.02495 3.7
pair_coeff       4 4 lj/cut 0.0103  3.4
pair_coeff       1 4 lj/cut 0.0516  3.7
pair_coeff       2 4 lj/cut 0.00497 3.4
pair_coeff       3 4 lj/cut 0.00497 3.4

# define groups

group            fe type 1
group            cnt type 2
group            c type 3
group            ar type 4

# initial velocities

compute          mobile_ar ar temp
compute          mobile_fe fe temp
compute          mobile_c c temp
velocity         c create 950.0 483800 temp mobile_c
velocity         fe create 950.0 483800 temp mobile_fe
velocity         ar create 950.0 483800 temp mobile_ar
fix              1 all nve
fix              5 fe temp/rescale 100 950.0 950.0 1.0 1.0
fix              6 ar temp/rescale 100 950.0 950.0 1.0 1.0
fix              7 c temp/rescale 100 950.0 950.0 1.0 1.0
#fix_modify       2 temp mobile
```
# static nanotube and metal

fix 20 cnt recenter INIT INIT INIT units box

# Run

compute en all pe/atom
timestep 0.000005

thermo 1000
thermo_style custom step atoms temp pe ke etotal evdwl
#thermo_modify temp mobile
thermo_modify lost ignore
dump 1 all custom 1000 dump.position.* type tag x y z c_en
dump 2 all xyz 10000 dump.xyz.*
rung 100000

unfix 20
fix 30 cnt recenter INIT INIT INIT units box

undump 1
undump 2
dump 3 all custom 10000 dump.position.* type tag x y z c_en
dump 4 all xyz 10000 dump.xyz.*
timestep 0.00002
run 200000

unfix 30
run 1700000
Typical LAMMPS data file to specify initial configuration for prediction of growth of carbon nanotubes:

# Lammps input file for carbon nanotube growth

9604 atoms
    0 bonds
    0 angles
    0 dihedrals
    0 impropers

4 atom types
    0 bond types

0.0 137.5 xlo xhi
0.0 27.5 ylo yhi
0.0 548.0 zlo zhi

Masses

1 55.847
2 12.0
3 12.0
4 39.94

Atoms

1 1 5.415496826 1.805165529 246.599990845
2 1 3.610331059 1.805165529 248.405166626

9603 2 62.796142578 17.188240051 233.135681152
9604 2 62.211509705 15.875138283 233.135681152
Typical LAMMPS input file for nanoscale thermal transport:

# 2-d LJ flow simulation

dimension 3
boundary p p p
units metal

atom_style atomic

# create geometry

lattice fcc 6.692
region box block 0 30 0 30 0 580 units box
create_box 2 box

mass 1 39.94
mass 2 55.85

# potentials

pair_style hybrid eam/fs lj/cut 10.0
pair_coeff 1 1 lj/cut 0.0103 3.4
pair_coeff * * eam/fs Fe_mm.eam.fs NULL Fe
pair_coeff 1 2 lj/cut 0.0516 3.7

# define groups

region 81 block INF INF INF INF 150 154 units box
create_atoms 1 region 81 units box
group liquid1 region 81

region 82 block INF INF INF INF 154 158 units box
create_atoms 1 region 82 units box
group liquid2 region 82

region 83 block INF INF INF INF 158 162 units box
create_atoms 1 region 83 units box
group liquid3 region 83

region 84 block INF INF INF INF 162 166 units box
create_atoms 1 region 84 units box
group liquid4 region 84

region 85 block INF INF INF INF 166 170 units box
create_atoms 1 region 85 units box
  group liquid5 region 85
region 86 block INF INF INF INF 170 210 units box
create_atoms 1 region 86 units box
  group liquid6 region 86
region 87 block INF INF INF INF 210 250 units box
create_atoms 1 region 87 units box
  group liquid7 region 87
region 88 block INF INF INF INF 250 290 units box
create_atoms 1 region 88 units box
  group liquid8 region 88
region 89 block INF INF INF INF 290 330 units box
create_atoms 1 region 89 units box
  group liquid9 region 89
region 90 block INF INF INF INF 330 370 units box
create_atoms 1 region 90 units box
  group liquid10 region 90
region 91 block INF INF INF INF 370 410 units box
create_atoms 1 region 91 units box
  group liquid11 region 91
region 92 block INF INF INF INF 410 414 units box
create_atoms 1 region 92 units box
  group liquid12 region 92
region 93 block INF INF INF INF 414 418 units box
create_atoms 1 region 93 units box
  group liquid13 region 93
region 94 block INF INF INF INF 418 422 units box
create_atoms 1 region 94 units box
  group liquid14 region 94
region 95 block INF INF INF INF 422 426 units box
create_atoms 1 region 95 units box
  group liquid15 region 95
region 96 block INF INF INF INF 426 430 units box
create_atoms 1 region 96 units box
  group liquid16 region 96
region 97 block INF INF INF INF 140 units box
create_atoms 1 region 97 units box
group liquid17 region 97

region 98 block INF INF INF INF 440 580 units box
create_atoms 1 region 98 units box
group liquid18 region 98

lattice     bcc 2.87

region 1 block INF INF INF INF 140 150 units box
create_atoms 2 region 1 units box
group lower region 1

region 2 block INF INF INF INF 430 440 units box
create_atoms 2 region 2 units box
group upper region 2

group boundary union lower upper

group flowsides union liquid17 liquid18


group flow subtract all boundary

group flow2 subtract flow flowsides

### compute temperatures

compute temp_1 flow temp/region 81
compute temp_2 flow temp/region 82
compute temp_3 flow temp/region 83
compute temp_4 flow temp/region 84
compute temp_5 flow temp/region 85
compute temp_6 flow temp/region 86
compute temp_7 flow temp/region 87
compute temp_8 flow temp/region 88
compute temp_9 flow temp/region 89
compute temp_10 flow temp/region 90
compute temp_11 flow temp/region 91
compute temp_12 flow temp/region 92
compute temp_13 flow temp/region 93
compute temp_14 flow temp/region 94
compute temp_15 flow temp/region 95
compute temp_16 flow temp/region 96
compute temp_lower lower temp
compute temp_upper upper temp
compute temp_flow flow temp
compute energy1 lower group/group flow
compute energy2 upper group/group flow
compute energy1a lower group/group flow2
compute energy2a upper group/group flow2

# initial velocities

velocity      flow create 100.0 581275 units box

fix           111 all nve

fix           1 liquid1 temp/rescale 10 100.0 100.0 0.001 1.0
fix           2 liquid2 temp/rescale 10 100.0 100.0 0.001 1.0
fix           3 liquid3 temp/rescale 10 100.0 100.0 0.001 1.0
fix           4 liquid4 temp/rescale 10 100.0 100.0 0.001 1.0
fix           5 liquid5 temp/rescale 10 100.0 100.0 0.001 1.0
fix           6 liquid6 temp/rescale 10 100.0 100.0 0.001 1.0
fix           7 liquid7 temp/rescale 10 100.0 100.0 0.001 1.0
fix           8 liquid8 temp/rescale 10 100.0 100.0 0.001 1.0
fix           9 liquid9 temp/rescale 10 100.0 100.0 0.001 1.0
fix          10 liquid10 temp/rescale 10 100.0 100.0 0.001 1.0
fix          11 liquid11 temp/rescale 10 100.0 100.0 0.001 1.0
fix          12 liquid12 temp/rescale 10 100.0 100.0 0.001 1.0
fix          13 liquid13 temp/rescale 10 100.0 100.0 0.001 1.0
fix          14 liquid14 temp/rescale 10 100.0 100.0 0.001 1.0
fix          15 liquid15 temp/rescale 10 100.0 100.0 0.001 1.0
fix          16 liquid16 temp/rescale 10 100.0 100.0 0.001 1.0
fix          17 liquid17 temp/rescale 10 100.0 100.0 0.001 1.0
fix          18 liquid18 temp/rescale 10 100.0 100.0 0.001 1.0

velocity      lower create 100.0 281375 units box
velocity      upper create 100.0 281375 units box

fix           221 lower temp/rescale 100 100.0 100.0 0.001 1.0
fix           222 upper temp/rescale 100 100.0 100.0 0.001 1.0

fix           20 lower momentum 10 linear 1 1 1
fix           21 upper momentum 10 linear 1 1 1
fix           22 flow momentum 10 linear 1 1 1

fix           91 flow ave/time 10 10000 100000 c_temp_1 c_temp_2 c_temp_3 c_temp_4 c_temp_5 c_temp_6 c_temp_7 c_temp_8 file heat_fluid1.out
fix           92 flow ave/time 10 10000 100000 c_temp_9 c_temp_10 c_temp_11 c_temp_12 c_temp_13 c_temp_14 c_temp_15 c_temp_16 file heat_fluid2.out
fix           94 upper ave/time 5 10000 1000005 c_temp_upper file heat_upper.out
fix 95 lower ave/time 5 10000 100005 c_temp_lower file heat_lower.out
fix 96 all ave/time 100 1000 100000 c_energy1 c_energy1a c_energy1[1] c_energy1[2] c_energy1[3] c_energy2a c_energy2 file force1.out

# Run

  timestep 0.001
  thermo 1000
  thermo_modify lost ignore temp temp_flow

dump 1 all custom 100000 dump.kapitza.* type tag x y z vx vy vz
run 300000

unfix 1
unfix 2
unfix 3
unfix 4
unfix 5
unfix 6
unfix 7
unfix 8
unfix 9
unfix 10
unfix 11
unfix 12
unfix 13
unfix 14
unfix 15
unfix 16
unfix 17
unfix 18

restart 1000000 therm.restart
run 700000

unfix 221
unfix 222
fix 221 lower temp/rescale 100 125 125 0.001 1.0
fix 222 upper temp/rescale 100 125 125 0.001 1.0

run 7000000