Nanomechanics of carbon nanotubes creep, inter-tubular friction, and their interactions with graphene oxide

Yang, Tianyi

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**NANOMECHANICS OF CARBON NANOTUBES CREEP, INTER-
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GRAPHENE OXIDE**

YANT TIANYI

School of Chemical & Biomedical Engineering

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A thesis submitted to the Nanyang Technological University
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Doctor of Philosophy

2012

Essentially, all models are wrong, but some are useful.

George E.P. Box

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Nanomechanics of Carbon Nanotubes Creep, Inter-tubular Friction, and their Interactions with Graphene Oxide

by

YANG Tianyi

LIAO Kin, Supervisor

Abstract

Carbon nanotubes (CNTs) are of great interest for load-bearing applications because of their excellent mechanical properties. While much effort has been made in the last decade in order to address problems that obscure the applications of CNTs with their remarkable properties fully exploited from both experimental and theoretical perspectives, some fundamental issues regarding the nanomechanical behavior of individual CNTs at noncritical stress, the interaction between CNTs in their assembled forms and, along with the development of a method for effectively dispersing CNTs in aqueous and polymer media with their intrinsic properties retained are far from being settled.

In this study, we first focus on probing the fracture mechanisms of CNTs creep using classical molecular dynamics (MD) and nudged elastic band (NEB) methods. The long-timescale microstructural evolution of CNTs at relatively low external stress is modeled by dividing the continuous process into a series of successive discrete transitions between metastable states. Our results indicate that there exist bifurcation states of the failure mechanism in armchair CNT: brittle-type fracture dominates the fracture if external stress exceeds 42.2 GPa for a (8, 8) CNT; alternatively, plastic deformation caused by the nucleation and diffusion of a specific

type of defects, 5|7 dislocations, takes place, leads to the necking of the CNT before eventual fracture.

Since the time-dependent behavior in CNT is only meaningfully characterized in engineering applications by deformation rate, and the relevant quantities that require sampling over a time dimension too large for atomistic simulation to reach, we adopt the concept from kinetic fracture theory. That is, the results from MD simulations are incorporated into a refined empirical kinetic function, which provides each metastable state along the structural evolution route with a time unit and a deformation unit, such that, the time-strain curves are obtained for characterizing the time-dependent behavior of CNTs creep. The curves are subsequently fitted into Maxwell model. The viscoelastic parameters obtained can serve as the benchmark for the engineering design of applying CNTs as load-bearing materials. The simulation results are also compared to experimental data from creep tests of a bundle of CNTs. We find that the creep behavior of CNT bundle is due to the combined effect of the inter-tubular frictional motion and brittle fracture of zigzag and other low chiral angle CNTs.

In order to determine the inter-tubular friction energy between CNTs, we have developed a straightforward calculation scheme, from which the normalized linear frictional stress within a bundle of CNTs was calculated. The average value obtained is 0.22 Nm^{-1} , which is comparable to the interlayer cohesive energy within graphite. The result is further verified by molecular mechanics simulations of single or a bundle of CNTs pulled out from an array of closely packed CNTs. This numerical value offers an important design parameter for mechanical applications of CNTs in their assembled forms.

The high frictional stress obtained implies the existence of strong adhesion between CNTs, which makes it very difficult to effectively disperse CNTs in water or polymer matrices. In the last part of this work, the nature of the interactions between CNT and graphene oxide (GO) and the role of GO as a dispersing agent for CNT dispersion have been systematically studied using MD methods. Strong affinity

between CNT and GO has been probed; the flat GO structure is driven into a scroll-like structure, wrapping around CNT with hydrophilic surface of GO exposed to water. The CNT-GO hybrid can be well dispersed in water. Calculation of the CNT-GO binding free energy via thermodynamic integration suggests that the self-assembly process is thermodynamically favorable in aqueous solution, and the strong adhesion primarily results from the π - π stacking. Moreover, the insights from simulations were implemented in experiments. Through adding GO and CNTs together into poly(vinyl alcohol) (PVA), a novel ternary composite were prepared. It is confirmed that dispersion of CNTs in water and PVA matrix can be significantly improved by adding GO. Besides, a synergistic effect arises from the combination of CNT and GO. The CNT-GO/PVA composite exhibits superior mechanical performances in comparison with PVA enhanced by CNT or GO alone.

Chapter 1 Introduction

1.1 Background

In his famous and visionary lecture given in 1959, ‘There’s Plenty of Room at the Bottom’, Richard P. Feynman, a Nobel laureate in Physics (1965), described the possibility of direct manipulation of individual molecules to fabricate new kinds of materials with novel and fascinating properties at very small length scale [1].

‘I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle... It might tell us much of great interest about the strange phenomena that occur in complex situations... It would have an enormous number of technical applications... What I want to talk about is the problem of manipulating and controlling things on a small scale... In the great future – we can arrange the atoms the way we want; the very atoms, all the way down! What would happen if we could arrange the atoms one by one the way we want them... They would be very interesting to investigate theoretically... I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do... At the atomic level, we have new kinds of forces and new kinds of possibilities, new kinds of effects...’

What Professor Feynman was referring to, half a century ago, is generally known as *Nanotechnology* nowadays, which involves developing, manipulating, and characterizing structures at the scale of 100 nanometers or smaller in at least one dimension [2], where novel phenomena and properties in many aspects (chemical, physical, biological, etc.) could be exploited. As substantial efforts have been made in the last two decades and promising results have been obtained, we might witness a big breakthrough in *Nanotechnology* this century. It has the potential to create many new products and advanced materials with a wide range of applications, such as chemical catalyst, drug delivery, nanoelectromechanical systems (NEMS), and

super strong and multi-functional materials. With the advance of *Nanotechnology*, the design of brand new materials with tailored properties through rearranging their structures at atomic or molecular level could be possible.

Why dose the idea of *Nanotechnology* loom so large and become so popular among scientists? In spite of the fact that it can provide us with so many applications with great features, *Nanotechnology* also holds the *Holy Grail* for physicists to understand and validate many fundamental physical theorems and conjectures. Graphene, for instance, a structure consists of an isolated single layer of carbon atoms packed in a honeycomb crystal lattice, is an ideal candidate to study one of the most striking phenomena in condensed-matter physics, *Quantum Hall* effect, which needs electrons to be confined within a two-dimensional structure [3-5]. And carbon nanotubes with their intrinsic uniformity and the extraordinary strength of sp^2 - σ carbon-carbon bond, offer a great intact, at least in principle, macromolecular model to study the materials fracture mechanisms, and to determine the extreme resistance of materials to mechanical stress at atomic level [6]. The fabrication and manipulation of these novel nanomaterials make all these studies possible, and the refined physical science in its turn is being used to boost the progress of *Nanotechnology*. It provides accurate atomic simulation methods (Classical, Statistical, Quantum Mechanical) to model, design, and predict the properties of condensed-matter systems.

One of the most prominent milestones in the progress of *Nanotechnology* is the re-discovery (spotted via transmission electron microcopy) of aforementioned Carbon Nanotubes (CNTs) in 1991 by Iijima at NEC laboratory [7]. Owing to their unique symmetric, cylindrical structure and the known features of their hybridized covalent bond, CNTs have many remarkable properties. For instance, they are excellent thermal conductors along their longitudinal axis, but good insulators laterally; they are the strongest and stiffest materials yet discovered with tensile strength twenty times higher than that of high strength steel; and metallic carbon nanotubes have a 1000 times larger electrical conductivity than that of copper [8].

Promising applications of CNTs are widely ranging from high strength composites reinforcement in materials science, novel transistors in electronics, supersensitive sensors in chemistry, hydrogen storage in new energy to drug delivery in medicine. Jamieson even once suggested that *Nanotechnology*, mainly fueled by the outstanding properties of CNTs, may have a greater impact on the advance of technology than the silicon revolution [9].

While the extraordinary physical properties of CNTs may offer a wide variety of anticipated applications [10-13], in the present work, we focus on revealing the nanomechanical behavior of CNTs, and tackling the fundamental problems that are concerned with using carbon nanotubes as load-bearing components for mechanical applications. The high stiffness and strength make CNTs ideal candidates as polymer composite reinforcing fillers or structural materials in NEMS. Computational simulations predict that the Young's modulus of CNTs is on the order of 1 TPa [14], which is later confirmed by experimental work [15, 16], making nanotubes probably the ultimate high-stiffness reinforcing materials. Moreover, the recoverable elastic strains of the CNTs can be as large as 5%, which may lead to one order of magnitude increase in tensile strength when compared with conventional composites. Besides, the extremely high strength/stiffness to mass ratios suggest the possibility of substantial weight savings for weight critical applications, such as the fabrication of airplane or spacecraft materials. In addition to the remarkable mechanical properties, CNTs have also shown exceptional thermal and electrical related properties, implying the systems may be designed to possess multifunctional specifications. Comparing with neat polymers, some results suggest that CNT-reinforced polymers exhibit large increase in the glass transition temperature [12], which extends the working temperature range of the polymer in practical applications.

Despite all these potential advantages, several critical issues must be addressed before the benefits of using CNTs as load-bearing components can be fully exploited. Such issues include:

- *A thorough understanding on the nanomechanical behavior and fracture mechanisms of CNTs.* It has been more than one decade now since the scientists started the investigation of the mechanical properties of CNTs. However, there are only a handful of experimental results available regarding the direct measurement of strength or elastic modulus of CNTs, due to the limitations of the current experimental techniques when manipulating nanomaterials. However, in the theoretical investigations, although enormous simulation work has been performed, current research mainly focuses on fracture under critical conditions, at high stresses, large strains. However, in practical applications, CNTs will most likely be loaded at much lower strains but for a prolonged time, yet no systematic study has been carried out.
- *The effect of the interaction between CNTs.* In order to reduce the surface energy, CNTs tend to appear in the form of densely packed bundles or ropes. Due to their nanoscale sizes, CNTs possess very high surface-to-volume ratio, which leaves CNTs with large surface area, such that the interaction between CNTs that closely contact with each other has important impacts on the materials performances when the CNTs are subjected to external load.
- *Dispersion of CNTs in the polymer matrices.* Since CNTs are likely to aggregate together to form bundles and other forms of assemblies, which unfortunately, compromises the mechanical performances due to intertubular sliding, the pursuit of the effective dispersion of CNTs in polymer media is necessary and fundamental for the fabrication of CNT-reinforced polymers with optimal, and more importantly, uniformly distributed mechanical properties.

Among these issues, the study of the mechanical properties of CNT is the foundation. Only after gaining a better understanding on the mechanical behavior and underlying mechanisms of these nanometer-sized tubes can we exploit them

with more confidence in structural applications. However, in practical applications, CNTs are most likely to appear in assembled forms, which makes the study of the interactions between them becomes important. The numerical value obtained can serve as an important design parameter for mechanical application of CNT arrays, ropes, etc. Besides, knowing how strong the CNTs interact with each other can help us to find a way to overcome this interaction in order that CNTs can be effectively dispersed in solutions. Thus, CNT-reinforced composite can reach its utmost mechanical properties with CNTs being uniformly distributed in the matrix.

On one hand, as nanomaterials, individual CNTs are not convenient and easy to observe, manipulate, and characterize, for they are too small and the testing instruments that are capable of measuring nanoscale materials are usually expensive and limited by the operational conditions. On the other hand, the length and time scales of CNTs and their physical phenomena have approached to a point where computer simulation and theoretical modeling can directly address the problems with high accuracy. Modeling methods, such as atomic simulation, provide an accurate, economic, and systematic way to understand the fundamental properties of materials. Atomic simulations have been playing a very important role in designing nanoscale devices, and in making theoretical predictions about the behavior of these systems. In addition, unlike the traditional computational methods, such as finite element analysis, the results obtained from these theoretical computations contains explicit atomic details, which can serve as complementary information to shed light on the experimental results of nanomaterials. Besides, with the ever-increasing power of modern high performance computing systems, the calculation results from atomic simulations can be more accurate and predictive for large-scale molecular systems.

1.2 Overall objectives

We report herein results of efforts in the long journey of pursuing the ultimate solutions of some critical issues that obscure the utilizations of CNTs as mechanical

applications with its extraordinary mechanical properties. Particularly, we focus on the understanding of the nanomechanical behavior of CNTs with explicit atomic rearrangement information at intramolecular level, the study of the interactions at the interface between carbon nanotubes in their assembly forms at molecular level, and the development of novel and more effective CNTs dispersion techniques that can effectively disperse CNTs into matrix solutions without compromising their inherent mechanical properties. The flow chart showing the objectives of this thesis is given in Figure 1.1.

Figure 1.1 The overview of the structure of this thesis.

1.3 Novelty and significance of research

Recent experimental studies demonstrate that, in comparison with traditional polymer composites, substantial improvement in the mechanical and thermo-mechanical behavior can be achieved through adding CNTs of different forms into polymer matrices [17-24]. The new class of CNT-reinforced composites will find immediate engineering application in many areas, like personal armor, sports good,

aerospace structural materials, and as functional materials, etc., especially in the weight and temperature critical environments. Moreover, apart from the above applications, CNTs are widely used as structural components in NEMS devices, which are designed to serve as novel electromechanical rigs, or lab-on-a-chip biosensors [25-30].

However, in order to design the CNTs-based application from an engineering point of view, first of all, a thorough understanding of CNTs fracture mechanisms is highly needed, which can be used as an engineering baseline in the design of such systems. In practice, the CNT-based composites or NEMS are expected to be used as load-bearing materials that can serve for a prolonged period of time, so the time-dependent behavior of CNTs at low strains should be studied with high priority, which however, is an extremely challenging task from both experimental and theoretical perspectives, since the sizes of CNTs are too small for the traditional mechanical testers and the timescale of this slow dynamical process is beyond the capability that atomic simulations can reach. Second, the interaction between CNTs in bundle state is critical for their mechanical behavior, but a quantitative expression for this intermolecular interaction remains unknown. Third, the poor dispersion of CNTs in polymer matrices is always being regarded as the *Achilles' Heel* of CNTs-based composites that limits their mechanical performances, and remains an open questions for a long time [31-33]. In this project, systemic computational and experimental studies have been carried out in order to seek the solutions of these problems, so that we can use the model and methods developed to design and produce CNT-based applications with confidence, which will allow CNTs and their composites to replace conventional materials in a broad spectrum of applications.

1.4 Specific aims

In order to address the aforementioned problems, four specific aims have been developed in this work: probing the atomic rearrangement mechanisms of CNTs

under non-critical conditions; determination of time-dependent behavior of CNTs at constant stress; estimation of friction energy within CNTs bundle; revealing the interactions between CNTs and Graphene Oxide (GO), a versatile material that has been long discovered yet only received attention very recently [34], and its application in effectively dispersing CNTs. These aims are briefly discussed herein:

- *To probe the atomic rearrangement mechanism of CNTs under non-critical conditions.* The competition between crack/defects initiation and structural evolution routes of CNTs under low tensile stress and strain have been extensively investigated through quantitative analysis of the activation energies calculated from molecular simulations of individual CNTs with different defects propagation schemes. Widely known failure modes of CNTs, including bond dissociation, Stone Wales dislocations, and dislocation climb, have been studied and compared.
- *To determine the time-dependent behavior of CNTs.* Knowing the crack propagation route of individual CNTs under relatively low tensile stress, the time-dependent behavior of CNTs at constant stress has been studied via incorporating results from classical molecular dynamics simulations into models based on transition state theory, in order that phenomena or behavior far beyond the timescale of molecular simulation can be evaluated.
- *To estimate the friction effect within CNT bundles.* Upon development of a straightforward empirical mathematical model based on results from tensile test of CNT bundles, normalized frictional energy between carbon nanotubes in their assembly form have been determined. This result is further verified through molecular mechanics simulations of single nanotubes or a bundle of nanotubes pulled out from a nanotube bundles.
- *To reveal the interactions between CNTs and Graphene Oxide (GO) and its*

application in CNTs dispersion in aqueous and polymer media. Molecular dynamics simulations have been carried out to determine the hybrid structures formed via the interaction between CNTs and GO. The size effect from both the CNT and GO perspective has been studied. The thermodynamic nature of CNT-GO interactions in water solution has been explored in detail. The simulation results have been subsequently tested in experimental studies. Novel CNT-GO/Poly(vinyl alcohol) tertiary composites have been developed. Tensile tests have been carried out and the results are compared with those only mixed with CNT.

1.5 Significant findings

The main results and findings of this thesis are briefly introduced below:

- The fracture mechanisms of CNTs of different chirality at relatively low external stresses have been determined using classical molecular dynamics and nudged elastic band methods. We find that there exist bifurcation states of the failure mechanism in armchair CNT. Brittle fracture dominates the failure process if the external stress exceeds 42.2 GPa for a (8, 8) CNT. Alternatively, plastic deformation takes place, which leads to the necking of the CNT before eventual failure.
- The time-strain curves of CNTs at constant external stresses have been obtained to characterize the time-dependent behavior of CNTs creep through incorporating simulation results into a refined empirical kinetic theory function. The results are compared to experimental data from creep tests of a bundle of CNTs. We find that the creep behavior of CNT bundle is due to the combined effect of the inter-tubular frictional motion and brittle fracture of zigzag and other low chiral angle CNTs.

- We have developed a straightforward calculation scheme to calculate the inter-tubular friction energy between CNTs. We find that the average value of linear frictional stress within a bundle of CNTs is about 0.22 Nm^{-1} . The result has been further verified by molecular mechanics simulations.
- Strong affinity between CNT and GO has been probed using simulation methods. The GO has been driven into a scroll-like structure, wrapping around CNT. The hybrid with hydrophilic surface exposed to water can be well dispersed. Calculation of the binding free energy suggests that the self-assembly process is thermodynamically favorable in water, and the strong adhesion is caused by π - π stacking. Moreover, through adding GO and CNTs into poly(vinyl alcohol) (PVA), a novel ternary composite were developed. We find that the dispersion of CNTs in water and PVA matrix can be significantly improved by adding GO. The CNT-GO/PVA composite exhibits superior mechanical performances.

1.6 This thesis

A deeper understanding of CNTs, CNT-CNT and CNT-GO interactions lies at the frontier of fundamental research in nanotechnology and will enable fascinating applications of these nanomaterials or hybrid assemblies. In order to meet this need, this thesis presents the collective results of a series of molecular simulations to investigate the energetics, structural, and dynamic properties of CNTs, CNT-CNT, and CNT-GO systems, and provides data from experiments to support and compare with simulation results.

In the next chapter, the background about CNTs and current theoretical and experimental studies on their nanomechanical behavior and failure mechanisms are reviewed. It also contains the properties and applications of CNT assemblies and the important role of the tube-tube interactions in their properties with an overview of the known methods for CNTs dispersion.

In chapter 3, we turn our attention to the intramolecular level studies of the failure mechanisms of CNTs with explicit atomic information under noncritical stress. That is, how the CNT structures evolve under an external stress that is substantially lower than the tensile strength. First, an outline of the computational methods employed, such as molecular dynamics, minimization techniques, and nudged elastic band method, are presented. The variation of activation energy at each step of defects or crack propagation has been examined. And the most kinetically favored CNT structural evolution route has been determined. Subsequently, the results of time-dependent behavior of CNTs under a variety of constant stresses has been presented in chapter 4. In this chapter, viscoelastic models for the creep of CNTs have been developed, and the results are compared with experimental data of CNT bundles.

Chapter 5 includes an experimental and theoretical study of frictional energy within CNT bundles. Using a straightforward empirical method, the normalized tube-tube linear frictional shear stress has been deduced from experiments. The results are verified via molecular mechanics simulations.

In chapter 6, results from extensive molecular dynamics simulations are presented to elucidate the interactions between CNT and GO molecules and to reveal the role of this interaction in the application of using GO as a novel dispersing agent for CNTs dispersion. Promising experimental results from tensile tests suggest the existence of a synergistic effect through adding CNT and GO together into the polymer matrix. Finally, in chapter 7, the last chapter, we conclude this work with a summary of the key findings and offer an outlook for future work.

Chapter 2 Literature Review

In this chapter, the background and the literature contains the previous studies within the scope of this thesis are reviewed. Starting with a brief introduction of the structure of CNTs, which is naturally followed by a comprehensive discussion on the nanomechanical properties and mechanical behavior of CNTs, we next present recent experimental and theoretical results from the studies of various CNTs assembly systems, where inter-tubular friction between nanotubes is playing an important part in their properties exhibited. Later, the dispersion methods that have been developed for CNTs over the last decade are introduced and discussed. All this background information serves as foundations for the following chapters, in which we will present computation methods, modeling strategies, and experimental techniques that have been adopted and developed to address the problems that are introduced in the last chapter.

2.1 Structure of carbon nanotubes

Taking one single molecular sheet of graphite (graphene), which is a simple planar structure that contains carbon atoms hold together in a honeycomb lattice, and rolling it up, one would end up with a cylindrical structure, consisting of a shell of carbon atoms. It would have properties similar to those of graphene, but would be less flexible and hard to stretch. This kind of tubular-shape carbonaceous material is usually micrometers long, with diameter ranging from less than 1 nm to 20 nm [35, 36]. These cylinders could be assembled in form of bundles, or nested with increasing diameters to obtain multi-walled carbon nanotubes (MWCNTs), as shown in Figure 2.1.

Figure 2.1 Schematics of a SWCNT, a MWCNT and a bundle of SWCNTs assembled together.

As the fourth form that has been discovered of carbon (the first three are graphite, diamond, and fullerenes), it was first fabricated in form of MWCNTs in 1991 [7]. After that, much effort has been made to fabricate, characterize, modify, and manipulate such tubular carbon structures. Although there are some debates on when the first batch of MWCNTs have been made [37], it is perfectly clear that the fabrication of single-walled carbon nanotubes (SWCNTs) was first reported in 1993 [38, 39].

It is well known that a carbon atom has six electrons in sum. Two of them fill the 1s orbital and the other four occupy the 2s and 2p orbitals; these valence orbitals can hybridize to form sp , sp^2 or sp^3 orbitals, depending on the bonding structures of the carbon polymorphs. In CNTs, the 2s orbital is mixed with two of the three available 2p orbitals, giving rise to three sp^2 orbitals, which could form three in-plane sp^2 - σ bonds (sp^2 - σ bond possess a binding energy of 420 kcal/mol, which is 60 kcal/mol higher than that of sp^3 - σ bonds in diamond), as shown in Figure 2.2. However, the curvature of the nanotube wall makes the σ bonds slightly out of plane

and the π orbital delocalized compared with those in graphene. This unique bonding structure results in the hexagonal lattice of CNTs and gives them their extraordinary properties.

Figure 2.2 Basic hexagonal bonding structure in CNTs. The out-of-plane π bond is responsible for the interlayer connection in graphite.

A SWCNT is illustrated as a graphene sheet rolled into a hollow cylindrical shape in Figure 2.3; the diameter is usually ranging from 0.4 to 10 nm. It could be considered as a one-dimensional structure because of the large length to diameter ratio, which can be as high as 100,000.

Figure 2.3 Rolling a graphene sheet into a SWCNT.

SWCNTs can be classified as either achiral (symmorphic) or chiral (non-symmorphic) depending on the chirality symmetry. If the mirror image of a carbon nanotube parallel to the tube axis has an identical shape as the original one, it is called an achiral tube. There are only two cases where this happens: armchair and zigzag. For the rest of the cases, the mirror image cannot be the same as the original one. The symmetry of CNTs is defined by the chiral vector, C_h , which is given as:

$$C_h = na_1 + ma_2 \equiv (n, m) \quad (2.1)$$

where a_1 and a_2 are the real space unit vectors, n and m are integers that satisfy the condition of $0 \leq m \leq n$, since the hexagonal symmetry of CNTs lattice structure. As shown in Figure 2.4, in an unrolled graphene sheet, the vector $\overline{OA}$ and $\overline{OB}$ describe the chiral vector C_h and the translational vector T , respectively. An armchair CNT occurs when $n = m$, and a zigzag one forms when $m = 0$. All other (n, m) vectors represent chiral nanotubes. The bottom part of Figure 2.4 illustrates examples of three types of CNTs.

The diameter of a (n, m) carbon nanotube is expressed as

$$d_t = \frac{|C_h|}{\pi} = \frac{a\sqrt{n^2 + m^2 + nm}}{\pi} \quad (2.2)$$

where a is the lattice constant of the graphene lattice, $a = 1.42 \times \sqrt{3} = 2.46 \text{ \AA}$. From figure 2.4 the $\sin(\theta)$ and $\cos(\theta)$ can be derived, where θ is the chiral angle between C_h and a_1

$$\sin \theta = \frac{\sqrt{3}m}{2\sqrt{n^2 + nm + m^2}}, \quad \cos \theta = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}} \quad (2.3)$$

Figure 2.4 Top: Graphene unit cell and chiral vector, the CNT is formed by connecting OB and AB'. Bottom: Examples of SWCNTs with different chirality: A. armchair (8, 8) B. zigzag (14, 0), and C. chiral (10, 6).

Therefore, the chiral angle θ can be defined within the range of $0 \leq \theta \leq 30^\circ$ as

$$\theta = \tan^{-1} \left(\frac{\sqrt{3}m}{2n+m} \right) \quad (2.4)$$

For instance, zigzag and armchair nanotubes correspond to $\theta = 0^\circ$ and $\theta = 30^\circ$, respectively. Another vector used in the characterization of CNTs is the

translational vector T , which is normal to the chiral vector C_h and parallel to the nanotube axis, defining the length of the nanotube. It can be expressed in terms of a_1 and a_2 as:

$$T = t_1 a_1 + t_2 a_2 \equiv (t_1, t_2) \quad (2.5)$$

in which t_1 and t_2 are integers given by

$$t_1 = \frac{n+2m}{d_R}, \quad t_2 = \frac{2n+m}{d_R} \quad (2.6)$$

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

where d is the greatest common divisor of n and m . And the length of the translational vector can be simplified to

$$T = \frac{\sqrt{3}C_h}{d_R}$$

Therefore, the number of hexagons per unit cell can be determined using the area of the unit cell, $|T \times C_h|$ divides by the area of the hexagon $|a_1 \times a_2|$:

$$N = \frac{|C_h \times T|}{|a_1 \times a_2|} = \frac{2(n^2 + nm + m^2)}{d_R} \quad (2.7)$$

Considering there are two carbon atoms per hexagonal lattice, each unit cell of the nanotube contains $2N$ carbon atoms.

2.2 Mechanical properties of carbon nanotubes

Despite the fact that CNTs possess extraordinary electrical, thermal, and optical properties, research on their mechanical properties is an area that has attracted intensive studies in the last decade. In this section, we review the computational

and theoretical work that has been carried out on this topic and present the representative experimental evidence that, in spite of the complications that come along when manipulating such small objects, has been reported concerning the measurements of mechanical behaviors of CNTs.

2.2.1 Elastic modulus of carbon nanotubes

Much of the initial work studying the mechanical behavior of CNTs has been using computational methods either derived from classic mechanical theories or based on quantum mechanics approaches. Only later were several experimental methods developed to directly determine the elastic modulus of CNTs.

Theoretical prediction of the mechanical properties of CNTs was first explored by Robertson *et al.* in 1992 [40]. Using both empirical potential and *ab initio* methods, they examined the strain energy and the elastic behavior of CNTs with radii smaller than 0.9 nm and obtained an elastic modulus of 1.06 TPa, which can be dependent on the tube radius with a relationship of $1/r^2$. Later, assuming the wall thickness of CNTs to be 0.066 nm, which is obtained from the calculation of flexural rigidity and in plane stiffness [14], Yakobson *et al.* found that the elastic modulus of CNTs to be about 5.5 TPa from the calculations based on the first generation Brenner potential [41-43]. Another pioneer work, using quenched molecular dynamics (MD) simulations and a wall thickness of 0.34 nm, which is the *van der Waals* separation distance between neighboring layers in graphite, obtained the elastic modulus of 1.0 TPa [44]. Clearly, the difference in the wall thickness used in the calculations directly influences the cross-sectional area that is needed in the calculation of elastic modulus, thus has a significant impact on the value obtained. The methods employing universal force field with torsional energy term were also used to predict the mechanical properties of CNTs [45, 46]. The elastic modulus calculated is around 1.0 TPa, with the nanotube thickness also being set as 0.34 nm. Besides, in Ref 44, since MWCNTs can be considered as concentric SWCNTs separated by the same distance as in graphite, molecular simulations found that the modulus of MWCNTs correlates to the number of CNT walls. Alternatively, with the derived

Born's perturbation implemented in a lattice-dynamical model, the elastic modulus also has been estimated to be 1.0 TPa [47].

There are also values of elastic modulus of CNTs calculated from quantum mechanics and tight binding methods. Using a non-orthogonal tight binding formalism with both electronic structure effects and empirical terms considered, the elastic modulus of SWCNTs was computed as 1.24 TPa for various chiralities [48]. In another work, applying an $O(N)$ tight binding method, Ozaki *et al.* gave an estimate of the elastic modulus of 0.98 TPa [49]. Moreover, Lier and coworkers presented an all-electron *ab initio* study for a number of SWCNTs at the Hartree-Fock 6-31 G* level, and deduced the elastic modulus to be slightly higher than 1 TPa [50].

Imagine the small size of individual CNTs. It is not trivial to carry out direct experimental mechanical tests of their elastic modulus. Due to the remarkable effort made in the last decade, several experimental techniques have been developed to measure the mechanical behavior of CNTs. Through observing the amplitude of the freestanding thermal vibrations in transmission electron microscopy, Treacy *et al.* first successfully obtained an elastic modulus of 1.8 TPa for isolated MWCNTs [51]. Using the same method, the value for SWCNTs that are around 1 nm in diameter, and 30 nm long, was estimated as 1.25 TPa by Krishnan [52]. In other works, bending tests of CNTs were conducted with the assistance of atomic force microscopy (AFM) [53-55]; and using this method, the elastic modulus of CNTs was measured in the range of 1.2 – 1.3 TPa. In the mean time, Raman spectroscopy has also been adopted to determine the elastic modulus [56-60] in Wagner's group with typical value obtained as high as 3.6 TPa from calculating the shift of D*-band. Later, constructing a refined nano-manipulation apparatus that combines the power of scanning electron microscopy (SEM) and AFM, Yu *et al.* [16, 61-63], for the first time, directly conducted the tensile tests for SWCNTs rope and MWCNTs through external force applied and measured by AFM probes. The experimental stress-strain curves for CNTs were obtained and analyzed, as shown in

Figure 2.5. The values calculated for elastic modulus are ranging from 0.32 to 1.47 TPa and 0.27 to 0.95 TPa for SWCNTs rope and MWCNTs, respectively. The large scattering of the results is attributed to complications of the testing methods and the individual difference of the CNTs samples used, which were formed *in situ* by induced deposition of carbonaceous materials via localized electron beam.

Figure 2.5 (a) SEM images showing the MWCNT mounted between two opposing AFM tips, the squared region in (a) is shown in (b) at a larger magnification in SEM. (c) Plot of the stress-strain curves for the MWCNTs measured. (d) Plot of the stress-strain curves from the tensile loading experiments on individual SWCNT ropes (Reproduced with permission from Ref. [16] and [61]).

In sum, the elastic modulus of CNTs has been determined to be around 1 TPa by majority of theoretical work using classical molecular dynamics and quantum mechanics methods. Later, the experimental results validated the computational predictions with elastic modulus of CNTs measured mainly ranging from 0.27 to 1.8 TPa. The relatively lower values obtained in experiments compared to theoretical results should be ascribed to the imperfect structure of the samples that have been tested, which is not considered in these computational studies.

2.2.2 Tensile strength and fracture mechanism

It is generally believed that for an object to attain the highest tensile strength it should possess utmost uniformity and perfection of its structure, even a single defect can cause significant loss of strength. Therefore, it has been suggested CNTs (especially CNTs with low density of defects) may approach the theoretical limits of strength, and are an ideal candidate to help understand the failure mechanism of materials at molecular level.

In theoretical work, harnessing the advantages of atomic molecular simulations, Yakobson and coworkers first proposed a theory concerned with dislocations initiation and motion, which are found to be energetically favorable for the mechanical relaxation in CNTs under tensile stress [64-68]. The theory involves the formation of a specific kind of defect that is introduced through bond rotation, known as Stone-Wales isomerization [69]. This rotation leads to the appearance of a pair of 5|7 dislocations embedded in the CNT hexagonal lattice. The 5|7 dislocations dipole can either glide away from each other along the CNT helical surface, giving rise to a plastic flow or deformation, or can evolve toward a larger crack to result in a brittle failure. Based on such theory and taking into account the impact of defect dipole formation rate on the CNT strength, Samsonidze *et al.* reported a CNTs fracture strain near 17%, and predicted a yield strength between 150-180 GPa [70, 71]. However, it is suggested that the formation of 5|7 dipole needs the help from thermal activation, and is only be favored at high temperatures [65, 66]. Later, Dumitrica and Yakobson introduced an alternative route for CNT fracture at room temperature, it is believed that the CNTs undergo a series of direct brittle bond breaking steps at high strains with a sequence of “lattice-trapped” states can be identified in the energy landscape. In another work, Belytschko *et al.*, using molecular mechanics simulation with modified Morse and Brenner potentials, calculated the fracture strains of CNTs ranging from 10 to 15%, correspond to tensile strength varies between 65 to 93 GPa [72]. They subsequently considered the influence of defects on the CNT strength, and the results indicated that the

failure strength of CNT under tensile stress falls in the range of 36 to 64 GPa [73, 74]. There are also subsequent reports on simulating how the pre-existing defects of various kinds can reduce the CNT strength [75-77].

On the experimental side, Yu *et al.*, using the aforementioned nano-manipulation platform, carried out tensile tests at nanometer scale to study the strength and fracture of CNTs. Combining use of AFM and SEM allows these researchers to measure the breaking strain and to observe the failure pattern image in real time [62, 78-80]. The maximum tensile strain was measured to be 5.3% for SWCNTs ropes, while the tensile strength was calculated ranging from 13 to 53 GPa based on 15 samples [62]. Similar tests of MWCNT demonstrated that the failure of MWCNT followed a 'sword-in-sheath' mechanism, and the failure strain reached up to 12% due to the pulled-out effect. The strength of outer shell of the MWCNT was obtained in the range of 11 – 63 GPa. In other groups, using a microelectromechanical system (MEMS) coupled in a TEM, Demczyk *et al.*, measured the tensile strength for individual MWCNTs at 150 GPa. The observed values of failure strain were scattered from 2% to 19% because of the variability of the samples and measurement conditions. Using the same technique, Oleg *et al.* conducted mechanical test for a very small strand of SWCNTs, and the tensile strength was estimated around 140 GPa [81]. Besides, in a very recent study, using Raman spectroscopy to monitor the change of CNT structures with respect to tensile force that is provided by van der Waals introduced friction between SWCNTs rope and substrate, Chang *et al.* successfully achieved a strain up to 13.7%, and the tensile strength was estimated to be 99 GPa.

Tensile tests of SWCNT at elevated temperature (higher than 2,000 °C) were also performed inside a TEM empowered with a piezo manipulator by Huang's *et al.* [82]. They were able to achieve a superb 280% tensile strain for SWCNTs at high temperatures in contrast to less than 15% for their room temperature counterparts. The super-plasticity discovered was attributed to the full activation of kinks and defects in CNTs [83-86], which agrees well with the defect motion mechanism

deduced from MD simulations.

While tremendous efforts have been made to look at the failure mechanisms of CNTs under critical conditions, only a handful of studies have been carried out to investigate the time-dependent behavior of CNTs at moderate levels of stress or strain, such as CNT creep and fatigue. In a previous work conducted in our group, assuming a brittle-type fracture, Xiao *et al.* calculated the lifetime of a zigzag CNT through incorporating results from molecular mechanics simulation at 0 K into kinetic fracture model [87]. Later, the model was expanded to study the time-depend behavior of CNTs with different chiralities and preexisting defects [77]. It is found that armchair CNT exhibits higher static fatigue strength than the zigzag one of similar size and defects shorten the lifetime of CNT at constant external stresses.

In order to have a clear perspective on the elastic modulus and tensile strength of CNTs, representative properties of several widely used materials for mechanical reinforcement are shown in Table 2.1, from which we can easily tell that the mechanical properties of CNTs are at least one order of magnitude greater than those of others with smaller density. While the measured or calculated properties of CNTs are quite favorable in comparison with traditional micrometer sized materials, a thorough understanding of the CNTs mechanical behavior must be developed such that the remarkable properties of CNTs can be fully utilized.

Table 2.1 Comparison of properties of widely used materials for structural reinforcement (information collected from Ref [88]).

Fiber	Diameter (μm)	Density (g/cm^3)	Elastic Modulus (GPa)	Tensile Strength (GPa)
CNTs	0.001-0.02	1.33	Up to ~ 1000	Up to ~ 100
Carbon	7	1.66	120-170	2.4-3.1
S-glass	7	2.50	90	3.4-4.6
Aramid	12	1.44	70-170	2.8
Quartz	9	2.2	70	3.4

Boron	~100	2.50	400	3.5
SiC	10-20	2.3	190	2.8

2.3 Assemblies of carbon nanotubes

While synthesis, manipulation, and characterization of individual CNTs are extremely challenging, the direct fabrication of macroscopic assemblies of nanotubes, CNT fibers, films, and arrays for example (as shown in Figure 2.6), provides us with an alternative way for using CNTs in practical applications at macroscopic level. These assemblies that inherit the remarkable properties from individual CNTs, are easy to handle, and are endowed with unique characteristics because of the unique interfacial regions between individual CNT blocks within the assemblies. The progress in this relatively new area is briefly presented in this section. After a summary of the mechanical properties of CNTs assemblies, their potential applications are introduced.

Figure 2.6 (a) SEM image of a CNT fiber in the process of being drawn and twisted from a nanotube array. (b) A resulting CNT fiber. (Reproduced with permission from Ref. [89]) (c) SEM image of a 250 nm thick CNT film. (d) SEM image

of SWCNT network in a single layer of the film. (Reproduced with permission from Ref. [90]) (e) SEM image of SWCNT forest array. (f) SWCNT array at a magnified resolution, scale bar is 1 μm . (Reproduced with permission from Ref. [91])

2.3.1 Mechanical performance of CNT assemblies

CNT fibers with individual nanotubes aligned parallel with each other along the fiber axis is the most natural form among various CNT assemblies, and could maximize the mechanical properties in the longitudinal dimension inherited from its CNT constituents. A representative work conducted by Koziol *et al.* proved that the optimized CNT fibers exhibit extraordinary mechanical properties with elastic modulus of 356 GPa, strength of 8.8 GPa, and fracture energy of 121 J/g, which are substantially higher than those commercial high-strength fibers.

Subsequently, it has been confirmed that two factor weight heavily on the mechanical properties of CNT fibers, one is the structure of individual CNTs, and the other the fiber conformation geometries. The nanotube structure, including chirality, length, and defects, has great influence on the mechanical behavior of fiber. Fibers consisted of SWCNTs have a elastic modulus of 130 GPa and strength of 0.2 GPa [92], which is relatively low due to the high curvature of SWCNT wall results in small interaction surface. MWCNTs fibers, on the other hand, possess a tensile strength of 0.5 GPa or 0.6 N/tex (tex is the linear density, grams per kilometers), which is also benefited from the spinning fabrication technique used [89]. The spinning tightens the fiber and increases the friction between individual tubes. Motta *et al.* fabricated fibers with SWCNTs and double-walled carbon nanotubes (DWCNTs), and those made by DWCNTs with aspect ratio of 100,000 showed the best mechanical properties, the elastic modulus is around 160 N/tex with strength of 2.2 N/tex, and the toughness of 46 J/g, which are higher than the best traditional fiber materials [93]. The improvement is attributed to the large diameter DWCNTs used in the experiments, which offers flattened tubular surface that maximizes the tube-tube contact area, facilitating the stress transfer among the CNTs during the tensile test. Later, it has been found that long few-walled carbon nanotubes (double,

triple-walled) are the best candidates for producing CNT fibers of optimized mechanical properties, for MWCNTs with more CNT layers are difficult to deform their cross sections, leading to a 47% - 183% lower values of strength [94].

In addition, the geometric conformation of CNT fibers also plays an important part in their mechanical behaviors. Twist is generally introduced to CNT fibers, in order that the nanotubes are tightly packed in the fibers with intertubular spaces reduced [89, 95-98]. In these studies, CNTs were drawn and twisted via stripping out nanotubes from well-aligned CNT arrays, as presented in Figure 2.6(a); and the tensile strength varies from several hundreds of MPa to a highest value of 3 GPa [99, 100]. In addition to the effort of applying mechanical interlocking, other works have been carried out to strengthen CNT fibers through noncovalent and covalent bonding [101-103]. Besides, Ma *et al.* fabricated CNT fibers with reticulate architecture, which is a load-transfer-favored network structure [17]. A tensile strength of 1.5 GPa was obtained for the fibers after epoxy-infiltration. Despite the differences between these methods being used to change the geometric structure of CNT fibers, they all share the same virtue, improving the shear strength at the interfacial area between nanotubes. Further theoretical and experimental studies suggested that the substantially lower elastic modulus and tensile strength in CNT fibers in comparison with the mechanical properties of individual CNTs is attributed to the tube-tube slippage when the fibers subject to tensile extension. Fitting data from both experiments and computational simulations, Vilatela *et al.* developed a model to predict the strength of CNT fibers, which is estimated to be 3.5 N/tex [104]. Their results suggest that the strength of CNT fibers is limited by the correlation within the CNT network other than the strength of individual CNTs. Using *in situ* Raman spectroscopy analysis, Li *et al.* were able to make a more directly observation on the CNT fiber failure mechanism [105]. They found that the yield of CNT fibers is caused by accumulation of slippage between CNTs with only elastic deformation occurred on the individual CNTs inside.

2.3.2 Application of CNT Assemblies

Since the attempts of direct adding CNTs into polymer matrices for structural reinforcement have been quite disappointing in most cases because of the difficulties in achieving effective dispersion of CNTs, oriented-CNT alignment, and optimizing interfacial properties [12, 106-108], boosted by the fabrication of high performance CNT fibers and arrays, the use of CNT assemblies in polymer composites has attracted much study in recent years. Composites of various components have been developed and surprising results have been obtained, some even beyond expectation. Mora *et al.* mixed CNT fibers with epoxy up to a high volume ratio of over 25% [109]. Although the reinforcing efficiency obtained was similar to that of traditional composites using carbon fibers, great improvement has been achieved under compressive load, which is rare in the high-stiffness fiber reinforced composites. The results was soon verified by Gao *et al.* [110]. Using *in situ* Raman spectroscopy, they identified the interaction between individual nanotubes within the fibers that were added in the composites is responsible for this improvement. Thus, the CNTs fibers possess remarkable flexibility without permanent buckling or failure under compression. That is to say, CNT fibers reinforced composites have the potential to combine supreme stiffness, strength, and flexibility altogether for applications as advanced structural materials.

In an earlier work, Suhr *et al.* dispersed dense packing of CNT arrays into epoxy resin and applied shear load to the sample prepared, from which they measured strong viscoelastic response of the composites with up to 1,400% increase in loss factor than in the baseline epoxy [111]. Monitoring the shear stress on the interface, the drastic improvement of mechanical damping is attributed to the frictional energy dissipation effect associated to inter-tubular sliding, which is confirmed by later works [112-116]. Harnessing unique interfacial properties with large interface area, the CNT arrays-based composites have promising applications for structural damping without sacrificing the other mechanical performances [117-120]. Studies on the CNT arrays themselves, which consist of aligned freestanding CNTs, also

confirmed that the tube-tube interfacial sliding plays a major role in their exceptional viscous property [121, 122].

Aside from the mechanical applications, CNT assemblies are also advantageous in producing optoelectronics and electrochemical devices. With their fascinating optical, electrical, and mechanical properties, transparent and conductive CNT films have been developed for a variety of applications, like super-capacitor for energy storage, integrated digital circuits, and novel electrodes [123-126]. It has also been suggested that the chemical and electrical properties of CNT films can be effectively modulated through mechanical deformation [127, 128], making the design and fabrication of next generation chemical/biological sensors that can be triggered by external force possible, and indicating the importance of pursuing a thorough understanding of interaction between individual tubes within CNTs assemblies, since it plays an important role in the mechanical behavior exhibited.

2.4 Dispersion of carbon nanotubes in solvents and polymers

Practical applications of CNTs are still limited because the lack of low-cost CNT production methods and the immature technologies for effectively dispersing CNTs in the matrices. The latter, in particular, is a tremendous hurdle that must be overcome before the merits for using CNTs as structural reinforcement in composite can be fully utilized [129-132]. Although composites that contain CNTs in their assembly forms have been developed, as overviewed in last section, only moderate improvements in terms of stiffness and tensile strength have been achieved in comparison to the properties of conventional composites. And the mechanical properties of composites enhanced by directly adding CNTs are also well below the expectation [133]. It is believed that the poorly dispersed nanotubes in polymers are responsible for the limited improvement of mechanical, which weaken, instead of enhance, the matrices [134-136]. And scientists have never stopped seeking new methods for improving CNT dispersion. The difficulties in effectively dispersing CNTs into solvents or polymers are inevitably related to the inherent assembling or

entangling nature of nanotubes that originates in the existence of strong van der Waals force between CNTs, the large surface area, and the smooth nanotube sidewalls.

There are generally three categories of methods to improve the dispersion of CNTs in solvent media, namely, optimum physical blending, *in situ* polymerization (for polymer matrices), and surface modification. Due to the limited effect of the first method and the restriction in the matrices of the second, in this thesis, we mainly focus on the third method, which, in fact, contains two major types of modification techniques: covalent and non-covalent surface modification.

2.4.1 Covalent surface modification

Because of the delocalized π orbital (Figure 2.1) of the sp^2 carbon atoms, CNTs are more reactive than flat graphene sheet with an improved tendency to covalently bond to other chemical groups [137]. Harnessing this unique advantage of CNTs, various techniques have been developed to introduce surface modifiers (chemical species or molecules) onto CNTs surface. In the initial attempts, different kinds of strong oxidizers, like nitric acid [138, 139], a mixture of nitric acid and sulfuric acid [140, 141], sulfuric acid hydrogen peroxide [142], and ozone [143], have been used to attach oxygen-bearing chemical species, such as carbonyl, carboxylic, ester, or hydroxyl groups onto the nanotube sidewalls. However, the oxidization of CNTs causes severe damage to the CNT structures, resulting in the fragmentation of nanotubes [144, 145]. Later, it is found that fluorination can preserve the nanotube structure. Reacting with aromatic or alky peroxides, the CNTs after fluorination can be used to introduce aromatic or alky groups, which improve the dispersion of CNTs [146]. In another study, Holzinger *et al.* used dipyrityl imidazolidene, a nucleophilic addition, to react with electrophilic SWCNTs [147]. The reaction successfully transferred a negative charge to the nanotube surface, giving rise to negatively charged CNTs, which can be homogeneously dispersed into solution because of electrostatic repulsion. Using buckypaper as electrode, Bahr *et al.* added Aryl groups on the CNT in an electrochemical environment [148], which makes it

possible to realize solvent-free modification that can directly produce dispersible and heavily functionalized CNTs in polymer matrices [149]. Cycloaddition has also been employed to modify the CNT surface. In Holzinger's work, an aziridine ring has been formed on CNTs by cycloaddition of nitrenes, which leads to crosslinking between CNTs and a substantial increase in solubility of CNTs in organic solvents [150, 151].

The various methods discussed above, which introduce chemical groups on CNTs surface, provide researchers with the access to subsequently graft the nanotubes onto other molecules, like various polymers [152, 153], peptides and other biomolecules, forming a multi-molecular cluster, which not only improve the dispersibility but also add new functions to the nanotube. There have been increasing effort in immobilizing various kinds of proteins and DNA strands of different sequences on nanotubes, from which both dispersibility and biocompatibilities of CNTs can be improved [154-156].

2.4.2 Non-covalent surface modification

In contrast with covalent functionalization, which locally disrupted the intrinsic CNT symmetry by changing sp^2 hybridization to sp^3 , non-covalent surface modification is of particular interest for it conserves the CNTs bonding structures, thus does not compromise their physical properties. This type of modification mainly involves the use of organic mediating molecules (surfactant, polymers, or biomolecules) that can be adsorbed or wrapped onto the CNTs

One of the simplest and most natural ways to increase the dispersibility of CNTs without any destruction should be the adsorption of amphiphilic molecules onto CNT sidewalls. Surfactant, amphiphilic copolymers, and polyaromatic derivatives that contain both hydrophilic and hydrophobic moieties, are ideal candidates for dispersing CNT into solvent environments. Their hydrophilic end interacts with polarized solvent molecules, and the hydrophobic counterpart adsorbs onto CNT, forming a soluble micelle [157], which indicate that the dispersion capacity of these

amphiphilic molecules strongly depends on the types of hydrophilic groups and the length and flexibility of the hydrophobic end. Results from extensive studies suggest that nonionic surfactants, like Triton X [158], improve the dispersion of CNTs by forming a relatively large solvation shell through the hydrophilic region of the surfactants adsorbed around the CNTs; ionic surfactants, such as sodium dodecylsulfate (SDS) [159] and sodium dodecylbenzene sulfonate (NaDDBS) [160], on the other hand, facilitate the CNT dispersion by van der Waals repulsion between the micelles. Islam *et al*, discovered that the stabilization of CNT suspensions depends on the length of the head groups within the surfactant that affiliate onto the nanotube surface [161]. The same study also shows the polyaromatic molecules possess unique advantages in being adsorbed onto CNTs since the formation of strong π - π stacking between aromatic groups and nanotubes. They compared the dispersibility between SDS and NaDDBS, which has an addition phenyl ring in comparison with SDS structure, and found that NaDDBS is more effective in dispersing SWCNTs in water solution due to the strong interaction between phenyl group and nanotube.

Motivated by the idea of utilizing this strong π - π stacking between aromatic derivatives and CNTs, conjugated polymers that are rich in aromatic groups have been drafted to functionalize CNTs in order to improve their solubility. Poly(m-phenylene vinylene) and poly(3-hexylthiophene) were found to be able to wrap themselves around CNTs, driving by the strong interaction between the polymers and CNTs [162, 163]. The van der Waals interactions between nanotubes are weakened during the wrapping, which causes an effective disentanglement effect on CNTs, and the dispersibility of CNT is improved. Considering the limited solubility and stability of conjugated polymers-CNT hybrids in aqueous solutions, Zou *et al*. developed a novel block polymer, P3HT-b-PS, which consists of both conjugated and non-conjugated parts, the latter exhibits good solubility, which significantly enhanced the dispersibility of CNTs [164, 165]. Other polymers that display relatively low π - π interactions with CNTs, polystyrene-block-poly(acrylic acid) and poly(styrene sulfonate) for example, can also wrap themselves onto CNTs [166].

Further investigations showed that while the wrapping of random-coil polymers onto CNTs significantly limits the degree of freedom of the polymers, decreasing the entropy of polymer, which is entropic unfavorable, the drop in surface energy of CNTs in solvent can be as high as 136 kJ/mol after wrapping, much higher than the energetic penalty from the decrease of entropy, which is 17kJ/mol at room temperature, making the wrapping process thermodynamically favorable [167].

2.4.3 Computational simulations of the dispersion mechanisms

In order to pursue deeper understandings of how surfactant molecules are adsorbed on and interact with CNTs and how the structures of CNT-polymers or biomolecules complex are formed, computational simulations, classical molecular dynamics in particular, are widely used. These simulations elaborate the energy variation and dynamic process over the course of adsorption or wrapping at molecular level.

Performing large-scale MD simulations for SDS and SWCNTs systems, Xu *et al.*, demonstrated a cylinder-like structure of SDS on CNT surface, and identified that the sodium ions between the nanotubes are crucial in the dispersion, which provide both the van der Waals repulsion force that facilitates the dispersion and Coulomb attraction that hinders the dispersion, known as screening effect [168]. This finding provides a microscopic mechanism of the function of counterion in the dispersion of CNTs, which fits well with the experimental result that shows initially, the addition of sodium 4-styrenesulfonate (NaSS) improves the dispersion, and a further increase of the NaSS concentration reduces it [169]. The affinities between CNTs and polymer molecules have also been quantitatively characterized. Zheng *et al.* reported that the interaction between the SWCNT and polymers strongly depends on the aromatic ring structures within the polymer, which tend to lay parallel to the tube surface after the simulations, and the binding energy increases when the nanotube has a larger radius [170].

The binding mechanism between biomolecules and CNTs has also been explored. In a study that probed the interaction between reversible cyclic peptide and SWCNT, Chiu *et al.* proved that peptide backbone is thermodynamically favorable to cyclize around CNT in water solution with a free energy of -12.1 kcal/mol, the ring-like structures in the peptide lay flat on the nanotube surface, providing sufficient energy for the cyclization [171]. In addition, several peptides can wrap onto the same CNT forming energetic favorable antiparallel β -sheet-like peptide stacking with hydrogen bonds hold them together. At the same time, the self-assembly mechanism and structures of CNT-DNA hybrid system have also been investigated using MD simulations. Spontaneous conformation changes in single-stranded DNA (ssDNA) structures driven by π - π stacking between ssDNA bases and CNT were spotted during the simulations, giving rise to right or left handed helices that wrap around CNT, which facilitate CNT dispersion [172]. A more detailed study shows that guanine (G) possesses the highest binding affinity among the four (G > A > T > C) bases of DNA structure due to it has highest π - π stacking interaction with CNT [173].

2.5 Summary and Discussion

2.5.1 Summary

Carbon nanotubes, a cylindrical carbon network, in which each atom is equivalently tied to its neighbors through high strength sp^2 - σ carbon-carbon bond, possess intrinsic uniformity with no apparent weak spot, leading to an ultimate resistance to mechanical tension. Owing to their remarkable mechanical performances, CNTs have received significant attention for next generation mechanical applications in scientific community. Much progress has been made in determining the elastic modulus, tensile strength, and failure mechanisms in the past decade in both theoretical and experimental studies. The impressive results revealed make the CNTs ideal candidates for NEMS structural load bearing and

composite reinforcement, for the mechanical properties of CNTs are orders of magnitude higher than those of traditional reinforcement.

Due to the high inter-tubular adhesion between CNTs, it is considerably difficult to effectively isolate the CNTs at molecular level. Two approaches are currently being pursued, in order that practical applications of CNTs can be realized with full utilization of their extraordinary mechanical properties. One is the use of CNTs in their assembly forms instead of individual nanotubes, and the other the development of novel CNT dispersing techniques. Researchers who adopt the first approach, like adding CNT fiber, film, array, into the matrices, see a significant improvement of the mechanical properties under compressions or cyclic mechanical damping with the compressive strength 20 times higher than that of neat polymer [174]. The improvement is owing to the incredible large interfacial area between CNTs and the high flexibility resulted from the inter-tubular slippage within the CNT array. However, only moderate enhancement in their tensile strength has been reported, which is because both the Young's modulus and strength of CNT assemblies fall in a wide range of 30-357 GPa and 0.2-8.8 GPa, respectively. Such variation makes it very difficult to compete with conventional high-strength reinforcing materials, like Kevlar and carbon fibers. As to the second approach, developing novel surface modification methods is the most promising way to achieving effective dispersion. And two types of modification methods are widely used to disperse CNTs in solvent media: covalent and non-covalent modifications.

2.5.2 Discussion

Even though the mechanical properties of CNTs have been extensively studied, it is also fair to say that all these works, no matter theoretical or experimental, are limited to the yielding and fracture behaviors at relatively high strains (>10%), and the CNTs fracture mechanisms that have been established are also based on the responses of CNTs under critical mechanical conditions. While, in practice, CNTs are most likely to be loaded at small strains, bearing a moderate level of stress with the expectation for a long-term service, few studies have looked at the time-dependent

behavior of CNTs [77, 87]. The failure mechanism under such conditions remains unclear.

Besides, CNTs assemblies (fiber, array) reinforced polymer composites exhibit extraordinary anti-compression properties and remarkable mechanical damping behaviors, both of which are aroused from the energy dissipated in the CNT assemblies because of the frictional sliding and the improved flexibility due to tube-tube slippage. However, a normalized value that can quantitatively express this friction force between CNTs is still unknown.

Although various CNT surface modification techniques have been developed for effectively dispersing CNTs into solutions and polymer matrices, the covalent approach drastically damages the intrinsic sp^2 bonding structure of CNTs and the physical properties that come with the structure, compromising their mechanical performances [175, 176]; the non-covalent modification methods available that use conjugated polymers for functionalization suffers from their limited dispersibility and the instability of the CNT-polymer complex due to their strand-like molecular structure cannot effectively cover the CNTs hydrophobic surface, and those use biomolecules for dispersion are not cost-friendly, and are not realistic for mass production for composites reinforcement. Thus, an economical method that can not only effectively disperse CNTs but also preserves the exceptional physical properties of CNTs is still highly desirable.

Besides, from the discussion in sections 2.2.1, 2.2.2, and 2.5.3, we can find that computational simulation is a useful tool to understand, analyze, and provide quantitative information on the structures, physical properties, and dynamic behaviors of these nanoscale materials at molecular level, all these are difficult or unable to be probed under even the most state-of-art experimental instruments. In addition, it also provides theoretical insights for experimental results. Thus, computational simulation is extensively used in this work.

Next, we will start this journey of exploration and discovery. It begins with the probe of the failure mechanisms of CNTs under a spectrum of noncritical tensile stresses. Besides, the simulation methods and strategies that have been employed and developed to help tackle the problem will also be presented.

Chapter 3 Probing the Failure Mechanisms of Carbon Nanotubes under Noncritical External Tensile Stresses

In this chapter, after summarizing the scientific background, the simulation methods and calculation schemes used are introduced, which is followed by the simulation results and discussion. The CNTs fracture mechanisms under a spectrum of noncritical tensile stresses are explored. Various failure mechanisms, including defects nucleation and diffusion, crack initiation and propagation, are considered and their initiation conditions are quantitatively analyzed.

3.1 Background

It has been previously reported that in tensile tests, two alternative failure mechanisms are involved in the CNTs fracture process: first, the 5|7 defect dipole initiation (via Stone-Wales (S-W) transformation) and diffusion, which give rise to a ductile failure of CNTs after plastic deformation; and second, the brittle-type straightforward bond breaking mechanism [65, 66, 177]. Both of these mechanisms have found their respective experimental evidence to support the validity, which is favored, depends on the intrinsic structure of CNTs (the chirality) and the conditions of the tensile tests [80, 82]. It is suggested that the nucleation of 5|7 defects is preferred at elevated temperatures, and the brittle rupture resulted from bond dissociation dominates the failure mechanism at high strains and low temperatures under mechanical tension [6, 66]. Limited by the computational and experimental methods used in identifying these failure modes, in which the CNTs were continuously being stretched until rupture, both fracture mechanisms were probed while a fast increasing tensile load was applied to carbon nanotubes, such that the initiation of defects or crack was immediately brought to the successive structural configuration, the one follows, and so on, along the fracture route towards the eventual failure, driving by the increasingly larger tensile stress. Therefore, the

CNTs yield or fracture mechanisms under noncritical conditions (low constant stress with a moderate strain level) are still missing, which is, however, of great importance, since CNTs are of great interests for potential applications like load-bearing components in NEMS and structural reinforcement in advanced composites. In both cases they are expected to be serving for a long term under loads far below their critical stress, such that it is essential to explore the failure mechanisms under such conditions. In the absence of an increasing stress, the CNT structure has sufficient time to rearrange itself, leading to a more strain-release favored configuration, and the CNT failure mechanisms based on current understanding cannot be applied to such cases. Only after gaining a better understanding on the underlying failure mechanisms of CNTs under noncritical stresses can we deploy them with more confidence in practical applications.

3.2 Methodology

The progressive deformation of materials under a constant load is generally known as creep, or “static fatigue”, which is a very slow dynamic process. Finding its fracture mechanisms and their relations with the materials atomic structures is a daunting and a long standing problem [178-180]. On one hand, due to the relatively low external stress applied, the strain rate in creep is very small, for example, the creep rate for a land-based turbine is around 10^{-11} s^{-1} [181], such that extrapolation to this rate from those measurable in experiments is unimaginable. In our case, not to mention the rigorous experimental conditions required and the complications come along when one needs to manipulate objects as small as CNTs, which make the direct measurement of creep behavior of CNTs impossible. On the other hand, although the length scale of CNTs falls within the range atomistic computation is capable of, the time scale of this slow dynamic process, which can be as long as 10^{11} s, is far beyond the limit molecular dynamics (MD) simulations can reach. Even with the most state-of-art large-scale parallel implementations, the MD itself is still fundamentally restricted by the requirement of the finite numerical integration

method used for solving the equation of motion, in which computational steps cannot exceed several femtoseconds. It means that we need to break the simulation time into at least 10^{25} discrete units to meet the challenge of simulating a phenomenon that lasts 10^{11} s, which seems never practical.

Since the creep of CNTs cannot be directly simulated in MD simulations, the tackling of this slow dynamic problem needs an alternative approach; and understand why this process takes such a long time in nature is very important. According to the transition-state theory [182], the rate of a transition event follows an $\exp(-\Delta U/k_B T)$ relationship, in which k_B is Boltzmann constant, T is temperature, and the rate strongly depends on the energy barrier ΔU . As carbon nanotubes spend most of the time being trapped in their energy minima states, without the aid from an increasing external stress, the transition between two adjacent energy minima over the saddle point becomes a rare event. And structural evolution of CNTs under a relatively low stress is the accumulated result of many such unusual transitions, which MD simulation, in its time scope, cannot sample enough states to reproduce this process.

In this thesis, rather than directly probing the exact dynamical trajectory of CNTs under such conditions using MD, this long-term intra-molecular structural evolution is tracked through abstracting the whole process into individual state-transition units between energy minima that are applicable to the CNT structure. Such an inspiring concept has been successfully implemented before in the analysis of simple defects diffusion problems in solid [183]. However, the challenge lies in directing the computational simulations to cover sufficient samples of the transitions, and in investigating the correlations between the energy states and atomistic details within our CNT structural framework. As mentioned earlier, multiple atomistic rearrange modes involves in the fracture of CNT, making the investigation a complicated problem. In this chapter, we use this approach to study the slow dynamic behavior of CNT under a spectrum of constant stresses below the critical value, and to track the most favorable structural evolution route under

different conditions. In next section, we first introduce the computational methods that have been adopted in this work.

3.3 Molecular Simulations

3.3.1 Computer simulation methods

Computer simulation that complements experimental studies is an excellent tool in the study of condensed matters. There are various computational methods available for simulating nanoscale system at different levels of precision and timescale (Figure 3.1). No single method itself has the ability to offer complete information of a system. Thus, for a given system, choosing an appropriate simulation technique is very important in order to find the useful answers for the questions of interest.

Figure 3.1 Time and length scales applicable to different computer simulation methods.

In atomistic scale, two types of energy model are widely used to simulate system at molecular level: *ab initio* methods and empirical force field methods. The former,

such as Hartree-Fock and density functional theory (DFT)-based simulations, is based on quantum mechanics theory, solving Schrodinger's equation at the electronic level to obtain the energy of the system. Since it does not rely on any phenomenological models, *ab initio* methods are very versatile and extremely accurate. However, these calculations are computational intensive, in which the processing time grows according to $O(N^3)$, N is the number of electrons in the system. Therefore, they can only be used to study very small systems (~ 100 atoms) for a short period of time (~ 10 ps). On the other hand, Newtonian mechanics-based empirical methods, which are derived from fitting results from *ab initio* computations and experimental data, implement many approximations. They provide a good compromise between simulation efficiency and accuracy. Accordingly, the size and time scales of the simulation system this type of methods can handle are up to 1,000 – 1,000,000 atoms and 1 – 100 ns, respectively. Coarse grain method usually shares the same empirical models as those in atomistic methods. The difference lies in particles represent a group of atoms in coarse grain. Thus, the computational burden is much smaller with the absence of some details about atomistic motions. Noteworthy is that *ab initio*, classical atomistic, coarse grain methods can all be implemented in molecular dynamics and Monte Carlo calculation schemes. However, in the scope of this thesis, the term, MD, specifically refers to empirical model-based atomistic molecular dynamics simulation. A brief comparison of these methods is listed in Table 3.1.

Table 3.1 Comparison of different computational methods.

Computational method	Theory	Advantage	Disadvantage
<i>Ab initio</i> methods	Quantum mechanics	Very accurate with effects from electrons	Low efficiency
Classical Molecular Dynamics	Classical force field Newton's law of motion	Dynamics properties and accurate	Long time simulation is ill-conditioned

Classical Monte Carlo	Classical force field Random sampling	Efficient	No dynamics information
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From Table 3.1, it is seen that atomistic simulation, classical MD that based on empirical models in particular, is most desirable for our CNT loading simulations. Since we are trying to probe failure mechanism that involves bond dissociation, defects initiation and diffusion, retaining atomistic details of CNT is vital for capturing its structural rearrangement. Besides, applying external load is a progressively evolving process that needs the dynamic information provided in MD simulations.

3.3.2 Molecular dynamics for carbon nanotubes

Tracking the trajectory of each atom over a given time, MD method provides scientists with a window to observe the microscopic behavior of molecular systems; it is an extremely powerful tool for simulating dynamic and equilibrium properties for a given system. In MD, the motion of atoms evolves according to classical Newtonian mechanics with the assumption that all electrons are always stay in their ground states, known as Born-Oppenheimer approximation, which implies phenomena that involve electron transfer and chemical reaction cannot be studied in MD frame. In addition, the interactions between atoms within the system that are defined by empirical potential functions need to be specified first, which are derived from either *ab initio* calculations or experimental physical properties. The schematic flow chart of a typical MD is illustrated in Figure 3.2. In the following sections, based on the procedures shown in the figure, the MD simulation scheme employed in this work with specific application for CNTs will be introduced.

3.3.2.1 System initialization

The simulation systems are generally initiated via constructing the atomistic structure of CNTs. An ad-hoc versatile program that can generate CNTs structure of

arbitrary chirality and periodic units based on its geometric characteristics introduced in section 2.1 is developed to create CNT models used in this work. Geometry optimizations were performed to the obtained structures in order to translate the systems to their local minimum states.

Figure 3.2 Schematic flow chart of a general MD simulation (the terms in the flow chart will be explained in detail in the following sections).

3.3.2.2 Force calculation

Calculation and summation of forces on each atom is the most time-consuming part of MD simulations. According to Newtonian mechanics, the force vector F_i applied on a particle i is equal to the product of the mass m_i and the acceleration a_i given by

$$F_i = m_i a_i = m \frac{d^2 r}{dt^2} \quad (3.1)$$

in which r_i is the position of atom i defined in last section. Rewriting equation 3.1 as the gradient of empirical potential functions,

$$F_i = -\nabla_i U = -\frac{\partial U(r_1, r_2, \dots, r_n)}{\partial r_i} \quad (3.2)$$

the force on each atom can be evaluated from differentiating the potential functions with respect to its atom coordinates. As force is one of the most important physical parameters in a dynamic process, robust empirical potential functions (also known as force field) that can accurately reproduce the physical properties of the system are crucial for successful simulations. Generally, two types of interactions are considered in an empirical force field: bond order interactions and non-bonded interactions. While bond order interactions reflect the physical nature of bond stretching, bending, and torsion, the non-bonded term consists of van der Waals electrostatic interaction, the latter is usually neglected in CNTs simulation.

There exists a spectrum of empirical potentials for carbon and carbonaceous chemicals [41, 43, 72, 184-188]. However, the second generation Brenner potential (hereafter referred to as Brenner potential), a reactive empirical bond order potential, is widely used in the simulations of mechanical properties of CNTs [189-191] and a good agreement with the results from *ab initio* methods has been reported [177]. Moreover, being parameterized in a bond order functional frame, Brenner potential possesses the ability to simulate carbon-carbon bond formation and dissociation via updating the atomistic neighbor-list at each MD step, which is vital for our problem and is generally lacked in other universal-style potentials, since in these potentials the neighbor-list is defined by user in the initialization stage and cannot be changed during the simulation.

The concept of bond order model is first proposed by Abell [192], in which he suggested that the bond energy of a system can be described by pairwise

interactions. An extension to carbonaceous system was made by Tersoff [41]. However, it lacks the ability to model intermediate bonding, such as delocalized bonding in benzene structure. Later, an improved form of Tersoff potential, Brenner potential, was developed [43], in which modified expressions for intramolecular interactions and a broad experimental database for parameters fitting are used, eliminated the nonphysical effects in Tersoff version. In addition, Brenner released an upgraded version of Brenner potential in 2002 [185]. It provides more accurate structural geometry, energy, and thermal properties for hydrocarbon system, including CNTs [193, 194].

In the Brenner potential, the total potential energy is given by

$$E_{total} = \frac{1}{2} \sum_i E_i = \frac{1}{2} \sum_i \sum_{j \neq i} E^B(r_{ij}) \quad (3-3)$$

where E_i is the potential energy of atom i and $E^B(r_{ij})$ is the interaction between atom i and its nearest neighbors, j , based on the form given by Tersoff,

$$E_{ij}^B = V_{ij}^R - b_{ij} V_{ij}^A \quad (3-4)$$

in which repulsive and attractive energies from the interactions between atom i and j are combined in a ratio, b_{ij} , the bond order term. V_{ij}^R represents the pair-wised repulsive potential, including the nucleus-nucleus and electron-electron interactions, while V_{ij}^A corresponds to the attractive term that accounts for nucleus-electron interactions. The bond order function, b_{ij} , includes the impacts from many-bond effect on the pair-wised interaction. It is the most remarkable feature of the Brenner potential. Various many-body factors, such as coordination numbers, angle bending, bond torsion, and covalent conjugations, are considered in this term. It adjusts the interaction strength with respect to the change of the local environment where the pairwise correlation locates in. Thus, weighing the bond strength, Brenner potential can simulate the bond formation and dissociation process, which usually can only be observed in quantum methods. A more detailed functional

expressions and the adjustments made in this work of Brenner potential are attached in Appendix A.

The Lennard-Jones (LJ) Potential is widely used to describe the van der Waals interactions between non-bonded atoms or molecules for its simplicity and efficiency [195]. The basic form of the potential function is described as

$$V_{ij}(r_{ij}) = 4\varepsilon \left[\left(\frac{r_0}{r_{ij}} \right)^{12} - \left(\frac{r_0}{r_{ij}} \right)^6 \right] \quad (3.5)$$

where ε and r_0 are the depth of potential well and the distance at which the potential is zero, respectively, and r_{ij} is the distance between the atom i and j . The r^{-12} term represents the short-range repulsive interaction between atoms according to Pauli principle. The repulsive energy increases abruptly if electron clouds of two atoms overlap. The r^{-6} term corresponds to the long-range attractive interaction caused by dipole-dipole interaction. In this work, an adapted form of this potential is used to describe the long-range interactions within the CNTs network, since they are missing in Brenner potential.

There are several methods to embed non-bonded interactions into Tersoff-like potential. One is to simply include the non-bonded term at the distance larger than the bond range [196]. However, this causes high repulsive energy barriers for long-range interacting carbon atoms and is not consistent with the original Brenner term, resulting in spurious results. In this work, LJ potential has been incorporated into Brenner potential in a more delicate way with two sets of switching functions employed, and the complete expression for the long-range interactions is given by

$$E_{ij}^{LJ} = S(t_r(r_{ij}))S(t_b(b_{ij}))C_{ij}V_{ij}(r_{ij}) + [1 - S(t_r(r_{ij}))]C_{ij}V_{ij}(r_{ij}) \quad (3.6)$$

in which $S(t)$ is a switching function to evaluate the “on and off” of LJ terms according to the distance between and bond order of the atom i and j , and C_{ij} is a connectivity checking switch so that there is no LJ interaction if atom i and j are connected by one or two intermediate neighbors. $S(t)$ is expressed by,

$$S(t) = \Theta(-t) + \Theta(t)\Theta(1-t)[1 - t^2(3 - 2t)] \quad (3.7)$$

where $\Theta(t)$ corresponds to the Heaviside step function, the scaling factor t varies

from 0 to 1, and has two expressions, which stand for the distance and bond order term, respectively,

$$\begin{aligned} t_r(r_{ij}) &= \frac{r_{ij} - r_{LJ}^{MIN}}{r_{LJ}^{MAX} - r_{LJ}^{MIN}} \\ t_b(b_{ij}) &= \frac{b_{ij} - b_{LJ}^{MIN}}{b_{LJ}^{MAX} - b_{LJ}^{MIN}} \end{aligned} \quad (3.8)$$

The revised LJ potential allows the non-bond interactions to be tuned smoothly with respect to the change of local environment, and fully compatible with the Brenner potential.

3.3.2.3 Integration of equation of motion

Knowing the net force acting on each atom, the trajectory can be evaluated through Newton's 2nd law:

$$m_i \frac{d^2 r_i}{dt^2} = \sum_i F_i \quad (3.9)$$

Using finite difference method, Equation 3.9 can be numerically solved at discrete time unit Δt . Here, an effective and stable algorithm, velocity verlet [197], is implemented in our MD simulations, in which the position and velocity evolutions are given as:

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{F(t)}{2m} \Delta t^2 \quad (3.10)$$

$$v(t + \Delta t) = v(t) + \frac{F(t) + F(t + \Delta t)}{2m} \Delta t \quad (3.11)$$

The above equations contains a local error of $O(\Delta t^4)$. Therefore, the time step Δt must be significantly smaller than the atomic oscillation time τ , which is associated with thermal vibrational motion. For carbon system using Brenner potential, a typical Δt is 0.5 fs.

3.3.2.4 Regulation of temperature and pressure

In MD simulations, the interactions among atoms are defined by classical force field, such that the system energy is a constant of kinetic motion. However, in

practice, systems usually stay in their thermal equilibrium state at a constant temperature T . In order to add the thermal effect into the calculation, thermal ensembles can be used in the simulations. Canonical ensemble (NVT), in which number of atoms, volume, and temperature are constant, can be applied to give an isothermal condition. Langvin, Nose-Hoover, and Berendsen thermostats are widely used schemes for the control of temperature [197]. Besides, the NPT (number of atoms, pressure, and temperature are constant) ensemble can be used for the control of pressure (barostats) and temperature at the same time in a system. In their microscopic definitions, T and P are given as

$$T = \frac{2}{3Nk_B} \langle K \rangle; \quad P = \frac{1}{V} \left[Nk_B T + \frac{1}{3} \left\langle \sum_{i>j} f(r_{ij}) \cdot r_{ij} \right\rangle \right]$$

where, $\langle K \rangle$ in the first equation is the average of kinetic energy and $f(r_{ij})$ in the second one is the force between atom i and j . Thus, rescaling the atomistic velocity and system volume, the thermostats and barostats can maintain the simulation system at a constant T and P , respectively.

3.3.3 Exploration of Energy landscape

As discussed in the methodology (3.2), rare-event phenomena, like creep, cannot be directly probed in MD simulations due to the insurmountable gap between the time-scale of numerical time step in MD and the long-term nature of slow dynamics. After using MD to apply specific loads on CNTs, our approach to this problem relies on the exploration of the system energy landscape through searching the energy minima and saddle points along the structural evolution route. How we identify these topological characteristics on the energetic landscape is thus of extreme importance.

3.3.3.1 Energy minima

Considering the complexity and the large dimensionality of a system's energy landscape, it is very difficult to locate the minima state via analytically solving for

the exact zero in first order derivative of the energy with respect to atom coordinates. In order to overcome this problem, some numerical methods have been developed, such as steepest descent (SD) and conjugate gradient (CG) [198], in which through following the downward path (gradient < 0) along the energy space, the local minima can be reached from an initial guess. More refined techniques that involve the construction of inverse Hessian matrix, like limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) method [199], could improve the minimizing efficiency for some cases. Besides, applying a damping parameter along the current force vector on the atoms during minimization, SD-based FIRE algorithm [200], a damping dynamics method, is also efficient in searching the local energy minima, especially when the initial structure is not well defined. In this work, all of the above methods have been implemented for tracking the energy minima, which is employed is based on their proficiency and performance in different conditions.

3.3.3.2 Energy saddle points

An energy saddle point lies in the range between two neighboring energy minima. The energy difference from saddle point to initial state defines the energy barrier of the respective transition. While there are a variety of techniques for saddle points searching, the climbing-image nudged elastic band (NEB) method is adopted in this work for its efficiency and stability [201, 202]. Here, the essential algorithm of NEB is summarized.

As a numerical variant of chain-of-states methods, NEB uses a string of discrete sequential images of the atomic geometric configurations that are connected via spring forces along the reaction route to find the minimum energy path (MEP) between a pair of local minima on the energy landscape (Figure 3.3). In NEB method, the initial reaction route can efficiently converge to the MEP, and the resolution depends on the number of images sampled. These images are relaxed to the MEP via the NEB force, F_i^{NEB} . It comprises two orthogonal components: the

spring force, F_i^S , that acts parallel to the elastic band direction τ , and the potential force, $F_i^\perp$, which is perpendicular to τ .

$$F_i^{NEB} = F_i^\perp + F_i^S \quad (3.12)$$

Here, F_i^S connects the neighboring images, and $F_i^\perp$ allows the energy to evolve towards the MEP but not directly slide down to the minimum. They are given as:

$$F_i^S = k \left(|R_{i+1} - R_i| - |R_i - R_{i-1}| \right) \tau_i \quad (3.13)$$

$$F_i^\perp = -\nabla(R_i) + \nabla(R_i) \cdot \tau_i \tau_i \quad (3.14)$$

In Equation 3.13 and 3.14, k is the spring force constant and R_i is the position of i th image. The initial and final energy minima states need to be specified before NEB calculation and, along with the number of images need to be sampled, such that the initial reaction path can be constructed by linearly interpolating the energy space at regular intervals between the two minima. The calculation is iterated until the convergence condition is satisfied. The transition state and energy barrier can be obtained through searching the saddle point along the MEP.

Figure 3.3 The force-projection computational scheme of the NEB method: the spring force F_i^S , along the elastic band direction τ , connects the images together; the potential force $F_i^\perp$, perpendicular to the band, directs the NEB reaction route toward MEP until convergence is reached during the calculation cycle.

3.3.4 Programing of the methods

Brenner potential is especially parameterized for hydrocarbon systems. On one hand, although it has higher accuracy for such systems, the widely used powerful molecular dynamics packages, like GROMAC [203], NAMD [204], and AMBER [205], do not implement this potential for its limited applicable elements and the programming architecture for this kind of pair-wised many-body potential is not the same as the universal force field. Besides, since the pair-wised energy strongly depends on the many-body term, the neighbor-list of each atom needs to be reassigned at each time step. On the other hand, available programs [206-208] that include Brenner potential are not robust and efficient enough to handle the problems we need to explore. These codes are all programmed in a serial way, and can only be performed on a single processor, significantly restricting their computational capacity. In addition, these programs do not include the long-range

van der Waals interaction. This term is very important for the system we are interested in, since our simulation models generally comprise thousands of atoms among which the long-range interactions cannot be neglected.

Because there is a lack of an adequate simulation package, we embark on making our own. A customized program has been developed. Using message passing interface (MPI), it is capable of performing MD simulations (according to the aforementioned methods) and NEB calculations with respect to Brenner potential for carbon nanotubes with thousands of atoms in a parallel mode (spatial decomposition of the system domain). The program is coded in C++ with standard libraries from the GNU Compiler Collection (GCC) for its powerful methods in memory control. While the intensive mathematical calculations of Brenner potential are completed in the function manner, the program can be easily incorporated into other implementations, and be called by external packages. Here, we do not discuss the details of the programming techniques. Starting from the next section, we will use the program developed to explore the energy landscape and the respective atomic configuration of CNTs.

3.3.4 Simulation protocol

All molecular simulations for CNTs were conducted in vacuum with sufficient space between the ends of CNTs and the boundaries of periodical boundary box, ensuring no interference across the boundaries is involved. Trajectories were integrated using the velocity verlet algorithm with a time step at 0.5 fs in the NVT ensemble using the Nose-Hoover thermostat. The temperature was relaxed every 100 time steps, minimizing the temperature fluctuation and the system interference from the thermocouple. All carbon atoms of the CNTs interact with each other according to Brenner potential at bond order with a cut-off at 2 Å and revised LJ potential under non-bonded conditions if the carbon-carbon atom distance falls in the range between 2 to 10.2 Å. Prior to the simulations, all CNTs models constructed were gradually heated up to 1000 °C over a time span of 25 ps in NPT ensembles at 0 atm, then the structures were relaxed at 1000 °C for another 25 ps,

followed by annealing to the simulation temperature, and ended with an energy minimization to reach the equilibrated state. All simulations were run across 8-32 processors on Nanyang Analytical HPC cluster. Analysis and visualization of MD log files and trajectories were performed with in-house Python and TCL scripts together with Visual Molecular Dynamics (VMD) [209].

3.4 Creep failure mechanism of carbon nanotubes

In this section, using the aforementioned methods, the creep failure mechanisms of CNTs under different constant tensile loadings are explored. Two SWCNTs models were considered in this work, one is an armchair type with chirality of (8, 8), the other a zigzag one with chiral index of (14, 0). Both SWCNTs are about 120 nm long and around 1.1 nm in diameter. As nanoscale materials, it is suggested that the mechanical properties of CNTs strongly depend on their chirality, since CNTs cannot be treated as continuous models for the orientation of the carbon-carbon bond within the structure has significant impact on their mechanical behaviors. Representing the two extreme cases of CNTs geometric structural varieties, this pair of CNTs adopted here will cover the spectrum of the mechanical behaviors that CNTs of other chiralities are likely to exhibit.

3.4.1 Mechanical behavior of CNTs under tensile test

Before we start sketching the energy landscape of the CNTs under constant stresses, the mechanical properties of the nanotubes need to be first determined from conventional tensile tests. In our MD simulations, the CNTs were deformed under tensile stress in its axial direction z at a constant strain rate until final failure. Two layers of carbon atoms at each end of the nanotubes were constrained against movement along the axial direction via imposing zero velocity and force on these regions (but these atoms were free to move in the other dimensions). With the implementation of these constraints, the CNTs were first relaxed for 20000 time steps, a homogeneous strain of 0.001 was subsequently applied to the nanotubes

through rescaling all the atom coordinates in the z direction, followed by another 20000 MD steps of structural relaxation. Considering the time step is 0.5 fs, this provides an average strain-rate of 0.01% ps⁻¹. This stretching and relaxation procedure was sequentially iterated until the complete fracture of CNTs. These MD simulations were performed in an NVT ensemble at room temperature of 298 K.

In order to obtain the stress-strain curves from tensile deformation process, the virial stress on each carbon atom was calculated according to the following expression:

$$\sigma_{ij}^a = \frac{1}{\Omega^a} \left(\frac{1}{2} m^a v_i^a v_j^a + \sum_{b=1,n} r_{ab}^j f_{ab}^i \right) \quad (3.15)$$

where, i and j represent the vector indices of the Cartesian coordinate system, a and b denote the carbon atoms within the interaction range, and m and v are the mass and velocity of the atom, respectively; while r_{ab} and f_{ab} stand for the distance and force between atom a and b , Ω^a is the atomic volume of atom a , which is taken from the initial CNT structures prior to deformation with a thickness of 3.4 Å. There are six virial stress vectors; here, we only consider the one in the axial direction, σ_{zz}^a . Once the virial stress of each atom was calculated, the stress on the entire nanotube was determined via averaging over all the carbon atoms in the simulation system every 200 time steps. Besides, these values were subsequently averaged over the latter 10000 time steps of the relaxation time, in order that the influences from thermal fluctuation can be eliminated. Therefore, both a spatial and temporal average of the stresses can be obtained. This process gives an averaged stress for each strain increment, allowing us to get the stress-strain relationship for the CNTs, as shown in Figure 3.4.

Figure 3.4 Stress-strain relationships of an armchair (8, 8) and a zigzag (14, 0) CNTs from MD simulations.

Table 3.2 Mechanical properties of (8, 8) and (14, 0) CNTs.

Chirality	Young's Modulus	Tensile Strength	Failure strain
	GPa	GPa	
(8, 8)	437.1	97.2	53.3
(14, 0)	491.6	77.5	31.8

The mechanical properties listed in Table 3.2 agree well with the simulation results from Belytschko *et al.* Using the same Brenner potential, they obtained the tensile strength of CNTs ranging from 65 to 93 GPa [72]. It is clear that the chirality of CNTs has a significant impact on their mechanical behavior under tension. While the zigzag carbon nanotube is more rigid with slightly higher Young's modulus in the initial stage (strain < 10%) of the tensile test, armchair tube possesses much higher tensile strength and failure strain, 25% and 68% higher than those of (14, 0),

respectively, indicating the atomic conformation in armchair CNTs can accommodate more tensile strain energy in comparison with zigzag CNTs. The difference in the orientation of the carbon-carbon bond along the tube axial direction plays a significant part in these discrepancies. As one third of all bonds in armchair CNTs are orthogonal to the tube axis, these tubes have more potential to rearrange their atomic structures to release the tensile strain. However, their zigzag counterparts, in which 1/3 carbon-carbon bonds are parallel to the axis, have no possible dislocations initiation route to reduce the tensile stress. Since the material has sufficient time to relax its structure according to the external stress in creep tests, two different failure mechanisms are expected for zigzag and armchair CNTs. Besides, the strength for both the CNTs exceeds 75 GPa, which provides a reference for the selection of the dead pulling force in the following constant stress simulations.

3.4.2 Simulating creep tests *in silico*

Even though the transition states that occur in a slow dynamic process like material creep are unlikely to be captured within the time scope of MD simulations, MD is still useful in sampling the different system conformations that are at different energy minima while applying a noncritical tensile stress. In order to realize this in MD simulation, a stretching scheme that is different from the one used in 3.4.1 has to be developed, since in a typical tensile test, we are usually interested in the control of strain rate (rescaling the system size in axial direction), however, in a creep test, the strain rate is an unknown value that needs to be evaluated after the test, and the key in creep tests is the control of the tensile force that is applied to the sample. In this work, an external force field is introduced to give prescribed tensile loads in z direction on the end atoms of CNTs. This additional potential term is added into the total energy Hamiltonian of the system, giving by:

$$U_{tension} = -f_p \sum_{i=1}^{N_{End}} r_z^i \quad (3.16)$$

in which f_p is the external pulling force, r_z^i is the z coordinate (axial direction) of an atom i at one end of the CNT, and N_{end} denotes the total number of end atoms. This external force field changes the system Hamiltonian without disturbing the Brenner formulation. However, the side effect is bond dissociation tends to take place near the end atoms when the force applied becomes increasingly large. To eliminate this artificial phenomenon, a position restraint term of the harmonic form is applied the bonds that are connected to the end atoms of CNTs:

$$U_{res} = k_{res} \sum_{i=1}^{N_{bond}} (r_i - r_{i0})^2 \quad (3.17)$$

where k_{res} , r_i , r_{i0} , N_{bond} , are force constant, bond length, initial bond length, and number of bonds, respectively. Here, k_{res} is taken as $8 \text{ eV} \cdot \text{\AA}^{-2}$ to strengthen the bonds at the ends of CNT, maintaining the bond length around the initial equilibrated value. Implementing Equation 3.14 and 3.15 in our simulation package, we are able simulate the mechanical response of CNTs that are subject to imposed dead external forces.

As potential energy of the system and atomic virial stress has been biased by the external force field, which provides an unchanged artificial external force regardless the potential response from the system. Thus, they cannot be used to calculate stress. Here, stress are evaluated via finite differencing energy contributions from pairwise (Brenner and LJ) terms with respect to the corresponding strains at different external loadings, given by

$$\sigma = \frac{F}{A} = \frac{1}{A} \frac{dU}{d(L\varepsilon)} = \frac{\Delta U}{\pi d t \Delta L} \quad (3.18)$$

where ΔU , ΔL is the change of pairwise potential energy and the elongation, respectively. D is the diameter of CNT and t , the thickness of CNT shell, is taken as 0.34 nm . The stresses calculated here agree well with the values shown in Figure 3.4. Besides, the relation between the pulling force applied on each end atom and the respective stress produced on CNT are shown in Figure 3.5. Interestingly, the

curves of this relation for both armchair and zigzag tubes can be divided into two distinct stages. As shown in Figure 3.5, the stress rises rapidly in the first stage till the force reaches a critical value of 2.5 eV/Å (4 nN). Subsequently, in the second stage, the stress steadily increases in a moderate rate up to the failure stress. This change in the stress increase rate is attributed to the structural transformation caused by the increasingly larger external force applied. In the initial stage, the CNT network is in its relaxed states, and is more flexible with respect to external force. However, as pulling force approaches the critical value, the bond and CNT lattice network is tightened, the entire CNT structure becomes highly-strained and more rigid, further elongation requires higher strain energy. The first stage can be well fitted into a second order polynomial and the second is well described by a linear equation as

$$\sigma' = a_1 f_p^2 + a_2 f_p \quad (3.19)$$

$$\sigma'' = b_1 f_p + b_2 \quad (3.20)$$

in which σ' and σ'' represent the stress in first and second stage, respectively. The parameters for each CNT simulated are tabulated in Table 3.2. With Equation 3.19 and 3.20, the pulling force specified in MD simulations can be transferred to engineering stress for further comparison.

Table 3.3 The empirical parameters in Equation 3.19 and 3.20 for (8, 8) and (14, 0) CNTs.

Chirality	a_1	a_2	b_1	b_2
(8, 8)	4.62	18.98	5.92	70.02
(14, 0)	3.96	16.08	8.05	48.77

Figure 3.5 the pulling force versus the respective stress produced on (8, 8) and (14, 0) CNTs. Symbols represent the simulation results, and colored lines indicate the fitting equation.

3.4.3 Route towards the rupture

In the carbon lattice within CNTs, two fracture mechanisms, namely, bond rupture and 5|7 dislocations dipole initiation and diffusion are involved and play important roles in the mechanical failure of CNTs. In this section, using MD simulations and NEB method, we evaluate which transition is favored at each step on the route towards the eventual fracture under different levels of noncritical load. Upon exploration of the energy landscape of different configurations of a CNT, the failure route is determined according to two criteria: first, the evolved structure should be able to release more strain energy compared to its preceding structural conformation; second, among the different possibilities that meet the first criterion, the state transition that leads to the new conformation requires the lowest activation energy.

Our tensile tests results and previous studies have found that S-W transformation is impeded in zigzag carbon nanotubes [6, 177], especially under low stress levels,

since the carbon-carbon bonds within their structure are already highly ordered towards the axial direction, such that the initiation of 5|7 dislocations is unlikely to further relax their structure. This suggests that no atomic rearrangement scheme is involved in the creep of zigzag tubes. Their failure mechanism under mechanical tension is solely dominated by bond dissociation of those parallel to the tube axis, forming a flat crack surface around the circumference of zigzag nanotube. This failure mode was also adopted by Xiao *et al.* in their calculation of the mechanical failure of a zigzag CNT [87]. Therefore, the focus of this work is the determination of the failure mechanism for Armchair CNT, in which different possible strain-releasing paths are in play and competing with each other at different stress levels and fracture stages.

3.4.3.1 The first step: defect initiation or bond rupture

In an intact armchair CNT, two possible ways could be taken to release the mechanical stress: the nucleation of a pair of 5|7 defects through S-W transformation and the initiation of a crack via bond rupture. As shown in Figure 3.6 (a) and (b), a 5|7 dislocations dipole and a dissociated bond are embedded into an intact (8, 8) CNT lattice network, respectively. Prescribed noncritical pulling forces ranging from 0.25 to 4.25 eV/Å are applied to these conformations using MD simulations. The local minima and the respective structures obtained from MD at different loading levels were collected and served as reference states in the following NEB calculations to evaluate the activation energy. In the NEB calculations, the initial and final states were defined as the energy minima of intact CNT and the evolved CNT, respectively. Twenty images were inserted between the two local minima according to the procedure introduced in section 3.3.3.2. A spring constant of $1 \times 10^5 \text{ eV} \cdot \text{\AA}^{-2}$ was adopted in all the NEB calculations to connect the identical atom pairs across the neighboring replica. And the MEP seeking is considered to be converged if the force component on each image perpendicular to the elastic band is less than $0.05 \text{ eV} \cdot \text{\AA}^{-1}$.

Figure 3.6 (8, 8) armchair CNT structures (zoom in snap shot) with embedded 5|7 dislocations dipole (a) and a crack formed by bond rupture (b).

The profile of the change of potential energy over NEB reaction coordinates under different pulling forces for 5|7 dipole nucleation and bond dissociation are displayed in Figure 3.7 (a) and (b), respectively. In the energy curve for a specific pulling force, the saddle point (point with the highest energy) represents the transition state, as shown in Figure 3.8. It involves the bond breakage of the two marked bonds in the initial states, and the S-W transformation follows as the bond rotates 90° and form another two bonds in the final state. Through identifying the saddle point, the activation energy needed for the state transition can be obtained. While the energy barrier of both transitions decreases as the increase of pulling force, there exists a significant difference in the rate of this decrease. In the CNT with 5|7 dipole, the energy barrier drops rapidly and becomes negligible when the force reaches $2 \text{ eV/\AA}$. In contrary, we only see slight reduction in the energy barrier for bond rupture when the pulling force gets higher in the initial stage, it only reduces $\sim 1 \text{ eV}$ (about $1.60 \times 10^{-19} \text{ J}$) when the pulling force is already $1.5 \text{ eV/\AA}$, which corresponds to 40 GPa according to Equation 3.19, and remains high even f_p reaches $2.25 \text{ eV/\AA}$. However, the energy barrier suddenly vanishes when f_p gets to the previous identified critical value of $2.5 \text{ eV/\AA}$, which corresponds to a fully tightened-up CNT lattice network with strain around 40%.

(a)

(b)

Figure 3.7 The minimum energy paths (MEP) of the two competing mechanisms from NEB calculations: MEP curves for the initiation of 5|7 dislocations dipole (a) and bond rupture (b) under different external forces (indicated by number).

Figure 3.8 Snapshots of the formation of a 5|7 dislocations dipole in the armchair CNT: (a) initial state, (b) transition state, (c) final state.

The trend of the change of activation energy barrier with respect to external force f_p for both transitions are summarized and compared in the Figure 3.9. It is evident that the energy barrier for the nucleation of 5|7 dislocations dipole is significantly lower than those from bond rupture. The energy barrier for 5|7 dislocation nucleation becomes negative when f_p approaches $2.0 \text{ eV/\AA}$, while the activation energy for bond rupture is still insurmountable high under the same pulling force. Therefore, the transition of local CNT structure to 5|7 dislocations will take place first. This suggests that under noncritical tensile stresses, the initiation of 5|7 dipole is thermodynamically favored in a pristine CNT structure in comparison with direct bond dissociation, the latter is only applicable at high strain level.

Figure 3.9 The activation energies for the initiation of 5|7 dislocations dipole and bond rupture under various external forces.

Besides, the length difference of the CNT after the initiation 5|7 dislocations and intact tube are compared with the length change due to bond rupture under different f_p , as shown in Figure 3.9. It is clear that the lengths of CNT after the nucleation of 5|7 dislocations are significantly longer than those from bond dissociation, which implies that more strain energy can be released through the S-W transformation. The nanotube lengths upon bond rupture almost remain unchanged. The strain energy only could be released when f_p approaches 2.0 eV/Å where subsequent bond dissociations take place, leading to a series of shallow energy minima for following bond dissociations in the highly strained nanotube lattice. This is consistent with results from quantum mechanics simulations [210]. Therefore, harnessing lower activation energy and better capacity in releasing strain energy, the initiation of 5|7 dipole should be favored under relative low external stresses from both the thermodynamic and structural relaxation perspective.

Figure 3.10 The change of CNT length between the intact CNT and those after the initiation of 5|7 dislocations dipole and bond rupture under a range of external forces.

3.4.3.2 The second step: diffusion of defect or growing into a crack

After the first transition, a 5|7 dipole is nucleated in the hexagonal network of (8, 8) CNT; the CNT has evolved into a structure shown in Figure 3.11(a). Unlike the initial state of the first step (intact CNT) in which two categories of carbon-carbon bond orientation (either parallel or orthogonal to the tube axis) are involved and only two state-transition possibilities are competing with each other, the possible defect evolution modes of the second step are more subtle, for the presence of a 5|7 dipole not only changed the bond orientation within the defect but also altered the orientation of the surrounding hexagonal lattices. Moreover, the entire failure mechanism largely depends on the structural evolution made in this step. The 5|7 defects could either grow into a larger crack, leading to a brittle failure, or slide away from each other, rearranging the CNTs lattice network through defect diffusion. It should be noted that the term, “crack”, used here refers to the large open carbon rings with size larger than $2a$ ($a = 2.46 \text{ Å}$, is the lattice constant) caused by the local structural transition within CNTs. A crack can be formed from direct

bond dissociations (Figure 3.11 (b-d)). Carbon bonds with three kinds of orientations within the 5|7|7|5 defect local environment are prone to bearing more strain energy under tension: the bond parallel to the tube axis and connects the two pentagon rings (position 1 in Figure 3.11(a), shown in Figure 3.11(b)); the one on the “shoulder” of the 5|7 dislocation (position 2 in Figure 3.11(a), shown in Figure 3.11(c)); and the bond lies on the side of the heptagon and shared by the adjacent hexagonal carbon ring (position 3 in Figure 3.11(a), shown in Figure 3.11(d)). Alternatively, stone-wales transformation of a strictly azimuthal bond (position 4 in Figure 3.11(a), shown in Figure 3.11(e)) can also result in a crack-like octagonal structure between two heptagonal (7|8|7) carbon rings.

Figure 3.11 Different possible structural evolution scenarios of (8, 8) CNT with a pre-existence 5|7 dislocations dipole: (a) the initial state in step 2; (b) rupture of the bond connects the two pentagon; (c) rupture of the bond at the “shoulder” of a 5|7 dislocation core; (d) rupture of the bond shared by the heptagonal and hexagonal carbon rings; (e) S-W transformation of the strictly azimuthal bond; (f) Diffusion of the 5|7 dislocations dipole.

Apart from the formation of a crack, a more interesting structural evolution scenario for releasing strain energy is the defects diffusion, which is a well recognized structural rearrangement mechanism in solid under creep deformation [183, 211]. However, its role in the long-term behavior of CNT under static stress has yet been studied. For each 5|7 defects dipole, there exist six possible directions on three sets of planes for dislocations diffusion. As shown in Figure 3.12(a), b_1 , b_2 , b_3 are the Burgers vectors, $\frac{a}{3}\langle\bar{1}\bar{1}20\rangle$ ($a = 0.246\text{ nm}$, is the lattice constant), in a perfect graphene lattice, each corresponds to a dislocations motion plane. Since the energy barriers for defect diffusion in $b_3\langle002\rangle$ direction are insurmountable high in CNT, here we only consider the situations associated with the defects motion in $b_1\pm(1,0)$ and $b_2\pm(0,1)$ directions in this work (Figure 3.12(b)).

For an Armchair CNT with chiral index of (C_1, C_2) , the dislocations motion in the directions of Burgers vector $\pm(0,1)$ leads to a separation of the 5|7 dislocations dipole by one lattice constant for each step, leaving a trail of recovered hexagonal structure with altered bond orientations and tube chiralities (Figure 3.12(c-f)). The chiral index of the region between the 5|7 dipole has been changed to (C_1, C_2-1) . However, in its counterpart that moves in directions of $\pm(1,0)$, the diffusion will result in a CNT segment with chirality of (C_1-1, C_2) , which is the mirror image of the first scenario (Figure 3.12(b)) if $C_1=C_2$. Due to the symmetric nature of armchair nanotube, these two Burgers vectors are equivalent in the first step of the diffusion process. In this work, the dislocations motion in $\pm(0,1)$ directions was selected, which was introduced by a stone-wales transformation of the bond on the “shoulder” of the 5|7 dislocation (position 5 in Figure 3.11(a), shown in Figure 3.11(f)).

Figure 3.12 (a) A 5|7 dislocations dipole in a graphite sheet. b_1 , b_2 , b_3 are the three Burgers vectors, corresponding to the three sets of possible dislocations diffusion planes. a_1 and a_2 are the basis vectors. (b) The 5|7 dislocations can slide away from each other in two distinct directions. (c→d) Schematics of the initiation of a 5|7 dislocations dipole in (8, 8) CNT. (d→e) the second S-W transformation separates the two 5|7 dislocations by one hexagonal lattice. (e→f) a subsequent rotation separates them by two hexagonal rings with altered chirality of (8, 7).

MD simulations and NEB calculations were performed for all the scenarios discussed above and their activation energies at different loading levels were collected from NEB curves and are summarized in Figure 3.13. In the cases in which bond rupture occurs, the dissociation of the bonds shared by the heptagonal and hexagonal rings (position 3) requires the lowest activation energy and is prone to rupture. In contrast, the bond dissociation at position 1 is highly unfavorable under low tensile forces, indicating that although the bond connect the two pentagon is geometrically parallel to the loading direction and is highly strained, it is quite stable under tension and only would rupture when the pulling force is close to the critical value. The reason lies in the two heptagons at either side of this bond, which are more flexible than the pentagonal and original hexagonal carbon rings and

reduce the strain energy concentrated on the bond at position 1. This agrees well with results from molecular mechanics calculations [77]. However, in that work, the author only considered the possibility of bond ruptures. From Figure 3.12, it is evident that the activation energy barriers for the two structural evolution routes in which S-W transformations take place are substantially lower and should be energetically favored.

Figure 3.13 Activation energy versus external pulling force for the different structural evolution scenarios considered in this section.

Interesting results are seen in the change of the activation energy for the two different sites of S-W transformation (position 4 and 5). While the activation energies for both S-W transformations drop rapidly and significantly faster than those for bond dissociations, the decrease rates are different, leading to bifurcation states of the CNT fracture. It is seen that the activation energy for defects diffusion is lower under relatively low external forces, and the separation of 5|7 dislocations is favored in such conditions. However, since the activation energy decreasing rate with respect to the external force for the formation of 7|8|7 crack is higher than that of 5|7 dislocations diffusion, the appearance of a 7|8|7 crack is preferred as f_p increases. A critical value of 1.6 eV/Å (corresponding to a stress of 42.2 GPa

according to Equation) has been identified, which represents the bifurcation point for the different state transitions, when f_p bellows $1.6 \text{ eV/\AA}$, dislocations diffusion dominates the failure mechanism, giving rise to a series of plastic flow (details will be discussed later). In contrast, if f_p exceeds this value, the 5|7 dislocations dipole will grow into a crack contains 7|8|7 carbon rings, which will subsequently evolve into a 7|8|8|7 crack due to another S-W transformation of the azimuthal bond, and form a series of 7|8|...|8|7 cracks around the circumference of CNT. This elevates the strain concentration on the bond shared by the two octagons, resulting in a large opening crack and a brittle fracture of the entire structure.

The elongations of the CNT upon these transitions in comparison with the initial states (the structure shown in Figure 3.11(a)) were calculated to evaluated the structural relaxation effects. The results are compared in Figure 3.14, from which we can find that among the three bond rupture scenarios, the bond dissociation at position 3 can most effectively relax the structure and reduce the strain energy. It also should be noted that the bond dissociation at position 1 leads to a shorter nanotube at low external loadings, implying that this bond is under compression stress initially, thus is very stable, which is in good agreement with its activation energy profile. The comparison between the two S-W transformations shows that the formation of 7|8|7 can release more strain energy through structure relaxation, and the difference becomes apparent when the force gets increasingly larger. This is attributed to the two vertical bonds formed in the octagonal structure, which facilitate the increase of tube length, resulting in a more relaxed structure compared with the structure results from 5|7 dislocations diffusion. The later increases the length of CNT by $\Delta L = (a^2/2\pi d)\sin(2\alpha)$ (a is the lattice constant, d is the tube diameter, and α is the 5|7 dislocation orientation angle) upon each diffusion step .

Figure 3.14 The change of CNT length between the CNT in its initial state of step 2 (Figure 3.10(a)) and those after the different transitions under a range of external forces.

3.4.3.3 A series of plastic flow

The results from last section indicate that the dislocations diffusion directs the structural evolution route of armchair CNT under relatively low stress levels (<42.2 GPa). The initiation of the first gilding step between the 5|7 dislocations will invoke a series of subsequent gilding steps, making the two 5|7 dislocation cores move away from each other and leaving the region in between with altered chirality.

The separating dislocation cores need to travel through 15 lattice units to finish one helix circle on the curved surface of a (8, 8) CNT. In the lateral dimension, the two 5|7 dislocation cores first glide away from each other; and after being separated by 7 pairs of hexagonal rings, they are located at two opposite sides of the CNT, as shown in Figure 3.15(c), and further movement will put them to the same side again when one cycle of diffusion ends (Figure 3.15(d))

Figure 3.15 The diffusion process of a pair of 5|7 dislocations dipole: (a) the initial state before diffusion; (b) the dislocations has been separated by 1 lattice unit; (c) the dislocations has traveled through 7 lattice units and are located in two opposite sides of CNT; (d) finish one helix circle of diffusion.

The step-by-step activation energies for a complete helix circle of 5|7 dislocations diffusion (an entire cycle on the helical gliding path) were calculated under different external pulling forces. The results are shown in Figure 3.16(a). First, it is evident that the external loads drastically reduce the activation energies required for the motion of 5|7 dislocations. The activation energies are already close to zero when a relatively low pulling force of $0.8 \text{ eV/\AA}$ is applied, which is corresponding to a stress of 18 GPa in the intact CNT structure. The trivial activation energy needed suggests the dislocations diffusion can be easily activated either under a moderate level of external stress or at an elevated temperature. Second, the dislocations migration energy barriers also see a rapid decrease as the two 5|7 dislocation cores glide away from each other in the initial few steps, indicating there exists an attractive mechanical restraint between the two dislocation cores when they are close to each other. Besides, the energy barriers saturate after the dislocations cores are separated by 8 pairs of hexagonal rings, and remains stable after the following diffusion steps, implying that the indifferent length of this attractive effect between dislocation cores is around $8 \cdot a$ (a is the lattice constant, 0.246 nm) in the defects

diffusion direction b_2 , which is 1.97 nm. This value agrees well with a previous work on the defects interactions of CNT, in which using molecular mechanics method, the authors found the indifferent distances between 5|7 defects in an armchair CNT are within the range between 1.2 nm and 2.3 nm [76]. However, our results also show that as the 5|7 dislocation cores continue their movements and get spatially closer when they are located in the same side of the CNT after traveling through one helix circle, there is no apparent increase in the energy barrier, which indicates that it is not the spatial distance between dislocation cores that matters but the distance in the circle helix way around the cylindrical surface of CNT.

The activation energy landscape as a function of both separation coordinates and external forces are also constructed and displayed in a 3D graph as shown in Figure 3.16(b). It is clear that the energy barriers for dislocations diffusion in most of cases are negative or under 1 eV, which is accessible by thermal motion of atoms under room temperature. Once the diffusion of defects is initiated, it will continue until the dislocations meet the tube boundaries or are hindered by other dislocation cores. The relatively high energy barrier in the first few steps under low external stresses (<20 GPa) can be overcome at an exceedingly long time or if an elevated temperature facilitates the transitions according to the transition state theory, which will be introduced in the next Chapter. Besides, these activation energies are still significantly lower than those from forming a crack in the CNT.

Figure 3.16 (a) Activation energy upon each diffusion step in the (8, 8) CNT under different external pulling forces. (b) Activation energy landscape for the dislocations diffusion process as a function of both separation coordinate and external pulling force.

3.4.3.4 Further structural evolution in the asymmetric CNT after plastic flow

The plastic flow introduced through the diffusion of 5|7 dislocations rearranges the atomic configuration within the carbon nanotube. As shown in Figure 3.17(a), the chirality of the region between the two dislocation cores has changed to (8, 7) according to the diffusion direction (Burgers vector (0, 1)) with a stepwise reduction in diameter, resulting in a (8, 8)|(8, 7)|(8, 8) hetero-junction. This phenomenon can also be interpreted as mechanical necking when materials are subject to external tensile stress. The necking of CNT elongates its length in the axial direction via reducing its diameter in the lateral dimensions, effectively releasing the strain energy. However, it also leads to an asymmetric structure: the indentation caused by CNT necking only appears in one side of the CNT (the side where the dislocations are located), such that there exists difference of mechanical tension between the side that is close to the preexisting dislocations and the opposite one. Thus, it is in our interests to find out which is favored for the nucleation of next defect or bond rupture.

In Figure 3.17 (c) and (d), cracks of two-lattice length caused by bond rupture have been embedded into the CNT structures in the same and opposite side of the preexisting 5|7 dislocation cores, respectively. Besides, CNT models contain a new nucleation of 5|7 dislocations in both sides of the asymmetric structure have also been constructed (Figure (e) and (g)). Their activation energies under a range of external pulling force up to 1.6 eV/Å are summarized and presented in Figure 3.18, from which we can see that the energy barriers for bond rupture remain high and no significant difference is seen in these two cases considered, indicating the occurrence of bond rupture has no preference between the two sides in the asymmetric structure. A closer inspection at these two curves show that as the pulling force increases, the activation energy for bond rupture in the indented side is lower, for this side is more mechanically strained under tension, and prone to bond rupture.

Figure 3.17 Different possible structural evolution routes of (8, 8) CNT after a series of plastic flow. The initial state: side view (a) and top view (b); the bond rupture occurs in the opposite side (c) and same side (d) of the preexisting dislocations; the nucleation of a second pair of 5|7 dislocations in the opposite side ((e) side view, (f) top view), and same side ((g) side view, (h) top view) of the preexisting dislocations.

Figure 3.18 Activation energy versus external pulling force for the different structural evolution routes after a series of plastic flow.

Although the bond rupture does not have preference on the side within the necking region, the energy barriers for the initiation of a second 5|7 dislocations dipole in the same side of the preexisting ones are apparently lower than the energy needed for nucleation on the opposite position. This implies that a new initiation of 5|7 dislocations dipole tends to occur in a place that is spatially closer to the preexisting ones. The nature of this preference lies in the interaction between dislocations on a cylindrical CNT surface. The linear defects motion route in a flat graphene (dashed line in Figure 3.19) needs to be transferred to a helical pathway on the convex surface of CNT. Thus, the interaction of dislocations within CNT should be affected by the distance between the dislocations in the circle helix dimension rather than the spatial distance. In figure 3.19, it is manifest that the two defects nucleation sites are subjected to different mechanical restraints from the preexisting 5|7 dislocation cores. The initiation of the 5|7 dislocations in the opposite side (indicated by red color in Figure 3.19) is situated right on the dislocations diffusion plane of the preexisting defects. Sharing the same gliding pathway, the dislocations initiated on the opposite are actually closer to the

preexisting ones in a helix measure, and experience stronger mechanical restraints from the preexisting dislocations. In contrast, although the blue dislocations dipole is spatially closer to the preexisting defects, it is far away from its defects diffusing plane, thus, is subject to lower constraints and requires less activation energy to complete the transition.

Figure 3.19 A schematic illustration of the cylindrical CNT surface on a flat plane, showing the positions of 5|7 dislocations dipoles (in real case, AB is connected with A'B', rolling up to form a CNT). The preexisting separated 5|7 dislocations are displayed in green color, while the red 5|7 dipole is initiated on the opposite of the preexisting dislocations, the blue 5|7 dipole is nucleated on the same side, spatially closes to the preexisting dislocations. Red dotted lines denote the dislocations diffusion routes in the direction of Burgers vector b_2 .

To sum up, our analysis shows that after the plastic flow, the initiation of a second 5|7 dipole within the necking region in the side spatially close to the preexisting dislocations, which is the site away from the gliding plane of the preexisting defects, and is energetically favored in comparison with bond ruptures and nucleation of a pair of 5|7 dislocations on the opposite side. Thus, after the nucleation, a new cycle of dislocations diffusion of the second 5|7 dipole could be triggered, such that in order to complete our failure mechanism for armchair CNT,

only one last question left: where is this change of tube chirality caused by defects diffusion towards?

3.4.3.5 Retain an armchair type or slide towards a zigzag nanotube

The diffusion of the first dislocations dipole not only causes the asymmetric necking of CNT, but also leads to a segment between the separated dislocation cores of an altered chirality with asymmetric structure. The newly initiated 5|7 dislocations discussed in last section is located within this region (Figure 3.20(a)). Different from the CNT structure analyzed in step 2 (section 3.4.3.2), in which the 5|7 dislocations are geometrically symmetric about the tube axis and the diffusions in directions of Burgers vector b_1 and b_2 lead to equivalent chiralities of (7, 8) and (8, 7), respectively, which are mirror images of each other, in the current asymmetric CNT structure (chiral index: (8, 7)), defects motion in b_1 (1, 0) and b_2 (0, 1) directions will result in two distinct CNT structures. While an armchair CNT configuration will be retained if the defects glide away from each other in direction b_1 (1, 0), giving rise to a (7, 7) region in the nanotube; the CNT chirality will slide towards a zigzag type if the second dislocation cores continue their motion in the direction b_2 (0, 1), that is, the same direction that the preexisting dipole follows, leading to a CNT segment with chiral index of (8, 6). A 3D model that illustrates the two directions for dislocations diffusion is shown in Figure 3.21. The separated 5|7 dislocation cores glide away from each other following two potential circle helix pathways on the CNT surface.

Figure 3.20 Different possible structural evolution routes of (8, 8) CNT after the initiation of a second pair of 5|7 dislocations: (a) The initial state; (b) bond rupture of the bond shared by heptagonal and hexagonal rings; (c) the formation of a 7|8|7 crack; (d) dislocations diffusion in b_1 direction; (e) dislocations diffusion in b_2 direction.

Figure 3.21 3D images showing the two possible dislocations diffusion pathways in circle helix form on the cylindrical surface of CNT: (a) diffusion in Burgers vector b_2 ; (b) diffusion in Burgers vector b_1 .

CNT models contains the second 5|7 dislocations dipole glides away from each other in both $b_1 (1, 0)$ and $b_2 (0, 1)$ directions have been constructed, and are shown in Figure 3.20 (d) and (e), respectively. It is clear that the regions between the separating 5|7 dislocation cores have different chiralities. An armchair configuration emerges if the dislocations move in b_1 direction (labeled with 3 in Figure 3.20); and the chirality is changing towards a zigzag type in another case (labeled with 4 in Figure 3.20). Moreover, CNT structures contains a subsequent bond rupture of the bond shared by heptagonal and hexagonal carbon rings (Figure 3.20(b)) and a formation of 7|8|7 crack (Figure 3.20(c)) have also been considered for comparison.

Figure 3.22 Activation energy versus external pulling force for the different structural evolution routes after the nucleation of a second pair of 5|7 dislocations.

The activation energies for the different transitions discussed above are shown in Figure 3.22. The bond rupture still requires high activation energy and is not feasible under these relatively low external forces. In addition, the energies needed to form a 7|8|7 crack ring are also higher than those from defects diffusions, indicating the CNT will go through another round of plastic flow. Even when the

pulling force increases to the critical value of $1.6 \text{ eV/\AA}$, the defects diffusion is still favored. It suggests that the strain releasing effect from forming a $7|8|7$ crack is weakened in the tilted CNT structure. Comparing the activation energy for diffusion at Burgers vectors b_1 and b_2 , it is apparent that the diffusive motion in b_2 direction entails less activation energy. Thus, instead of retaining an armchair configuration, the CNT segment between the separating dislocations will evolve to a region with chiral index of $(8, 6)$, which will be followed by $(8, 5)$, $(8, 4)$ *etc.*, towards a zigzag configuration. This transformation can be understood in a geometric way. Note that in considering two pristine hexagonal carbon rings in armchair and zigzag formations, the one with the zigzag orientation has longer distance in its axial direction and the armchair tube, however, is longer in the lateral dimension. Under tensile stress, the atoms within the armchair tube are driven by an axial pulling force, gradually transferring to a more axial direction orientated structure through dislocations diffusion. During this process, the bonds that previously form a 30° angle with the tube axis in the original armchair configuration progressively rearrange their orientation, becoming parallel to the tube axis, which increases the intrinsic tube length, thus, facilitates the release of strain energy.

The structural relaxation effects of different state transitions were also analyzed and the elongation of the CNT are summarized in Figure 3.23. It is seen that the CNT upon dislocations diffusion in the b_2 direction has the longest tube length compared with those of other transitions. The differences between the elongations caused by diffusion in b_1 and b_2 directions are attributed to the different bonds orientation with in the region between the two dislocation cores. A $(8, 6)$ CNT segment resulted from diffusion in b_2 direction is more axial orientated than a $(7, 7)$ segment, possessing better structural relaxation effect and releasing more tensile stress. Also noteworthy is, previously, the forming of $7|8|7$ cracking ring could achieve the best structural relaxation effect, as discussed in step 2, however, in an asymmetric CNT structure, this is impeded by the tilted atomistic arrangement. Therefore, the plastic deformation caused by $5|7$ dislocations motion dominates the failure mechanism under the critical external force of $1.6 \text{ eV/\AA}$ until final rupture.

Figure 3.23 The change of CNT length between the CNT in its initial state after the initiation of a second pair of 5|7 dislocations (Figure 3.20(a)) and those after the different transitions considered in this section under a range of external forces.

3.4.4 The whole picture

The activation energy and mechanical relaxation effect of different state transitions applicable to CNT structure under various constant tensile stresses have been systemically evaluated. While the fracture route is relatively straightforward for zigzag tubes with only bonds ruptures take place in their highly axial orientated structure, the fracture mechanism of armchair CNTs is much more complicated. It involves the nucleation of 5|7 dislocations dipole, initiation of crack through either bond dissociation or further S-W transformation in the existing defects, and the diffusion of 5|7 dislocation cores, which not only releases the strain energy but also changes the chirality of CNTs within the region between the two separated dislocation cores.

Our calculations indicate that the nucleation of 5|7 dislocations dipole in an intact armchair CNT under noncritical stress entails lower energy barrier than that of

bond rupture, thus, is thermodynamically favored. It also has better structural relaxation effect. After the nucleation of a 5|7 dislocations dipole in the CNT structure, two different fracture routes could be taken, which one is favored depends on the external stress applied. If the stress is above a critical value of 42.2 GPa, a 7|8|7 crack could be formed by a S-W transformation of the azimuthal bond in the 5|7 dislocations dipole, followed by forming a chain of 7|8|...|8|7 cracks and a brittle fracture afterward. Alternatively, a series of plastic flow caused by 5|7 dislocations diffusion in either b_1 or b_2 direction dominates the failure mechanism if the stress is below 42.2 GPa, leading to a necking effect and the chirality change within the region between the separated 5|7 dislocation cores. NEB calculations show that the activation energy required for this process is accessible by thermal motion under moderate levels of external stress at room temperature. Thereafter, a site within the necking region and is spatially close to the preexisting dislocations is prone to the nucleation of another pair of 5|7 dislocations, which is followed by another round of defects diffusion. During this process, the second set of dislocations tend to follow the same diffusive direction the first pair of dislocations takes, thus the CNT abandons its original armchair configuration, gradually rearranging itself towards the zigzag configuration. The external stress applied in the axial direction is the driving force behind this transformation. After n th round of 5|7 defects nucleation and diffusion, the CNT would have a chiral index of $(8, 8-n)$ with elongated length but reduced diameter in the necking region.

The snapshots of the hetero-junction region of CNT after different cycles of 5|7 dislocations initiation and diffusion are shown in Figure 3.24. It is clear that the diameter of CNT between the dislocation cores shrinks as more defects are initiated and glide away from each other. Considering the total atom mass is conserved in this process, there is also a significant elongation effect in the axial direction of the CNT structure, facilitating the release of tensile stress. Besides, within the necking area, the carbon-carbon bonds that form a 30° angle with the tube axis in the intact nanotube progressively turn parallel to the axial direction (indicated by arrows in Figure 3.23), providing additional structural relaxation effect.

Figure 3.24 Snapshots of CNT structures after the initiation of different number of 5|7 dislocations dipoles. The necking region is highlighted in the structures with their respective chiral index labeled. The arrows indicate the direction of the bonds that form 30° angle with the tube axis in the intact structure.

The activation energy landscape for the nucleation of 5|7 dislocations at different stages are shown in Figure 3.25, in which we see an apparent reduction of the energy barrier for the initiation of a 5|7 dislocations dipole as the progress of CNT necking. This suggests that the 5|7 defects can be more easily initiated in a CNT with high surface curvature. The convex surface of CNT admixes a small amount of delocalized sp^3 bonding to the in plane sp^2 bonds, known as sp^2 - sp^3 re-hybridization, which weakens the strength of the original sp^2 - σ bonds. This effect is found to be proportional to the local curvature [212]. Therefore, in a CNT with high-curvature surface, that is to say, smaller diameter, it would require less energy to dissociate the carbon-carbon bonds during the S-W transformations. It also can be deduced

that following this tendency, the initiation of a 5|7 dislocations dipole in a planar graphene should require the highest activation energy.

The external load also plays an important role in the initiation of 5|7 dislocations. As the driving force, it provides an external aid for the transition, in addition to the effect from internal thermal motion. The higher the external force, the lower the energy barrier. We have identified that an external per atom pulling force of 2.0 eV/Å (56 GPa) is needed for a barrier-free nucleation of 5|7 dipole in the intact CNT structure. This threshold drops as the decrease of the activation energy needed for the 5|7 defects initiation. After the nucleation of 7th pair of 5|7 defects, the activation energy becomes negligible (<0.5 eV) (considering thermal motion of atoms) even under a low f_p of 0.2 eV/Å (4 GPa), which indicates the CNT structure is already very unstable and the subsequent failure is instantaneous. This can be understood in terms of the stress concentration in the necking region. The local stress in this area becomes increasingly large as the necking process continues, and fracture takes place once the local stress within the necking segment of the hetero-junction structure reaches its critical value (the blank in the surface indicates tube failure occurs).

Also noteworthy is through exploring the failure mechanism of armchair CNT, we have actually been through the examination of fracture routes for CNTs with a variety of chiral angles from 30° of (8, 8) to 5° of (8, 1). Therefore, the failure mechanisms identified here not only applicable to the armchair CNTs, but also cover the fracture patterns for CNTs with other chiral indexes. A flow chart that demonstrates the complete failure mechanisms of a (8, 8) CNT under noncritical stresses is given in Figure 3.26.

Figure 3.25 Activation energy landscape for the initiation of 5|7 dislocations dipole in a (8, 8) CNT as a function of both number of dislocations dipole nucleated and external pulling force (blank denotes the CNT has already ruptured).

Figure 3.26 Flow chart of the complete failure mechanisms of a (8, 8) armchair CNT under noncritical stresses.

3.5 Summary

In this chapter, we presented the results of a series of atomistic MD and NEB simulations that explore the different structural configurations, activation energy landscape, and mechanical relaxation effect of CNT under a spectrum of noncritical tensile stresses at intra-molecular level. MD simulations were performed to apply prescribed external forces to the CNT structures; minimization methods were employed to probe the energy minima states applicable to transitions; and NEB calculations were carried out to find the minimum energy path between energy minima and to calculate the energy barrier.

The competition between different potential failure routes involved in the CNT fracture, such as 5|7 dislocations nucleation and diffusion and crack propagation through bond dissociation, have been quantitatively evaluated under different levels of external stress. Our results show that after the nucleation of a pair of 5|7 dislocations in the armchair CNT structure, there exist bifurcation states in CNT fracture: brittle failure caused by the growth of cracks dominates the fracture mechanism if external stress is over 42.2 GPa; otherwise, plastic deformation due to dislocations diffusion takes place. Moreover, the details of the dislocations diffusion process have been systematically studied, in which the CNT gradually elongates its length in the axial direction via reducing the diameter in the lateral dimensions, leading to the necking of CNT and a hetero-junction structure contains CNT segment with altered chirality until the eventual fracture.

In the following chapter, using the CNT evolution structures obtained here, the strain rate during this slow dynamic process will be studied. The results obtained will be described by phenomenological viscoelastic model.

Chapter 4 Calculations of Strain Rate of Long-timescale Atomistic Structural Evolution of Carbon Nanotubes

In this chapter, a computational scheme for calculating the strain rate of slow dynamic process of CNTs creep is presented. We first introduce the background of this study. Thereafter, empirical function from kinetic fracture theory is adopted to calculate the time needed for each discrete transition along the structural evolution route determined in the last chapter. The time obtained is subsequently connected to the respective strain of those individual CNT metastable-state geometries at constant external stress, such that, the time-dependent behaviors of CNTs creep can be obtained. The results are further analyzed using phenomenological viscoelastic model and are compared with experimental results.

4.1 Background

In the last chapter, using molecular dynamics (MD) and nudged elastic band (NEB) methods, we coarse-grain the energy landscape of carbon nanotube (CNT) out to discrete energy minima and transition states. While we abandon directly probing the microstructural transformations in MD, we direct the computer simulations specifically at searching for possible state transitions in order to reveal the failure mechanisms of CNTs creep. And the structural evolution routes under different noncritical external stresses have been obtained. However, in order to fulfill the requirements of mechanical design in engineering, the determination of the failure mechanisms is only the beginning [213]. Different from in a tensile test, the plastic deformation of materials under a constant load is time-dependent, which implies that the strain rate is an unknown value that traditionally needs to be evaluated from experimental creep tests, which, however, is impractical for an object so small as CNT.

As CNTs are of great interests for applications as loading-bearing materials for its remarkable mechanical properties, it is not enough to only consider the tensile strength (will they break under certain amount of stress?) but also should take into account the creep behavior (how long can they stay functional?), since experimental evidence indicates the fracture of CNTs also takes place at low stress levels after a relatively long period of time [214]. To answer this question, it is essential to know the strain rate during this slow dynamic process, that is, how long will it take to finish each transition that have been identified in the last chapter along the structural evolution route? However, creep is a long-timescale phenomenon, during which the atomistic structural evolution takes a prolonged time to finish. It is also well known that simulation techniques that are able to track the dynamical behavior with explicit atomistic details are restricted to their microscopic time scales. Thus, an alternative approach is needed to connect the structural evolution with the time required for each transition.

4.2 Kinetic fracture theory

Materials fracture can be seen as the result of accumulation of defects nucleation/diffusion and bond breakage, which causes the loss of the stability of materials until the eventual breakdown. While an increasingly larger external force provides the energy needed for such events in a tensile test; the structural evolution is controlled by thermally activated atomic motion in materials creep. In classical continuum mechanics, such as Griffith-type methods [179, 215], the materials are treated as uniform objects, which fail to consider the microscopic inhomogeneous nature of the structures of interest in our nanoscale CNTs network. However, kinetic fracture theory, in which the atomic bonds are viewed as coupled oscillators in a state of constant thermal vibration, explicitly includes the effect of inhomogeneous distribution of the external load among atomic bond in a microscopic way. The phenomenological model of kinetic fracture theory was first

proposed by Kramers in 1940 [216]. It is assumed that the rate of a thermal activated escape in a diffusive process, ν , takes an Arrhenius form,

$$\nu = \nu_0 \exp(-U_0 / k_B T) \quad (4.1)$$

in which ν_0 is called Kramers attempt frequency, which is associated to the atomic thermal motion and is given by $\nu_0 = k_B T / h$ (k_B is Boltzmann's constant, T is temperature, and h is Plank constant); U_0 is the intrinsic energy barrier for the transition, which is usually significant larger than the thermal activation energy $k_B T$ in a slow dynamic process. This equation has been extensively used in the studies of fracture of solids [217] and rupture of bimolecular adhesion bonds [218]. It is found that if an external stress σ applied, the energy barrier ΔU is reduced proportionally to the external field, as

$$U(\sigma) = U_0 - \gamma^\ddagger \sigma \quad (4.2)$$

where $\gamma^\ddagger$ is the activation volume whose dimension is of the order of the bond length. This linear relation was first proposed by Tobolsky and Eyring in their study of the mechanical properties of polymers [219], which was later extended to different kinds of solid material by Zhurkov [220]. Combing Equation 4.1 and 4.2 and taking its inverse expression, the lifetime of an atomic bond, τ , under external stress can be written as,

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma^\ddagger \sigma}{k_B T}\right) \quad (4.3)$$

in which $\tau_0 = 1/\nu_0$ is the time interval for each escape attempt. We rewrite the above equation as,

$$\tau = \tau_0 \exp\left(\frac{U_0 - x^\ddagger f}{k_B T}\right) = \tau_0 \exp\left(\frac{U_0(1 - f/f_c)}{k_B T}\right) \quad (4.4)$$

where, $x^\ddagger = \gamma^\ddagger / A$ (A is the atomic area) denotes the distance between the bound and transition state, and $f_c = U_0 / x^\ddagger$ is the critical external force, where the energy barrier to escape vanishes, as shown in Figure 4.1. From Equation 4.4, we can find that in kinetic fracture theory, chemical bonds break according to thermal fluctuation of atoms, and the possibility of this process strongly depends on the external load, which lowers the intrinsic energy barrier and excites the bond being ruptured (Figure 4.1). And this decrease of the energy barrier also associates with the activation volume, which takes into account the microscopic structural effect: the overstress on a specific area compared to the average value.

Figure 4.1 Conceptual illustration of the bond binding energy landscape being biased when subjected to an external load. The energy barrier has been lowered with the distance between the minimum and saddle point decreased. For a given load, the probability of finding the atom in dissociated states at time t can be described as a function of f in a diffusive process.

Two kinds of transitions are involved in the fracture mechanisms of CNT as discussed in the last chapter; one is the S-W transformation, the other the direct bond rupture. According to Equation 4.4, the calculation of time required for bond rupture in CNT is straightforward, which is simply,

$$\tau = \frac{\tau_0}{n_{site}} \exp\left(\frac{\Delta U(f)}{k_B T}\right) = \frac{\tau_0}{n_{site}} \exp\left(\frac{U_0(1-f/f_c)}{k_B T}\right) \quad (4.5)$$

where n_{site} is the number of site available for transitions (taken as the number of non-boundary atoms in the intact CNT, and the number of equivalent sites for transition in the following CNT geometries). The problem lies in the incorporation of the S-W transformation into the computational framework of kinetic fracture theory. Using NEB calculations, we identified the excited state during S-W transformation in section 3.4.2.1. It involves the simultaneous breakage of two neighboring bonds of the one that rotates 90° to become parallel to the tube axis. To solve for the time needed for such transitions, we assume a situation in which the applied external force rises from zero to a constant value f^* in a time span t . During this process, a cumulative probability of bond dissociation, P , can be expressed by the integral of Equation 4.5,

$$P = v_0 n_{site} \int_0^{f^*} \dot{f}^{-1} \exp\left(\frac{-\Delta U(f)}{k_B T}\right) df = v_0 n_{site} t \frac{k_B T}{\Delta U(f^*)} \exp\left(\frac{-\Delta U(f^*)}{k_B T}\right) \quad (4.6)$$

The probability function in Equation 4.6 indicates that the bond rupture is kinetically favorable (P approaches 100%) at large t , or under high temperature, or the f^* is close to the critical bond-breaking load f_c . Thus, the probability of two neighboring bonds dissociate altogether to reach the transition state in a S-W transformation is given by,

$$P_{sw} = P \cdot C_{n_{site}}^1 \cdot P = n_{site} \left[v_0 t \frac{k_B T}{\Delta U(f^*)} \exp\left(\frac{-\Delta U(f^*)}{k_B T}\right) \right]^2 \quad (4.7)$$

in which $C_{n_{site}}^1$ limits the second site for bond dissociation to the neighboring position. As the time needed for each transition is inversely proportional to its probability, the time for S-W transformation, τ_{sw} , reads as $\tau_{sw} = (P / P_{sw})\tau$. Note that comparing Equation 4.6 and 4.7, one may find that in kinetic fracture theory, the S-W transformation is a more rare event than bond rupture, which seems in conflict with the results obtained in the last chapter. This is because in diffusion-based kinetic theory, the bond dissociation is a reversible process when the formation energy E_f is positive (energy of the final state is higher than that of the initial state), which only becomes irreversible when $E_f < 0$ [71]. And the formation energy for S-W transformation is far below that of bond rupture as the increase of external force, thus it is still kinetically favorable. This also implies that the reach of excitation state is not necessarily leading to the final state during a reversible diffusion process. Therefore, our approach for calculating the time of each transition is an underestimation of its true lifetime, which is, however, viable in engineering design.

4.3 Simulation methods

For the sake of consistency, the same zigzag (14, 0) and armchair (8, 8) CNT models as discussed in the last chapter are used here. Therefore, for these CNT structures at a specific temperature, one needs to know the intrinsic bond dissociation energy U_0 , the force applied on the local atom f at certain amount of external stress, and the critical bond-breaking force f_c to solve for the time of each transition according to Equation 4.5. Among these parameters, U_0 is a constant for each CNT chirality. The reason it differs by CNT chirality is that except the bond stretching, there also exists a significant structural tightening effect in CNTs when subject to tensile stress, the latter largely depends on the chirality of CNT, for example, the armchair CNTs are able to accommodate more strain energy through structural tightening than zigzag tubes of the same diameter as aforementioned in chapter 3. Consider CNTs with all kinds of chirality have the same sp^2 - σ carbon-carbon bond in their structural network. The energy needed for dissociating a bond

in the armchair configurations should be higher than that of their zigzag counterparts.

Different from U_0 , which is a constant throughout the structural evolution process, f and f_c reflect the change of the overstress within the crack propagation area. As illustrated in Figure 4.1, the bonding energy landscape is tilted by the external local load f with energy barrier reduced and distance between the bound and transition state decreased. It indicates that both f and f_c change according to the microscopic structural evolution along the route towards eventual failure. And the ratio between f and f_c is the modulating factor of the energy barrier for each transition. The higher the ratio, the faster the transition takes place.

In this work, MD simulations were conducted to solve for f and f_c for a series of successive structures based on the CNTs fracture mechanism identified in the last chapter at a number of noncritical external stress. For the (14, 0) zigzag CNT, a crack propagation process of up to eight bonds have been ruptured around the circumference of CNT was studied, as shown in Figure 4.2. And the local strain of the crack-front carbon-carbon bond was monitored. For the (8, 8) armchair CNT, nanotube structures of the nucleation and diffusion of the first five 5|7 dislocations dipoles have been extracted from the structure evolution route. In both cases, the strain energies of the atoms that are about to reach their transition state were calculated and recorded for further analysis.

Figure 4.2 Crack initiation and propagation in a (14, 0) zigzag CNT. i denotes the number of carbon-carbon bonds that have been ruptured within the crack.

Using the same stretching scheme discussed in Section 3.4.1, we applied an extreme strain rate to the CNT structures in order to compensate, in a brute-force fashion, for the MD's intrinsic inability to investigate long-term problems. That is, the energy barrier of the creep deformation that results in the slow dynamics is overcome by the extreme strain rate applied in the simulations ($1 \times 10^8 \text{ s}^{-1}$). However, this approach leads to a problem that since it has been previously reported that the energy needed for bond dissociation in CNT has a logarithmic dependence on the strain rate [221], the bond dissociation energy determined in a high strain rate simulation is an overestimation of the real energy needed in a slow dynamic process. To address this issue, the Equation 4.3 is rewritten as,

$$\tau(\epsilon, T) = \tau_0(T) \exp\left(\frac{U_0 - \gamma^\ddagger k\epsilon}{k_B T}\right) \quad (4.8)$$

in which k is elastic constant and ε is local strain. Therefore, the strain rate needed for bond dissociation at a given strain is,

$$\dot{\varepsilon} = \dot{\varepsilon}_0(T) \exp\left(-\frac{U_0 - \gamma^\ddagger k \varepsilon}{k_B T}\right) \quad (4.9)$$

where $\dot{\varepsilon}$ and $\dot{\varepsilon}_0$ are applied strain rate and intrinsic vibration strain rate, respectively. Thus, rearranging Equation 4.9, we obtain the bond-breaking strain as,

$$\varepsilon_f(T, \dot{\varepsilon}, \dot{\varepsilon}_0(T)) = \frac{U_0}{\gamma^\ddagger k} + \frac{k_B T}{\gamma^\ddagger k} \ln \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0(T)} \quad (4.10)$$

From Equation 4.10, we find that the strain applied for bond-breaking depends on two external factors: the strain rate and temperature, such that the bond dissociation at lower strain rates and low temperatures can be simulated at faster strain rates with the kinetic energy compensation from high temperatures. The two are able to yield equivalent failure strain for carbon-carbon bond, and the energy barrier needs in a slow dynamic process can be obtained from high strain-rate MD simulations according to,

$$\varepsilon_f(T_{sd}, \dot{\varepsilon}_{sd}, \dot{\varepsilon}_0(T_{sd})) = \varepsilon_f(T_{md}, \dot{\varepsilon}_{md}, \dot{\varepsilon}_0(T_{md})) \quad (4.11)$$

where the former part stands for the failure strain of slow dynamic process, and the latter represents that of MD simulations. It is known that the strain rate in our MD simulation is $1 \times 10^8 \text{ s}^{-1}$. Consider the creep of CNT at room temperature of 298 K and an exceedingly slow strain rate of 0.01 yr^{-1} , ensuring that the energy barriers are not being overestimated. Substituting these values into Equation 4.11 and using recursive method, we obtain the temperature, T_{md} , required in our MD simulations as 1228 K.

4.4 Results and discussion

4.4.1 Solve for the time needed for each transition

Curves about the strain energy of the atom that is about to be exited to transition state versus its local tensile strain for a series of successive CNT structures along the structural evolution route are obtained from MD simulations and shown in Figure 4.3. From the curves for intact zigzag and armchair nanotubes, the inflection points and their respective strain energy are identified, which correspond to the intrinsic bond dissociation energy U_0 ($U_0=1.18$ eV for (14, 0) CNT and 1.48 eV for (8, 8) CNT). The U_0 obtained here for the zigzag CNT can be compared to the value adopted in Ref [77, 87], in which examining the yield point on the potential energy profile of carbon-carbon interaction, they calculated an intrinsic energy barrier for bond dissociation as 1.14 eV. The consistency between this value and the U_0 we obtained for zigzag CNT indicates the elongation in zigzag CNT are largely caused by the stretching of carbon-carbon bonds, with minimum structure tightening effect involved. However, the U_0 for the CNT of armchair configuration is significantly higher than that of zigzag, which implies the armchair CNT structure could absorb more strain energy through structure tightening. Besides, while the inflection strain decreases as the evolution of CNT structure for both of the CNTs, the reduction is more significant in the zigzag tube, indicating the existence of a crack due to bond dissociation will cause much more damage on the integrity and stability of CNT structure than the initiation and diffusion of 5|7 defects.

Figure 4.3 Strain energy of the atom subjected to transition versus axial tensile strain: (a) curves for (14, 0) zigzag CNT, the number of broken carbon-carbon bonds is denoted by parameter i ; (b) symbols are simulation results of the intact (14, 0) CNT and after the dissociation of the first bond, the colored lines are the regression curves given by Equation 4.12; (c) curves for (8, 8) armchair CNT, the structures are extracted from the fracture route determined in Chapter 3; (d) symbols are simulation results of the intact (8, 8) CNT and after the initiation of first 5|7 dislocations dipole, the colored lines are the regression curves given by Equation 4.12.

Based on the curves displayed in Figure 4.3 (a) and (c), for each CNT geometry, the strain energy, E , can be well fitted into a two-parameter cubic function as (typical regression curves are shown in Figure 4.3 (b) and (d)) [222],

$$E(\epsilon) = a\epsilon^2 + b\epsilon^3 \quad (4.12)$$

where a and b are in energy unit (eV), which characterize the degree of the stress concentration from the local structural effect as a result of an existing flaw in the CNTs structures. The values of parameters a and b , and the R^2 of the regression curves for the different structures of (14, 0) and (8, 8) CNTs are tabulated in Table 4.1 and 4.2, respectively. The high R^2 indicates the good agreement between the simulation results and fitted curves.

Table 4.1 Values of coefficient a and b for (14, 0) zigzag CNT, both are in eV unit. R^2 indicates the goodness of the fitted curve.

Coefficient	Intact	$i = 1$	$i = 2$	$i = 3$	$i = 4$
a	56.9	28.1	29.6	28.5	25.3
b	-149.6	-51.8	-82.1	-75.7	-52.5
R^2	0.999	0.997	0.997	0.997	0.998
Coefficient	$i = 5$	$i = 6$	$i = 7$	$i = 8$	
a	30.4	29.4	24.1	19.7	
b	-138.5	-162.5	-107.2	-78.2	
R^2	0.997	0.997	0.997	0.992	

Table 4.2 Values of coefficient a and b for (8, 8) armchair CNT, both are in eV unit. R^2 indicates the goodness of the fitted curve.

Coefficient	Intact	1 st 5 7 initiation	1 st 5 7 diffusion	2 nd 5 7 initiation	2 nd 5 7 diffusion	3 rd 5 7 initiation
a	26.8	23.7	23.0	21.9	24.7	24.6
b	-44.2	-34.5	-37.3	-28.6	-40.3	-42.5
R^2	0.999	0.998	0.999	0.997	0.997	0.998
Coefficient	3 rd 5 7 diffusion	4 th 5 7 initiation	4 th 5 7 diffusion	5 th 5 7 initiation	5 th 5 7 diffusion	
a	23.0	21.3	21.8	27.8	23.5	
b	-36.0	-37.5	-41.2	-97.2	-85.4	

R^2	0.999	0.999	0.997	0.998	0.997
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Therefore, the pulling force applied on the atom is given by the first-order derivative of the strain energy with respect to the bond elongation ΔL_b as:

$$f(\varepsilon) = \frac{\partial E}{\partial \Delta L_b} = \frac{\partial E}{x_0 \partial \varepsilon} = x_0^{-1}(2a\varepsilon + 3b\varepsilon^2) \quad (4.13)$$

where x_0 represents the bond length in its equilibrium state. And the bond-breaking critical force f_c reads as:

$$f_c = x_0^{-1}(2a\varepsilon_f + 3b\varepsilon_f^2) \quad (4.14)$$

in which ε_f is the bond rupture strain determined from the inflection point in the curves shown in Figure 4.3 (a) and (c). Substituting Equation 4.13 and 4.14 into Equation 4.5, the lifetime of each structural configuration along the structural evolution route can be calculated. And the evolution time needed for the transformation from geometry m to n is simply,

$$T_{mn} = \sum_{i=m}^n \tau_i = \sum_{i=m}^n \frac{\tau_0}{n_{site}} \exp\left(\frac{U_0(1 - f_i / f_c^i)}{k_B T}\right) \quad (4.15)$$

where i represents the geometry of CNT after i -1th transition and $m = 0$ denotes the accumulation of time starts with CNT in its intact form. However, in order to find the strain rate under a constant external stress, we are still short of one parameter, the strain of the whole CNT for different geometries.

4.4.2 Determine the stress-strain relationship for each geometry

To connect the lifetime of each transition with its corresponding strain with respect to the intact tube length, MD simulations with constant pulling force applied on the end atoms of CNTs were carried out for each CNT configurations of both chiralities. The stress-strain relationship is extracted from simulation results and

shown in Figure 4.4. It is seen that the strain grows linearly as the increase of external stress at these relatively low stress levels for almost all the CNT geometries. In the graph of zigzag case, we can find a clear increase of the slope in the stress-strain relationship as the growth of the number of broken carbon-carbon bond within the crack, which implies the decrease of the Young's modulus due to the crack propagation. It is also seen that the appearance of yield points (marked by circle in Figure 4.4a) in the stress-strain curves even under these relatively low stresses after four carbon-carbon bonds have broken. And both of the stress and strain of the yield point decrease as the propagation of crack continues, indicating the nanotube structure is already fragile. Also noteworthy is there is only slight difference in the strain when a small external stress (<5 GPa) applied in the zigzag tube, suggesting that in the absence of an external stress, the increase of intrinsic tube length is trivial after the broken of carbon-carbon bond, indicates that the bond rupture has limited effect in terms of the structural relaxation. Thus, the increasingly larger difference in the strain at the later stage when the stress becomes higher is largely attributed to the elongation of the crack-front bonds, which makes stress heavily concentrate on these bonds, and they are prone to rupture.

In contrast, no yield points are spotted on the stress-strain curves for all of the armchair CNT geometries, indicating that the nucleation and diffusion of 5|7 defects could better preserve the mechanical properties of CNT than the initiation of crack. which is also supported by the fact that there is no apparent increase in the slope of these stress-strain curves as the evolution of CNT structure. And the Young's modulus of CNT after the transitions remains the same until the necking effect becomes manifest after the diffusion of 4th 5|7 dislocations dipole. It corresponds to a (8, 8)|(8, 4)|(8, 8) hetero-junction structure within the CNT. This result suggests that unlike the zigzag CNT, which will go through significant stiffness degradation before rupture, the stiffness of armchair CNT barely decreased during the necking process until final failure. This is because the intrinsic hexagonal carbon lattice structure has been mostly retained in the diffusion of 5|7 dislocations in armchair

CNT. In addition, the stepwise increase of the strain between curves in Figure 4.4b shows that the intrinsic tube length has been significantly increased after the diffusion of 5|7 dislocations, which effectively relaxes CNT structure and releases the tensile stress.

All the stress-strain relationship are fitted into a linear function as,

$$\sigma = E_i \varepsilon_i + \varepsilon_0^i \quad (4.16)$$

where E_i represents the Young's modulus of i th geometry and ε_0^i is the intrinsic strain in the absence of external loads due to the structural relaxation effect after the i th transition.

Figure 4.4 Stress versus strain for a series of successive geometries along the structural evolution route of CNT: (a) the curves of (14, 0) zigzag CNT, i denotes the number of broken carbon-carbon bond, and circles mark the yield points; (b) the curves of (8, 8) armchair CNT.

4.4.3 Time-strain relationship

Combining Equation 4.15 and 4.16 and given a noncritical constant external stress, we are finally able to determine the strain rate for CNTs creep. The time-strain curves for (14, 0) and (8, 8) CNTs under an external tensile stress of 10 GPa are shown in Figure 4.5 (a) and (c), respectively. For the zigzag CNT, its time-strain relationship that can be subdivided into two stages exhibits typical characteristics of the brittle fracture of materials. The (14, 0) CNT spends almost all of its lifetime in the first stage, where the crack slowly grows from one ruptured carbon-carbon bond to a relatively large open ring that consists of four dissociated bonding interactions. At the same time, since no nucleation and diffusion of defects are involved in the failure mechanism of zigzag CNT, the increase of strain is largely due to the growth of crack caused by the concentration of strain energy. As a result of this insight, only slight increase in the strain is seen within this stage, indicating the stress has not been released through structural relaxation but has concentrated on the crack front areas, which leads to the quickly propagation of the increasingly large crack and the eventual fracture of CNT in a very short period of time in the second stage.

This result also suggests that the brittle failure of materials deduced in kinetic fracture model can also be interpreted as the crack propagation process described in the Griffith fracture theory. The latter states that the crack propagation in brittle materials is governed by the relationship between the release of strain energy due to the growth of crack and the free energy penalty of a newly created surface [179]. Therefore, the actual tensile strength of a brittle material largely depends on the size of the flaws nucleated in the material, rather than the intrinsic strength of its atomic bonds. In zigzag CNT, the length of crack increases by one lattice spacing (0.246 nm) upon each step of bond dissociation. And the crack propagation involves a series of such discrete process at the crack tip. It is seen in Figure 4.5 (a) that the dissociations of the first three carbon-carbon bonds in the initial stage after the initiation of a crack require an exceedingly long period of time. This is caused by the

corrugation of energy landscape due to the discreteness of the crystal lattice in CNT structure, known as 'lattice trapping' [210]. Therefore, the transition from one metastable state to the next along the crack propagation route needs to overcome the lattice trapping barrier through thermal or mechanical activation. And in our creep test, a long period of time is necessary. However, in the second stage, only minimum time for thermal activation is required for the crack propagation, which reflects as an abrupt increase in the strain in a very short period. It implies that the net change in the total energy of the CNT system vanishes upon the dissociation of fourth carbon-carbon bond at an external stress of 10 GPa, which corresponds to a critical Griffith crack length of five lattice spacing (1.23 nm) in the CNT surface. After this point, the CNT structure becomes very fragile and the crack quickly evolves until the final fracture.

We now turn our attention to the time-strain relationship of (8, 8) armchair CNT. Based on the time-strain behavior shown in Figure 4.5 (b), the strain rate curve can be divided into three regimes. After the initial instantaneous strain caused by the elastic deformation, the CNT undergoes a period of relatively steady increase of strain in Stage *I* that persists for a substantial portion of the CNT's lifetime, which corresponds to the initiation and diffusion of 1st 5|7 dislocations dipole in the CNT structure. After the initiation of 2nd pair of 5|7 dislocations, the creep response of CNT reflects characteristic of a strain softening process in Stage *II*. The increase of strain starts to accelerate, leading to a fast rising strain levels. And this strain softening effect continues in the tertiary stage until the final failure occurs. This increase of strain rate is attributed to the necking effect caused by the diffusion of 5|7 defects. Stress concentrates on the necking region for its reduced diameter, and energy barrier for the nucleation and diffusion of new 5|7 dislocations dipole becomes shallow. This effect becomes more evident in the tertiary stage after the initiation of 4th pair of 5|7 defects with only minimum thermal activation is needed to finish the following transitions. This is consistent with the previous analysis of the stress-strain behavior of (8, 8) CNT geometries. The Young's modulus of the CNT also starts to drop after the nucleation of 4th 5|7 dislocations dipole.

Figure 4.5 Time-strain curves of CNTs under an external constant stress of 10 GPa: (a) (14, 0) zigzag CNT; (b) (8, 8) armchair CNT.

If we look the whole picture of the time-strain curve of (8, 8) CNT, it can be taken as a continuous strain softening process, which is different from the creep behavior of traditional materials, like metals. In the creep of metallic materials, there exists a transient regime in the initial stage where the strain rate decreases (strain hardening) due to the rise of overall resistance to dislocations motion caused by

structural restraints, such as grain boundary. However, in single-molecule materials, like individual CNTs, there are no such restriction factors. Our simulation results in the last chapter show that the diffusion of 5|7 dislocations can proceed to the ends of a flawless CNT, and the energy barrier for diffusion decreases as they glides away from each other. Therefore, the increasingly lower energy barrier for defects nucleation and diffusion leads to the increase of strain rate observed in Figure 4.5(b).

Comparing the time-strain curves of zigzag and armchair CNTs, we can find the impact of the two different failure mechanisms on their time-dependent behavior. While the strain almost remains unchanged until the abrupt brittle rupture in the zigzag tube, substantial increase of the strain, which is due to the plastic deformation as a result of nucleation and diffusion of defects, can be seen throughout the time-strain curves of the armchair CNT. The lifetime of each configuration drops rapidly in the zigzag tube along the structural evolution route, and the CNT can hardly bear the stress after the broken of 4th carbon-carbon bond; in contrast, the mechanical properties of armchair CNT have been mostly preserved in the process of nucleation and diffusion of defects, and the (8, 8) CNT structure is only prone to rupture after the necking effect becomes manifest when the necking region has evolved into a (8, 4) segment. The outcome of this difference is although both of the CNTs can last an exceedingly long period of time at an external stress of 10 GPa (years at least), the lifetime of armchair CNT is five times longer than its zigzag counterpart (as shown in Table 4.3), thus the CNTs with armchair configuration possess better resistance to creep deformation.

Moreover, the influences from different levels of external stress on the time-dependent behavior of CNTs of both chiralities have also been studied (Figure 4.6). It is evident that the strain rate has been significantly accelerated due to the increase of external load, giving rise to a substantially shorter lifetime that the CNTs can last. When an elevated external stress applied, it greatly increases the degree of strain energy concentration on the defects or crack tip, reducing the distance

between metastable and transition state, such that the time required for thermal activation is reduced. Comparing Figure 4.6 (a) and (b), we can also see that the zigzag tube is more sensitive to the change of external stress, which is due to the crack front bonds are fully exposed to the increased stress, bearing more strain energy. As a result, the critical crack length required for an instantaneous fracture is also smaller than that needed at 10 GPa. However, in the armchair configuration, the integrity of CNT structure is better preserved in the nucleation and diffusion of defects. Therefore, these CNTs are able to survive a much longer time than the zigzag ones at elevated stress levels. Our calculations suggest that the ratio between the lifetime of (8, 8) and (14, 0) CNTs has increased from 5.24 at 10 GPa to a value of 54.75 at 20 GPa, as listed in Table 4.3.

Table 4.3 Lifetime of (14, 0) and (8, 8) CNTs at constant external stress

CNT	Lifetime (s)		
	10 GPa	20 GPa	30 GPa
(14, 0)	6.08×10^7	1.94×10^4	-
(8, 8)	3.19×10^8	1.06×10^6	3.54×10^3
(8, 8):(14, 0)	5.24	54.75	-

Figure 4.6 Time-strain relationship of CNTs under different external stresses: (a) (14, 0) zigzag CNT; (b) (8, 8) armchair CNT.

4.4.4 Fit to phenomenological viscoelastic model

The time-dependent mechanical response of materials has for many years been described by a number of mechanical models, which consist of different combinations of Hookean spring and Newtonian dashpot [223, 224]. These models

provide a useful physical picture of viscoelastic behavior. The spring component (Figure 4.7(a)) is intended to describe linear elastic response, its stress is given by $\sigma_s = k\epsilon$, where k is the spring constant with units of Pa. Therefore, the resulting strains are instantaneous and not a function of time. In contrast, the dashpot (Figure 4.7(b)) denotes viscous flow, in which stress is written as $\sigma_d = \eta \dot{\epsilon}$, where η is the viscosity in units of Pa-s and $\dot{\epsilon}$ is strain rate, such that the dashpot represents the time-dependent deformation. It is infinite rigid when $t = 0$, and with time, the viscous behavior becomes evident as strains develop that are linearly proportional to time.

Figure 4.7 Mechanical analogs modeling the time-dependent deformation process in solids: (a) elastic spring; (b) viscous dashpot; (c) Maxwell model for viscoelastic flow; (d) stress-strain-time diagram for Maxwell model.

In this work, since the CNTs of both chiralities spend most of their lifetime in the primary regime (Stage I) where the relationship between strain and time is linear with no transient behavior observed, we employ the Maxwell model to characterize the viscoelasticity of CNTS. It is simply a spring and a dashpot connected in series, as shown in Figure 4.7(c). Therefore, the stress on each component is the same and

equal to the external stress, while the resulting strain is the sum of the strain in each unit:

$$\sigma = \sigma_s = \sigma_d \quad (4.17)$$

$$\varepsilon = \varepsilon_s + \varepsilon_d \quad (4.18)$$

In order to seek a single equation connecting the stress to the strain, it is convenient to differentiate Equation 4.18 with respect to time,

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_s}{dt} + \frac{d\varepsilon_d}{dt} = \frac{1}{k} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (4.19)$$

And for a creep test under constant stress of σ_0 , the strain as a function of time is given by a linear function as,

$$\varepsilon = \frac{\sigma_0}{k} + \frac{\sigma_0}{\eta} t \quad (4.20)$$

The strain experienced by the Maxwell model is depicted in Figure 4.7(d). Note that in this viscoelastic model, elastic strains can be recovered, but the viscous strains arising from the creep process remain even after the stress is removed, which is a measure of the plastic deformation. Thus, in the time-dependent behavior of CNTs, the spring could be visualized as the elastic or energetic component (bond stretching, bond angle changing) of the overall response, while the dashpot represents the conformational or entropic (bond dissociation or nucleation and diffusion of defects) component.

Figure 4.8 Time-strain relationship of CNTs at external stress of 10 GPa fitted with Maxwell viscoelastic model: (a) (14, 0) zigzag CNT; (b) (8, 8) armchair CNT.

As shown in Figure 4.8, the time-strain relationship of the first stage can be well fitted into Equation 4.20 for (14, 0) and (8, 8) CNTs, indicating the creep behavior of CNTs can be well described by Maxwell model. The values of k and η for both CNTs at different external stress are tabulated in Table 4.4. Comparing the k values of zigzag and armchair CNTs, one can find that the zigzag tube is more rigid with slightly higher spring constant, which is in agreement with our tensile test results reported in Chapter 3. What is surprising is the viscosity of (14, 0) CNT is also higher than that of its armchair counterpart at a relatively low external stress of 10 GPa. This can be attributed to the fact that only the simulation results within the primary stage of the time-strain curve are used to fit against the Maxwell model and the zigzag CNT only experiences trivial deformation within this stage, which results in a very flat regression line and an extraordinary high viscosity value. However, this high resistance to deformation in the primary stage of zigzag CNT is obtained at the sacrifice of its structural stability through bond dissociation, which vanishes once the split reaches the critical Griffith crack length. The uncertainty of this resistance also reflects from the fact that the viscosity of zigzag tube already drops well below that of armchair CNT when the external stress is increased to 20 GPa. Besides, we also see a stress stiffening effect in the zigzag tube with increased spring constant at stress of 20 GPa than that obtained from 10 GPa, for the elevated stress

reduces the critical crack length needed for instantaneous fracture, making the CNT more rigid and undergo less deformation before rupture. In contrast, there exists a strain softening effect in armchair CNT with decreased value of k as the increase of external load. This is caused by the nucleation and diffusion of defects entail less activation energy at an elevated loading level, which facilitate the deformation of CNT.

Table 4.4 Viscoelastic parameters of Maxwell model of (14, 0) and (8, 8) CNTs. All values for k and η are in units of GPa and GPa-s, respectively.

CNT	10 GPa		20 GPa		30 GPa	
	k	η	k	η	k	η
(14, 0)	463.91	9.00×10^{11}	489.25	2.47×10^8	-	-
(8, 8)	452.02	1.07×10^{11}	451.49	8.83×10^8	416.19	5.19×10^6

4.4.5 Compare with experimental results

Since direct manipulation of individual CNT is already extremely challenging, not to mention the difficulties of conducting long-term creep test for these nanoscale materials, we chose to measure the time-dependent behavior of CNT bundles that consist of closely packed CNTs linearly aligned in their axial directions. This kind of CNT assembly should well reflect the mechanical properties of its individual components under tension.

CNT ropes comprised by SWCNTs with diameter around 1 nm (same as the diameter of CNTs constructed in the simulations) were adopted to prepare the bundle samples [225, 226]. CNT bundles were carefully separated from as-synthesized CNT ropes; each is about 1.5 mm in length and 1-10 μ m in diameter. Creep tests were carried out at room temperature on a micro-mechanical testing device developed in our lab. A constant load was applied to the CNT bundles and the deformations were monitored and recorded in real time. The details of the

testing device specifications and experimental process can be found in Ref. [227] and [228].

In order to compare the results from simulations and experiments, some adjustments have to be made, since the length scale of the CNTs used in simulations is much smaller than those tested in experiments. Both of the (14, 0) and (8, 8) CNTs are around 100 nm in length, which is 1.5×10^4 times shorter than the CNT bundle. Therefore, the number of available sites for transition in the CNT bundle should also be 1.5×10^4 times higher than the original scaling factor n_{site} used in Equation 4.5 to calculate the lifetime of each configuration. Applying the new scaling factor, we can obtain an estimation of the time-strain relationship for a 1.5 mm long CNT.

In Figure 4.9, the time-dependent behaviors of CNT between scaled simulation results and experimental data at a constant external stress of 10 GPa are compared. While the time-dependent behavior predicted from simulations of zigzag CNT is in good agreements with that of experiment, the lifetime of the armchair CNT is still exceedingly long, which goes beyond the scope of the graph. Moreover, one striking finding in the experimental time-strain curve is, unlike the results from simulations, the CNT bundle went through a period of transient response (highlighted in Figure 4.9) in the initial stage, where the strain rate decreases with time to a minimum steady-state value that lasts for the rest of the materials life. The reason behind this phenomenon could be attributed to the individual CNTs that comprise the CNT bundle are not perfectly aligned and are twisted or entangled to each other [229]. When external force applied, the CNTs first rearrange their conformation through tube-tube sliding, and as the increase of strain, the bundle is highly tightened and this inter-tubular motion becomes difficult and is restricted by the mechanical interlocking of the entangled CNTs structure, giving rise to the decrease of strain rate in the transient stage. However, with time, the brittle zigzag and other high chiral angle CNTs will break first, which breaks the balance between the inter-tubular motion and mechanical interlocking in the steady stage. Even though the

CNTs with armchair configuration still survive at this time, the broken CNTs will cause the collapse of the interlocked CNTs structure within the bundle, reactivating the sliding at the CNT-CNT interface, which leads to the final dissociation of the entire CNT bundle. Therefore, the time-dependent behavior of CNT bundle is resulted from the combined effects of inter-tubular frictional sliding and brittle rupture of zigzag CNTs and CNTs with high chiral angles.

Figure 4.9 Comparison of the time-strain curves between scaled simulation results and experimental data of CNT bundle at an external stress of 10 GPa. The transient stage in the experimental data has been highlighted. The arrow besides the simulation result of (8, 8) CNT indicates the CNT still survives.

4.5 Summary

We have presented an attempt to incorporate results from molecular dynamics simulations into empirical functions from kinetic fracture theory in the study of the creep deformation of CNTs with explicit atomistic details, motivated by the desire to investigate the time-dependent slow dynamic process using atomistic simulation

methods. A complete simulation procedure for calculating the strain rate of CNTs creep is illustrated in Figure 4.10. It is compiled from all the efforts have been made in Chapter 3 and 4. Through this computational workflow, time-strain relationships of both a zigzag and an armchair CNTs have been obtained under a number of constant external stresses. The results show that CNTs possess remarkable resistance to creep deformation, the flawless CNT structures can last for years at a stress of 10 GPa. Besides, this time-dependent behavior of CNTs strongly depends on their chirality. Simulation results indicate that CNTs of armchair configuration can last much longer than the zigzag nanotubes. And this discrepancy becomes more evident at an elevated external stress.

Figure 4.10 A diagram showing the complete computational process of time-strain relationship of CNTs.

Moreover, the time-strain relationships of CNTs have also been characterized by Maxwell viscoelastic model. The viscoelastic parameters derived from the

phenomenological model can serve as a benchmark for the engineering design of using CNTs as long-term structural and mechanical applications. In the end, the simulation results are compared with experimental data of the creep response of CNT bundle. A creep failure mechanism of the CNT bundle has been proposed. We find that the combined effects of brittle-type fracture of CNTs and the inter-tubular frictional sliding lead to the eventual dissociation of the CNT bundle under creep, in which the latter plays an important part in the overall viscoelastic behavior exhibited by the CNT bundle. In the next chapter, we will focus on this important intermolecular interaction between individual CNTs when they are closely packed in assembled forms, seeking a way to quantitatively characterize this frictional energy at the CNT-CNT interface.

Chapter 5 Estimation of Friction Energy within a Bundle of Single-Walled Carbon Nanotubes[†]

Carbon nanotubes often self assemble into bundles, arrays, and other forms, which are easier to produce and manipulate than individual CNTs. Inter-tubular frictional sliding is inevitable if an external load is applied to such CNT assembly systems. As discussed in last chapter, this frictional effect empower CNT bundle with its unique viscoelastic behavior under creep deformation, which is different from that of individual CNTs. In addition, it has been previously reported that the addition of dense-packing carbon nanotubes into polymers can significantly increase the damping ratio (loss factor) of the materials, producing composites with strong viscoelastic response [118, 120, 230]. The inter-tubular sliding is also considered to be responsible for this increase. In this chapter, normalized friction energy between single-walled carbon nanotubes (SWCNTs) has been experimentally determined from tensile testing of SWCNT bundles using a straightforward calculation scheme. The result is further verified by molecular simulations.

5.1 Background

It is known that single-walled carbon nanotubes (SWCNTs) may appear in closely packed stacking, forming self-assembled bundles [231], among other forms. Long and aligned bundles of SWCNTs can now be synthesized and used as components in many applications, including the fabrication of CNT-polymer composites [232]. To study the mechanical behaviors of CNT bundles, concepts for analyzing other types of twisted wires and fibers have been adopted [233]. A recent effort by Xiao *et al* modeled the force-strain behavior of a bundle of SWCNTs with no friction among them [227]. Apparently, the friction between SWCNTs or within a CNT bundle is

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difficult to measure directly through experiment. It has been previously reported that the friction between adjacent graphene layers in a multi-walled carbon nanotube was estimated to be 9 nN [234], and inter-tubular friction force within a CNT bundle was measured to be 1.4×10^{-4} N by field induced displacement [235]. However, a normalized, quantitative parameter independent of contact area, which can be used to estimate friction force between CNTs when they are closely packed together, remains unknown. In order to quantitatively characterize the energy dissipated in the system in terms of frictional sliding under mechanical load, it is essential to get a fundamental understanding on how these nanotubes interact with each other during inter-tubular motion, since the contribution from the interfacial force could be significant for long CNTs have high aspect ratio. In this study, we propose a straightforward computational scheme based on experimental data, with which friction among CNTs within a bundle can be determined.

5.2 Friction Energy Evaluation Methods

Consider a CNT bundle with a large number of CNTs under uniaxial loading with applied strain, ε . The total input energy dissipated in the bundle, U_t , is the sum of elastic energy under stretching, U_e , and frictional energy, U_f , due to inter-tube sliding,

$$U_t = U_e + U_f = \left(\frac{1}{2} \varepsilon^2 E \right) V + \gamma \Delta A \quad (5.1)$$

where E is the elastic modulus of the CNT bundle (treated as a constant when the strain is less than 2%) [236], V is the volume of CNTs within the bundle, and ΔA is the change of contact area between CNTs during sliding. The coefficient γ (unit in Nm^{-1} or Jm^{-2}) is the liner shear stress, representing the cohesive energy from interfacial frictional force of CNTs. U_t , the total input energy, is the area under a force-elongation curve of a tensile test, and U_e can be determined by knowing ε , E , and V . Subsequently, U_f and therefore γ , can be evaluated.

Figure 5.1 A mounted SWCNT bundle, in which the upper end is attached to the lead rod and the lower end is fixed on the surface of a rigid stage, is subjected to tensile loading: (a) before breaking, (b) moments after broken into two parts.

Bundles of straight, aligned SWCNTs about 3 mm long, carefully separated from SWCNT ropes synthesized by catalytic decomposition of hydrocarbons, were prepared for tensile testing using a micromechanical tester reported in the last chapter [214, 227]. Each SWCNT bundle was mounted vertically between a rigid stage and a replaceable lead rod that is firmly attached to a force transducer, using epoxy adhesive. The strain rate was controlled at 0.001 s^{-1} . Displacement, force, as well as images of a SWCNT bundle were recorded simultaneously during loading. No slipping of SWCNT bundle from the mounting ends was observed from the video images recorded. A total of 8 SWCNT bundles were successfully tested and results analyzed. All these samples failed in the region between the two mounting ends, typical images of a SWCNT bundle before and after tensile testing are shown in Figure 5.1.

Figure 5.2 An applied force versus elongation curve obtained from the uniaxial tensile test on SWCNT bundle, which is sample E shown in Table 5.1. Inset is the linear fit of force to strain while strain is below 2%, which gives the slope.

In order to solve for γ , the effective cross-sectional area, A , of a SWCNT bundle can be calculated through the stress-strain relation $F/A = E\epsilon$, where F is the applied force. The product of A and E can be obtained from the slope of the linear fit to the force-strain curve (the initial, nonlinear portion is excluded from the analysis) of each bundle when the applied strain is below 2%, as shown in the inset of Figure 5.2. As mentioned earlier, E is regarded as a constant (1.23 TPa), taken from a work by Salvétat *et al.* [15], therefore the value of A can be obtained. The effective areas calculated are in good agreement with images of SWCNTs from scanning electron microscopy (SEM). The volume of SWCNTs within a bundle can be obtained by multiplying the effective area by its length. Assuming that all SWCNTs in the bundles are aligned armchair nanotubes (10, 10), with a diameter, d , of 1.36 nm, the total number of SWCNTs in the bundle, N , can be calculated by dividing the effective area of the bundle by the area of an individual SWCNT, $\pi t d$, where $t = 0.34$ nm, is the wall thickness of a SWCNT. Thus, U_i can be rewritten as,

$$U_t = \left(\frac{1}{2} \varepsilon^2 E \right) Al + \gamma N \Delta l \pi d \quad (5.2)$$

Since the change of contact area between SWCNTs is $N \times \Delta l \pi d$, it follows that γ can be expressed as

$$\gamma = \frac{U_{total} - \left(\frac{1}{2} \varepsilon^2 E \right) Al}{N \varepsilon l \pi d} \quad (5.3)$$

5.3 Results and Discussion

5.3.1 Frictional energy deduced from experiments

The total energy is calculated by integrating the force-elongation curve within 1% applied strain in order to avoid the influence from failed SWCNTs during the tensile test. Thus, ε is set at 0.01 in above equation. Results for 8 samples are listed in Table 5.1.

It is seen from Table 5.1 that the γ obtained are quite consistent, nearly all of the values are of the same order of magnitude, with a mean of 0.22 Nm^{-1} . The 95% confidence interval for γ is $(0.15, 0.28) \text{ Nm}^{-1}$ from Student's t -test. This experimentally obtained value is comparable to the inter-layer cohesive energy of graphene (0.16 Nm^{-1}) [237], and a more recently calculated value of the binding energy for graphite (0.25 Nm^{-1}) [238]. The upper limit of γ obtained in present study is larger than the value of graphite may be attributed partially to the fact that SWCNTs in the bundles could be inter-twisted [239], which increases the normal force between SWCNTs under tensile stress.

Table 5.1 List of the SWCNT Bundles measured under uniaxial tensile test.

Sample	Area (m^2)	Elastic Energy (J)	Total Energy (J)	γ (Nm^{-1})
A	1.67×10^{-11}	2.14×10^{-6}	3.78×10^{-6}	2.89×10^{-1}
B	7.64×10^{-11}	1.99×10^{-5}	3.41×10^{-5}	2.71×10^{-1}
C	1.17×10^{-10}	2.29×10^{-5}	3.70×10^{-5}	2.33×10^{-1}
D	6.70×10^{-11}	1.49×10^{-5}	2.21×10^{-5}	1.84×10^{-1}
E ^a	3.49×10^{-11}	7.11×10^{-6}	9.04×10^{-6}	1.03×10^{-1}
F	3.46×10^{-11}	5.01×10^{-6}	9.02×10^{-6}	3.04×10^{-1}
G	6.88×10^{-11}	1.54×10^{-5}	2.00×10^{-5}	1.11×10^{-1}
H	8.45×10^{-11}	1.30×10^{-5}	2.16×10^{-5}	2.5×10^{-1}

As a comparison, the frictional energy at the later stage during a tensile test is also studied. As shown in Figure 5.2, a plateau region, highlighted in the force-elongation curve between two arrows, is selected (data in inverted triangle). Within this portion of the curve, essentially, only inter-tubular sliding occurs, since there is no significant change in applied force. Worth noticing are several kinks, big and small, appear throughout the curve until failure. These kinks or load drops is interpreted as failures of sub-bundles of SWCNTs, since the as-prepared SWCNT bundles consist primarily of many sub-bundles with diameter of ~ 40 nm. Assuming all of the SWCNTs within the bundle have the same elastic modulus, the amount of SWCNTs survived after a load drop is proportional to the ratio of the applied forces before and after the drop occurs. Thus the amount of intact, load-bearing SWCNTs at the starting point of the plateau can be calculated. By calculating the cumulative number of force-drop ratios, 61% SWCNTs survived at the beginning of the plateau region. This implies that the cross sectional area of the bundle at that point has decreased to 0.614. Using 0.614, we obtain $\gamma = 0.59 \text{ Nm}^{-1}$. This value is very close to the number obtained by Yu *et al* [61], which is more than twice compared to those shown in Table 5.1. The discrepancy could be explained by the edge effect, arising from the interactions of the dangling broken Carbon-Carbon bond on the edge of fractured SWCNTs cylinder. Since almost half of the SWCNTs have already been

broken at this stage, the edge effect cannot be neglected. Therefore, it is believed that the value determined here is an overestimation of the friction energy within SWCNT bundle. It should be pointed out that several assumptions are being made in carrying out the calculations that might influence the results obtained. However, independent measurements of some of the parameters (such as the effective area) are not possible. The method described here offers an indirect way of estimating the inter-tubular friction, represents initial effort to elucidate the friction energy within SWCNT bundle.

5.3.2 Molecular simulations

The experimental results of frictional energy are verified by molecular mechanics simulations. Molecular models of two SWCNT bundles, one with 7 individual tubes and the other with 19, were constructed. These tubes are of armchair configuration and are arranged in hexagonal arrays. SWCNTs of two different sizes (diameter 6.9 and 13.6 Å, length 37 Å) were used to examine size effect.

To determine the frictional energy, a nanotube or a bundle of nanotubes is pulled out from the host array and the frictional energy is obtained by dividing the total energy of pullout by the surface area of contact of the pulled-out tube (or bundle). For the 7-SWCNT bundle, a single tube at the center of the array was pulled out while for the 19-SWCNT bundle, 6 core SWCNTs were pulled out. The contact area for the single tube is $2\pi rL$, where r and L are the radius and the length of the SWCNT, respectively; the contact area of the 6 core SWCNTs is estimated as $2\pi RL$ for simplicity, where $2R$ is taken as the edge-to-edge diagonal of the 6-SWCNT hexagonal arrays.

Figure 5.3 Energy curves of a 7-SWCNT hexagonal arrays with varying center-to-center distance between the center SWCNT and the rest in the bundle.

In our simulations the inter-tubular distance (or the center-to-center distance) in the SWCNT arrays were varied. In Figure 5.3, the energy for a 7-SWCNT array (diameter 13.6 Å) is illustrated, with varying center-to-center distance. The difference between the energy curve of the “pulled-out state”, where a tube has already been pulled out from the bundle, and that of the “bundle state”, where all of the tubes are organized in hexagonal array, is the energy required for pullout, denoted W . The frictional energy per unit area, γ , is simply $W/2\pi rL$. For each case, γ is determined based on the maximum energy difference, and the results are summarized in Table 5.2. The frictional energies, γ , obtained from molecular mechanics simulations, ranged from 0.18 to 0.28 Nm^{-1} , are in very good agreement with the average value from the experiments, which is 0.22 Nm^{-1} .

Table 5.2 Results of Molecular Mechanics Simulation.

Case	No. of SWCNTs in array	SWCNT Diameter (Å)	No. of SWCNTs Pulled Out	Frictional Energy, (Nm ⁻¹)
1	7	6.9	1	2.8×10 ⁻¹
2	19	6.9	6	2.3×10 ⁻¹
3	7	13.6	1	2.1×10 ⁻¹
4	19	13.6	6	1.8×10 ⁻¹

It is seen from Figure 5.3 that friction energy decreases with an increase and decrease in inter-tubular spacing, away from the lowest energy position of the “bundle State”. It can thus be inferred that some of the low γ values obtained from experiments could be attributed to larger inter-tubular spacing. The kink of on the energy curve of the “bundle state” correspond to collapse of the center tube from circular shape under reduced inter-tubular spacing, which might occur under high lateral pressure. In addition, it is seen from Table 5.2 that there is a size effect: the bigger the tube, the lower the friction energy. Also, a bundle tends to have lower frictional energy than a single tube.

5.4 Summary

In sum, we have established a straightforward calculation scheme to determine the friction energy due to tube-tube sliding through uniaxial tensile test. Normalized friction shear stress has been derived from experimental data, with an average value at 0.22 Nm⁻¹.

This result is further verified by molecular mechanics simulation of single nanotube or a bundle of nanotubes pulled out from a nanotube bundle. This numerical value offers an important parameter for quantitative analysis of the significant increase in the viscoelastic response of dense-packing CNT assemblies.

Moreover, it is also useful in the design and development of CNT-based nanomechanical or nanoelectromechanical systems.

Chapter 6 Structure of Carbon Nanotube and Graphene Oxide Hybrids and its Role in Dispersion of Carbon Nanotubes[§]

A comprehensive molecular dynamics study on the intermolecular interactions between CNTs and graphene oxide (GO) is presented in this chapter. We start with probing the structural conformation of CNT-GO hybrid self-assembly, in which the variations of potential energy of both molecules are studied in details and, along with analysis of the impact from the chirality and size effects on the binding energy. Next, using thermodynamics integration method, the nature of the interaction between CNT and GO in aqueous solution is dissected; the binding free energy is calculated. The chapter ends with an experimental study that applies our simulation findings in development of a novel CNT-GO/polymer ternary composite.

6.1 Background

In the last chapter, the interaction between individual CNTs in bundle state has been determined from both experimental and theoretical studies. The normalized interfacial frictional shear stress obtained is quite high and can be compared to the inter-layer binding energy within graphite. This strong inter-tubular interaction combined with the natural tendency in reducing the surface energy result in the facts that CNTs tend to appear in aggregated forms and it is very difficult to disperse them. In addition, the hydrophobic nature of the pristine CNTs makes them prone to forming aggregations in the solution even after being fully dispersed through mechanical dispersion methods, like ultra-sonication, which is an important procedure in the preparation of composites consisted of CNTs and water-soluble polymers [11].

Lack of methods and techniques that can effectively disperse CNTs in water and polymer media has been a daunting problem that impedes the practical applications

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of CNTs for years. From the energetic perspective, dispersing CNTs is against the physical nature of CNTs, which is, however, exactly where surface modification methods look at: to modify the physical properties of CNTs surface. As discussed earlier in *section 2.4*, there exist a variety of techniques for grafting different types of functional chemical species onto CNTs surface such that the surface-modified CNTs can be effectively dispersed into solutions. While some promising results have been reported, the widely-used covalent modification methods usually cause severe damage, even fragmentation, to the intrinsic honeycomb lattice structure of CNTs and the mechanical properties of CNTs have been heavily compromised [145]; the non-covalent surface functionalizing methods either suffer from their limited dispersibility and unstable complex structure, or are not economic-friendly for the synthesis of special designed block copolymers, ssDNA, and proteins is not easy [155, 156, 164].

Besides, the macromolecules, either chemical or biological, that have been used to modify or functionalize the CNTs surface, usually have mechanical properties far below those of CNTs themselves. To some extent, this also results in the decrease of mechanical performance of the complex hybrid in comparison with pure CNTs. In order to fully exploit the benefits of using CNTs as reinforcement in composites, an efficient, cost-friendly surface modification method that can disperse CNTs without any compromise in their mechanical properties is highly desirable.

6.1.1 Graphene Oxide

In recent years, overwhelming research has been carried out to look at the properties and applications of graphene [5, 240-243], a “rising star” in *Nanotechnology*, which also brings graphene oxide (GO), simply two-dimensional oxidized graphene sheet, into the materials scientists’ interests for its unique structure and properties, and their anticipated application in advanced technologies [244]. Unlike the recently discovered graphene, the fabrication of GO has a history that can be extended back hundred of years to some earliest studies on the chemistry of graphite. In 1859, British chemist Brodie developed the first batch of

GO through adding potassium chlorate into a slurry of graphite mixed with fuming nitric acid [245]. The composition ratio of C:H:O of the GO obtained has been measured to be 61.04:1.85:37.11. His formula was improved by Staudenmaier 40 years later via adding the chlorate and concentrated sulfuric acid over the course of reaction [246]. And almost one century after Brodie's work, by adding graphite into a mixture of KMnO_4 and H_2SO_4 , Hummers *et al.* found an alternative approach and an effective way for the oxidation of graphite [247]. And little has changed after that. The current preparation methods for GO are either modified version of Hummers method or variants of the previous two. As a precursor in the fabrication of graphene (before reduction in chemical exfoliation methods) [244], the preparation of GO is simple, efficient and low-cost with only the reaction of graphite and oxidizer involved.

After the oxidization treatment of bulk graphite, graphene oxide, the single-atom thick two dimensional graphene layer that bears various oxygen functional groups, such as hydroxyl, epoxy, and carbonyl groups, on its basal plane and edges is exfoliated from the graphite host. These charged chemical groups interact with the polarized water molecules, forming hydrogen bonds, which provide GO with its intrinsic hydrophilic property. The dispersion of GO in water can be easily achieved by simple sonication, and the dispersed GO solution is very stable, no subsequent agglomeration observed after dispersion [244].

Moreover, in contrast to the dispersants like chemical surfactants, conjugate polymers, and biomolecules, GO molecules are inherently strong, possessing the excellent mechanical properties inherited from graphene. Theoretical and experimental studies suggest that GO sheets have an elastic modulus around 250 GPa and tensile strength as high as 60 GPa, comparable to CNTs. GO has also been incorporated into various polymer matrices, such as poly(vinyl alcohol) (PVA), epoxy, and others, as reinforcement fillers [244, 248, 249]. Many of these composites have shown significant improvement on the mechanical properties.

6.1.2 Motivations and Scope of this chapter

As previously discussed in section 2.4.2, strong π - π interaction is expected between aromatic derivatives and carbon nanotubes, driving the conjugate polymers and biomolecules to adsorb onto the CNTs. Therefore, it is natural for one to expect that GO molecule could also be tightly bound to CNT surface since even though part of the carbon atoms have been oxidized into sp^3 atoms in GO, there are still a lot of sp^2 carbon atoms available, which could form conjugated π - π interactions with CNT. Recently, Zhang *et al*, have shown that adding GO into aqueous media can effectively improve the dispersibility of MWCNTs [250]. It is suggested that the π - π interaction between CNT and GO is responsible for this improvement.

Although the feasibility of using GO as a novel dispersant for CNTs dispersion has been demonstrated experimentally, the extent of the structure of the hybrid complex, dynamics of self-assembly process, and the thermodynamic nature of this interaction, has not been studied yet. Because of the small size of these nanomaterials, structural information at atomic level resolution is highly desirable to fully understand and realize the potential of CNT-GO. At this moment, such atomic picture of this hybrid assembly is still missing. Besides, studies on the effect of using both GO and CNT at the same time for composite reinforcement is scarce. Herein we present results from all-atom molecular dynamics simulations to understand the structure and stability of CNT-GO hybrids, and the role of GO in the dispersion of CNT in water solution. The simulation work demonstrated here also exemplifies a computational framework to gain microscopic understanding of hybrid structure and interaction between CNT and other molecules. In the end, developing PVA based composites with CNT and GO as reinforcement fillers, experiments have been carried out to verify our simulation results.

6.2 Carbon nanotube and graphene oxide hybrid self-assembly

Since directly imaging the CNT-GO hybrid structure is experimentally difficult, a computational approach has been pursued to shed light on the nature of this intermolecular interaction. In particular, a series of MD simulations were performed to study the CNT-GO self-assembly dynamics.

6.2.1 Simulation details

6.2.1.1 Models of simulation system

The simulation systems consisted of an infinite (10, 10) single-walled carbon nanotube and a 6 nm × 5 nm GO molecule containing 2016 atoms with chemical composition of $C_{10}O_2(OH)_3$ (two epoxy and three hydroxyl groups per 10 carbon atoms were randomly distributed on either side of the graphene basal plane) was initialized in a 7.8×4.5×7.1 nm³ box. To model an infinite carbon nanotube, a SWCNT segment was aligned along the z-axis with a length commensurate with the respective dimension of simulation box, as shown in Figure 6.1. 50% of the carbon atoms within the GO molecule were oxidized, providing a ratio between carbon and oxygen atom as 2:1, consistent with the GO composition produced from the widely-used Hummers method [244], and a ratio of 3:2 for hydroxyl and epoxy groups was adopted as suggested by Gao *et al* [251]. Both the SWCNT and GO structures have been annealed at 2000°C, followed by quenching to room temperature and geometric optimization to reach their equilibrium states prior to the simulations.

Figure 6.1 Illustrations of the simulation box contains CNT and GO molecule in their initial states: (a) front view; (b) side view.

6.2.1.2 Potential for simulation

There are only a handful of computational studies on GO molecules available [252-254], and in these studies, the authors were using either *ab initio* methods or ReaxFF, a reactive force field based on results from quantum calculations, which, however, cannot well produce the properties of CNTs. Due to the lack of the ability to model electrostatic interaction and the missing of empirical parameters for oxygen atoms contained GO [185], the aforementioned Brenner potential cannot be implemented in the current simulation system. In this work, the interatomic interactions were described by a versatile force field, known as condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) [255]. COMPASS is parameterized and validated with respect to extensive quantum mechanics calculations and experimental data for various organic and inorganic molecules. The comprehensive functional forms used in COMPASS make it possible to be fitted against properties of elements with different covalent bonding conditions. It also explicitly contains the non-bonded interactions, in which the total potential energy is expressed as:

$$E_{pot} = E_{valence} + E_{cross-term} + E_{nonbonded} \quad (6.1)$$

where $E_{valence}$ is composed of the bond-order energy terms, such as bond stretching, angle bending, dihedral torsion, and out of plane restriction:

$$\begin{aligned}
E_{valence} = & \sum_b \left[K_2(b-b_0)^2 + K_3(b-b_0)^3 + K_4(b-b_0)^4 \right] \\
& + \sum_\theta \left[H_2(\theta-\theta_0)^2 + H_3(\theta-\theta_0)^3 + H_4(\theta-\theta_0)^4 \right] \\
& + \sum_\varphi \left[V_1[1-\cos(\varphi-\varphi_1)] + V_2[1-\cos(2\varphi-\varphi_2)] + V_3[1-\cos(3\varphi-\varphi_3)] \right] \\
& + \sum_x K_x \chi^2
\end{aligned} \tag{6.2}$$

in which, b and b' are the two neighboring bond lengths, θ is the bond angle, φ is the dihedral angle, and χ is the out of plane angle. $E_{cross-term}$ is a very important term for producing accurate dynamical properties of molecules in COMPASS, which is responsible for the bond and angle distortions caused by the neighboring atoms. It is given by:

$$\begin{aligned}
E_{cross-term} = & \sum_b \sum_{b'} F_{bb'}(b-b_0)(b'-b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta'_0) \\
& + \sum_b \sum_\theta F_{b\theta}(b-b_0)(\theta-\theta_0) + \sum_b \sum_\varphi F_{b\varphi}(b-b_0)[V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos \varphi] \\
& + \sum_{b'} \sum_\varphi F_{b'\varphi}(b'-b'_0)[V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos \varphi] \\
& + \sum_\theta \sum_\varphi F_{\theta\varphi}(\theta-\theta_0)[V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos \varphi] \\
& + \sum_\varphi \sum_\theta \sum_{\theta'} K_{\varphi\theta\theta'} \cos \varphi (\theta-\theta_0)(\theta'-\theta'_0)
\end{aligned} \tag{6.3}$$

The parameters in equations 6.2 and 6.3, such as b_0 , b'_0 , θ_0 , θ'_0 , K_b , H_b , φ_b , V_b , $F_{bb'}$, $F_{\theta\theta'}$, $F_{b\theta}$, $F_{b\varphi}$, $F_{b'\varphi}$, $F_{\theta\varphi}$, and $K_{\varphi\theta\theta'}$ are all derived from *ab initio* calculations and empirical data. The non-bonded energy is given by the summation of van der Waals and electrostatic interactions:

$$E_{nonbonded} = \sum_{i>j} \left(\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6} \right) + \sum_{i>j} \frac{q_i q_j}{\epsilon r_{ij}} \tag{6.4}$$

Instead of the 12th-power function in the LJ potential, an inverse 9th-power term is used for the repulsive van der Waals interactions in COMPASS. The electrostatic energy is represented by the Coulomb equation. In equation 6.4, A_{ij} and B_{ij} are empirical value, ϵ is the dielectric constant, and r_{ij} is the distance between atom i and j . For non-bonded interaction between two different types of atoms, these parameters are given as:

$$A_{ij} = \frac{1}{2}(A_i + A_j) \quad \epsilon = \sqrt{\epsilon_i \epsilon_j}$$

6.2.1.3 Setup the simulation systems

An atom-based cutoff of 15.5 Å was employed in the calculation of van der Waals interaction according to Equation 4.4, and Ewald method with sum tolerance of 10^{-4} kcal/mol ($1 \text{ kcal/mol} = 6.97 \times 10^{-21} \text{ J}$) was applied to obtain electrostatic energy. All simulations were performed at a time step of 0.5 fs in canonical ensemble (NVT) with Nose-Hoover thermostat to maintain a constant temperature at 298 K. The relaxed GO sheet was aligned parallel to the CNT with a separation of 15 Å in the initial configuration, as shown in Figure 6.1. No structural restraint has been applied to the system.

6.2.2 Results and discussion

6.2.2.1 Explore the structure rearrangement from simulations

Snapshots from the MD simulations are shown in Figure 6.2, illustrating the dynamical process of SWCNT-GO self-assembly. Despite the fact that the two molecules are separated at a distance of 15 Å at the initial state, the GO moves toward the SWCNT and attaches onto the nanotube surface. After the attachment, as the distance between SWCNT and GO is much closer, and the intermolecular force that acts on these molecules becomes much stronger, the GO molecule begins to curl up and wraps around the SWCNT, forming a scroll. The self-assembly of SWCNT-GO is driven by strong, attractive interactions between the SWCNT sidewall and the

graphene basal plane of GO. At 40 ps, the SWCNT-GO hybrid reaches its equilibrium structure, which evinced a nano-scroll conformation (Figure 6.2(b)). The conformation of this hybrid structure remains relative stable to 500 ps (when the simulation terminated).

In order to characterize the dynamic process of structural rearrangement of GO with respect to the SWCNT during the self-assembly, the radial distribution functions (RDF) were calculated (Figure 6.4) between the CNT and different atom groups in the GO molecules over a trajectory of 500 ps. The RDF curves give a statistical measure of the distances between the CNT sidewall and the atoms being considered during MD simulation, which is given by:

$$g_{AB}(r) = \frac{\langle \rho_B(r) \rangle}{\langle \rho_B \rangle_{local}} = \frac{1}{\langle \rho_B \rangle_{local}} \frac{1}{N_A} \sum_{i \in A} \sum_{j \in B} \frac{\delta(r_{ij} - r)}{4\pi r^2} \quad (6.5)$$

where $\langle \rho_B(r) \rangle$ is the particle density of type B atoms at a distance r in reference to type A atoms, and $\langle \rho_B \rangle_{local}$ is the particle density of type B averaged over all the sphere space around particles A within the simulation box. Here, r_{max} is defined as half of the box length, avoiding the interference from self-images.

Figure 6.2 Snapshots of a GO sheet interacting with a CNT: (a) snapshots at time intervals from 0 to 500 ps, (b) side-view of the conformation at 500 ps.

As shown in the RDF curve for GO in Figure 6.3, the molecule is most likely to be in the positions that are 4-6 Å away from the tube wall, confirming the GO has attached onto the CNT surface. Since the RDF is averaged over the entire simulation time scope, it also suggests that the hybrid complex remains a scroll-like structure to the end of the simulation. The RDF curves also show that there exists a close contact between the CNT and GO, for the onset of the curve starts deviating from zero at a distance as close as ~ 2 Å from the CNT sidewall, which should be attributed to the out-of-plane hydroxyl groups that point toward SWCNT. The two peaks shown in the curves for hydroxyl and epoxy groups indicate the presence of these chemical groups on the two sides of the GO surface. Worth noticing is the

distances from the first peak in the curves for hydroxyl and epoxy species to the peak of carbon basal plane are much farther in comparison with the distances from the second peaks, which implies that the covalent bonds in these chemical groups on the side towards the nanotube are being stretched due to the attraction force given by CNT. Therefore, strong interactions exist on the interface between CNT and GO.

Figure 6.3 RDF curves showing the distance between SWCNTs surface and different chemical groups of GO molecules.

Figure 6.4 Concentration profile of the equilibrium hybrid SWCNT-GO structures during the last 200 ps of the simulations trajectory.

The details of the interfacial region of the equilibrium structure of SWCNT-GO hybrid can be characterized by the atomic concentration distribution of the complex, which is the atom density profile in a given direction within the simulation box, as shown in Figure 6.4. Four distances, SWCNT-Hydroxyl group (d_{C-OH}), SWCNT-Epoxy group ($d_{C-Epoxy}$), CNT-Carbon basal plane (d_{C-C}), and SWCNT-GO (d_{C-GO}) have been defined and calculated. The densities are averaged over the last 200 ps of the trajectory file. From the figure, we can find that the d_{C-OH} is 2.62 Å, $d_{C-Epoxy}$ is 3.22 Å, d_{C-C} is 4.41 Å, and d_{C-GO} is 4.39 Å, respectively. Due to the steric hindrance effect aroused from the randomly distributed oxygen-bearing chemical groups on the GO surface, the distance between SWCNT and GO carbon backbone is slightly larger than the interlayer distance within graphite (3.4 Å) [256]. It is still close enough to generate strong adhesive binding between the two molecules, and is comparable to the intermolecular distance between SWCNT and conjugated polymers after adsorption, 4 Å [257]. This strong interaction is expected among aromatic, planar carbon structures and is referred to as the π - π stacking. Consider

the “anchoring sites” that provides this strong adhesion in a two dimensional GO sheet are much more than those from a string-like polymer backbone. The binding between SWCNT and GO should also be much stronger in comparison with CNT and conjugated polymers, which indicates the SWCNT-GO nano-scroll is considerably stable.

6.2.2.2 The energetic perspective of the assembly

In molecular simulations, the total energy is given by the Hamiltonian of the system, which is the summation of kinetic energy and potential energy. The former is related to the thermal fluctuation of the system, the variation of which is negligible in a constant temperature ensemble after equilibrium. The latter represents the interatomic interactions defined by the force field, which is very sensitive to the change of structural conformations and is a very useful tool for interpreting the dynamic process. The analysis of energy also provides a quantitative measure to look into the interactions of SWCNT-GO hybrid. In this section, the deformation energy of SWCNT and GO and the binding energy between SWCNT and GO have been calculated in order to study the energy variation and the respective molecular conformations during the self-scrolling process.

The deformation energies of SWCNT and GO ($E_{def-CNT}$ and E_{def-GO}) over the entire simulation time are shown in Figure 6.5. The deformation energy is defined as the potential energy difference (kinetic energy is excluded to eliminate the thermal fluctuation effects) between the energy after a number of time steps and the energy of the initial equilibrium state as,

$$E_{def}^p(t) = E^p(t) - E^p(t_0) \quad (6.6)$$

where t_0 denotes the initial state. As shown in Figure 6.5, it is clear that there are three stages for the change of $E_{def-CNT}$. In the first 40 ps, as the GO is moving toward the nanotube, the quickly increasing attractive forces act on the radial direction of SWCNT, resulting in the deformation of CNT with a rapid increase in its deformation energy. However, the evolution of SWCNT deformation energy does not just stop at

the end of the initial stage at 250 Kcal/mol. After the formation of a complete nano-scroll at 40 ps, the $E_{def-CNT}$ continues to increase until the simulation proceeds to 350 ps when the deformation energy reaches a plateau of 848 Kcal/mol, which indicates the stress induced by the intermolecular attractive forces in the radial direction of nanotube continuously deforms the SWCNT even after the finish of wrapping process. Although during the simulation time of the second stage (between 40 to 350 ps), the rate of the increase of $E_{def-CNT}$ is smaller than that of the initial phase, and the increase of $E_{def-CNT}$ is much larger with a total increment of 600 Kcal/mol. This interesting phenomenon suggests that the GO molecule that has wrapped onto SWCNT surface continuously compresses the nanotube, giving rise to a “squeezing effect”, which introduces pre-strain on SWCNT, increases the interfacial shear stress and is beneficial to forming a firm intermolecular binding. As the intermolecular π - π stacking is only responsible for inducing the wrapping of GO onto SWCNT, it saturates after the finish of the self-assembly process, indicating that π - π interactions cannot be the only driving force of this continuous deformation. In order to trace the source of this strong radial force on the SWCNT, we need to turn our attention to the deformation energy of GO.

Figure 6.5 Change of the deformation energy with respect to simulation time.

Perhaps the most striking result in the analysis of deformation energy is the trend pattern of the curve for E_{def-GO} . As seen in Figure 6.5, the change of E_{def-GO} can also be divided into three phases. It starts with an initial surge of E_{def-GO} , climbing to a highest value of 189 Kcal/mol at 18 ps, corresponds to the GO molecule begins to curl up. Worth noticing is there exists an energy barrier of ~ 300 Kcal/mol in the curling process. In contrast to the variation of $E_{def-CNT}$, which is a continuous increasing process, after the energy barrier, E_{def-GO} steady decreases and remains a negative value in the second stage until it saturates at around 400 ps, which imply that the curling of GO is an energetic favorable spontaneous process. That is to say, the potential energy of GO decreases as the molecule curls itself up. And this reduction in potential energy of GO after wrapping is the origin of the radial forces that deform SWCNT. It should also be pointed out that the existence of an energy barrier in the initial stage, which is overcome by the π - π interaction due to the presence of SWCNT, prohibits GO from curling up on its own.

To further explore how strong the adhesion is between CNT and GO, the binding energy of SWCNT-GO hybrid was calculated according the following equation,

$$E_{Bind} = E_{Hybrid} - (E_{CNT} + E_{GO}) \quad (6.7)$$

where E_{Hybrid} , E_{CNT} , and E_{GO} are the potential energies of Hybrid complex, SWCNT, and GO, respectively. We can observe from Figure 6.6 that the binding energy increases rapidly in the initial stage when the GO is approaching CNT, and the increase becomes even faster after the GO has been attached to CNT and starts to wrap around the tube, suggesting the existence of a strong attractive force between the two molecules. The binding energy continues to increase until $t = 40$ ps, when the whole surface of the CNT is nearly wrapped by the GO molecule. In our case, the saturated binding energy is around -916 Kcal/mol for a 5×6 nm² GO wrapped onto a (10, 10) SWCNT. This high binding energy between CNT and GO suggests that strong adhesion between them, and the nano-scroll structure formed is very stable. The saturated binding energy after 40 ps also confirms that the increase of

deformation energy of SWCNT is caused by the squeezing effect from GO molecule rather than the intermolecular π - π stacking.

Figure 6.6 Evolution of the binding energy between SWCNT and GO. Inset: the variation in the total potential energy of the system as a function of simulation time.

Therefore, our analysis on the simulation system energy indicates that two factors in the SWCNT-GO hybrid system contribute to the strong binding in the resulted nano-scroll structure. One is the strong π - π stacking between the sp^2 delocalized carbon atoms on the SWCNT and GO carbon backbone. The other the “squeezing effect” due to the spontaneous deformation of GO driven by the reduction of potential energy after wrapping around the nanotube, resulting in a pre-strain effect on the SWCNT and an enhanced interfacial shear stress between SWCNT and GO.

In addition, the binding energy of a SWCNT within a bundle of SWCNTs was also calculated to investigate the agglomeration effect. This binding energy is then compared with the one between GO and CNT to find which process is more thermodynamically favorable. It is known that CNTs tend to self-assemble into

bundles or agglomerates, forming closed packed hexagonal array [258]. For this kind of configuration, a newly bind SWCNT, to the bundle, is most likely to interact with two or three other CNTs. A molecular model of a (10,10) SWCNT bundle with 7 individual tubes was constructed. The length of these SWCNTs is the same as that of the tube we used in calculating CNT-GO interaction. The binding energy calculated is summarized in Table 6.1 and the result is compared with the binding energy between CNT and GO. It is manifested that the binding between CNT and GO is much more thermodynamically favorable, as the formation of CNT bundle is 291.1 Kcal/mol less stable than that for the CNT-GO complex. From the normalized binding energy (energy per unit length of CNT), the energy difference is as large as 5.6×10^4 Kcal/mol for a 1 μm long CNT. Therefore, in the presence of GO in the solution, CNTs tend to be wrapped by GO to form a nano-scroll structure rather than self-assembling into bundles. Because of the excellent dispersibility of GO in water [259], once GO has been wrapped onto the wall of a CNT, the hydrophobic surface of the CNT is covered by GO and the CNT-water interface is replaced with the hydrophilic surface of GO – which entails good dispersion in water.

Table 6.1 The binding energies of SWCNT bundles and SWCNT-GO complex.

	E_{Bind} (Kcal/mol)	Normalized E_{Bind} (Kcal/mol/nm)	ΔE_{Bind} (Kcal/mol)
CNTs Bundle	-624.7	-127.5	291.1
GO-CNT Complex	-915.8	-183.2	0

6.2.2.3 Chirality and size effects

It is known that the physical properties of CNTs, such as conductivity and mechanical behavior, significantly depend on their chirality [260]. It has been previously demonstrated through experiments that some conjugated copolymers and DNA biomolecules prefer to bind with CNTs of specific chiralities [261, 262]. To investigate the impact of chirality on the binding energy, we performed MD simulations for GO molecule interacts with SWCNTs of different chiralities. Here,

five SWCNTs of similar length and diameter but with increasing chiral angle θ , rising from 0 to 30°, were constructed, as shown in Figure 6.7. The details of these CNTs are tabulated in Table 6.2.

Figure 6.7 Structural schematics of the five SWCNTs with different chirality but similar geometric parameters constructed in the MD simulations.

Table 6.2 Geometric details of the carbon nanotubes used in the simulation with different chiralities.

Chiral index of SWCNT	SWCNT diameter Å	SWCNT length Å	Number of carbon atoms	Chiral angle
(10, 10)	13.56	71.33	1200	30.00
(12, 8)	13.65	74.28	1216	23.41
(14, 5)	13.36	72.67	1164	14.70
(16, 2)	13.38	72.79	1168	5.82
(17, 0)	13.31	72.42	1156	0.00

The binding energies between GO molecule and SWCNTs with different chiral index are shown in Figure 6.8, which are averaged from the last 200 ps of 500 ps

long MD trajectories after the hybrid structures reached their equilibrium state. The results suggest that GO molecule is able to wrap around the CNTs surface of each chirality considered here, forming scroll-like structures with high binding energy around -900 Kcal/mol. Thus, the CNT chirality has a negligible effect on the CNT-GO intermolecular binding and GO molecules could be used to disperse CNTs regardless their chiral angles.

Figure 6.8 Comparison of the binding energy between GO molecules and SWCNTs with different chiral index but similar length and diameter.

In addition to the chiral effect, the influence from the size of CNTs on the CNT-GO interactions has also been studied. We have previously identified that there exists an energy barrier for GO molecule when it starts to curl up, which needs to be overcome by the attractive π - π interaction between CNT and GO. However, this interaction strongly depends on the size of the interface between the two molecules. A series of armchair SWCNTs (n, n) ($5 \leq n \leq 12$) with same length and increasing diameters have been constructed. And their binding energy with GO molecule were calculated and summarized in Figure 6.9. It is apparent that the size of CNTs has a significant effect on the SWCNT-GO binding energy. The change of binding energy

can be divided into three regimes. Initially, when the SWCNTs is small ($n \leq 6$), the limited CNTs surface cannot provide sufficient interface to induce the GO molecule to overcome the energy barrier and to fully wrap itself around the SWCNTs, such that, in these cases, GO is only adsorbed onto the CNTs, which results in the relatively low binding energy. The threshold of the CNT diameter for forming a nano-scroll structure through interacting with GO is identified to be 9.5 Å when the chiral index increases to (7, 7), which reflected in the curve as an abrupt increase of the binding energy. After that, GO molecule is able to wrap around all the SWCNTs with larger diameters. And the SWCNT-GO binding energy saturates when $n = 9$, as all the available GO surface has been bound with SWCNTs.

Figure 6.9 Comparison of the binding energy between GO molecules and a series of armchair CNTs with increasing diameters.

GO molecules of smaller sizes should require less activation energy to curl up. Therefore, we reduce the length of GO to $\pi(d_{(6,6)} + 2t)$, where $d_{(6,6)}$ is 8.14 Å, the diameter of (6, 6) SWCNTs, and $t = 4.39$ Å, the distance between CNT surface and GO backbone. However, simulation results suggest that the GO molecule of a smaller size still cannot form a scroll-like structure with (6, 6) SWCNT. A close inspection on the GO structure after absorption indicates except the energetic factor, the

wrapping of GO onto CNTs is also restricted by the intrinsic properties of GO structure. The flexibility of graphene has been reduced upon oxidization in GO. The out-of-plane epoxy and hydroxyl groups on GO surface will produce high repulsive interaction when the CNT diameter is small, impeding GO to wrap on a high curvature surface, (Figure 6.10). For cylindrical surface of CNTs, the curvature κ is simply given by $\kappa = 1/R$ (R is the radius of CNT). Thus, our results suggest that the nano-scroll SWCNT-GO hybrid can only be formed if the curvature of the nanotube is smaller than $0.246 \text{ \AA}^{-1}$ ($2/d_{(6,6)}$).

Figure 6.10 Schematic illustration showing the wrapping of GO around SWCNTs surface with increasing curvature (decreasing diameter).

6.3 The thermodynamic nature of SWCNT-GO interaction

Our pervious simulations have demonstrated that SWCNT-GO spontaneously self-assembles into a nano-scroll structure through high affinity interactions between SWCNT sidewall and GO carbon backbone. During the assembly process, GO gradually curls up and wraps onto carbon nanotube due to the strong π - π stacking. The importance of SWCNT-GO stacking on the stability of the hybrid structure has been studied and the binding energy has been derived. While the binding energy is useful for providing us with information about SWCNT-GO adhesion strength, it

does not offer a complete understanding of the relevant issues involved in the self-assembly dynamics. Since, in practice, SWCNT and GO are usually added together and assembled in aqueous solutions at room temperature, it is expected that SWCNT-GO interactions includes a complex interplay of thermodynamic effects, such as the variation of system entropy and enthalpy, and solvent mediated effects. Simply calculating the SWCNT-GO binding energy does not offer any insight into these important issues. Therefore, gaining a better understanding on the thermodynamic behavior of SWCNT-GO interaction in aqueous environment is essential. The physical quantity that captures these thermodynamic effects is the SWCNT-GO binding free energy ΔA_{bind} in water solution. In this section, we use alchemical free energy methods to calculate ΔA_{bind} , thermodynamic integration, in particular, is employed.

6.3.1 Simulation details

6.3.1.1 Thermodynamic integration (TI)

From a thermodynamic prospective, the natural tendency of a system is to achieve a state with minimum free energy. The change of free energy ΔA when the system transforms from one to another state is an important measure of the system's thermodynamic nature. ΔA , known as the change of Helmholtz free energy, is the work exchanged with the surrounding environment during a state transformation at constant volume and temperature, and is given as

$$\Delta A = \Delta E - T \Delta S \quad (6.8)$$

where, ΔE is the change of total energy, ΔS is the change of entropy, and T is the system temperature. While a spontaneous transformation between states releases energy to the surroundings with $\Delta A < 0$, a transformation with $\Delta A > 0$ consumes energy from the environment and is thermodynamic unfavorable. In classical statistical mechanics, the Helmholtz free energy is defined by the partition function

Z as $A = -k_B T \ln Z$, in canonical ensemble, Z is an integral over the entire accessible system phase space,

$$Z = \frac{1}{N!h^{3N}} \iint \exp[-\beta H(p, q)] dp dq \quad (6.9)$$

However, Z is not an average of the system states and cannot be directly probed in MD simulations. Thermodynamic integration is an alchemical free energy method that enables computation of ΔA from two well-defined states using MD. In TI, a coupling parameter λ is introduced into the Hamiltonian H , changing it into $H(p, q, \lambda)$. And a serial of intermediate unphysical states with finite different λ values ranging from 0 to 1 are interpolated between the initial state A ($\lambda = 0$) and final state B ($\lambda = 1$). Thus, it is possible to evaluate Equation 6.8 as an ensemble average via differentiating H with respect to λ :

$$\frac{dA}{d\lambda} = \frac{\iint \frac{\partial H}{\partial \lambda} \exp[-\beta H(p, q, \lambda)] dp dq}{\iint \exp[-\beta H(p, q, \lambda)] dp dq} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_{NVT; \lambda} \quad (6.10)$$

Therefore, the difference in free energy between A and B can be estimated by integrating the above derivative over different λ :

$$A^B(V, T) - A^A(V, T) = \int_0^1 \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_{NVT; \lambda} d\lambda \quad (6.11)$$

In MD simulations, a discrete set of λ values are predefined to obtain $\langle \partial H / \partial \lambda \rangle$, and the integral can be calculated by numerical finite difference method, from which large free energy difference between two states of system can be evaluated.

6.3.1.2 Implementation of TI method for determining the SWCNT-GO free energy

In this work, TI method is used to calculate the SWCNT-GO binding free energy ΔA_{bind} in water solution. ΔA_{bind} , the measure of the attraction between SWCNT and GO molecules and their preference for binding, is obtained as the difference of free

energy of the bound and unbound states of the SWCNT-GO system. In practice, this was realized by evaluating free energy differences along the thermodynamic circle illustrated in Figure 6.11. With the circle ΔA_{bind} is determined by computing the ΔA_{ann}^{unb} and ΔA_{cre}^b , the free energy change for annihilating and creating the GO in the unbound and bound states, respectively. Since Figure 6.11 defines a closed thermodynamic circle, the total free energy change of the entire circle is zero, ΔA for SWCNT and GO binding is subsequently written as:

$$\Delta A_{bind} = \Delta A_{ann}^{unb} + \Delta A_{cre}^b \quad (6.12)$$

Figure 6.11 Illustration of the thermodynamic circle used to compute the binding free energy, ΔA_{bind} , of the CNT-GO interaction.

From Equation 6.12, we can see that the computation of binding free energy involves the evaluation of the free energy differences upon annihilation and creation

of GO in the unbound and bound states. And these free energy variations were calculated using the following procedure:

- Electrostatic interactions (attraction and repulsion among charged atoms) were tuned between off and on by changing the charge on atoms q according to λ values between 0 and 1 with an increment step as 0.2. The atomic charge is defined by $q(\lambda) = (1 - \lambda)q_0$, in which q_0 is the initial charge.
- van der Waals interactions U_{vdW} were then turned on and off based on a modified form of the van der Waals calculation equation introduced in Equation. The singularity in the r^{-9} part causes slow convergence of $\langle \partial H / \partial \lambda \rangle$, which can be overcome by the “soft-core” form of the equation as $U_{vdW}(\lambda)$. It is given by

$$U_{vdW}(\lambda) = \varepsilon(1 - \lambda) \left[2 \frac{\sigma^9}{(\alpha \sigma^{9/2} \lambda^p + r^{9/2})^2} - 3 \frac{\sigma^6}{(\alpha \sigma^6 \lambda^p + r^6)} \right]$$

The soft-core parameters were set as $\alpha = 0.5$ and λ power $p = 1$. And 21 λ values with increment of 0.05 were used to obtain sufficient samples for integration.

At each λ , $\langle \partial H / \partial \lambda \rangle$ was calculated from the last 2 ns of a 10 ns simulation and the result was analyzed via the block averaging method.

6.3.1.3 Setup the simulation system

The complete simulation system for binding free energy calculation consists of two structural conformations, an unbound state and a bound state for SWCNT and GO, and each of the conformation is then composed of an annihilated and a created state. In the annihilated systems, the GO has atomic charges and van der Waals energy potentials set as zero, such that there exists no interaction between GO and water, GO and SWCNT, and within GO itself. Bound state simulation system comprised a GO molecule (contains 498 atoms with the same composition as in section 6.2.1.1) wrapped onto an infinite (10,10) CNT in water solution (3029 water

molecules, treated as simple point charge (SPC) model) in a 5.0×5.0×4.9 nm³ box. Unbounded system contained the same GO molecule, which is separated with CNT at a distance of 15 Å.

It is known that the epoxy and hydroxyl groups dominate the number of chemical species on the basal plane of GO [244, 263]. In order to study the influence of the different chemical groups on the binding free energy, two additional GO molecules with only hydroxyl (GO_H) or epoxy (GO_E) groups on the surface towards the SWCNT sidewall were constructed. The numbers of oxidized carbon on the side that bears the single type chemical group in these GO molecules are set to be the same for comparison, and the other side of GO remains untouched as the original model.

Before the TI calculations, using Nose-Hoover barostat and thermostat, all structures in the systems were first equilibrated in NPT ensemble at 1 atm over a time span of 2.5 ns to ensure a proper system volume and solvent density. The simulation boxes were gradually heated from 10 to 500 K in 500 ps, then annealed at 500 K for another 500 ps, and subsequently quenched to 298 K over the next 500 ps. Finally, the systems stayed and relaxed at 298 K for 1 ns, reaching the fully equilibrated conformation of the structure. Each TI calculation was conducted in canonical ensemble within an equilibrated volume and at room temperature of 298 K.

It has been previously reported that the polarization and charge transfer effects are negligible in the π - π stacking process of CNT and other molecules [264]. Therefore, the classical force field method implemented in this work should provide a reasonable estimate for ΔA_{bind} .

Moreover, in the bound state, the GO is held in place through intermolecular interactions with CNT. Perturbing this interaction in TI calculations will enable the GO to escape from the binding site and explore the whole simulation box, which results in the $\langle \partial H / \partial \lambda \rangle$ to converge very slowly during the transformation. In order to alleviate this problem, harmonic restriction force of 5 kcal•mol⁻¹•Å⁻² was applied

to GO in the bound state, and the free energy contribution from the position restraints ΔA_{res} was calculated as:

$$\Delta A_{res} = k_B T \ln \left(\frac{V_{std}}{V_{bound}} \right) \quad (6.13)$$

in which, $V_{std} = 4037.5 \text{ \AA}^3$ is the standard unbound state volume occupied by one single GO molecule used in the simulation. $V_{bound} = \pi(r_{max}^2 - r_{min}^2)L_{SWCNT}$ is the accessible volume for the GO in the bound state, where L_{SWCNT} is 4.9 nm and r_{max} , r_{min} , the maximum and minimum radial distances that are accessible to GO from SWCNT surface to GO mass center, are defined by

$$r_{max} = \langle r \rangle + 2\sigma \quad r_{min} = \langle r \rangle - 2\sigma$$

where $\langle r \rangle$ is the average of the radial position of the GO molecule and σ is the standard deviation, which is calculated from equilibrated trajectory after binding. With Equation, the free energy contribution from the restraints applied is accounted for to ensure that the net free energy between the unbound annihilated and bound annihilated system remains zero.

Note that the above method for calculating the restraints part in the free energy does not include the energy required for the motion of GO on the SWCNT surface after self-assembly. This is acceptable because the sidewall of pristine SWCNT is quite smooth and the adsorbed GO can slide laterally along SWCNT surface according to the simulation trajectory. It indicates that the energy barrier for lateral motion of GO after binding with SWCNT is less than thermal energy $k_B T$. Once the GO molecule has been firmly attached onto SWCNT sidewall, it undergoes minor fluctuations in the radial direction. Thus, our restraints applied to the GO in the bound state are reasonable. After the implementation of the restrictions, while GO can access the space freely in the axial direction on the circumferential dimensions of the SWCNT, it experiences an infinite potential well that prohibits GO from moving in the radial direction except within the region between r_{min} and r_{max} .

6.3.2 Results and discussion

6.3.2.1 Binding free energy

The binding free energy ΔA_{bind} of different GO molecules along with ΔA_{conf} , ΔA_{vdW} , ΔA_{ele} , ΔA_{ele} , and ΔA_{res} , representing the energy contribution from conformation, van der Waals, electrostatic, and positions restraint, respectively, are presented in Table 6. Among the models constructed, GO with only epoxy groups (GO_E) on the side binding to CNT has the lowest ΔA_{bind} , suggesting it possess the highest affinity for carbon nanotubes. In contrast, ΔA_{bind} of GO_H is the highest, and thus it has the lowest binding affinity. ΔA_{bind} for the three GO models follows, $\Delta A_{bind}^{GO-E} < \Delta A_{bind}^{GO} < \Delta A_{bind}^{GO-H}$. Worth noticing is that the magnitude of all the ΔA_{bind} values is on the order of ~ 200 Kcal/mol for small GO molecules of 2.4×3.0 nm², indicating the existence of strong SWCNT-GO binding. It is clear that among each contribution that composes ΔA_{bind} , van der Waals interaction plays a dominant role in the state transformation of SWCNT-GO binding. The change of potential energy caused by structural rearrangement during the course of self-assembly also favors the binding, which is in line with the results from our previous simulations in vacuum. Besides, there are only minor contributions from ΔA_{ele} and ΔA_{res} .

The different contributions from energetic ΔE_{bind} and entropic ΔS_{bind} terms were also evaluated by carrying out the free energy calculations at other temperatures of 278 K and 318 K. Using finite differences method, the entropic change ΔS_{bind} is given by:

$$\Delta S(T) = \frac{\Delta A(T - \Delta T) - \Delta A(T + \Delta T)}{2\Delta T} \quad (6.14)$$

However, the ΔA_{bind} obtained at 278 K and 318 K were approximately the same after repeating the simulations 5 times. Consider $\Delta A = \Delta E - T\Delta S$. The binding free energy has negligible influence from the temperature, indicating $T\Delta S \ll \Delta E$. This result is expected since unlike string-like polymer backbones that usually are quite

flexible before binding to CNTs, thus the binding orders and restrains the polymers structures, causing a significantly decrease of the systems entropy, the two-dimensional GO structures are already ordered conformations, such that the absorption has little impact on the total entropy. The SWCNT-GO binding is dominated by the energetic factor with $\Delta A_{bind} \approx \Delta E_{bind}$.

Table 6.3 Binding free energy and individual energy contributions of the interaction between CNT and GO molecules.

GO Molecule	ΔA_{conf} Kcal/mol	ΔA_{vdW} Kcal/mol	ΔA_{ele} Kcal/mol	ΔA_{res} Kcal/mol	ΔA_{bind} Kcal/mol
GO	-44.43	-215.41	-9.66	8.69	-260.80
GO _H	-54.51	-131.14	-9.44	6.29	-188.79
GO _E	-41.26	-292.55	-14.23	11.22	-336.61

6.3.2.2 Dissection of the energetic term

ΔE_{bind} is the summation of the energetic influences from the pairwise interactions among the three components of the simulation system, carbon nanotube (CNT), graphene oxide (GO), and water (W), and is expanded as

$$\Delta E_{bind} = \Delta E_{CNT-GO} + \Delta E_{GO} + \Delta E_{CNT} + \Delta E_{GO-W} + \Delta E_{CNT-W} + \Delta E_W \quad (6.15)$$

Each term in Equation were evaluated for the three GO models and summarized in Figure 6.12. As previously discussed, strong van der Waals interaction exists between GO and CNT, which is also referred as π - π stacking. Since SWCNT model adopted here was uncharged, SWCNT experience no electrostatic interactions with the surroundings. Thus, $\Delta E_{CNT-GO} = \Delta E_{\pi-\pi}$, and the stacking energy of the three GO molecules follows the same trend as ΔA_{bind} , $\Delta E_{bind}^{GO-E} < \Delta E_{bind}^{GO} < \Delta E_{bind}^{GO-H}$, which is understandable from geometric characteristics of epoxy and hydroxyl groups. As a type of non-bond long-range (1.55 nm) interactions, the strength of π - π stacking

strongly depends on the distance between the two interacting groups. Beyond the repulsive range (atomic volume), the closer the two groups, the higher the interaction strength. The steric hindrance effect from the out of plane hydroxyl groups on the carbon basal plane is more significant compared to epoxy group, because while in an epoxy group the oxygen is restrained on the backbone surface by two oxygen-carbon bonds, the single oxygen-carbon bond in hydroxyl group is more flexible and the hydrogen in the end of the group also extends the distance to the carbon backbone. An analysis on the atomic concentration of the equilibrated structures of SWCNT-GO_E and SWCNT- GO_H hybrids is shown in Figure 6.13. The distances between the GO carbon bone and SWCNT surface are defined as d_{c-c}^E and d_{c-c}^H for GO_E and GO_H, respectively. The analysis suggests that d_{c-c}^E is nearly 1 Å shorter than d_{c-c}^H ($d_{c-c}^E = 4.2$ Å, $d_{c-c}^H = 5.1$ Å), which explains the stronger π - π stacking between SWCNT-GO_E. The results indicate that GO molecules contain higher epoxy concentration are more favorable in binding with SWCNTs.

The energetic contribution from the change of potential energy due to structural rearrangement consists of two parts, ΔE_{GO} and ΔE_{CNT} , representing the deformation energy of GO and SWCNT, respectively. The results is analogous to those from *in-vacuum* simulations with the structural change of GO during the assembly is favored for binding. However, the deformation energy of CNT is significantly smaller than the results in vacuum, which should be attributed to the presence of hydrogen bonds between GO and water molecules. The water molecules reduce the squeezing effect from GO on SWCNT, leading to a decreased ΔE_{CNT} . Combining these two components, the change of potential energy due to the deformation of SWCNT and GO still favors the binding.

Figure 6.12 Different energetic contributions of binding free energy: $E_{\pi-\pi}$, van der Waals interaction; ΔE_{GO} , potential energy change of GO; ΔE_{CNT} , potential energy change of CNT; ΔE_{GO-W} , GO-water energy variation; ΔE_{CNT-W} , CNT-water energy variation; ΔE_{W-W} , water-water energy variation. The sum of these terms is approximately equal to ΔA_{bind} .

Figure 6.13 Concentration profile of the equilibrium hybrid structures of CNT and different GO models.

In contrast to the π - π stacking and change of conformation energy just discussed, which provide negative (favored) contribution to ΔA_{bind} , ΔE_{GO-w} and ΔE_{CNT-w} , the desolvation penalty effect from SWCNT-GO binding, are positive. Before the assembly, both the GO and SWCNT are completely surrounded by water (Figure 6.14). However, in the bound state, the water molecules are excluded from the interfacial area of the hybrid, which reduces the attractive component within GO/SWCNT-water interactions and increasing the total energy in associate with the interactions with water molecules. The penalty for GO molecule is much higher since one side of the hydrophilic GO surface is bound to SWCNT and could no longer form attractive hydrogen bond with water molecules. It is also evident that the penalty for the GO surface that only contains hydroxyl group is more significant than its epoxy counterpart, since hydroxyl group is more likely to form hydrogen bond in water. This penalty effect plays a major part in the positive component of the binding free energy, and is one of the main reasons (apart from the aforementioned π - π stacking) epoxy group is more thermodynamically favorable in binding with SWCNT.

From the water density profile illustrated in Figure 6.14, we can see that even though the water are completely excluded from the binding side in the assembled state, the hydrophilic surface on the other side is still well-immersed in the aqueous solvent. The binding to SWCNT does not impede the formation of hydrogen bond between GO and water molecules. Since GO wraps around SWCNT convex surface, water molecules are able to solvent the whole SWCNT-GO hybrid with the hydrophobic SWCNT surface previously exposed to water has been transferred to binding interface between SWCNT and GO.

Figure 6.14 Water density of the simulation box: (a) front view of unbound state; (b) side view of unbound state; (c) front view of bound state; (d) side view of bound state.

The last term in Equation 6.15 is the change of water-water interactions upon SWCNT-GO binding. ΔE_w is negative for all GO models, which partially compensates the desolvation penalties. In Figure 6.14 (a) and (b), the hydrophobic SWCNT is completely surrounded by water molecules, giving rise to unfavorable dangling hydrogen bonds at SWCNT-water interface [265]. However, in the bound state, the GO wraps around SWCNT, which decreases the hydrophobic surface accessible to water. This also reduces the number of unfavorable dangling hydrogen bonds, leading to a negative change of water-water interactions.

To sum up, the results presented suggest that the binding between SWCNT and GO is thermodynamically favorable in aqueous solution and GO in the bound state has high affinity to SWCNT. While one specific type of SWCNT (10, 10) was adopted

in our analysis of binding free energy of SWCNT-GO hybrid, the results can be generalized and applied to SWCNTs of other chiralities, for there is no favorable selections in terms of CNT chirality in the binding process of CNT and GO, as has been shown. Moreover, our simulations indicate the GO molecules with higher ratio of epoxy groups (other than hydroxyl group) possess higher binding affinity to SWCNT. Among all the individual energetic factors, the intermolecular π - π stacking contributes a major part to the strong binding energy, this interaction becomes stronger when the CNT and GO backbone get closer to each other. Since GO has a planar structure and lays parallel to the CNT convex surface upon wrapping around the nanotube, it is expected if CNT curvature increases (smaller diameter) the contacts between CNT and GO will be affected, which weakens the π - π interaction.

6.4 CNTs-GO hybrid for effectively dispersing CNTs and as mechanical reinforcement for poly(vinyl alcohol) based composite

It is demonstrated by the computer simulations that the GO molecules are able to self-assemble onto the CNT surface, giving rise to a stable nano-scroll structure and the two molecules are tightly bound together via strong π - π stacking. The adsorption process is thermodynamic favorable in aqueous solution. In the CNT-GO hybrid, hydrophilic GO molecule covers the CNT sidewall through wrapping around the nanotube, modifying the intrinsic hydrophobic surface of CNTs, should significantly improve the dispersibility of CNTs in water solution, and subsequently result in a more well-dispersed CNT-reinforced water-soluble polymer composites.

In order to verify our simulation-based results and assumptions, we carried out experimental studies, introducing GO into CNTs-polymer composites to effectively disperse CNTs into polymer matrix and to improve the mechanical performance of the composites; poly(vinyl alcohol) (PVA), a water-soluble polymer, was used as base matrix in particular.

6.4.1 Experimental details

6.4.1.1 Materials

As suggested in the simulation part, CNTs of larger diameters, that is smaller surface curvature, can more effectively induce GO to wrap on their surface. Therefore, Multi-walled CNTs (MWCNTs) of diameter 10-20 nm were employed in the experiments. Graphite powder with particle size below 20 μm and PVA with molecular weight of 80,000 were purchased from Sigma-Aldrich Co. Ltd.

6.4.4.2 Preparation of graphene oxide

GO was prepared with aforementioned modified Hummer's method [266], which generally consists of two steps: the pretreatment and oxidization. To pretreat the powder, graphite of 12 g was added into the acidic solution that contains $\text{K}_2\text{S}_2\text{O}_8$ (10 g), P_2O_5 (10 g), and concentrated H_2SO_4 (50 ml) at 80 $^\circ\text{C}$. The resulting mixture was stirred at 80 $^\circ\text{C}$ for 4.5 h and followed by cooling to room temperature. The solution was diluted with 2 L de-ionized (DI) water and was allowed to stand overnight. Decanting the supernatant, the pretreated graphite powder was obtained by centrifugation and DI water wash. This pretreated powder (2g) was put into concentrated H_2SO_4 (46 ml) with ice bath for oxidization. KMnO_4 (6 g) was added gradually with magnetic stirring with the temperature of the solution was kept below 10 $^\circ\text{C}$. The mixture was then stirred at 35 $^\circ\text{C}$ for 2 h. Adding 96 ml DI water, the solution was stirred for another 30 min, the oxidization was then terminated by adding 300 ml of DI water and 5 ml of 30% H_2O_2 solution. The mixture was centrifugation and subjected to several rounds of suspension in 5% HCl solution and separated by centrifugation. In order to completely remove metal ions and acids, the graphite oxide was subjected to cycles of washing with DI water and separation with centrifugation until the pH value of the supernatant reached 6. The GO product was suspended in distilled water to give a viscous, brown dispersion (15 mg/ml).

6.4.1.2 Fabrication of CNT-GO reinforced PVA films

The GO suspension prepared was diluted to 1 mg/ml, and certain amount of pristine MWCNTs was added to the solution with the following GO to CNTs weight ratio: 0.25:1, 0.5:1, 1:1, 2:1, and 5:1. The mixtures were ultrasonicated for 1 h. PVA (10 g) was dissolved in DI water (90 g) at 90 °C for 1 h to give a 10 percent by weight (wt%) solution. The GO dispersed CNTs (CNT-GO) solution prepared was subsequently mixed with PVA solution (2ml, 10 wt%). After ultrasonication for an hour at room temperature, the CNT-GO/PVA solution was casted onto PET sheets and dried at room temperature for 24 h, and heated up to 60 °C for another 12 h. The size of the composite films obtained was 3 cm × 10 cm, and about 10 µm in thickness. In addition, CNT/PVA, GO/PVA composite films were also fabricated with the similar procedure for comparison. The details of the CNT and GO compositions of the PVA composite films are listed in Table 6.4.

Table 6.4 The different compositions of CNT-GO reinforced PVA films.

Composition	1	2	3	4	5	6	8	9
CNT wt%	0	0.5	0.5	0.5	0.5	0.5	0.5	0
GO wt%	0	0	0.125	0.25	0.5	1	2	1

6.4.1.3 Tensile tests

In order to characterize the mechanical performance of the CNT-GO reinforced PVA films, the tensile behavior of the composites with different compositions were measured using an Instron 8848 Microforce Tester at a loading rate of 2 mm/min and a gauge length of 10 mm. All composites films prepared in the last section were cut into strips of 30 mm × 5 mm. For each composition, 10 samples were tested, from which the mean and standard deviation of the mechanical parameters were calculated.

6.4.1.4 Characterization of structural morphology

The structural morphologies of pure multi-walled CNTs and CNT-GO hybrid in aqueous solutions were characterized through a JEOL JSM-6700F field-emission scanning electron microscopy (FE-SEM). Optical microscopy was used to study the impact of different composition ratios of CNT and GO on the dispersion of CNTs within PVA matrix.

6.4.2 Results and discussion

6.4.2.1 Effective dispersion of CNT in water and PVA

A representative FE-SEM image of pristine MWCNTs that were dispersed in aqueous solution with ultrasonication for 1 h is shown in Figure 6.15(a). It is evident that the MWCNTs still appear in the form of bundles that are microns in diameter and several lumps of agglomerated nanotubes can be observed even after the mechanical dispersion, indicating the existence of strong tube-tube adhesion. In contrast, the FE-SEM image of GO dispersed MWCNTs (MWCNT to GO weight ratio as 1:2) is shown in Figure 6.15(b), the magnification is two times higher than that of pure MWCNTs. With the presence of GO, even in the magnified image, we cannot find any big MWCNT bundles or agglomerated lumps. The diameter of MWCNTs in the image is in the range of nanometers, suggesting that the MWCNTs have been effectively dispersed into individual tubes or very small bundle. Besides, no GO sheet-like structure can be seen in the MWCNT-GO hybrid, which implies that all GO molecules were homogeneously mixed with and adsorbed onto the nanotubes. These images confirm our simulation results that the CNT-GO hybrid structure can be used to effectively disperse CNTs in aqueous solution.

Figure 6.15 (a) Typical SEM image of pristine MWCNTs; (b) SEM image of GO dispersed MWCNTs.

Next, we study the effectiveness of using GO as a dispersant for CNTs in PVA matrix, since it is suggested that in order to achieve the maximum advantage of applying CNTs as high-strength reinforcement, the homogenous dispersion of CNTs in the matrices is crucial [267]. First, CNT/PVA composite films with 0.5 wt% CNTs were made by solution casting and drying. The solution was prepared through directly mixing of CNTs and PVA in water with 1 h ultrasonication. As shown in Figure 6.16(a), large MWCNT agglomerates are visible in the photo image, suggesting the CNTs were not well dispersed in the composites. Due to the heavy agglomeration of the MWCNTs, the film is not translucent. From a more detailed optical microscopy image of pure MWCNT/PVA composites (Figure 6.17(a)), we can find the size of MWCNT agglomerates can be as large as 100 μm .

In order to improve the dispersion of MWCNTs in the polymer matrix, GO was added into the MWCNTs solution before mixing with PVA. Ternary composites contain MWCNTs, GO, and PVA were fabricated with different weight ratios. For comparison, the optical photo image of pure GO(1 wt%)/PVA and MWCNT(0.5 wt%)-GO(1 wt%)/PVA composite films are shown in Figure 6.16 (b) and (c), respectively. Pure GO/PVA film exhibits a homogeneous brown color, indicating that GO can be intrinsically well dispersed in PVA matrix. Besides, the MWCNT-GO

hybrid inherits this good dispersibility from GO in PVA. The MWCNT-GO/PVA composite film displays perfect uniformity with black color, and no big particles or agglomerated CNTs can be observed, in contrast with the film made by adding MWCNTs only (Figure 6.16(a)).

Figure 6.16 Optical images of composite films: (a) MWCNT/PVA (0.5 wt% MWCNTs); (b) GO/PVA (1 wt% GO); (c) MWCNT-GO/PVA (0.5 wt% MWCNTs and 1 wt% GO).

MWCNT-GO/PVA films with different MWCNT-to-GO weight ratio were prepared to study the effect of GO on the dispersion of CNTs in the polymer matrix, and the microscope images of these films are shown in Figure 6.17. With the addition of GO, the agglomeration of MWCNTs in PVA matrix was diminished significantly. It is manifest that both the size and number of the agglomerated MWCNTs lumps in the PVA matrix decrease with an increase in the GO added. When the MWCNT-GO weight ratio is ranging from 1:0 to 1:2, the particle size of CNT agglomerates decrease from the order of 100 μm to a just a few microns. However, no further reduction in the size and number of agglomerates is seen at higher GO/MWCNT weight ratios. The visible agglomerates remained might be the impurity particles introduced along with the MWCNTs used, which cannot be dispersed by GO. Thus, a GO/CNT weight ratio of 2:1 is identified as the optimized GO-to-MWCNT ratio.

Figure 6.17 Optical microscope images of MWCNT/PVA and MWCNT-GO/PVA composites film of different weight ratios.

Therefore, experimental studies have successfully demonstrated that the dispersibility of CNTs in both aqueous solution and polymer matrix can be significantly improved through adding GO into the mixture, confirms our previous simulation results. No obvious agglomeration of CNTs can be seen in the composites with a MWCNT-to-GO weigh ratio of 1:2. Polymer composites with homogenously dispersed CNTs are expected to possess enhanced mechanical properties.

6.4.2.2 The mechanical properties of MWCNT-GO/PVA composite

The stress-strain curves of pure PVA, MWCNT/PVA, and MWCNT-GO/PVA are shown in Figure 6.18, details of the results are listed in Table 6.5. Comparing with pure PVA films, the mechanical performance of MWCNT/PVA and GO/PVA composite films are improved. As shown in Figure 6.19, The yield strength and Young's modulus of PVA with 1 wt% GO have been increased by 29% and 13%, respectively. However, due to heavy agglomeration of MWCNT, the yield strength and Young's modulus of PVA with 0.5 wt% MWCNT only seen a 6% and 3% increase, respectively. In view of the good GO-assisted CNT dispersion, it is expected that the mechanical properties of the MWCNT-GO/PVA ternary composite would be considerably better than that of CNT/PVA and GO/PVA composite. As shown in Figure 6.19, the yield strength and Young's modulus of MWCNT-GO/PVA composite films with 0.5 wt% MWCNT and 1 wt% GO are 88.5 MPa and 4.1 GPa, respectively. Using the the results of neat PVA as references, the yield strength and Young's modulus have increased by 48% and 31%, respectively, which are also much higher than the percent improvement of MWCNT/PVA and GO/PVA combined (yield strength: (6%+29%); Young's modulus: (3%+13%)).

Table 6.5 The yield strength, tensile strength, failure strain, and Young's modulus of pure PVA, MWCNT/PVA, GO/PVA, and MWCNT-GO/PVA composites

Composition (wt%)		Yield Strength (MPa)		Tensile Strength (MPa)		Failure Strain (%)		Young's Modulus (GPa)	
CNT	GO	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0	0	59.6	4.6	57.3	5.1	115.8	40.0	3.1	0.28
0.5	0	63.1	5.4	56.2	4.0	29.7	20.8	3.2	0.37
0	1	77.0	9.1	73.4	9.0	8.0	4.0	3.5	0.51
0.5	1	88.5	6.8	80.7	6.4	24.7	17.2	4.1	0.40

Figure 6.18 Typical stress-strain curves of pure PVA, MWCNT/PVA, GO/PVA, and MWCNT-GO/PVA composite films.

Figure 6.19 Comparison of Young's modulus (a) and yield strength (b) of pure PVA, MWCNT/PVA, GO/PVA, and MWCNT-GO/PVA composite films (Standard deviations were calculated from tensile test of 10 samples for each composition).

From rule of mixture [176], the Young's modulus of non-aligned, short fibers enhanced composite can be described as:

$$Y_c = (\eta_0 \eta_l Y_f - Y_m) V_f + Y_m \quad (6.16)$$

where η_0 is the orientation efficiency factor, for randomly oriented fiber $\eta_0=0.2$, η_l is length efficiency factor and it approaches 1 for the filler with aspect ratio higher than 10. Y_c , Y_f and Y_m represent the Young's modulus of MWCNT-GO/PVA, MWCNT/PVA, and GO/PVA composites, respectively. V_f and V_m denote the volume fraction of CNT and the matrix, respectively. The Young's modulus of 1 wt% GO enhanced PVA composites film is 3.5 GPa from the experimental results. Here, the Young's modulus of MWCNTs is taken as 1 TPa [12]. The densities of the GO/PVA matrix and MWCNT filler are about 1.3 and 2.1 g·cm⁻³, respectively. Thus, the V_f of 0.5 wt% CNTs is about 0.31 percent by volume (v%). Substituting these parameters into Equation 6.16, Y_c is determined as 4.11 GPa, which agrees well with the experimental result of 4.10 GPa. This agreement between the experimental determined Young's modulus of MWCNT-GO/PVA and the prediction by the simple rule of mixture equation suggests that CNTs are fully dispersed in polymer matrix and the external tensile loads is effectively transmitted to the MWCNT-GO filler within the polymer matrix.

The tensile tests results indicate that both the reinforcement effect of CNT and GO can be fully exploited in the MWCNT-GO/PVA composite. In addition, for GO/PVA composites, although the strength and Young's modulus were enhanced with the incorporation of GO sheets, the failure strain of GO/PVA composite with 1 wt% GO sheets is only 8 %. Compared with pure PVA films, the ductility of GO/PVA is debilitated. However, for MWCNT-GO/PVA composite, the failure strain can be as high as 24.7%. Although it is still lower than that of pure PVA, the failure strain is tripled compared with GO/PVA. These results show that GO dispersed CNT as a new kind of hybrid reinforcement filler exerts a synergistic effect, not only the tensile strength and Young's modulus of the composite are significantly improved, most of the ductility is also retained.

6.5 Summary

In this chapter, we carried out a series of MD simulations in order to explore the nature of CNT-GO interaction. The CNT-GO hybrid structure, energetic profile, self-assembly mechanisms, and the role of GO in CNT dispersion in water solution have been studied. Simulation results suggest that the adhesion between CNT and GO is strong and is energetically preferred compared to the agglomeration of CNTs. The scroll-like structure formed with the hydrophilic surface of GO exposed to water can be well dispersed in aqueous solution. Further studies indicate GO molecules can self-assemble onto CNT with arbitrary chiral angles. However, we also find that the assembling process strongly depends on the size of CNT, for GO molecules need sufficient attractive force from CNT to overcome the energy barrier when it starts to curl up at the initial stage and the oxidized graphene backbone is quite rigid, which cannot accomplish a full wrapping if the curvature of the CNT surface is larger than $0.246 \text{ \AA}^{-1}$.

The binding free energy of CNT-GO hybrid in aqueous solution has also been calculated using TI method, which confirms that the adsorption of GO on the CNT surface is thermodynamically favorable. Detailed analysis of various energetic factors shows the π - π stacking plays a major role in the binding between CNT and GO. Besides, GO molecules with high epoxy/hydroxyl group ratio possess stronger affinity to CNT.

Moreover, in order to verify our simulation findings, we utilized GO as a dispersing agent to fabricate PVA-based composites containing CNTs. Through the strong affinity between CNTs and GO, excellent dispersion of CNTs in the PVA matrix has been achieved with the weight ratio of CNT:GO about 1:2. The PVA composite films containing GO dispersed CNTs exhibit synergistic effects with superior mechanical properties than those of single CNT or GO enhanced PVA composite films. Furthermore, the agreement between the Young's modulus of GO-CNT/PVA from experiments and those predicted by the rule of mixture indicates that the CNTs

were fully dispersed in the polymer matrix and that both the reinforcement effect of GO and CNT were fully exploited in the GO-CNT/PVA composite.

Chapter 7 Summary and Conclusions

In this thesis, we employed both computational and experimental techniques to investigate some fundamental issues that obscure the application of CNTs with their remarkable properties fully exploited. At the intramolecular level, the time-dependent failure mechanisms of individual CNTs have been systematically studied and determined. To tackle this daunting problem, we broke down the overall deformation process into discrete transitions and subsequently developed a strategy for the understanding of the rate of deformation upon these transitions using concept of kinetic fracture theory. The comparison of the time-dependent behavior between our simulation results of individual tubes and experimental data of a bundle of CNTs indicates that there exist two distinct failure mechanisms in these two cases. The intermolecular level tube-tube sliding within the CNTs bundles when tensile stress applied is responsible for this discrepancy, which leads to our following studies on the estimation of the inter-tubular interactions within a bundle of CNTs. Using a straightforward computational scheme, a normalized linear shear stress has been deduced, and the results are verified by molecular simulations. Knowing the existence of high affinities among individual CNTs in their assembly states, we turned our attention to the development of an effective CNT dispersion method to break down this inter-tubular adhesion. Through the investigation of the nature of the intermolecular interaction between CNT and GO, the mechanism of using GO as a dispersing agent for CNT dispersion has been revealed. Experimental studies have also been carried out to check the effect of adding GO and CNT together into a polymer matrix in practice. The solving strategies and key findings of all these studies presented in this thesis are summarized herein.

This project starts with the investigation of fracture mechanism of individual CNTs at relatively low external stress. The slow dynamic nature of this process brings us into a dilemma since direct experimental measurement is impractical and MD simulations cannot probe phenomena of long-time scale. To tackle this problem,

the continuous deformation of CNT creep was decomposed into a series of successive metastable states according to the bond rupture and defects nucleation mechanisms applicable to CNTs structure. While the structural evolution pathways of CNTs are complicated and tedious to compile, we successfully identified the thermodynamically favored CNT fracture route under a spectrum of external stress through searching all the possible nearest neighboring transitions. NEB methods were used to calculate the activation energy for a list of plausible jumps between CNT metastable states. The competition between the nucleation/diffusion of 5|7 defects and bond rupture at different structural evolution stages have been evaluated. Simulation results indicate for a (8, 8) armchair CNT, after the emerge of a pair of 5|7 dislocations, there exist bifurcation states in CNT fracture: brittle failure governs the fracture mechanism if stress exceeds 42.2 GPa; otherwise, plastic deformation caused by dislocations diffusion takes place. The CNT gradually elongates its length through the motion of 5|7 dislocations to release strain energy. At the same time, its diameter between the separated dislocations shrinks with chirality changing toward a zigzag configuration. This leads to the necking of CNT till the eventual fracture due to the stress concentration within the necking region.

However, the determination of the fracture mechanisms of CNTs creep is just the beginning. In order to quantitatively characterize the time-dependent behavior of CNTs, we embarked on a calculation of the strain rate of this slow dynamic process. Concept from kinetic fracture theory has been adopted to bridge the gap between the long-term nature of CNT creep and the timescale of atomistic MD simulation. Results from MD simulations have been incorporated into a kinetic empirical function, in order that the time needed for each transition between the CNT metastable states previously identified can be evaluated. With time and the strain of each evolved geometry with respect to the original length of CNT, the time-strain curves were obtained for (14, 0) zigzag and (8, 8) armchair CNTs at a number of external stresses. Modeling results suggest that flawless CNTs possess remarkable resistance to creep deformation. Theoretically, they can last for years at a stress of 10 GPa. Besides, the chirality of CNT plays an important part in the CNTs time-

dependent behavior. CNTs of armchair configuration can survive a much longer time than the zigzag nanotubes of the similar size. And this discrepancy becomes more apparent at elevated stress levels. The time-strain curves are also characterized using Maxwell model. The viscoelastic parameters obtained can serve as the benchmark for the engineering design of applying CNTs as load-bearing materials. The simulation results are compared to experimental data from creep tests of a bundle of CNTs. We find that the mechanical response of creep of CNT bundle is due to the combined effect of the inter-tubular frictional motion and brittle fracture of zigzag and other low chiral angle CNTs. And the sliding at the interface between the CNTs is responsible for the viscoelastic behavior exhibited by CNT bundle, which is different from that of individual CNTs. This motivated us to seek a way that can quantitatively characterize this frictional intermolecular interaction.

Using data from experimental uniaxial tensile test, we have established a straightforward calculation scheme to evaluate the frictional energy due to tube-tube sliding. Normalized frictional shear stress has been derived through partitioning the total tensile strain energy into different contributions, with an average value of 0.22 Nm^{-1} , which is comparable to the cohesive energy between graphene layers in graphite. The result is subsequently verified by molecular mechanics simulation of single CNT or a bundle of CNT pulled out from an array of CNTs. This numerical value offers an important parameter for quantitative analysis of the significant increase in the viscoelastic response of closely packed CNT assemblies. Moreover, it is also useful in the design and development of CNT-based nanomechanical or nanoelectromechanical systems, like electric motor [268], in which the friction between CNTs is an important factor.

The high inter-tubular frictional energy indicates there exist strong interactions between individual CNTs, which lead to the agglomeration of CNTs in aqueous solution, and it is very difficult to disperse them. The heavily agglomerated CNTs weakens the mechanical properties of CNTs-reinforced composites, limits the use of CNTs in practical applications. Among various CNT dispersion methods,

noncovalent surface modification is one of the most promising ways that can both achieve good dispersion effect and retain the intrinsic properties of CNTs, in which the dispersing agents usually adsorb onto the CNTs surface through intermolecular interactions. In this study, the nature of the interactions between CNT and GO has been systematically studied using a series of MD simulations. Strong adhesion between CNT and GO has been probed, which results primarily from π - π stacking. And the binding is energetically preferred compared to the agglomeration of CNTs. Using TI method, binding free energy between GO and CNT in aqueous solution was calculated, which reveals the GO-CNT interaction is thermodynamically favorable. The scroll-like structure emerged with the hydrophilic GO exposed to water can be well dispersed in aqueous solution. Further studies indicate the chirality of CNT has negligible effect on the binding energy with GO. However, the assembling process strongly depends on the diameter of CNT. The CNT with diameter smaller than 9.5 Å cannot provide GO with sufficient attractive force to overcome the energy barrier upon curling up. Besides, the forming of CNT-GO nano-scroll is also restricted by the curvature of CNT, for the repulsive interaction between the oxygenated chemical groups on the GO surface impedes the GO to accomplish a full wrapping if the curvature is higher than 0.246 Å^{-1} .

Furthermore, in the last part of this thesis, insights from simulation results were implemented in our experiments. GO was utilized as a dispersing agent to fabricate a novel CNT-GO/PVA ternary composite. Owing to the strong adhesion between CNT and GO, excellent dispersion of CNTs in both water and PVA has been achieved. Results from tensile tests suggest the PVA composite films containing both GO and CNTs exhibit synergistic effects with superior mechanical properties than those of single CNT or GO enhanced PVA composite films, not only the tensile strength and Young' modulus of the composites have been substantially enhanced in CNT-GO/PVA ternary composite, but most of the ductility of pure PVA is also retained.

7.1 Recommendations for Future Research

While this thesis has attempted to provide deeper understandings of some fundamental issues regarding CNTs mechanical properties and applications, future work is still needed in order that CNTs and their composites can replace conventional materials in a broad spectrum of applications. In the determination of the failure mechanisms of CNTs at noncritical stress, the main focus of this study is ideal, flawless CNTs. However, it is suggested that the as-synthesized CNTs usually contain vacancies, dislocations, and impurities in their structure [73, 74, 269]. The effects of these preexisting defects on the energy barriers of state transitions between metastable states in CNTs have yet been evaluated. Besides, it has been reported that the ad-atom can significantly change the mechanical properties of CNTs [270]. It is also interesting to see how the presence of ad-atom affects the activation conditions of the two alternative fracture mechanisms: brittle and plastic deformation of CNTs. Furthermore, some of the energy states representing the key transition structure can be refined by more-precise *ab initio* computations.

Our experimental results suggest that adding CNT and GO together into polymer matrix can lead to a synergistic effect on the mechanical properties. However, despite the contribution from a more homogeneously dispersed CNT, a thorough understanding on the enhancing mechanism within the ternary composite is still unclear. MD simulation can be directed to probe the structure of this novel composite and the mechanical properties can be quantitatively characterized for composites with different volume content of CNT and GO. Moreover, a recent study also suggests that the mechanical properties of GO molecules strongly depend on the presence of water molecules, which can form a hydrogen bond network between GO layers [249]. Therefore, studies could also be carried out to look at the effect from the water content on the mechanical performances of CNT-GO/polymer composites.

Scientific research is the search for knowledge, with an open mind, to establish novel facts, prove new ideas, and develop new theories for the advancement of human beings [271]. In this process of seeking the concealed meaning of the matters provided to us by the creator, even the most mundane facts and long-established theories are subject to re-examination as new findings and theories come in. This is not the weakness of science, but rather its strength; it is constantly moving forward. No endeavor rivals science in its incremental progress towards a more accurate understanding of the problems in front of us. In the search and 're-search', scientists step by step approach the truth of each problem. Thus, as the author completes this journey by writing these last few words of this thesis, it seems only appropriate to conclude as: the exploration and discovery of the fascinating properties of these nanoscale materials should and are always 'to be continued...'

Appendix A Functional Expressions of Second Generation Brenner Potential and the Adjustments

In the Brenner potential, the total potential energy is given by [185]

$$E_{total} = \frac{1}{2} \sum_i E_i = \frac{1}{2} \sum_i \sum_{j \neq i} E^B(r_{ij}) \quad (A.1)$$

where E_i is the potential energy of atom i and $E^B(r_{ij})$ is the interaction between atom i and its nearest neighbors, j ,

$$E_{ij}^B = V_{ij}^R - b_{ij} V_{ij}^A \quad (A.2)$$

in which repulsive and attractive contributions from atom i and j are combined in a ratio determined by the bond order term b_{ij} . The function V_{ij}^R represents the pair-wised repulsive potential including the core-core and electron-electron interactions, while V_{ij}^A corresponds to the attractive potential caused by core-electron interactions. Both of these terms rely on the distance, r_{ij} , between the two atoms, i and j .

The repulsive term has the form given by Brenner as,

$$V_{ij}^R = f_c(r_{ij}) \left[1 + \frac{Q_{ij}}{r_{ij}} \right] A_{ij} e^{-\alpha_{ij} r_{ij}} \quad (A.3)$$

where the parameters Q_{ij} , A_{ij} and α_{ij} are two body coefficients determined by the atom types of i and j , so they hold constant for carbon system. This term goes to infinity as the inter-particle distance approaches zero.

The attractive interactions is given by a triple exponential,

$$V_{ij}^A = f_c(r_{ij}) \sum_{n=1}^3 B_{ij}^n e^{-\beta_{ij}^n r_{ij}} \quad (\text{A.4})$$

This term has sufficient flexibility to produce accurate bond properties. B_{ij} and β_{ij} also depend on the type of interaction. The function, $f_c(r_{ij})$, is the cut-off function, which limits the range of the covalent interactions to insure that the interactions are restricted within the nearest neighbors, it is written as

$$f_c(r_{ij}) = \begin{cases} 1 & \text{if } r_{ij} < D_{ij}^{\min} \\ \frac{1 + \cos\left(\frac{r_{ij} - D_{ij}^{\min}}{D_{ij}^{\max} - D_{ij}^{\min}}\right)}{2} & \text{if } D_{ij}^{\min} \leq r_{ij} \leq D_{ij}^{\max} \\ 0 & \text{if } r_{ij} > D_{ij}^{\max} \end{cases} \quad (\text{A.5})$$

Here, $D_{ij}^{\max} - D_{ij}^{\min}$ defines the range over which the covalent contribution from the repulsive and attractive interactions varies from one to zero.

The bond order function, b_{ij} , represents the influences on the energy from many bond effect. This term is expressed by

$$b_{ij} = \frac{1}{2} [p_{ij}^{\sigma\pi} + p_{ji}^{\sigma\pi}] + \pi_{ij}^{rc} + \pi_{ij}^{dh} \quad (\text{A.6})$$

Each of the terms within the Eq. (A.6) is a many body term that depends on the bonding environment surrounding atom i and j . The first two terms, $P_{ij}^{\sigma\pi}$ and $P_{ji}^{\sigma\pi}$, are the covalent bonding interactions, and are the most important components, given as,

$$p_{ij}^{\sigma\pi} = \left[1 + \sum_{k \neq i, j} f_c(r_{ik}) g_i(\cos \theta_{jik}) e^{\lambda_{jik}} + P_{ij}(N_i^C) \right]^{-1/2} \quad (\text{A.7})$$

in which $g_i(\cos\theta_{jik})$ manages the influence of the nearest neighbor atoms on the bond order term according to bond angle among atom i, j and k . The function P_{ij} is a two dimensional cubic spline that represents the distinct chemical environment around atom i , and N_i^C is the number of neighboring carbon atoms of atom i , which is also scaled by the cut-off function,

$$N_i^C = \sum_{k(\neq i, j)}^{carbon} f_c(r_{ik})$$

According to the above function, the number of neighboring atoms of atom i , excluding atom j , can be calculated and the value ranges from 0 to 1 for each atom, so that the bond order term is continuous during bond breaking.

The last two components that contribute to the bond order function are the radial and dihedral terms. The term π_{ij}^{rc} depends on whether the bond between atom i and j has a radical nature or is part of a conjugated system. It is written as

$$\pi_{ij}^{rc} = F_{ij}(N_i^t, N_j^t, N_{ij}^{conj})$$

where F_{ij} is a tri-cubic spline, in which the first two variables are the total number of neighbors of bonded atoms i and j , and the third one is a function that depends on local conjugation, the value of N_{ij}^{conj} is given by

$$N_{ij}^{conj} = 1 + \left[\sum_{k(i \neq j)}^{carbon} f_c(r_{ik}) F(x_{ik}) \right]^2 + \left[\sum_{k(i \neq j)}^{carbon} f_c(r_{jl}) F(x_{jl}) \right]^2 \quad (\text{A.8})$$

in which, $x_{ik} = N_k^t - f_c(r_{ik})$ and

$$F(x_{ik}) = \begin{cases} 1 & \text{if } x_{ik} < 2 \\ \frac{1 + \cos[2\pi(x_{ik} - 2)]}{2} & \text{if } 2 \leq x_{ik} \leq 3 \\ 0 & \text{if } x_{ik} \geq 3 \end{cases} \quad (\text{A.9})$$

The last term, π_{ij}^{dh} , corresponds to the dihedral angle for carbon-carbon bonds, which represents the torsional effect in the molecule and is given by

$$\pi_{ij}^{dh} = T_{ij}(N_i^t, N_j^t, N_{ij}^{conj}) \left[\sum \sum (1 - \cos^2(\Theta_{ijkl})) f_c(r_{ik}) f_c(r_{jl}) \right] \quad (\text{A.10})$$

where Θ_{ijkl} is the torsional angle between atoms i, j, k , and l , these four atoms are linked via chemical bond as a chain. The T_{ij} here is another three-dimensional cubic spline. In these functions, the standard equations for describing the rotational forces about dihedral angles for carbon-carbon bonds is embedded into the analytic bond order term of Brenner formula.

It has been previously reported that directly using Brenner potential for mechanical simulation could lead to an overestimation of the force needed to dissociate a carbon-carbon bond [50, 82, 95, 103-105]. This spurious result is due to the form of the cutoff function used in the potential, which has a discontinuity in the second order derivative of the potential with respect to interatomic distance; thus, it artificially increases the bond binding force for distances within the cutoff range, which is 1.7 to 2.0 Å. Therefore, in this work, a modified version of Brenner potential is adopted by increasing the onset distance of the cutoff functions for the Brenner term from 1.7 to 1.92 Å. This revision does not have any side effects on the applications of the potential for modeling CNTs under tensile stress.

Bibliography

1. Feynman, R.P., *There's Plenty of Room at the Bottom*. Journal of Engineering and Science, 1960. **4**(2): p. 23-36.
2. Fritz Allhoff, P.L., Daniel Moore, *What is nanotechnology and why does it matter?: from science to ethics* 2010: John Wiley and Sons. 304.
3. Wang, Z., et al., *Observation of unidirectional backscattering-immune topological electromagnetic states*. Nature, 2009. **461**(7265): p. 772-U20.
4. Williams, J.R., L. DiCarlo, and C.M. Marcus, *Quantum hall effect in a gate-controlled p-n junction of graphene*. Science, 2007. **317**(5838): p. 638-641.
5. Zhang, Y., et al., *Experimental observation of the quantum Hall effect and Berry's phase in graphene*. Nature, 2005. **438**(7065): p. 201-204.
6. Dumitrica, T., M. Hua, and B. Yakobson, *Symmetry-, time-, and temperature-dependent strength of carbon nanotubes*. P Natl Acad Sci Usa, 2006. **103**(16): p. 6105-6109.
7. Iijima, S., *Helical microtubules of graphitic carbon*. Nature, 1991. **354**(6348): p. 56-58.
8. Hong, S. and S. Myung, *Nanotube Electronics: A flexible approach to mobility*. Nat Nano, 2007. **2**(4): p. 207-208.
9. Jamieson, V., *Carbon Nanotubes Roll On*. Physics World, 2000. **13**(6).
10. Andrews, R. and M. Weisenberger, *Carbon nanotube polymer composites*. Curr Opin Solid St M, 2004. **8**(1): p. 31-37.
11. Coleman, J., U. Khan, and Y. Gun'ko, *Mechanical reinforcement of polymers using carbon nanotubes*. Adv Mater, 2006. **18**(6): p. 689-706.
12. Coleman, J.N., et al., *Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites*. Carbon, 2006. **44**(9): p. 1624-1652.
13. Velasco-Santos, C., A. Martinez-Hernandez, and V. Castano, *Carbon nanotube-polymer nanocomposites: The role of interfaces*. Compos Interface, 2005. **11**(8-9): p. 567-586.
14. Yakobson, B., C. Brabec, and J. Bernholc, *Nanomechanics of carbon tubes: Instabilities beyond linear response*. Phys Rev Lett, 1996. **76**(14): p. 2511-2514.
15. Salvétat, J., et al., *Elastic and shear moduli of single-walled carbon nanotube ropes*. Phys Rev Lett, 1999. **82**(5): p. 944-947.
16. Yu, M., et al., *Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load*. Science, 2000. **287**(5453): p. 637-640.
17. Ma, W., et al., *High-Strength Composite Fibers: Realizing True Potential of Carbon Nanotubes in Polymer Matrix through Continuous Reticulate Architecture and Molecular Level Couplings*. Nano Lett, 2009. **9**(8): p. 2855-2861.
18. Liang, S., et al., *Shear enhanced interfacial interaction between carbon nanotubes and polyethylene and formation of nanohybrid shish-kebabs*. Polymer, 2008. **49**(23): p. 4925-4929.

19. Lahiff, E., et al., *Physical properties of novel free-standing polymer-nanotube thin films*. Carbon, 2006. **44**(8): p. 1525-1529.
20. Zhao, C., et al., *Synthesis and characterization of multi-walled carbon nanotubes reinforced polyamide 6 via in situ polymerization*. Polymer, 2005. **46**(14): p. 5125-5132.
21. Wall, A., J.N. Coleman, and M.S. Ferreira, *Physical mechanism for the mechanical reinforcement in nanotube-polymer composite materials*. Physical Review B - Condensed Matter and Materials Physics, 2005. **71**(12): p. 1-5.
22. Qin, S., et al., *Covalent cross-linked polymer/single-wall carbon nanotube multilayer films*. Chemistry of Materials, 2005. **17**(8): p. 2131-2135.
23. Manchado, M.A.L., et al., *Thermal and mechanical properties of single-walled carbon nanotubes-polypropylene composites prepared by melt processing*. Carbon, 2005. **43**(7): p. 1499-1505.
24. Gao, J., et al., *Continuous spinning of a single-walled carbon nanotube-nylon composite fiber*. Journal of the American Chemical Society, 2005. **127**(11): p. 3847-3854.
25. Liao, M. and Y. Koide, *Carbon-based materials: Growth, properties, MEMS/NEMS technologies, and MEM/NEM switches*. Critical reviews in solid state and materials sciences, 2011. **36**(2): p. 66-101.
26. Lee, D., et al. *Suspended carbon nanotube thin film structures with high degree of alignment for NEMS switch applications*. 2011.
27. Lee, D. and T. Cui, *Suspended carbon nanotube nanocomposite beams with a high mechanical strength via layer-by-layer nano-self-assembly*. Nanotechnology, 2011. **22**(16).
28. Bunch, J.S., *NEMS: Putting a damper on nanoresonators*. Nature Nanotechnology, 2011. **6**(6): p. 331-332.
29. Arun, A., et al., *SWNT array resonant gate MOS transistor*. Nanotechnology, 2011. **22**(5).
30. Yamada, T., et al., *A stretchable carbon nanotube strain sensor for human-motion detection*. Nature Nanotechnology, 2011. **6**(000290301300010): p. 296-301.
31. Xie, X.L., Y.W. Mai, and X.P. Zhou, *Dispersion and alignment of carbon nanotubes in polymer matrix: A review*. Materials Science and Engineering R: Reports, 2005. **49**(4).
32. Pang, J., et al., *Dispersing carbon nanotubes in aqueous solutions by a silicon surfactant: Experimental and molecular dynamics simulation study*. Colloid Surface A, 2009. **350**(1-3): p. 101-108.
33. Li, Q., M. Zaiser, and V. Koutsos, *Carbon nanotube/epoxy resin composites using a block copolymer as a dispersing agent*. Physica Status Solidi (A) Applied Research, 2004. **201**(13): p. R89-R91.
34. Dreyer, D.R., et al., *The chemistry of graphene oxide*. Chemical Society Reviews, 2010. **39**(1): p. 228-240.
35. Zhao, X., et al., *Smallest carbon nanotube is 3 angstrom in diameter*. Phys Rev Lett, 2004. **92**(12): p. 125502.
36. Qin, L., et al., *Materials science - The smallest carbon nanotube*. Nature, 2000. **408**(6808): p. 50-50.

37. Monthioux, M. and V. Kuznetsov, *Who should be given the credit for the discovery of carbon nanotubes?* Carbon, 2006. **44**(9): p. 1621-1623.
38. Iijima, S. and T. Ichihashi, *Single-shell carbon nanotubes of 1-nm diameter.* Nature, 1993. **363**(6430): p. 603-605.
39. Bethune, D.S., et al., *Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls.* Nature, 1993. **363**(6430): p. 605-607.
40. Robertson, D., D. Brenner, and J. Mintmire, *Energetic of nanoscale graphitic tubules.* Phys Rev B, 1992. **45**(21): p. 12592-12595.
41. Tersoff, J., *Empirical interatomic potential for carbon, with applications to amorphous-carbon.* Phys Rev Lett, 1988. **61**(25): p. 2879-2882.
42. Tersoff, J., *Empirical interatomic potential for silicon with improved elastic properties.* Phys Rev B, 1988. **38**(14): p. 9902-9905.
43. Brenner, D., *Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films.* Phys Rev B, 1990. **42**(15): p. 9458-9471.
44. Cornwell, C. and L. Wille, *Elastic properties of single-walled carbon nanotubes in compression.* Solid State Commun, 1997. **101**(8): p. 555-558.
45. Yao, N. and V. Lordi, *Young's modulus of single-walled carbon nanotubes.* J Appl Phys, 1998. **84**(4): p. 1939-1943.
46. Lu, J., *Elastic properties of carbon nanotubes and nanoropes.* Phys Rev Lett, 1997. **79**(7): p. 1297-1300.
47. Popov, V., V. Van Doren, and M. Balkanski, *Elastic properties of single-walled carbon nanotubes.* Phys Rev B, 2000. **61**(4): p. 3078-3084.
48. Hernandez, E., et al., *Elastic properties of C and BxCyNz composite nanotubes.* Phys Rev Lett, 1998. **80**(20): p. 4502-4505.
49. Ozaki, T., Y. Iwasa, and T. Mitani, *Stiffness of single-walled carbon nanotubes under large strain.* Phys Rev Lett, 2000. **84**(8): p. 1712-1715.
50. Van Lier, G., et al., *Ab initio study of the elastic properties of single-walled carbon nanotubes and graphene.* Chem Phys Lett, 2000. **326**(1-2): p. 181-185.
51. Treacy, M.M.J., T.W. Ebbesen, and J.M. Gibson, *Exceptionally high Young's modulus observed for individual carbon nanotubes.* Nature, 1996. **381**(6584): p. 678-680.
52. Krishnan, A., et al., *Young's modulus of single-walled nanotubes.* Phys Rev B, 1998. **58**(20): p. 14013-14019.
53. Wong, E.W., P.E. Sheehan, and C.M. Lieber, *Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes.* Science, 1997. **277**(5334): p. 1971-1975.
54. Salvétat, J., et al., *Mechanical properties of carbon nanotubes.* Appl Phys A-Mater, 1999. **69**(3): p. 255-260.
55. Tombler, T., et al., *Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation.* Nature, 2000. **405**(6788): p. 769-772.
56. Lourie, O. and H. Wagner, *Transmission electron microscopy observations of fracture of single-wall carbon nanotubes under axial tension.* Appl Phys Lett, 1998. **73**(24): p. 3527-3529.

57. Wood, J.R., et al., *Mechanical response of carbon nanotubes under molecular and macroscopic pressures*. Journal of Physical Chemistry B, 1999. **103**(47): p. 10388-10392.
58. Wood, J.R., et al., Phys. Rev. B, 2000. **62**: p. 7371-7375.
59. Zhao, Q., M.D. Frogley, and H.D. Wagner, *Direction-sensitive strain-mapping with carbon nanotube sensors*. Composites Science and Technology, 2002. **62**(1): p. 147-150.
60. Zhao, Q., M.D. Frogley, and H.D. Wagner, *Direction-sensitive stress measurements with carbon nanotube sensors*. Polymers for Advanced Technologies, 2002. **13**(10-12): p. 759-764.
61. Yu, M., B. Yakobson, and R. Ruoff, *Controlled sliding and pullout of nested shells in individual multiwalled carbon nanotubes*. J Phys Chem B, 2000. **104**(37): p. 8764-8767.
62. Yu, M., et al., *Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties*. Phys Rev Lett, 2000. **84**(24): p. 5552-5555.
63. Yu, M., et al., *Three-dimensional manipulation of carbon nanotubes under a scanning electron microscope*. Nanotechnology, 1999. **10**(3): p. 244-252.
64. Samsonidze, G., G. Samsonidze, and B. Yakobson, *Kinetic theory of symmetry-dependent strength in carbon nanotubes*. Phys Rev Lett, 2002. **88**(6): p. 065501.
65. Yakobson, B., *Mechanical relaxation and "intramolecular plasticity" in carbon nanotubes*. Applied Physics Letters, 1998. **72**(8): p. 918-920.
66. Nardelli, M., B. Yakobson, and J. Bernholc, *Brittle and ductile behavior in carbon nanotubes*. Phys Rev Lett, 1998. **81**(21): p. 4656-4659.
67. Bernholc, J., et al., *Theory of growth and mechanical properties of nanotubes*. Appl Phys A-Mater, 1998. **67**(1): p. 39-46.
68. Yakobson, B.I., et al., *High strain rate fracture and C-chain unraveling in carbon nanotubes*. Computational Materials Science, 1997. **8**(4): p. 341-348.
69. Stone, A. and D. Wales, *Theoretical-studies of icosahedral C₆₀ and some related species*. Chem Phys Lett, 1986. **128**(5-6): p. 501-503.
70. Samsonidze, G.G. and B.I. Yakobson, *Kinetic theory of symmetry-dependent strength in carbon nanotubes*. Physical Review Letters, 2002. **88**(6): p. 065501/1-065501/4.
71. Samsonidze, G.G., G.G. Samsonidze, and B.I. Yakobson, *Energetics of Stone-Wales defects in deformations of monoatomic hexagonal layers*. Computational Materials Science, 2002. **23**(1-4): p. 62-72.
72. Belytschko, T., et al., *Atomistic simulations of nanotube fracture*. Phys Rev B, 2002. **65**(23): p. 235430.
73. Zhang, S., et al., *Mechanics of defects in carbon nanotubes: Atomistic and multiscale simulations*. Phys Rev B, 2005. **71**(11): p. 115403.
74. Mielke, S., et al., *The role of vacancy defects and holes in the fracture of carbon nanotubes*. Chem Phys Lett, 2004. **390**(4-6): p. 413-420.
75. Huhtala, M., et al., *Improved mechanical load transfer between shells of multiwalled carbon nanotubes*. Phys Rev B, 2004. **70**(4): p. 045404.
76. Huq, A.M.A., et al., *On defect interactions in axially loaded single-walled carbon nanotubes*. J Appl Phys, 2008. **103**(5): p. 054306.

77. Ren, Y., T. Xiao, and K. Liao, *Time-dependent fracture behavior of single-walled carbon nanotubes with and without Stone-Wales defects*. Phys Rev B, 2006. **74**(4): p. 045410.
78. Demczyk, B.G., et al., *Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes*. Materials Science and Engineering A, 2002. **334**(1-2): p. 173-178.
79. Bozovic, D., et al., *Plastic deformations in mechanically strained single-walled carbon nanotubes*. Phys Rev B, 2003. **67**(3): p. 033407.
80. Troiani, H., et al., *Direct observation of the mechanical properties of single-walled carbon nanotubes and their junctions at the atomic level*. Nano Lett., 2003. **3**(6): p. 751-755.
81. Lourie, O., et al., *Mechanics of Carbon Nanotubes*. MRS Spring Meeting, San Francisco, CA, 2001.
82. Huang, J., et al., *Superplastic carbon nanotubes - Conditions have been discovered that allow extensive deformation of rigid single-walled nanotubes*. Nature, 2006. **439**(7074): p. 281-281.
83. Ding, F., et al., *Pseudoclimb and dislocation dynamics in superplastic nanotubes*. Phys Rev Lett, 2007. **98**(7): p. 075503.
84. Ding, F., J.Y. Huang, and B.I. Yakobson, *Comment on "Mechanism for Superelongation of Carbon Nanotubes at High Temperatures"*. Phys. Rev. Lett., 2009. **103**(3): p. 039601.
85. Tang, C., W. Guo, and C. Chen, *Mechanism for superelongation of carbon nanotubes at high temperatures*. Phys. Rev. Lett., 2008. **100**(17): p. 175501.
86. Tang, C., W. Guo, and C. Chen, *Comment on "Mechanism for Superelongation of Carbon Nanotubes at High Temperatures" Reply*. Phys. Rev. Lett., 2009. **103**(3): p. 039602.
87. Xiao, T., Y. Ren, and K. Liao, *A kinetic model for time-dependent fracture of carbon nanotubes*. Nano Lett., 2004. **4**(6): p. 1139-1142.
88. Ho-ming Herbert Tong, N.J.C., Lee E. Fitzpatrick, *Characterization of Polymers*. Materials characterization series 1994, University of Michigan: Butterworth-Heinemann.
89. Zhang, M., K. Atkinson, and R. Baughman, *Multifunctional carbon nanotube yarns by downsizing an ancient technology*. Science, 2004. **306**(5700): p. 1358-1361.
90. Ma, W., et al., *Directly synthesized strong, highly conducting, transparent single-walled carbon nanotube films*. Nano Letters, 2007. **7**(8): p. 2307-2311.
91. Hata, K., et al., *Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes*. Science, 2004. **306**(5700): p. 1362-1364.
92. Ericson, L.M., et al., *Macroscopic, neat, single-walled carbon nanotube fibers*. Science, 2004. **305**(5689): p. 1447-1450.
93. Motta, M., et al., *High performance fibres from 'dog bone' carbon nanotubes*. Advanced Materials, 2007. **19**(21): p. 3721-3726.
94. Jia, J., et al., *A comparison of the mechanical properties of fibers spun from different carbon nanotubes*. Carbon, 2011. **49**(4): p. 1333-1339.
95. Li, Q., et al., *Sustained growth of ultralong carbon nanotube arrays for fiber spinning*. Advanced Materials, 2006. **18**(23): p. 3160-3163.

96. Zhang, X., et al., *Ultrastrong, stiff, and lightweight carbon-nanotube fibers*. Advanced Materials, 2007. **19**(23): p. 4198-4201.
97. Zhang, X., et al., *Strong carbon-nanotube fibers spun from long carbon-nanotube arrays*. Small, 2007. **3**(2): p. 244-248.
98. Lu, W., et al., *State of the Art of Carbon Nanotube Fibers: Opportunities and Challenges*, in Adv. Mater. 2012. p. 1805-1833.
99. Tran, C.D., et al., *Improving the tensile strength of carbon nanotube spun yarns using a modified spinning process*. Carbon, 2009. **47**(11): p. 2662-2670.
100. Zheng, L., G. Sun, and Z. Zhan, *Tuning array morphology for high-strength carbon-nanotube fibers*. Small, 2010. **6**(1): p. 132-137.
101. Vigolo, B., et al., *Improved structure and properties of single-wall carbon nanotube spun fibers*. Applied Physics Letters, 2002. **81**(7): p. 1210-1212.
102. Vigolo, B., et al., *Macroscopic fibers and ribbons of oriented carbon nanotubes*. Science, 2000. **290**(5495): p. 1331-1334.
103. Kis, A., et al., *Reinforcement of single-walled carbon nanotube bundles by intertube bridging*. Nature Materials, 2004. **3**(3): p. 153-157.
104. Vilatela, J.J., J.A. Elliott, and A.H. Windle, *A Model for the Strength of Yarn-like Carbon Nanotube Fibers*. ACS Nano, 2011. **5**(3): p. 1921-1927.
105. Li, Q., et al., *Deformation mechanisms of carbon nanotube fibres under tensile loading by in situ Raman spectroscopy analysis*. Nanotechnology, 2011. **22**(22): p. 225704.
106. Ajayan, P.M. and J.M. Tour, *Materials science: Nanotube composites*. Nature, 2007. **447**(7148): p. 1066-1068.
107. Moniruzzaman, M. and K.I. Winey, *Polymer nanocomposites containing carbon nanotubes*. Macromolecules, 2006. **39**(16): p. 5194-5205.
108. Xiao, L., et al., *Flexible, stretchable, transparent carbon nanotube thin film loudspeakers*. Nano Letters, 2008. **8**(12): p. 4539-4545.
109. Mora, R.J., J.J. Vilatela, and A.H. Windle, *Properties of composites of carbon nanotube fibres*. Composites Science and Technology, 2009. **69**(10): p. 1558-1563.
110. Gao, Y., et al., *Axial compression of hierarchically structured carbon nanotube fiber embedded in epoxy*. Advanced Functional Materials, 2010. **20**(21): p. 3797-3803.
111. Suhr, J., et al., *Fatigue resistance of aligned carbon nanotube arrays under cyclic compression*. Nature Nanotechnology, 2007. **2**(7): p. 417-421.
112. Xu, M., et al., *Tailoring temperature invariant viscoelasticity of carbon nanotube material*. Nano Letters, 2011. **11**(8): p. 3279-3284.
113. Wang, Z., et al., *Vibration reduction ability of MWCNT PVAc composites measured under high frequency for acoustic device application*. Journal of Materials Chemistry, 2011. **21**(12): p. 4150-4155.
114. Zeng, Y., et al., *Design and reinforcement: Vertically aligned carbon nanotube-based sandwich composites*. ACS Nano, 2010. **4**(11): p. 6798-6804.
115. Verdejo, R., et al., *Enhanced acoustic damping in flexible polyurethane foams filled with carbon nanotubes*. Composites Science and Technology, 2009. **69**(10): p. 1564-1569.

116. Deng, C.F., et al., *Damping characteristics of carbon nanotube reinforced aluminum composite*. Materials Letters, 2007. **61**(14-15): p. 3229-3231.
117. Sun, L., et al., *Energy absorption capability of nanocomposites: A review*. Compos Sci Technol, 2009. **69**(14): p. 2392-2409.
118. Suhr, J. and N.A. Koratkar, *Energy dissipation in carbon nanotube composites: a review*. J Mater Sci, 2008. **43**(13): p. 4370-4382.
119. Ci, L., et al., *Continuous carbon nanotube reinforced composites*. Nano Lett, 2008. **8**(9): p. 2762-2766.
120. Suhr, J., et al., *Fatigue resistance of aligned carbon nanotube arrays under cyclic compression*. Nat Nanotechnol, 2007. **2**(7): p. 417-421.
121. Teo, E.H.T., et al., *A carbon nanomattress: A new nanosystem with intrinsic, tunable, damping properties*. Adv Mater, 2007. **19**(19): p. 2941-+.
122. Pathak, S., et al., *Viscoelasticity and high buckling stress of dense carbon nanotube brushes*. Carbon, 2009. **47**(8): p. 1969-1976.
123. Cao, Q. and J.A. Rogers, *Ultrathin films of single-walled carbon nanotubes for electronics and sensors: A review of fundamental and applied aspects*. Advanced Materials, 2009. **21**(1): p. 29-53.
124. Gruner, G., *Carbon nanotube films for transparent and plastic electronics*. Journal of Materials Chemistry, 2006. **16**(35): p. 3533-3539.
125. Khang, D.Y., et al., *Molecular scale buckling mechanics in individual aligned single-wall carbon nanotubes on elastomeric substrates*. Nano Letters, 2008. **8**(1): p. 124-130.
126. Fan, Z., et al., *Toward the Development of Printable Nanowire Electronics and Sensors*. Advanced Materials, 2009. **21**(37): p. 3730-3743.
127. Srivastava, D., et al., *Predictions of enhanced chemical reactivity at regions of local conformational strain on carbon nanotubes: Kinky chemistry*. Journal of Physical Chemistry B, 1999. **103**(21): p. 4330-4337.
128. Tombler, T.W., et al., *Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation*. Nature, 2000. **405**(6788): p. 769-772.
129. Shaffer, M.S.P., X. Fan, and A.H. Windle, *Dispersion and packing of carbon nanotubes*. Carbon, 1998. **36**(11): p. 1603-1612.
130. Fan, S., et al., *Self-oriented regular arrays of carbon nanotubes and their field emission properties*. Science, 1999. **283**(5401): p. 512-514.
131. Yu, J., et al., *Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution*. Carbon, 2007. **45**(3): p. 618-623.
132. Ahn, Y.R., et al., *Compressional behavior of carbon nanotube reinforced mesophase pitch-based carbon fibers*. Fibers and Polymers, 2006. **7**(1): p. 85-87.
133. Kim, S.W., et al., *Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers*. Carbon, 2012. **50**(1): p. 3-33.
134. Hammel, E., et al., *Carbon nanofibers for composite applications*. Carbon, 2004. **42**(5-6): p. 1153-1158.
135. Liu, T., et al., *Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites*. Macromolecules, 2004. **37**(19): p. 7214-7222.

136. Song, Y.S. and J.R. Youn, *Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites*. Carbon, 2005. **43**(7): p. 1378-1385.
137. Niyogi, S., et al., *Chemistry of single-walled carbon nanotubes*. Accounts of Chemical Research, 2002. **35**(12): p. 1105-1113.
138. Dujardin, E., et al., *Purification of single-shell nanotubes*. Advanced Materials, 1998. **10**(8): p. 611-613.
139. Yang, S.J. and C.R. Park, *Facile preparation of monodisperse ZnO quantum dots with high quality photoluminescence characteristics*. Nanotechnology, 2008. **19**(3).
140. Liu, J., et al., *Fullerene pipes*. Science, 1998. **280**(5367): p. 1253-1256.
141. Kuznetsova, A., et al., *Oxygen-containing functional groups on single-wall carbon nanotubes: NEXAFS and vibrational spectroscopic studies*. Journal of the American Chemical Society, 2001. **123**(43): p. 10699-10704.
142. Ziegler, K.J., et al., *Controlled oxidative cutting of single-walled carbon nanotubes*. Journal of the American Chemical Society, 2005. **127**(5): p. 1541-1547.
143. Mawhinney, D.B., et al., *Infrared spectral evidence for the etching of carbon nanotubes: Ozone oxidation at 298 K [7]*. Journal of the American Chemical Society, 2000. **122**(10): p. 2383-2384.
144. Worsley, K.A., et al., *Functionalization and dissolution of nitric acid treated single-walled carbon nanotubes*. Journal of the American Chemical Society, 2009. **131**(50): p. 18153-18158.
145. Salzmann, C.G., et al., *The role of carboxylated carbonaceous fragments in the functionalization and spectroscopy of a single-walled carbon-nanotube material*. Advanced Materials, 2007. **19**(6): p. 883-887.
146. Khabashesku, V.N., W.E. Billups, and J.L. Margrave, *Fluorination of single-wall carbon nanotubes and subsequent derivatization reactions*. Accounts of Chemical Research, 2002. **35**(12): p. 1087-1095.
147. Holzinger, M., et al., *Sidewall functionalization of carbon nanotubes*. Angewandte Chemie - International Edition, 2001. **40**(21): p. 4002-4005.
148. Bahr, J.L., et al., *Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salts: A bucky paper electrode*. Journal of the American Chemical Society, 2001. **123**(27): p. 6536-6542.
149. Dyke, C.A. and J.M. Tour, *Solvent-free functionalization of carbon nanotubes*. Journal of the American Chemical Society, 2003. **125**(5): p. 1156-1157.
150. Holzinger, M., et al., *[2+1] Cycloaddition for cross-linking SWCNTs*. Carbon, 2004. **42**(5-6): p. 941-947.
151. Holzinger, M., et al., *Functionalization of single-walled carbon nanotubes with (R)-oxycarbonyl nitrenes*. Journal of the American Chemical Society, 2003. **125**(28): p. 8566-8580.
152. Zhao, B., et al., *Synthesis and characterization of water soluble single-walled carbon nanotube graft copolymers*. Journal of the American Chemical Society, 2005. **127**(22): p. 8197-8203.

153. Sun, Y.P., et al., *Soluble dendron-functionalized carbon nanotubes: Preparation, characterization, and properties*. Chemistry of Materials, 2001. **13**(9): p. 2864-2869.
154. Williams, K.A., et al., *Nanotechnology: Carbon nanotubes with DNA recognition*. Nature, 2002. **420**(6917): p. 761.
155. Hazani, M., et al., *Confocal fluorescence imaging of DNA-functionalized carbon nanotubes*. Nano Letters, 2003. **3**(2): p. 153-155.
156. Baker, S.E., et al., *Covalently Bonded Adducts of Deoxyribonucleic Acid (DNA) Oligonucleotides with Single-Wall Carbon Nanotubes: Synthesis and Hybridization*. Nano Letters, 2002. **2**(12): p. 1413-1417.
157. Li, X., et al., *Noncovalent assembly of carbon nanotube-inorganic hybrids*. Journal of Materials Chemistry, 2011. **21**(21): p. 7527-7547.
158. Moore, E.M., et al., *Enhancing the strength of polypropylene fibers with carbon nanotubes*. Journal of Applied Polymer Science, 2004. **93**(6): p. 2926-2933.
159. O'Connell, M.J., et al., *Band gap fluorescence from individual single-walled carbon nanotubes*. Science, 2002. **297**(5581): p. 593-596.
160. Tan, Y. and D.E. Resasco, *Dispersion of single-walled carbon nanotubes of narrow diameter distribution*. Journal of Physical Chemistry B, 2005. **109**(30): p. 14454-14460.
161. Islam, M.F., et al., *High weight fraction surfactant solubilization of single-wall carbon nanotubes in water*. Nano Letters, 2003. **3**(2): p. 269-273.
162. Star, A., et al., *Noncovalent side-wall functionalization of single-walled carbon nanotubes*. Macromolecules, 2003. **36**(3): p. 553-560.
163. Giulianini, M., et al., *Regioregular poly(3-hexyl-thiophene) helical self-organization on carbon nanotubes*. Applied Physics Letters, 2009. **95**(1).
164. Zou, J., et al., *Preparation of a superhydrophobic and conductive nanocomposite coating from a carbon-nanotube-conjugated block copolymer dispersion*. Advanced Materials, 2008. **20**(17): p. 3337-3341.
165. Zou, J., et al., *Dispersion of pristine carbon nanotubes using conjugated block copolymers*. Advanced Materials, 2008. **20**(11): p. 2055-2060.
166. Kang, Y. and T.A. Taton, *Micelle-encapsulated carbon nanotubes: A route to nanotube composites*. Journal of the American Chemical Society, 2003. **125**(19): p. 5650-5651.
167. O'Connell, M.J., et al., *Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping*. Chemical Physics Letters, 2001. **342**(3-4): p. 265-271.
168. Xu, Z., X. Yang, and Z. Yang, *A Molecular Simulation Probing of Structure and Interaction for Supramolecular Sodium Dodecyl Sulfate/Single-Wall Carbon Nanotube Assemblies*. Nano Lett, 2010. **10**(3): p. 985-991.
169. Doe, C., et al., *Charged rod-like nanoparticles assisting single-walled carbon nanotube dispersion in water*. Advanced Functional Materials, 2008. **18**(18): p. 2685-2691.
170. Zheng, Q., et al., *Investigation of molecular interactions between SWNT and polyethylene/polypropylene/polystyrene/polyaniline molecules*. J Phys Chem C, 2007. **111**(12): p. 4628-4635.

171. Chiu, C.-c., et al., *Molecular Dynamics Study of a Carbon Nanotube Binding Reversible Cyclic Peptide*. *Acs Nano*, 2010. **4**(5): p. 2539-2546.
172. Johnson, R.R., A.T.C. Johnson, and M.L. Klein, *Probing the structure of DNA-carbon nanotube hybrids with molecular dynamics*. *Nano Lett*, 2008. **8**(1): p. 69-75.
173. Johnson, R.R., A.T.C. Johnson, and M.L. Klein, *The Nature of DNA-Base-Carbon-Nanotube Interactions*. *Small*, 2010. **6**(1): p. 31-34.
174. Liu, L., W. Ma, and Z. Zhang, *Macroscopic Carbon Nanotube Assemblies: Preparation, Properties, and Potential Applications*. *Small*, 2011. **7**(11): p. 1504-1520.
175. Sahoo, N.G., et al., *Polymer nanocomposites based on functionalized carbon nanotubes*. *Progress in Polymer Science*, 2010. **35**(7): p. 837-867.
176. Peng, X. and S. Wong, *Functional Covalent Chemistry of Carbon Nanotube Surfaces*. *Advanced Materials*, 2009. **21**(000263492000001): p. 625-642.
177. Nardelli, M., B. Yakobson, and J. Bernholc, *Mechanism of strain release in carbon nanotubes*. *Phys Rev B*, 1998. **57**(8): p. R4277-R4280.
178. Lawn, B., *Fracture of Brittle Solids*, 1993.
179. Griffith, A.A., *The phenomena of rupture and flow in solids*. *Philos. Trans. R. Soc. London*, 1920. **221**: p. 163-198.
180. Freund, L.B., *Dynamic Fracture Mechanics*, 1998.
181. Nabarro, F.R.N., *Creep at very low rates*. *Metallurgical And Materials Transactions A-Physical Metallurgy And Materials Science*, 2002. **33**(000173776300002): p. 213-218.
182. George H, V., *Frequency factors and isotope effects in solid state rate processes*. *Journal of Physics and Chemistry of Solids*, 1957. **3**(1-2): p. 121-127.
183. Shewmon, P.G., *Diffusion in solids* 1989, Minerals, Metals, & Materials Society: Warrendale, Pa.
184. Brenner, D., et al., *Atomic modeling of carbon-based nanostructures as a tool for developing new materials and technologies*. *Cmes-Comp Model Eng*, 2002. **3**(5): p. 643-673.
185. Brenner, D., et al., *A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons*. *J Phys-Condens Mat*, 2002. **14**(4): p. 783-802.
186. Los, J.H., et al., *Improved long-range reactive bond-order potential for carbon. I. Construction*. *Physical Review B*, 2005. **72**(21).
187. Allinger, N., Y. Yuh, and J. Lii, *Molecular mechanics - the MM3 force-field for hydrocarbons.1*. *J Am Chem Soc*, 1989. **111**(23): p. 8551-8566.
188. van Duin, A., et al., *ReaxFF: A reactive force field for hydrocarbons*. *J Phys Chem A*, 2001. **105**(41): p. 9396-9409.
189. Ruoff, R., D. Qian, and W. Liu, *Mechanical properties of carbon nanotubes: theoretical predictions and experimental measurements*. *Cr Phys*, 2003. **4**(9): p. 993-1008.
190. Jeong, B.-W., J.-K. Lim, and S.B. Sinnott, *Tensile mechanical behavior of hollow and filled carbon nanotubes under tension or combined tension-torsion*. *Applied Physics Letters*, 2007. **90**(2): p. 023102.

191. Jeong, B.-W., J.-K. Lim, and S.B. Sinnott, *Tuning the torsional properties of carbon nanotube systems with axial prestress*. Applied Physics Letters, 2008. **92**(25): p. 253114.
192. Abell, G., *Empirical chemical pseudopotential theory of molecular and metallic bonding*. Phys Rev B, Phys Rev B, 1985. **31**(10): p. 6184-6196.
193. Zhou, L.G. and S.Q. Shi, *Molecular dynamic simulations on tensile mechanical properties of single-walled carbon nanotubes with and without hydrogen storage*. Computational Materials Science, 2002. **23**(1-4): p. 166-174.
194. Liew, K., X. He, and C. Wong, *On the study of elastic and plastic properties of multi-walled carbon nanotubes under axial tension using molecular dynamics simulation*. Acta Mater, 2004. **52**(9): p. 2521-2527.
195. Tuckerman, M., *Statistical Mechanics and Molecular Simulations*. 2010: p. 696.
196. Jeong, B.-W., J.-K. Lim, and S.B. Sinnott, *Torsional stiffening of carbon nanotube systems*. Applied Physics Letters, 2007. **91**(9): p. 093102.
197. Frenkel, D.S., B., *Understanding molecular simulation : from algorithms to applications*. 2nd ed2002, San Diego, Calif.: Academic Press.
198. Press, W.H., et al., *Numerical Recipes in C: The Art of Scientific Computation*. 2nd ed1992, Cambridge: Cambridge University Press.
199. Liu, D.C. and J. Nocedal, *On the limited memory BFGS method for large scale optimization*. Mathematical Programming, Series B, 1989. **45**(3): p. 503-528.
200. Bitzek, E., et al., *Structural relaxation made simple*. Physical Review Letters, 2006. **97**(17).
201. Henkelman, G. and H. Jonsson, *Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points*. Journal of Chemical Physics, 2000. **113**(22): p. 9978-9985.
202. Henkelman, G., B.P. Uberuaga, and H. Jonsson, *Climbing image nudged elastic band method for finding saddle points and minimum energy paths*. Journal of Chemical Physics, 2000. **113**(22): p. 9901-9904.
203. Spoel, D.V.D., A. Patriksson, and M.M. Seibert, *Protein folding properties from molecular dynamics simulations*, in *Proceedings of the 8th international conference on Applied parallel computing: state of the art in scientific computing2007*, Springer-Verlag: Umeå, Sweden. p. 109-115.
204. Phillips, J.C., et al., *Scalable molecular dynamics with NAMD*. Journal of Computational Chemistry, 2005. **26**(16): p. 1781-1802.
205. Salomon-Ferrer, R., D.A. Case, and R.C. Walker, *An overview of the Amber biomolecular simulation package*. Wiley Interdisciplinary Reviews: Computational Molecular Science, 2012: p. n/a-n/a.
206. Dommelen, L.V.; Available from: <http://www.eng.fsu.edu/~dommelen/research/nano/brenner/> 2009.
207. Mutat, T.; Available from: <http://phycomp.technion.ac.il/~talimu/code1.html> 2009.
208. GULP. Available from: <https://http://www.ivec.org/gulp/potentials.html> 2010.
209. William Humphrey, A.D., Klaus Schulten, *{VMD} -- {V}isual {M}olecular {D}ynamics*. Journal of Molecular Graphics, 1996. **14**: p. 33-38.

210. Dumitrica, T., T. Belytschko, and B. Yakobson, *Bond-breaking bifurcation states in carbon nanotube fracture*. J Chem Phys, 2003. **118**(21): p. 9485-9488.
211. Gorokhov, D.A. and G. Blatter, *Diffusion and creep of a particle in a random potential*. Physical Review B - Condensed Matter and Materials Physics, 1998. **58**(1): p. 213-217.
212. Dresselhaus, M., G. Dresselhaus, and A. Jorio, *Unusual properties and structure of carbon nanotubes*. Annu Rev Mater Res, 2004. **34**: p. 247-278.
213. Hess, H. and E.L. Dumont, *Fatigue Failure and Molecular Machine Design*. Small (Weinheim an der Bergstrasse, Germany), 2011(21574250).
214. Ma, G., et al., *How long can single-walled carbon nanotube ropes last under static or dynamic fatigue?* Applied Physics Letters, 2008. **92**(8): p. 033105.
215. Bernstein, N. and D. Hess, *Lattice trapping barriers to brittle fracture*. Phys Rev Lett, 2003. **91**(2): p. 025501.
216. Kramers, H., *Brownian motion in a field of force and the diffusion model of chemical reactions*. Physica, 1940. **7**: p. 284-304.
217. Curran, D., L. Seaman, and D. Shockey, *Dynamic failure of solids*. Phys Rep, 1987. **147**(5-6): p. 253-388.
218. Evans, E. and K. Ritchie, *Dynamic strength of molecular adhesion bonds*. Biophys J, 1997. **72**(4): p. 1541-1555.
219. Tobolsky, A. and H. Eyring, *Mechanical properties of polymeric materials*. J Chem Phys, 1943. **11**(3): p. 125-134.
220. Zhurkov, S., *Kinetic concept of strength of solids*. Int J Fract Mech, 1965. **1**(4): p. 311-&.
221. Wei, C., K. Cho, and D. Srivastava, *Tensile strength of carbon nanotubes under realistic temperature and strain rate*. Phys Rev B, 2003. **67**(11): p. 115407.
222. Xiao, T., X. Xu, and K. Liao, *Characterization of nonlinear elasticity and elastic instability in single-walled carbon nanotubes*. J Appl Phys, 2004. **95**(12): p. 8145-8148.
223. Tan, S.C.W., et al., *Viscoelastic behaviour of human mesenchymal stem cells*. BMC Cell Biol, 2008. **9**: p. 40.
224. Guevorkian, K., et al., *Aspiration of Biological Viscoelastic Drops*. Phys Rev Lett, 2010. **104**(21): p. 218101.
225. Liu, C., et al., *Synthesis of macroscopically long ropes of well-aligned single-walled carbon nanotubes*. Adv Mater, 2000. **12**(16): p. 1190-1192.
226. Cheng, H., et al., *Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons*. Applied Physics Letters, 1998. **72**(25): p. 3282-3284.
227. Xiao, T., et al., *Force-strain relation of bundles of carbon nanotubes*. Applied Physics Letters, 2006. **89**(3): p. 033116.
228. Guo, J., et al., *How long can single-walled carbon nanotube ropes last under static or dynamic fatigue?* Applied Physics Letters, 2008.
229. Liu, C., et al., *Synthesis of macroscopically long ropes of well-aligned single-walled carbon nanotubes*. Advanced Materials, 2000. **12**(16): p. 1190-1192.
230. Suhr, J., et al., *Viscoelasticity in carbon nanotube composites*. Nat Mater, 2005. **4**(2): p. 134-137.

231. Zhang, Y., et al., *Heterostructures of Single-Walled Carbon Nanotubes and Carbide Nanorods*. Science, 1999. **285**(5434): p. 1719.
232. Zhu, H., et al., *Direct Synthesis of Long Single-Walled Carbon Nanotube Strands*. Science, 2002. **296**(5569): p. 884.
233. Qian, D., et al., *Mechanics of carbon nanotubes*. Applied Mechanics Reviews, 2002. **55**: p. 495.
234. Cumings, J. and A. Zettl, *Low-friction nanoscale linear bearing realized from multiwall carbon nanotubes*. Science, 2000. **289**(5479): p. 602-604.
235. Syue, S.-H., et al., *Internanotube friction*. Applied Physics Letters, 2006. **89**(16): p. 163115.
236. Xiao, T. and K. Liao, *Nonlinear elastic properties of carbon nanotubes subjected to large axial deformations*. Phys Rev B, 2002. **66**(15): p. 153407.
237. Benedict, L., et al., *Microscopic determination of the interlayer binding energy in graphite*. Chem Phys Lett, 1998. **286**(5-6): p. 490-496.
238. Hasegawa, M., K. Nishidate, and H. Iyetomi, *Energetics of interlayer binding in graphite: The semiempirical approach revisited*. Phys Rev B, 2007. **76**(11): p. 115424.
239. Cheng, H., et al., *Bulk morphology and diameter distribution of single-walled carbon nanotubes synthesized by catalytic decomposition of hydrocarbons*. Chem Phys Lett, 1998. **289**(5-6): p. 602-610.
240. Sinitskii, A., et al., *Corrugation of Chemically Converted Graphene Monolayers on SiO₂*. Acs Nano, 2010. **4**(6): p. 3095-3102.
241. Neek-Amal, M. and F.M. Peeters, *Graphene nanoribbons subjected to axial stress*. Phys Rev B, 2010. **82**(8): p. 085432.
242. Rafiee, M.A., et al., *Fracture and Fatigue in Graphene Nanocomposites*. Small, 2010. **6**(2): p. 179-183.
243. Sen, D., et al., *Tearing Graphene Sheets From Adhesive Substrates Produces Tapered Nanoribbons*. Small, 2010. **6**(10): p. 1108-1116.
244. Compton, O.C. and S.T. Nguyen, *Graphene Oxide, Highly Reduced Graphene Oxide, and Graphene: Versatile Building Blocks for Carbon-Based Materials*. Small, 2010. **6**(6): p. 711-723.
245. Brodie, B.C., *On the Atomic Weight of Graphite*. Philos. Trans. R. Soc. London, 1859. **149**: p. 249-259.
246. Staudenmaier, L., *Verfahren zur Darstellung der Graphitsäure*. Berichte der deutschen chemischen Gesellschaft, 1898. **31**(2): p. 1481-1487.
247. Hummers, W.S. and R.E. Offeman, *Preparation of Graphitic Oxide*. Journal of the American Chemical Society, 1958. **80**(6): p. 1339-1339.
248. Liang, J., et al., *Molecular-Level Dispersion of Graphene into Poly(vinyl alcohol) and Effective Reinforcement of their Nanocomposites*. Adv. Funct. Mater., 2009. **19**(14): p. 2297-2302.
249. Medhekar, N.V., et al., *Hydrogen Bond Networks in Graphene Oxide Composite Paper: Structure and Mechanical Properties*. Acs Nano, 2010. **4**(4): p. 2300-2306.
250. Zhang, C., et al., *Graphene Oxide-Assisted Dispersion of Pristine Multiwalled Carbon Nanotubes in Aqueous Media*. J Phys Chem C, 2010. **114**(26): p. 11435-11440.

251. Gao, W., et al., *New insights into the structure and reduction of graphite oxide*. Nat Chem, 2009. **1**(5): p. 403-408.
252. Gao, X., J. Jang, and S. Nagase, *Hydrazine and Thermal Reduction of Graphene Oxide: Reaction Mechanisms, Product Structures, and Reaction Design*. J Phys Chem C, 2010. **114**(2): p. 832-842.
253. Bagri, A., et al., *Stability and Formation Mechanisms of Carbonyl- and Hydroxyl-Decorated Holes in Graphene Oxide*. J Phys Chem C, 2010. **114**(28): p. 12053-12061.
254. Bagri, A., et al., *Structural evolution during the reduction of chemically derived graphene oxide*. Nat Chem, 2010. **2**(7): p. 581-587.
255. Sun, H., *COMPASS: An ab initio force-field optimized for condensed-phase applications - Overview with details on alkane and benzene compounds*. J Phys Chem B, 1998. **102**(38): p. 7338-7364.
256. Palser, A.H.R., *Interlayer interactions in graphite and carbon nanotubes*. Physical Chemistry Chemical Physics, 1999. **1**(18): p. 4459-4464.
257. Foroutan, M. and A.T. Nasrabadi, *Investigation of the Interfacial Binding between Single-Walled Carbon Nanotubes and Heterocyclic Conjugated Polymers*. J Phys Chem B, 2010. **114**(16): p. 5320-5326.
258. Yang, T., et al., *Experimental estimation of friction energy within a bundle of single-walled carbon nanotubes*. Applied Physics Letters, 2008. **93**(4): p. 041914.
259. Kim, J., et al., *Graphene Oxide Sheets at Interfaces*. J Am Chem Soc, 2010. **132**(23): p. 8180-8186.
260. Dai, H., *Carbon nanotubes: Synthesis, integration, and properties*. Accounts of Chemical Research, 2002. **35**(12): p. 1035-1044.
261. Tu, X., et al., *DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes*. Nature, 2009. **460**(7252): p. 250-253.
262. Yan, L.Y., et al., *Enrichment of (8,4) Single-Walled Carbon Nanotubes Through Coextraction with Heparin*. Small, 2010. **6**(1): p. 110-118.
263. Dreyer, D.R., et al., *The chemistry of graphene oxide*. Chem Soc Rev, 2010. **39**(1): p. 228-240.
264. Ortmann, F., W.G. Schmidt, and F. Bechstedt, *Attracted by Long-Range Electron Correlation: Adenine on Graphite*. Physical Review Letters, 2005. **95**(18): p. 186101.
265. Gordillo, M.C. and J. Marti, *Structure of water adsorbed on a single graphene sheet*. Physical Review B, 2008. **78**(7): p. 075432.
266. Kovtyukhova, N.I., *Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations*. Chemistry of Materials, 1999. **11**(3): p. 771-778.
267. Hilding, J., et al., *Dispersion of carbon nanotubes in liquids*. Journal of Dispersion Science and Technology, 2003. **24**(1): p. 1-41.
268. Toth, G., et al., *Carbon-Nanotube-Based Electrical Brush Contacts*. Advanced Materials, 2009. **21**(20): p. 2054-2058.
269. *Defects in carbon nanotubes Implications for mechanical properties*. 2007: p. 1-109.

- 270. Zhou, L.G. and S.Q. Shi, *Computer simulation of the fracture of carbon nanotubes in a hydrogen environment*. Philosophical Magazine A: Physics of Condensed Matter, Structure, Defects and Mechanical Properties, 2002. **82**(17-18): p. 3201-3209.
- 271. *Research*. Available from: <http://en.wikipedia.org/wiki/Research> 2011.