ABSTRACT

JIN, YUN Atomistic Simulations of Fracture of 2D Graphene Systems and the Elastic Properties of Carbon Nanotubes. (Under the direction of Dr. Fuh-Gwo Yuan)

This dissertation has two main parts. The first part is the atomistic simulations of fracture of 2d graphene systems. In principle the macroscopic mechanical properties of materials are determined by the atoms and the basic laws of physics. For the fracture of materials, atomistic simulations can provide basic understanding of the origins of fracture due to the bond rupture. In this dissertation the fracture mechanism of a nanostructure material has been investigated by atomistic simulations. Macroscopic fracture parameters have been examined from both atomistic simulation and continuum models. Methods of calculating energy release rates in atomic systems have been successfully developed. The atomic descriptions of the stress field in front of crack tips were also obtained. These simulations showed that, in macroscopic fracture mechanics under small deformation, linear elastic fracture mechanics is sufficient for the description of cracking behavior for this covalently bonded material. The results merge the discrete (atomistic) and continuum (macroscopic) description of facture. Meanwhile, a method to calculate $J$-integral in the atomic system has been developed. The numerical results of $J$-integral agreed very well with the energy release rate in the linear elastic condition. After a necessary modification on the Tersoff-Brenner potential, the critical values of $J$-integral, denoted by $J_c$, have been obtained as the measure of the fracture toughness of graphene sheets.
In the second part of this dissertation the mechanical properties of single-walled carbon nanotube (SWNT) have been evaluated. The values of the in-plane Young’s modulus, rotational shear modulus, and in-plane Poisson’s ratio are in the range of existing theoretical and experimental results. Several elastic moduli of SWNTs have been obtained using molecular dynamic simulations. It has been shown from the simulations that the elastic constants of SWNTs are insensitive to the morphology pattern such as nanotube radius and thus the effect of curvature on the elastic constants can be neglected. Assumption of the transversely isotropic properties on the cylinder surface of the single-walled nanotube has been confirmed by numerical calculations. Besides the conventional energy approach, a new method, which denoted as force approach in the dissertation, has been developed to analyze the elastic properties of carbon nanotubes. The results from two approaches matched very well. The advantage of the force approach is that it can provide more accurate prediction than the energy approach. Furthermore, the force approach can predict the nonlinear behavior without assumption of assumed total potential energy in quadratic form described for small-strain deformation in the energy approach.
ATOMISTIC SIMULATIONS OF FRACTURE OF
2D GRAPHENE SYSTEMS AND
THE ELASTIC PROPERTIES OF CARBON NANOTUBES

by

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Chair of Advisory Committee
To my parents
Biography

Yun Jin was born on September 28, 1975 in Wuwei, Anhui Province, People’s Republic of China. He graduated from Wuwei High School, China and received a Bachelor of Science degree in Theoretical and Applied Mechanics from University of Science and Technology of China (USTC) in July 1997. He completed his Master of Engineering project in Solid Mechanics, Experimental and numerical studies on magneto-rheological fluids, under the direction of Professor Peiqiang Zhang in USTC in July 2000. Immediately thereafter, he entered the Ph.D. program of North Carolina State University (NCSU) in Mechanical Engineering under the direction of Dr. Fuh-Gwo Yuan. Yun Jin’s research at NCSU mainly focused on the atomistic simulations of elastic properties of carbon nanotubes and the fractures of nanostructure materials.
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NOMENCLATURE & ABBREVIATIONS

Brief definitions of the most frequently used symbols and abbreviations are listed as following. Some symbols necessarily have different definitions in different sections. In such conditions, definitions are provided locally and are used consistently within the section.

**Greek symbols**
- $\alpha$: Atom identity
- $\beta$: Atom identity
- $\Delta a$: Equilibrium interatomic distance, m
- $\Delta t$: time step, s
- $\varepsilon$: vector of dielectric permittivity $\varepsilon_{ij}$, F/in.
- $\varepsilon_{ij}$: Components of strain tensor
- $\kappa$: Parameter for plane stress or plane strain
- $\mu$: Elastic shear modulus, pa
- $\nu$: Poisson’s ratio
- $\sigma_{ij}$: Components of stress tensor, pa
- $\delta$: constant in Tersoff-Brenner potential

**Roman symbols**
- $a$: Half of the crack length, m
- $a_0$: Constant in Tersoff-Brenner potential
- $c_0$: Constant in Tersoff-Brenner potential
- $C_{ijkl}$: Components of stiffness matrix
$D_e$  Constant in Tersoff-Brenner potential, ev 

$d_0$  Constant in Tersoff-Brenner potential 

$E$  Young’s modulus, pa 

$F$  Interatomic force 

$fs$  Femto-second, $10^{-15}$ s 

$G, G_I, G_{II}$  Energy release rate, pa m 

$K_I, K_{II}$  Stress intensity factors 

$k_B$  Boltzmann constant 

$L$  Length, m 

$p$  $p$ atomic orbital 

$p_x, p_y, p_z$  Three different orientations in $p$ atomic orbital 

$ps$  Pico-second, $10^{-12}$ s 

$r$  Radius, m 

$r_e$  Constant in Tersoff-Brenner potential, m 

$r, \theta, z$  Cylindrical coordinates 

$S$  Constant in Tersoff-Brenner potential 

$s$  $s$ atomic orbital 

$t$  wall thickness of nanotube and graphene sheet, m 

$U$  Potential energy, J 

$V$  Volume of a domain, $m^3$ 

$x_1, x_2$  Cartesian coordinates of a plane 

$u_i, u_2$  Displacements in the directions of $x_1, x_2$, respectively, m
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>BCC</td>
<td>Body-Centered-Cubic</td>
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<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
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<tr>
<td>DFT</td>
<td>Density-Functional Theory</td>
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<tr>
<td>EDI</td>
<td>Equivalent Domain Integral</td>
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<tr>
<td>FCC</td>
<td>Faced-Centered-Cubic</td>
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<tr>
<td>FEA</td>
<td>Finite Element Analysis</td>
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<tr>
<td>GB</td>
<td>Ground Boundary</td>
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<tr>
<td>LEFM</td>
<td>Linear Elastic Fracture Mechanics</td>
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<td>MD</td>
<td>Molecular Dynamics</td>
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<td>MM</td>
<td>Molecular Mechanics</td>
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<tr>
<td>MWNT</td>
<td>Multi-Walled Nanotube</td>
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<tr>
<td>PVW</td>
<td>Principle of Virtual Work</td>
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<tr>
<td>SWNT</td>
<td>Single-Walled Nanotube</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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1 INTRODUCTION

Fracture mechanics has become an engineering discipline that has been studied by both atomistic and continuum approaches. In 1921, Griffith approached the fracture theory of brittle materials from the fundamental energy balance, by introducing a specific surface energy along the crack surface. All the atomic or internal structural factors are hidden in the surface energy. An important precursor to the Griffith theory was the elastic fields of an elliptical cavity based on continuum theory. Although Griffith formulated a fracture criterion in terms of macroscopic thermodynamic quantities, a complete description required an evaluation of events at the molecular level. The maximum stress at the tip of an equilibrium crack must correspond to the theoretical cohesive strength of the material; that is, the largest possible stress level that the molecular structure can sustain by virtue of its intrinsic bond strength. The global energy approach could not be extended easily to many different geometries and loading conditions encountered in a variety of experiments and practical structures.

In 1957, Irwin used a local force approach showed, for the first time, the local stresses around the crack tip in linear elastic materials. Irwin suggested that the singular stresses could be characterized in terms of a singular parameter, stress intensity factor. This factor combines the effect of geometry and load. As a consequence, the fracture characterization problem was reduced to the calculation of single quantity of universal significance. Furthermore, Irwin provided a quantitative relation between that strain energy release rate, a global parameter, and the stress intensity factor, a local crack-tip parameter. Since the stress intensity factor characterizes the failure at the crack tip as long
as process and inelastic zones are small compared with the macroscopic dimensions of the solids, so called small scale yielding, the Irwin theory can apply to non-brittle materials. Since then, the continuum based fracture mechanics has been of great interest in applying to ductile materials using other parameters such as $J$-integral and other advanced materials including composite materials. Various fracture criteria have been established from a macroscopic point of view. A damage tolerance philosophy based on fracture mechanics has been developed to provide structural integrity assessments in aerospace industry.

These continuum approaches have successfully described many fracture mechanisms in solid materials and continue to be of great use. Nevertheless, they still have some shortcomings, such as the spurious singularity of the stress field at crack tip. In principle, all the macroscopic mechanical responses of a material are governed by constitutive atoms and the basic laws of physics, in particular fracture associated with successive failure at atomic level. Hence, atomistic simulation may open new avenues in studies of microscopic origins of material failure behavior. Direct observations from transmission electron microscopy (TEM) have already proven the existence of sharp atomic crack, as can be seen in Figure 1.1 (Lawn et al., 1980). The dimensions in the figures indicated that the phenomena we are interested in are in the level of $10^2$ nm, especially the scales at crack tip is no more than 10 nm. Obviously, the underlying atomic structures of the material are definitely not able to be neglected for the investigations on such kind of small scale. Therefore the atomistic predictions would be necessary and enable us to gain more insights on the material behavior at the most fundamental level. A material studied in the prediction can be always perfectly characterized in terms of internal structure, composition, defects, etc., making the results often less ambiguous than in experiments. Continuum mechanics approach, on the other hand, is often based on
phenomenological constitutive models which can be an idealization of observed
deformation properties that may not be representative of actual physical mechanism. In
summary, to provide a basic understanding of the origins of facture due to the rupture of
the interatomic bonds, investigations on the atomic or molecular levels are necessary and
critical.

Fig 1.1 Transmission electron micrograph of cracks in silicon (After Lawn et al., 1980)

1.1 Literature review

The first attempt to explicitly analyze the interatomic forces which resist crack
extension is by Elliott (1947). In his approach the relationship between normal stress and
the displacement along the crack plane is deduced based on the linear elastic solution of a
cracked body under tension. By equating the area under the stress-displacement curve to
the surface energy and the maximum stress to the critical rupture stress for the material,
Elliott formulated a model with two semi-infinite solids that attract each other by the
atomistic force-separation curve. A very close relation with Griffith theory has been
found. Latter, Cribb and Tomkins (1967) proposed a more direct approach to evaluate the
distribution of interatomic forces across crack surface. They also derived the corresponding interatomic force-distance curve by the continuum theory of linear elasticity.

The above two works, though attempting to using discrete models to analyze the interactions and displacements around crack tip, were indeed still completely based on linear elastic continuum theory. One of the first achievements to develop direct numerical computations of atomic aspect of fracture may be the so called Goodier-Kanninen model (1966). Goodier and Kanninen investigated an elastic solid containing external plane cracks. The atomic model representing the crack tip structure is shown in Figure 1.2. They assumed that the interatomic forces bridging the crack surface were based on nonlinear force-separation law, while all other interatomic interactions are considered to be linearly elastic. In the model, four different functions were used to represent the principal features of the force-separation law, which are linear, sinusoidal, exponential, and inverse power functions. The Young’s modulus was obtained by calculating the initial slope of the force-separation curve, and the surface energy was taken as the area under the curve. For those atoms on the crack surface, only displacements in the vertical direction were considered. Plus considering the different treatment of the atoms on the crack surface and other places, these made the whole model actually representing two linearly elastic semi-infinite bodies connected by a series of non-linear springs. Subsequently, Kanninen and co-workers (Gehlen and Kanninen, 1970; Kanninen and Gehlen, 1971; Gehlen, Hahn, and Kanninen, 1973) extended the previous model to treat the atoms near the crack tip as atomic crystal structures, which leaded to three degrees of freedom for each atom. After detailed studied the atomic arrangements of body-centered-cubic (BCC) iron, an important fracture parameter, the critical applied stress at which crack propagates, is estimated.
Kanninen and co-workers’ approaches led us to a deeper understanding of the crack process, and more importantly, they contributed two basic ideas of atomistic modeling: 1) the construction of an atomic model to reflect the key physical features of the system; 2) proper selection of the interatomic force-separation laws to characterize fundamentally chemical bonding. Due to the lack of knowledge of interatomic potential functions and the limitation of computer speed at that time, the shortcomings of their models are also obvious. First of all, too few numbers of atoms (no more than 50) have been handled in the numerical computation which let the atomic displacements actually still being dominated by linear continuum elasticity. The representations of the atomic interactions were oversimplified and as the author recognized, the interactions between the atomic region and the continuum region were ignored. Here we want to mention a long-time misleading method in many approaches in which the Young’s modulus was always evaluated from the initial slope of local atomic force-separation laws. While the Young’s modulus of the material is not necessarily equal to the initial slope since the global strain of the whole structure can not be taken for granted as equivalent to the local strain of the atom pairs.
Almost at the same time Chang (1970) presented a similar work on simulating the atomic configurations and cohesive forces fields around crack tip in BCC and FCC (face-centered-cubic) metal. Atom-relaxation methods, which were first applied to compute theoretical maximum strengths of preface crystals in brittle solids by Tyson (1966) and subsequently developed by Chang (1967), were employed to integrate the classical motion equations. The basic idea of atom-relaxation methods is to evaluate the total kinetic energy at each step of the integration of the motion equations. Whenever the total kinetic energy got to the maximum, all the velocities are set to zero. Therefore the potential energy will drop monotonically towards the minimum. Cracks were formed by removing a single plane of atoms, and external tensile strains were applied normal to the crack. The results showed that the crack tip force fields mainly depend on the orientation of the crack with respect to the crystallite. However, the concept of the shearing component of the forces mentioned in the paper is vague, and the method of computing the shearing force was also arguable.

Sinclair and Lawn (1972 a, b, c) considered atomically sharp cracks in diamond, silicon and germanium. Both continuum approach and atomistic approach were applied. The results indicated that continuum theory is capable of giving remarkably accurate predictions of the crack-tip displacement field, except very near to the crack tip. The atomistic approach was actually coupling the atomic and continuum region together. It differed primarily from the previous work such as Kanninen’s is that, instead of applying the rigid boundary condition, a flexible boundary condition which let the outer continuum region be able to adjust as the response of the motion of the inner atomic zone. The later works of Sinclair (1975, 1978) extended their calculations and investigated the effect of the kinks at the crack front.
Another approach to model the crack in discrete system is the lattice theory. Thomson and co-worker (Thomson, Hsieh, and Rana, 1971; Hsieh and Thomson, 1973; Fuller and Thomson, 1977) developed a discrete quasi-one-dimensional chain model of a crack in lattice static, as shown in Figure 1.3. The model consists of two semi-infinite chains of atoms that are bonded with two types of interactions which were modeled as spring elements: nonlinear in the crack tip bond and linear in other bonds. All displacements are assumed to be vertical. Latter a two-dimensional lattice model was proposed. They studied the fracture in atomic lattices, especially the fundamental role of the surface energy in brittle fracture. Ashurst et al. (1976) described the crack propagation in the two-dimensional triangular lattice.

With the fast progress on high-speed computers, researchers can handle even multi-million atoms computations in molecular dynamics (MD) simulation using supercomputer and parallel algorithms in the last decade. Most of the works were mainly focused on describing the phenomena of the dynamic crack propagation.

Holian and Ravelo (1995) used MD simulation to simulation the crack propagation under mode-I tensile deformation at high strain rates. They also discussed the
distinction between brittle and ductile behavior for dynamical cracks in the paper. A similar approach pursued by Zhang et al., (1995) to study the brittle and ductile fracture in metal crystals led to the results that geometry of crack and crystal orientation has strong effect on the crack tip processes. Also, generally it has been assumed that a brittle failure implies that the crack propagates without the emission of dislocations while the materials where dislocations are emitted are generally believed to be ductile materials. This view implies a description of brittle-ductile behavior in terms of the processes occurring at the crack tip. While an atomistic simulation shows controversy phenomenon that the emitted dislocations can actually lead to brittle failure under certain condition (Farkas, 1998). There are also many other articles focused on the simulation of profiles of crack tip process in different atomic models (Ludwig and Gumbsch, 1998; Trebin et al., 1999; Gall et al., 2000; Gao et al., 2001; Rountree et al., 2002; and etc.)

Meanwhile, Marder and Liu (1993) investigated the instabilities in crack propagation and the crack-front speed in a 2-dimensional system consists of coupled springs which would snap beyond a critical displacement. The results showed that the local crack branches appear when the crack-front speed exceeds $0.66V_R$ where $V_R$ is the Rayleigh wave speed in the material. Consequently, Omeltchenko et al. (1997) simulated the crack propagation under tensile mode in a graphite sheet containing a million carbon atoms by MD simulation based on Brenner’s reactive empirical bond-order potential. The fracture profiles and the speeds of the crack propagation have been obtained. A latter study provided a multi-scale modeling of brittle-crack propagation and applied it to the fracture growth in a 2-dimensional Ag plate in macroscopic dimensions (Rafii-Tabar et al., 1998). The critical crack velocity has been predicted.
In this thesis our investigation of atomic fracture is mainly performed in a 2-dimensional graphene system. Therefore, recent works closely related to the atomic fracture of carbon allotropes are emphasized as following.

Shenderova et al. (2000) proposed an atomistic model of the fracture of polycrystalline diamond. Fracture stresses for two orientated Grain Boundaries (GB’s) were evaluated. Also, the cleavage energies for GB’s were computed through both density-functional theory (DFT) and molecular dynamic simulations (MD). Their results showed that the theoretical fracture stresses of individual GB is related mainly by GB type, such as orientation, rather than by the cleavage energies. Belytschko et al. (2002) studied the fracture of carbon nanotubes by molecular mechanics simulations. The fracture behavior is found to be almost independent of the separation energy and to depend primarily on the inflection point in the interatomic potential. Their numerical results shows that the fracture strain of a zigzag nanotube is 10%-15% and the range of fracture stresses is 65-93 GPa. However, the interatomic potential function used in the paper is a combination of an empirical potential function, the modified Morse potential, and a simple unrealistic bending function. As there is no more fundamental proof of the validity of this combination, it would be questionable how much key physical features the potential function reveals without further examination by physicist and chemist.

1.2 Plan of Investigation

Ever-increasing computational power, advancement in the description of atomic interactions in materials, and a strong desire in developing lightweight nano-structured materials, such as nanotubes and nanowires, have revealed the emergence of interest in predicting the properties of materials in the atomic level before they are synthesized. Strain energy release rate, stress intensity factor, and \( J \)-integral are the representative
mechanical parameters which always give the criterion of crack propagation in the continuum mechanics. On the other hand, when describing the essential phenomena of fracture in atomistic simulation, characteristics are needed to know to evaluate and predict quantitatively the mechanical properties of the damaged mechanical field. However, there are few studies focused on such problems in the previous references.

Nakatani et al. (2000) proposed a method to estimate the $J$-integral in amorphous metal model under mode I deformation in molecular dynamics simulation. But during the computation of each term in the $J$-integral, the displacement gradients calculated in the paper were actually dependent on the selection of a weighted function, which is a normal distribution function in their calculation. That led to different numerical results of the $J$-integral when choosing different statistical distributions. Based on the above reviews and discussions, to systematically investigate the macroscopic parameters in the atomic fracture and develop reliable approach of the calculation of those parameters in atomic system become our primary interests.

In this dissertation macroscopic fracture parameters are examined from both atomic-scale and macroscopic continuum model. The following is a simple structure of the dissertation. Chapter 2 is the methodology of atomistic simulation. A brief introduction of basic chemistry of carbon covalent bond is presented in the beginning. Then the atomistic simulation we used in our investigation, MD simulation, is introduced, together with the description of a many-body empirical interatomic potential, the so-called Tersoff-Brenner potential function. The last part in chapter 2 is the method of calculating the atomic stress in the previous works. Simulations of elastic properties of single-walled carbon nanotubes are provided in chapter 3. The Young’s modulus, Poisson’s ratio and shear modulus is obtained under different deformation modes. Both force and energy approaches that link the behavior at the atomic and macroscopic scales
of the nanotubes are used to predict the selected effective elastic moduli. A comparison of the elastic constants obtained from MD simulations with available experimental data is made. Chapter 4 introduces the method to calculate the energy release rates under Mode I and II small deformation. Two methods, global energy approach and local force approach are both adopted to compute the energy release rates. The energy release rates and deformed crack surface profiles are also calculated from linear elastic fracture mechanics (LEFM) through homogenized material properties for comparison. Also atomic stress fields near the crack tip in a semi-infinite atomic region are evaluated by applying remote Mode I and Mode II deformations. Chapter 5 presents the approach of the calculation of $J$-integral. The independency of the $J$-integral in atomic system is examined firstly. Then the results are compared to the elastic energy release rate obtained from atomic and continuum approaches in linear conditions. Finally the nonlinear fracture toughness, $J_c$, is estimated in different crack length. Chapter 6 provides the summary of our investigation and some recommendations for future work.
2 METHODOLOGY OF ATOMISTIC SIMULATIONS

Atomistic simulations model the behavior of molecular system at atomic level. The usefulness and physical significance of atomistic simulations has been demonstrated by numerous work in the last two decades since the high-speed computer came up. Alternative quantum mechanics methods are usually more accurate but also much more computationally expensive which make it not feasible to handle molecular systems consisting of more than hundreds of atoms. In this chapter we will introduced some methodologies of atomistic simulation associated with our research. The organization of this chapter is as follows. In the first section the basic chemistry of carbon bonding mechanism will be briefly discussed. Section 2 provides the introduction of molecular dynamics simulation, the integration algorithm and a detailed description of interatomic potential function including interatomic forces derived from it. The last section is the calculation method of stress in atomic system.

2.1 Basic Chemistry of Carbon Bonds

This section is a brief explanation of the molecular bonding mechanism of carbon atoms. First of all let us introduce several basic chemical concepts that will be used in the following parts. It is well known that every atom consists of a positively charged nucleus surrounded by a charged cloud of electrons. The electrons moving around the nucleus have different energy levels which are normally identified as atomic orbital. As we know, completely different from the common sense of macroscopic theory, the exact location of an electron in an atom is never possible to determine not only by experiment observations
but also by theoretical analysis. Therefore, the atomic orbital actually represents a three-dimensional volume of space within which an electron with specified energy level would have a certain probability to be there. For carbon atoms there are only two kinds of atomic orbital: $s$ and $p$ orbital. As shown in Figure 2.1, the shape of $s$ orbital is spherical while $p$ orbital has three orientations, denoted as $p_x$, $p_y$, and $p_z$, lie along three perpendicular axes. The chemical bond is in fact the exchange and share of electrons between atom pair. When atoms get close enough, the atomic orbital on the individual atoms will be able to overlap so that the three-dimensional probability regions share a common volume part.

![s and p atomic orbital](image)

Fig. 2.1 The illustration of $s$ and $p$ atomic orbital.

Carbon atom has 6 electrons and the electronic ground state configuration is $1s^22s^22p^2$, where $s$ and $p$ denote different atomic orbital and the superscripts indicate the number of electron that stay on the orbital, the number in front of the orbital represent different electron shells. During the chemical reaction the atom may rearrange its atomic orbital prior to the bond formation. Instead of using the original atomic orbital directly, mixtures of them (hybrids) are formed. For carbon the hybridization is limited to mixing
one 2s and three 2p orbital, which is \( sp^3 \), \( sp^2 \) and \( sp \) hybridization. These terms specifically refer to the hybridization of the atom and indicate the number of \( p \) orbital used to form hybrids. The balanced angle separations between the hybrid orbital are 109\(^0\), 120\(^0\) and 180\(^0\) for the \( sp^3 \), \( sp^2 \) and \( sp \) hybrid bond respectively, as shown in Figure 2.2.

A typical \( sp^3 \) hybridization material in the natural world is the diamond, while the graphite and graphite-related materials, such as carbon nanotube, have \( sp^2 \) bonding. In this dissertation, our study is mainly focused on the graphite and carbon nanotube. An ideal crystal structure of graphite consists of periodical hexagonal structures. In such structure the carbon covalent bonds are formed between a carbon atom and its three nearest neighbors from one s-orbital (2s) and two p-orbital electrons (2\( p_x \), 2\( p_y \)). The three bonds angles are 120\(^0\) to each other within a plane. This in-plane bond is referred to as a \( \sigma \)-bond. The \( \sigma \)-bond is a strong covalent bond, which is the fundamental reason of the high stiffness and high strength in-plane properties of graphite and carbon nanotube. The remaining \( p \)-orbital, which is 2\( p_z \) as atomic notation, is perpendicular to the plane of \( \sigma \)-bond and provides only weak interplanar bonding, which is named as \( \pi \)-bond (Fig. 2.3)
2.2 Molecular Mechanics and Dynamics Simulation

2.2.1 Introduction of Molecular Dynamics Simulation

Molecular dynamics simulation (MD simulation) provides the methodology for detailed microscopic modeling on the molecular scale. It is deterministic and based on Newton’s second law. Though not considering quantum chemistry, the MD simulation can still accurately describe some molecular phenomena by choosing proper interatomic potential functions (Hinchliffe, 1995). Therefore MD simulation is always regarded as one of the principal tools in the theoretical study of chemical molecules system.

The basic principle of MD simulation is to compute the motions of individual molecules, which are always treated as rigid body particles, in models of solids, liquids and gases. It is based on Newton’s second law, \( F_i = m_i a_i \), where \( F_i \) is the force exerted on atom \( i \), \( m_i \) is the mass of atom \( i \) and \( a_i \) is its acceleration. From knowledge of the force on each atom, the acceleration of each atom in the system can be determined.
Numerical integration of the equations of motion then yields a trajectory that describes
the positions, velocities, and accelerations of the atoms as they vary with time. From this
trajectory, the average values of properties can be estimated.

The mutual interaction force, $F_i$, which exerted on atom $i$, can be determined by
the gradient of the total potential energy of the carbon nanotubes, as given by

$$F_i = -\nabla_i U$$  \hspace{1cm} (2.1)

where $U$ is the total potential energy of the system. Then the acceleration of atoms
can be expressed by the derivative of the total potential energy.

$$a_i = -\frac{1}{m_i} \nabla_i U$$ \hspace{1cm} (2.2)

Therefore, to determine the trajectory of the atoms in the system, only the initial
positions of the atoms and initial distribution of velocities is needed. The initial positions
can be obtained from experimental structures. The initial atoms velocities, $v_i$, are often
chosen randomly from a Maxwell-Boltzmann distribution at a given temperature which
gives the probability that an atom $i$ has a velocity $v_i^{\alpha}$ in the direction given by.

$$p(v_i^{\alpha}) = \left(\frac{m_i}{2\pi k_b T}\right)^{1/2} \exp\left[-\frac{m_i v_i^{\alpha 2}}{2 k_b T}\right]$$ \hspace{1cm} (2.3)

where $k_b$ is the Boltzmann constant, $T$ is the temperature which can be calculated
from the velocities of the atoms

$$T = \frac{1}{2 N k_b} \sum_{i=1}^{N} m_i v_i^{2}$$ \hspace{1cm} (2.4)
where $N$ is the total number of the atoms in the system.

If the thermo effect is not considered, which means the temperature of the system is set at 0K, the simulation is molecular mechanics, which is known by the acronym MM.

### 2.2.2 Integration Algorithm

To have a reliable computation on the atoms trajectories, appropriate numerical method are required to be applied to solve those differential equations. A number of robust algorithms are used to integrate governing motion equations of atoms, such as Verlet’s algorithm, leapfrog algorithm, and *etc.* The finite-difference method that has been used in our MD simulation is Verlet’s algorithm. This algorithm is a combination of two Taylor expansions, as given by:

\[
x(t + \Delta t) = x(t) + \frac{dx}{dt} \Delta t + \frac{1}{2} \frac{d^2x}{dt^2} \Delta t^2 + \frac{1}{6} \frac{d^3x}{dt^3} \Delta t^3 + O(\Delta t^4)
\]  

\[
x(t - \Delta t) = x(t) - \frac{dx}{dt} \Delta t + \frac{1}{2} \frac{d^2x}{dt^2} \Delta t^2 - \frac{1}{6} \frac{d^3x}{dt^3} \Delta t^3 + O(\Delta t^4)
\]

Adding these two equations gives the Verlet algorithm, which is:

\[
x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \frac{d^2x}{dt^2} \Delta t^2
\]

where the local truncation error is in the order of $\Delta t^4$. Typically $\Delta t$ is on the order of femto-second ($10^{-15}$ s).

And normally the velocity can be estimated as first-order central difference.

\[
v(t) = \frac{x(t+\Delta t) - x(t-\Delta t)}{2\Delta t}
\]
2.2.3 Interatomic Potential Function

Developing the interatomic potential function is the key issue of molecular simulation. Many researchers have been working over the past two decades to derive functional forms and parameters for potential function of general applicability to organic molecules. A natural starting is to describe the total interatomic potential energy in terms of three different mechanical interactions among atoms, which are bond stretching, bond bending and bond torsion respectively. This potential function is a general function that can be applied to most atomic structures and are much less relatively computationally demanding. However it has several limitations to reflect the real chemical bond reactions. For example, analysis of the vibration spectrum shows that real diatomic molecules do not vibrate as if they were simple particles at the ends of classical springs. Another limitation is due to the fixed set of atom types. In the actual chemical structure the atom properties always depend on a particular bond environment, i.e., the carbon atom in ethyne is obviously chemically different from a carbon atom in a diamond molecule. However, when using this potential to describe the two different chemical systems listed above, the bond properties simulated by this potential would be exactly the same with each other, which is unphysical. To avoid such limitations, a Tersoff-Brenner potential energy function that can reproduce the realistic chemical bonds properties of hydrocarbon molecules more accurately is adopted to investigate the fracture parameters at the atomic level. A detailed description of the Tersoff-Brenner potential energy function will be provided in the following.

Tersoff-Brenner potential is an empirical many-body potential energy function, which is capable of modeling intramolecular chemical bonding of diamond and graphite as well as a number of essential hydrocarbons molecules (Brenner, 1990). The potential is
based on Tersoff’s covalent-bonding formalism with corrections for functions of neighboring atoms on local environment (Tersoff, 1988a, b, and c). For carbon atoms, the so-called Tersoff-Brenner potential energy function is given by:

$$U = \sum_{i} \sum_{j(\neq i)} [V_{R}(r_{g}) - \bar{B}_{ij}V_{A}(r_{g})]$$

(2.9)

where $U$ is the total interatomic potential energy of the system. $i$ refers to the atom of interest, $j$ refers to neighboring atoms, and $r_{g}$ is the distance between atoms $i$ and $j$. Figure 2.4 is a schematic diagram of the atomic structure of graphite which illustrates the atom distance and neighboring atoms in the Tersoff-Brenner potential function more clearly. From the figure we can see that an arbitrary atom $i$ has three neighboring atoms, denoted by $j$, $k_{1}$, $k_{2}$, respectively.

The functions $V_{R}(r_{g})$ and $V_{A}(r_{g})$ are the short-range pair potential describing repulsive and attractive interactions between atoms $i$ and $j$ respectively given by

$$V_{R}(r_{g}) = f(r_{g}) \frac{D_{r}}{S-1} e^{-\frac{S}{S} \beta (r_{g}-r_{e})}$$

(2.10)

$$V_{A}(r_{g}) = f(r_{g}) \frac{D_{S} S}{S-1} e^{-\frac{S}{S} \beta (r_{g}-r_{e})}$$

(2.11)

where $r_{e}$ is the equilibrium distance of two free carbon atoms without any neighboring atoms. $D_{r}$, $S$ and $\beta$ are constants.
The cut-off function $f(r_{ij})$, which restricts the pair potential to nearest neighbors, is simply taken as:

$$f(r_{ij}) = \begin{cases} 
1 & r_{ij} < r_1 \\
\frac{1}{2} \left[ 1 + \cos \left( \frac{\pi (r_{ij} - r_1)}{r_2 - r_1} \right) \right] & r_1 \leq r_{ij} \leq r_2 \\
0 & r_{ij} > r_2 
\end{cases}$$

(2.12)

which has a continuous value from 1 to 0 in the range of $r_1$ and $r_2$. $r_2$ is the cut-off distance.

The function $B_{ij}$ is the critical feature of the potential. It represents a measure of the number of bonds between atoms in a material and bond angle, and is assumed to be a monotonically decreasing function of the coordination of atoms $i$ and $j$ because the more neighbors an atom has, the weaker the bond to each neighbor is. Since $B_{ij}$ can reflect the change of local atomic environment, the Tersoff-Brenner potential then has the capability to accurately describe different hydrocarbon systems within the same set of parameters.

The form of $B_{ij}$ is given by:
\[
\overline{B}_{ij} = \frac{1}{2} (B_{ij} + B_{ji})
\]  
(2.13)

where

\[
B_{ij} = \left[ 1 + \sum_{k(\neq i,j)} G(\theta_{ijk}) f(r_{ik}) \right]^{-\delta}
\]  
(2.14)

\(\delta\) is the constant. \(G(\theta_{ijk})\), which is the function of the angle \(\theta_{ijk}\) between bonds \(i-j\) and \(i-k\), is given by

\[
G(\theta) = a_0 \left[ 1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + (1 + \cos \theta)^2} \right]
\]  
(2.15)

where \(a_0\), \(c_0\), \(d_0\) are constants. All the constants in the Tersoff-Brenner potential are listed in Table 2.1:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_e)</td>
<td>0.139 nm</td>
</tr>
<tr>
<td>(D)</td>
<td>6.0 ev</td>
</tr>
<tr>
<td>(S)</td>
<td>1.22</td>
</tr>
<tr>
<td>(\beta)</td>
<td>21 nm(^{-1})</td>
</tr>
<tr>
<td>(R_1)</td>
<td>0.17 nm</td>
</tr>
<tr>
<td>(R_2)</td>
<td>0.20 nm</td>
</tr>
<tr>
<td>(\delta)</td>
<td>0.5</td>
</tr>
<tr>
<td>(a_0)</td>
<td>0.00020813</td>
</tr>
<tr>
<td>(c_0^2)</td>
<td>330(^2)</td>
</tr>
<tr>
<td>(d_0^2)</td>
<td>3.5(^2)</td>
</tr>
</tbody>
</table>
Note that $r_e$ in the potential function (Eq. 2.10 and 2.11) is not the real equilibrium bond length in any arbitrary system. Only when $\overline{B}_{ij}=1.0$ is $r_e$ the equilibrium bond length. The equilibrium bond length is determined by minimizing the interatomic potential with regard to $r_{ij}$, that is $\partial U / \partial r_{ij} = 0$. Apparently, the equilibrium bond length is a function of $\overline{B}_{ij}$ which represents the influence of nearby neighboring atoms exerting on the bond $i$-$j$. Therefore for different bond conditions, such as $sp^2$ hybridization and $sp^3$ bond, this potential can automatically determine the equilibrium bond length in different systems within the same set of parameters in the potential function. This new feature also provides a way to describe the phenomenon of bond breaking and forming. This lead to the equilibrium interatomic distance for the graphene sheet equal to $r_0 = 0.145$ nm.

To give a brief picture of Tersoff-Brenner potential function, Figure 2.5 describes the interatomic force and potential energy versus bond length for a single bond between atom $i$ and $j$ in a graphene sheet. In both figures the bond $i$-$j$ reaches equilibrium at point $A$; at point $B$ the bond length equals to $r_1$ and at point $C$ equals to $r_2$, which is the cut-off distance. In Fig. 2.5a the interatomic force increases dramatically when the bond length reaches 0.17 nm. This awkward phenomenon results from the cut-off function $f(r_{ij})$ in the Tersoff-Brenner potential. Thus, a proper adjustment in the potential function is necessary to avoid this problem when studying the mechanical properties of a bond in the range of the cut-off distance. In this dissertation, during the investigation of the elastic properties of carbon nanotube and the facture properties of graphene sheet in linear condition the external deformation fields applied to the atomic system are sufficiently small so that the range of local bonds length in the system is always much smaller than $r_1$. 
For the evaluation of the fracture behavior in nonlinearity a detailed discussion on this issue is proposed in chapter 5.

![Graphs of interatomic force and potential energy versus bond length](image)

(a) Interatomic force versus bond length  
(b) Potential energy versus bond length

Fig. 2.5 The interatomic force and potential energy versus bond length obtained by Tersoff-Brenner potential.

### 2.3 Stress in Atomic System

In macroscopic continuous media stress denotes the magnitude of the forces per unit area of the surface on which they act. At the atomic scale, the concept of stress, which is related to the interatomic forces among neighboring atoms, can also be used as a physically appropriate description of the mechanical response of the local atomic structure. The stress calculations in the atomistic simulations have been formulated over years (e.g., Tsai, 1979; Swenson, 1983; Vitek and Egami, 1987; Lutsko, 1988; Cheung and Yip, 1991; Cormier et al., 2001; Zhou, 2003). The atomic stress is normally based on the virial theorem of Clausius (1870) and the general form of the atomic stress is given by

$$\sigma_{\alpha\beta} = -\frac{1}{V_0} m_i \nu_i^\alpha \nu_i^\beta - \frac{1}{2V_0} F_{\gamma\gamma}^\beta \nu_{\gamma\gamma}^\alpha$$

(2.16)
where $\sigma_{\alpha\beta}^i$ is the atomic stress tensor in the Cartesian coordinates at atom $i$. $V_0$ is the volume per atom. $m_i$ is the mass of atom $i$ and $v_i^\alpha$ is the velocity of atom $i$ in $\alpha$ direction. $r_{ij}^\beta = |\mathbf{r}_i^\alpha - \mathbf{r}_j^\alpha|$ is the distance between atom $i$ and $j$ projected on $\alpha$ direction. $F_{ij}^{\beta}$ is the $\beta$ component of the interatomic force exerted on atom $i$ by atom $j$.

Swenson has given a derivation of the expression above for the atomic stress tensor from a classical virial theorem (Swenson, 1983). To get a better understanding of the microscopic stress, a brief derivation is listed in the following part.

Consider a system of $N$ atoms in a volume $V$. For atom $i$, there is:

$$F_i^\alpha = \frac{dp_i^\alpha}{dt} \quad (2.17)$$

where $F_i^\alpha$ is the $\alpha$-th component of the force exert on atom $i$, $p_i^\alpha$ is the $\alpha$-th component of momentum of atom $i$. Multiplying Eq. (2.16) by $x_i^\beta$, which is the $\beta$-th component of the coordinate of atom $i$, summing over all the atoms, and taking a time average give

$$\frac{1}{\tau} \int_0^\tau \sum_{i=1}^N x_i^\beta F_i^\alpha \, dt + \frac{1}{\tau} \int_0^\tau \sum_{i=1}^N \frac{p_i^\beta p_i^\alpha}{m_i} \, dt = \frac{1}{\tau} \sum_{i=1}^N x_i^\beta p_i^\alpha \bigg|_0^\tau \quad (2.18)$$

where $m_i$ is the mass of atom $i$.

The basic assumption leading to a classical virial theorem is either (a) the system is periodic and $\tau$ is chosen to be a multiple of a period, or (b) the system is bounded and $\tau$ is chosen to be large. In either case, the right-hand side of Eq. (2.18) vanishes. Then:

$$V^{\alpha\beta} + K^{\alpha\beta} = 0 \quad (2.19)$$
Now assume that the force on atom $i$ is due to a wall force, $w_i$, and interatomic forces, $F_{ij}$, exerted by atom $j$. Thus:

$$V^{\alpha\beta} = V^{\alpha\beta}_W + V^{\alpha\beta}_I$$

(2.22)

where

$$V^{\alpha\beta}_W = \frac{1}{\tau} \int_{\tau_0}^{\tau} \sum_{i=1}^{N} x_i^\beta w_i^\alpha \, dt$$

(2.23)

$$V^{\alpha\beta}_I = \frac{1}{\tau} \int_{\tau_0}^{\tau} \sum_{i=1}^{N} x_i^\beta F_{ij}^\alpha \, dt$$

(2.24)

The wall force part, $V^{\alpha\beta}_W$, is related to the stress tensor. To see this assume that on a macroscopic scale the wall force is very short ranged so that only atoms very close to the wall will contribute to $V^{\alpha\beta}_W$. In the vicinity of the wall, all of the atoms in a volume $dV$ will contribute to $V^{\alpha\beta}_W$ if $dV$ is defined as the product of an element of wall area $dS$ times the range of the wall force $d$. Let $n$ be a unit normal to the surface area $dS$ and $r$ be the position vector of the center of the volume element. Then from atoms in $dV$ at some instant of time there is
\[ \delta V_{w}^{ag} = \sum_{dv} x_{i}^{\beta} w_{i}^{\alpha} \]
\[ = \sum_{dv} (x_{i}^{\beta} - r_{i}^{\beta}) w_{i}^{\alpha} + r_{i}^{\beta} \sum_{dv} w_{i}^{\alpha} \] (2.25)

On a macroscopic scale \( x_{i}^{\beta} \) and \( r_{i}^{\beta} \) are essentially equal, then Eq. (2.25) is approximated by

\[ \delta V_{w}^{ag} = r_{i}^{\beta} \sum_{dv} w_{i}^{\alpha} \] (2.26)

Taking the time average, Eq. (2.26) turns to be:

\[ \frac{1}{\tau} \int_{0}^{\tau} \delta V_{w}^{ag} dt = r_{i}^{\beta} \cdot \frac{1}{\tau} \int_{0}^{\tau} \sum w_{i}^{\alpha} dt \] (2.27)

And the factor of \( r_{i}^{\beta} \) is identified with the stress vector \( T \), the average force per unit area exerted by the wall on the system, which is,

\[ \frac{1}{\tau} \int_{0}^{\tau} \delta V_{w}^{ag} dt = r_{i}^{\beta} T^{\alpha} dS \] (2.28)

Define the macroscopic stress tensor \( \sigma_{ag} \) in the usual way, \( T^{\alpha} = \sigma_{ag} n_{\beta} \). Where repeated indices are summed. Thus:

\[ V_{w}^{ag} = \iint_{\text{surface}} r_{i}^{\beta} \sigma_{ag} n_{\beta} dS \] (2.29)

Using the divergence theorem, Eq. (2.29) can be expressed as

\[ V_{w}^{ag} = \iiint_{V} \frac{\partial}{\partial r_{i}} (r_{i}^{\beta} \sigma_{ag}) dV \] (2.30)

Based on the equation of equilibrium:
\[
\frac{\partial \sigma_{\alpha\gamma}}{\partial r_i^\gamma} = 0
\]  

(2.31)

Then Eq. (2.31) turns to be:

\[
V_{W}^{\alpha\beta} = \sigma_{\alpha\gamma} \int \int \int \frac{\partial F_i^{\beta}}{\partial r_i^\gamma} dV = V \sigma^{\alpha\beta}
\]  

(2.32)

Then an expression for the macroscopic stress tensor can be derived from Eq. (2.19) as:

\[
\sigma_{\alpha\beta} = -\frac{1}{V} (K^{\alpha\beta} + V_{i}^{\alpha\beta})
\]

\[
= -\frac{1}{V} \frac{1}{\tau} \int_{0}^{\tau} \sum_{i=1}^{N} \frac{p_i^{\beta}}{m_i} F_i^{\alpha} dt - \frac{1}{2V} \frac{1}{\tau} \int_{0}^{\tau} \sum_{i \neq j}^{N} (x_i^{\beta} - x_j^{\beta}) F_{ij}^{\alpha} dt
\]

(2.33)

In a static, periodic model structure, Eq. (2.33) can be shown to be

\[
\sigma_{\alpha\beta} = -\frac{1}{2V_0} r_{ij}^{\beta} F_{ij}^{\alpha}
\]

(2.34)
3 ELASTIC PROPERTIES OF SINGLE-WALLED CARBON NANOTUBES

In this chapter, selected effective elastic moduli of single-walled carbon nanotubes are simulated numerically. This effective macroscopic behavior is studied using molecular dynamics (MD) simulations in which the dynamic response and mutual force interaction among atoms of the nanostructures are obtained when subjected to small-strain deformation. Both force and energy approaches that link the behavior at the atomic and macroscopic scales of the nanotubes are used to predict the elastic moduli under different deformation modes. A comparison of the elastic constants obtained from MD simulation with available experimental data is made.

3.1 Introduction

Iijima (1991) first reported the formation and observation of carbon nanotubes (CNTs). Since then, research on CNTs has been attracting much attention to explore their unusual electronic and material properties (e.g. Dresselhaus, 1997; Schadler et al., 1998; Dekker, 1999; Qian et al., 2000). Both experimental and theoretical studies indicated that CNTs are material with extraordinary high stiffness and axial strength. Due to their large aspect ratios and small diameters, CNTs have emerged as potentially attractive materials as reinforcing elements in light-weight and high strength structural composites.

Studies of the mechanical behavior of CNTs have focused mainly on the adoption of different empirical potentials and continuum models using elasticity theory. In
experimented approaches, the force-displacement response of a nanotube is measured and the axial Young’s modulus is obtained by comparison to an equivalent elastic beam. Treacy et al. (1996) showed an average value 1.8 TPa (with large scatter) for the axial Young’s modulus from the direct measurements with a transmission electron microscope of a variety of multi-walled nanotubes (MWNTs) of different inner and outer diameters using an analogy to the thermal vibration analysis of anchored tubes. The nanotubes with the smallest inner diameter were considerably stiffer, with a Young’s modulus of 3.70 TPa. Wong et al. (1997) used an atomic force microscopy (AFM) to measure force-displacement relations for anchored MWNTs on a substrate. From a comparison to elastic beam theory, the Young’s modulus can be extracted. An average of 1.28 ± 0.5 TPa with little dependence of nanotube diameter was reported. Lourie and Wagner (1998) obtained the axial Young’s modulus for a series of temperatures by micro-Raman spectroscopy from measurements of cooling-induced compressive deformation of nanotubes embedded in an epoxy matrix. At 81° K, the experimental results gave 3 TPa for single-walled nanotubes (SWNTs) with an average radius of 0.7 nm, and 2.4 TPa for MWNTs with an average radius of 5 to 10 nm.

In theoretical studies of predicting elastic properties of nanotubes using MD simulations, Yakobson et al. (1996) used a realistic many-body interatomic potential (Tersoff-Brenner potential) with a continuum shell model and obtained the axial SWNT modulus that ranged from 1.4 to 5.5 TPa. Note that the paper used the value 0.066 nm as the tube wall thickness while most other references use 0.34 nm instead. Cornwell and Wille (1997) reported a relatively low modulus of 1.0 TPa for open-ended, free-standing SWNT by using quenched molecular dynamics simulations using the Tersoff-Brenner potential. Lu (1997) used an empirical force-constant model to determine several elastic moduli of single- and multi-walled nanotubes and obtained the Young’s modulus of about
1 TPa and the rotational shear modulus of about 0.5 TPa. The analysis showed that the elastic properties were insensitive to the radius, helicity, and the number of walls. However, Yao and Lordi (1998) used MD simulations and found that changes in structure such as radius and helicity of the SMNTs could affect the Young’s modulus because their results showed that the torsional potential energy, which is the dominant component of total potential energy, increased as the quadratic function of the decreasing tube radius. Sinnott et al. (1998) estimated the axial Young’s modulus for carbon fibers composed of SWNTs aligned in the direction of tubular axis. The result showed that fibers, which were composed of smaller radius carbon nanotubes with a packing ration of 0.9, had a modulus of approximately 1.25-1.40 TPa. Hernandez et al. (1998) adopted a tight-binding method to obtain averaged values of Young’s modulus and Poisson’s ratio of SWNTs with different chiral vectors, which were found to be 1.24 TPa and 0.262, respectively. Zhou et al. (2000) claimed that both Young’s modulus and the wall thickness were independent of the radius and the helicity of SWNTs. They applied the strain energy of SWNTs directly from electronic band structure without introducing empirical potentials and continuum elasticity theory to describe the mechanical properties of SWNTs. The estimated value for the axial modulus was reported as 5.0 TPa, which is five times larger than the value of MWNTs.

In spite of the variety of theoretical studies on the macroscopic elastic behavior of CNTs, there still remain controversial issues regarding the effect of geometric structure of CNTs on elastic moduli, as evidence by the wide scatter among the elastic moduli reported in the literature. Meanwhile, the computations of elastic moduli are still not very completed, such as the numerical results of bulk modulus were not consisted with other elastic moduli obtained in Lu’s simulations (1997). The objective in this chapter is to reexamine the elastic behavior of CNTs in detail using two different approaches in polar
coordinate system which should be more appropriate for the investigation of the mechanical properties of CNTs. The organization of this chapter is as follows. In the next section, the morphological structure of carbon nanotubes will be briefly discussed. In Section 3.3, several elastic moduli are determined by applying different small-strain deformation modes. The elastic moduli are predicted using energy and force approaches. Numerical results and a summary are given in Section 3.4.

### 3.2 Structure of Carbon Nanotubes

Single-walled nanotubes are formed by folding a graphene sheet to form a hollow cylinder which is composed of hexagonal carbon ring units, which are also referred to as graphene units. The fundamental carbon nanotube structure can be classified into three categories: armchair, zigzag, and chiral, in terms of their helicity. Figure 3.1 shows a segment of a single graphite plane that can be transformed into a carbon nanotube by rolling it up into a cylinder. To describe this structure, a chiral vector is defined as $OA = na_1 + ma_2$, where $a_1$ and $a_2$ are unit vectors for the honeycomb lattice of the graphene sheet, $n$ and $m$ are two integers, along with a chiral angle $\theta$ which is the angle of the chiral vector with respect to the $x$ direction shown in Figure 3.1. This chiral vector, $OA$, will be denoted as $(n, m)$ which will also specify the structure of the carbon nanotube. Vector $OB$ is perpendicular to the vector $OA$. To construct a CNT, we cut off the quadrangles $OAB'B$ and roll it into a cylinder with $OB$ and $AB'$ overlapping each other. The relationship between the integers $(n, m)$ and the nanotube radius, $r$, and chiral angle, $\theta$, is given by

\[
r = \sqrt{3}a_e - (m^2 + mn + n^2)^{1/2} / 2\pi \quad (3.1)
\]

\[
\theta = \tan^{-1}[\sqrt{3}m / (m + 2n)] \quad (3.2)
\]
where $a_{c-c}$ is the length of the C-C bond

Generally there are three major categories of nanotubes based on the chiral angle $\theta$. Figure 3.2 is the examples of the three kinds of nanotubes.

$\theta = 0^\circ$ \hspace{1cm} Zigzag

$0^\circ < \theta < 30^\circ$ \hspace{1cm} Chiral

$\theta = 30^\circ$ \hspace{1cm} Arm Chair
3.3 Elastic Moduli

3.3.1 Stress-Strain Relationship of Carbon Nanotube

The general elastic characteristics of the carbon nanotubes will now be discussed. Because of the hexagonal symmetry properties in the cylindrical surface of nanotube, the nanotube exhibits transverse isotropy in the $\theta - z$ plane, which is defined by five independent elastic constants in the stress-strain relationships.

$$
\begin{bmatrix}
\sigma_{rr} \\
\sigma_{\theta\theta} \\
\sigma_{zz}
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{13} & C_{13} \\
C_{13} & C_{33} & C_{23} \\
C_{13} & C_{23} & C_{33}
\end{bmatrix}
\begin{bmatrix}
\epsilon_{rr} \\
\epsilon_{\theta\theta} \\
\epsilon_{zz}
\end{bmatrix}
$$

(3.3)
\[
\tau_{\theta z} = G_{\theta z} \gamma_{\theta z}, \quad \tau_{rz} = G_{r z} \gamma_{r z}, \quad \tau_{r \theta} = G_{r \theta} \gamma_{r \theta}
\] (3.4)

where \( G_{\theta z} = \frac{E_z}{2(1 + \nu_{\theta z})} \)

Eq. (3.3) can also be expressed in term of engineering constants as

\[
\begin{bmatrix}
\varepsilon_{rr} \\
\varepsilon_{\theta \phi} \\
\varepsilon_{zz}
\end{bmatrix} =
\begin{bmatrix}
\frac{1}{E_r} & -\frac{\nu_{rr}}{E_r} & -\frac{\nu_{rz}}{E_r} \\
-\frac{\nu_{rr}}{E_z} & \frac{1}{E_z} & -\frac{\nu_{r\theta}}{E_z} \\
-\frac{\nu_{rz}}{E_z} & -\frac{\nu_{r\theta}}{E_z} & \frac{1}{E_z}
\end{bmatrix}
\begin{bmatrix}
\sigma_{rr} \\
\sigma_{\theta \phi} \\
\sigma_{zz}
\end{bmatrix}
\] (3.5)

In the cylindrical coordinate system the relation of strain and displacement is given by

\[
\varepsilon_{rr} = \frac{\partial u_r}{\partial r}
\]

\[
\varepsilon_{\theta \phi} = \frac{u_r}{r} + \frac{1}{r} \frac{\partial u_\theta}{\partial \theta}
\]

\[
\varepsilon_{zz} = \frac{\partial u_z}{\partial z}
\]

\[
\gamma_{rr} = \frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}
\]

\[
\gamma_{\theta \phi} = \frac{\partial u_\theta}{\partial r} \frac{u_\theta}{r} + \frac{1}{r} \frac{\partial u_r}{\partial \theta}
\]

\[
\gamma_{z \theta} = \frac{1}{r} \frac{\partial u_r}{\partial \theta} + \frac{\partial u_\theta}{\partial z}
\] (3.6)
3.3.2 Calculations of Elastic Moduli

The potential energy expression under small-strain deformation in carbon nanotube is given by:

\[ U = U_0 + \frac{1}{2} V_0 C_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \]  \hspace{1cm} (3.7)

where \( U \) is the total potential energy at equilibrium, \( U_0 \) is the initial potential energy at equilibrium before deformation is applied, \( C_{ijkl} \) is the fourth-order tensor of elastic constants, \( V_0 \) is the initial volume of the carbon nanotube, which for a hollow cylinder is given by \( V_0 = 2\pi rtL \), where \( L \) is the length, \( r \) is the radius, and \( t \) is the assumed tube wall thickness.

In our simulation, both a force and energy approach is adopted to predict the elastic moduli of carbon nanotubes. In the force approach, based on the classical virial theorem discussed in the previous chapter, an expression of the stress tensor in a macroscopic and bounded system is given in the term of atom coordinates and interatomic forces. Thus the elastic moduli can be calculated by directly computing the averaged atom coordinates and interatomic forces in the nanotube. Meanwhile, the energy approach, which uses the second derivative of potential energy with respect to strain under each deformation mode, is also performed to obtain the elastic moduli. Equations (3.8) and (3.9) define the calculation of elastic moduli based on force approach and energy approach, respectively:

\[ \sigma_{\alpha\beta} = -\frac{1}{2V_0} F_{ij}^\alpha r_{ij}^\beta \]  \hspace{1cm} (3.8)
In Eqs. (3.8) and (3.9), the repeated subscripts indicate the sum of all atoms. \( \sigma_{\alpha\beta} \) is the average atomic-level stress tensor in the Cartesian coordinates, \( F_{ij} \) is the interatomic forces including bonding and nonbonding forces between two atoms \( i \) and \( j \).

Based on the two approaches, several elastic moduli are determined under small-strain deformation in the following parts by applying deformation modes similar with some previous elastic constants calculations (Hashin and Rosen, 1964; Yuan, Pagano, and Cai, 1990).

1) Calculation of \( E_z \) and \( \nu_{z\theta} \)

To calculate the axial Young’s modulus, \( E_z \), and the Poisson’s ratio, \( \nu_{z\theta} \), the atoms are displaced by \( u_z = \varepsilon_z^0 \). The average strain and stresses are:

\[
\varepsilon_z = \varepsilon_z^0 ,
\]

\[
\sigma_{zz} \neq 0 \text{, any other } \sigma_{ij} = 0 \quad (3.10)
\]

Through MD simulation, the longitudinal elastic modulus, \( E_z \), can be calculated by a force and energy approach using the following relationships:

\[
E_z = \frac{1}{V_0} \frac{\partial^2 U}{\partial \varepsilon_{zz}^0} \quad \text{Energy Approach}
\]

\[
E_z = \frac{\sigma_{zz}}{\varepsilon_{zz}^0} \quad \text{Force Approach} \quad (3.11)
\]
The Poisson’s ratio is obtained as:

\[ \nu_{z\theta} = -\frac{\varepsilon_{\theta\theta}}{\varepsilon_{zz}} \]  \hspace{1cm} (3.12)

2) Calculation of \( E_\theta \) and \( \nu_{\theta\theta} \)

If a radial displacement \( u_r = \varepsilon_{\theta\theta}^0 r \) is applied to every atom of the nanotube, then we obtain only a radial stress and can calculate a pure radial stress in which:

\[ \varepsilon_{\theta\theta} = \varepsilon_{\theta\theta}^0 \]

\[ \sigma_{\theta\theta} \neq 0, \text{ any other } \sigma_{ij} = 0 \]  \hspace{1cm} (3.13)

Hence, \( E_\theta \) and \( \nu_{\theta\theta} \) are given by:

\[ E_\theta = \frac{1}{V_0} \frac{\partial^2 U}{\partial \varepsilon_{\theta\theta}^0} \hspace{1cm} \text{--- Energy Approach} \]

\[ E_\theta = \frac{\sigma_{\theta\theta}}{\varepsilon_{\theta\theta}^0} \hspace{1cm} \text{--- Force Approach} \]  \hspace{1cm} (3.14)

\[ \nu_{\theta\theta} = -\frac{\varepsilon_{zz}}{\varepsilon_{\theta\theta}^0} \]  \hspace{1cm} (3.15)

3) Calculation of the Rotational Shear Modulus \( G_{\theta z} \)

The required displacement mode in this case is \( u_\theta = \gamma_{\theta z}^0 z \) which is applied to all atoms. The resulting strain and stresses are then given by:

\[ \gamma_{\theta z} = \gamma_{\theta z}^0, \text{ any other } \varepsilon_{ij} = 0 \]
\( \tau_{\theta z} \neq 0, \text{ any other } \sigma_{ij} = 0 \)  

(3.16)

Then the rotational shear modulus \( G_{\theta z} \) can then be calculated by:

\[
G_{\theta z} = \frac{1}{V_0} \frac{\partial^2 U}{\partial \gamma_{\theta z}^0} \quad \text{------Energy Approach}
\]

\[
G_{\theta z} = \frac{\tau_{\theta z}}{\gamma_{\theta z}^0} \quad \text{------Force Approach} \quad (3.17)
\]

4) Calculation of \( C_{23} \) and \( C_{33} \)

Here the carbon atoms are under deformation \( u_z = \epsilon_{zz}^0 \) and lateral displacements are constrained. The average strain state imposed is:

\( \epsilon_{zz} = \epsilon_{zz}^0, \text{ any other } \epsilon_{ij} = 0 \)  

(3.18)

Based on the relationship of stress and strain, \( C_{23} \) and \( C_{33} \) are given by:

\[
C_{33} = \frac{1}{V_0} \frac{\partial^2 U}{\partial \epsilon_{zz}^0} \quad \text{------Energy Approach}
\]

\[
C_{23} = \frac{\sigma_{\theta z}}{\epsilon_{zz}^0} \quad \text{------Force Approach} \quad (3.19)
\]

Although \( C_{13} \) can be calculated using a force approach, this modulus is small, on the order of 1 GPa, which is within the numerical error bounds of the present analysis. Therefore, the determination of \( C_{13} \) is not attempted.
3.3.3 Details of the Numerical Procedure for Calculating Moduli

In the present analysis, focus is placed on the elastic moduli of armchair nanotubes ranging from \( n = 6 \) to 20. The various geometric dimensions of the nanotubes are listed in Table 3.1. The aspect ratio of the nanotubes, which is the length-to-radius ratio, is set to be greater than 10 to ensure that edge effects can be neglected. A key issue here is that the wall thickness of the nanotubes needs to be specified in the continuum sense before predicting the values of elastic moduli for the single-walled carbon nanotubes. For multi-walled nanotubes, the distance between any two walls is close to that of the interlayer separation distance in graphite, which is 0.34 nm. This interlayer separation distance is used as the effective wall thickness of SWNTs. The general process of the simulation is as following. First the MD simulations are performed to obtain a minimum energy state of the nanotube without any applied deformation. The simulation run for approximately 5 ps with a time step of 1 fs after which the energy attained a constant minimum value. Then different types of deformation modes discussed above are applied to the nanotube by scaling atomic positions and applying boundary conditions along the appropriate coordinates. The nanotube reaches an equilibrium state over approximately 5 ps. After the equilibrium a 5 ps equilibrium period is carried out. By integrating molecular dynamic equations, the stresses and total potential energy are calculated from the averaged results from this equilibrium period. Then the value of elastic moduli can be obtained using force and energy approach through equations (3.8) and (3.9), respectively.

In the energy approach, the initial potential energy, \( U_0 \), is obtained from the MD simulation by minimizing the energy of the nanotube without any externally applied strain state. For each deformation mode, three constant strain values, 0.0005, 0.001, and
0.0015 are applied to calculate the total potential energies. A least-squares fit for the four potential energies is used to obtain the elastic moduli.

In the force approach, only an applied strain value of 0.001 for each deformation mode is used to calculate the elastic moduli. Note that the stresses calculated from Eq. (7) need to be transformed into polar coordinates for calculating some of the elastic moduli in the force approach.

<table>
<thead>
<tr>
<th>(n, n)</th>
<th>Number of Atoms</th>
<th>Radius (nm)</th>
<th>Length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6, 6)</td>
<td>456</td>
<td>0.407</td>
<td>4.427</td>
</tr>
<tr>
<td>(7, 7)</td>
<td>616</td>
<td>0.475</td>
<td>5.165</td>
</tr>
<tr>
<td>(8, 8)</td>
<td>800</td>
<td>0.543</td>
<td>5.903</td>
</tr>
<tr>
<td>(9, 9)</td>
<td>1008</td>
<td>0.611</td>
<td>6.641</td>
</tr>
<tr>
<td>(10, 10)</td>
<td>1240</td>
<td>0.678</td>
<td>7.379</td>
</tr>
<tr>
<td>(11, 11)</td>
<td>1496</td>
<td>0.746</td>
<td>8.116</td>
</tr>
<tr>
<td>(12, 12)</td>
<td>1776</td>
<td>0.814</td>
<td>8.854</td>
</tr>
<tr>
<td>(13, 13)</td>
<td>2080</td>
<td>0.882</td>
<td>9.592</td>
</tr>
<tr>
<td>(14, 14)</td>
<td>2408</td>
<td>0.950</td>
<td>10.330</td>
</tr>
<tr>
<td>(15, 15)</td>
<td>2760</td>
<td>1.018</td>
<td>11.068</td>
</tr>
<tr>
<td>(16, 16)</td>
<td>3136</td>
<td>1.085</td>
<td>11.806</td>
</tr>
<tr>
<td>(17, 17)</td>
<td>3536</td>
<td>1.153</td>
<td>12.544</td>
</tr>
<tr>
<td>(18, 18)</td>
<td>3960</td>
<td>1.221</td>
<td>13.281</td>
</tr>
<tr>
<td>(19, 19)</td>
<td>4408</td>
<td>1.289</td>
<td>14.019</td>
</tr>
<tr>
<td>(20, 20)</td>
<td>4880</td>
<td>1.357</td>
<td>14.757</td>
</tr>
</tbody>
</table>
3. 4 Results and Discussions

Figure 3.3 are the numerical values of $E_z$ and $E_\theta$ of different armchair single-walled carbon nanotubes with radii ranging from 0.407 to 1.357 nm obtained from the energy and force approaches. It is clearly shown that $E_z$ and $E_\theta$ have little dependence on the radius of nanotubes in both the energy and force approaches. The two set of predictions from the energy and force approach agree very well for all the nanotubes studied. This suggests that the carbon nanotube is essentially isotropic in the plane of cylindrical surface. The average values and relative errors of $E_z$ and $E_\theta$ for all the nanotubes investigated here are listed in Table 3.2.

<table>
<thead>
<tr>
<th></th>
<th>Energy Approach</th>
<th>Force Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_z$</td>
<td>0.708</td>
<td>0.708</td>
</tr>
<tr>
<td>$E_\theta$</td>
<td>0.697</td>
<td>0.682</td>
</tr>
<tr>
<td>Average</td>
<td>0.703 ± 0.006</td>
<td>0.695 ± 0.013</td>
</tr>
</tbody>
</table>

The above values show that the two approaches yield similar predictions of moduli of carbon nanotubes. Figures 3.4 and 3.5 show the Poisson’s ratio, $\nu_{rk}$ and $\nu_{z\theta}$, and shear modulus $G_{rk}$ as a function of carbon nanotube radii, respectively. From Figure 3.4 the average values of Poisson’s ratios are obtained as $\nu_{z\theta} = 0.404$ and $\nu_{rk} = 0.414$. Utilizing the relationship for the shear modulus in a transversely isotropic material,
\[ G_{r\theta} = \frac{E_i}{2(1 + \nu_{r\theta})}, \] a comparison between the direct numerical results for \( G_{r\theta} \) and the values derived from the elastic relation using \( E_i \) and \( \nu_{r\theta} \) is shown in Table 3.3. The comparison shows a close agreement and yields further confirmation of the transverse isotropic property of the nanotube. Again, the results of shear modulus demonstrate to be insensitive to the radius of the nanotube. Figure 3.6 depicts the predictions of the \( C_{33} \) elastic coefficients versus nanotubes radii. The average value of \( C_{33} \) is 1.065 TPa with a standard deviation 0.5% using the energy approach. Using the force approach, \( C_{33} \) shows an average value of 1.062 TPa with a standard deviation 0.1%. Figure 3.7 is the value of \( C_{23} \), which has an average 0.217 TPa with a standard deviation 0.1%, from force approach. All elastic moduli predicted through the simulations are listed in Table 3.4.

<table>
<thead>
<tr>
<th></th>
<th>Energy Approach</th>
<th>Force Approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_{r\theta} ) -- Numerical (TPa)</td>
<td>0.239</td>
<td>0.243</td>
</tr>
<tr>
<td>( G_{r\theta} ) -- Theoretical (TPa)</td>
<td>0.249</td>
<td>0.246</td>
</tr>
<tr>
<td>Relative error</td>
<td>4.0 %</td>
<td>1.2 %</td>
</tr>
</tbody>
</table>

Since the single-walled nanotube has a single carbon atom in the thickness direction, the engineering constants that are related to the radial direction, \( E_i \), \( \nu_{r\theta} \), and \( G_{r\theta} \) (or \( G_{r\theta} \)), are yet to be clearly defined. It has been shown from simulations using both force and energy approaches that overall the elastic constants of SWNTs are insensitive to
the morphology pattern such as nanotube radius and thus the effect of curvature on the elastic constants can be neglected. This confirmed the experimental results by Wong (Wong, et al., 1997) in which they found that the Young’s modulus had no dependence on tube diameter. The average numerical results in our simulations are in the same range with the previous experimental and numerical results, i.e. measurements using AFM showed a range of 0.3 –1.5 TPa of Young’s modulus (Yu, et al., 2000). In the simulation the results from energy approach agree remarkably well with the results from force approach. The force approach provides more information than that from the energy approach. In addition, the force approach provides more accurate prediction than the energy approach since the energy approach is required to calculate several total potential energy values under different strain levels and then uses a least-square fit to obtain the elastic moduli. Furthermore, the force approach can predict the nonlinear behavior without assumption of assumed total potential energy in quadratic form described in Equation 3.7 for small-strain deformation in the energy approach. Assumption of the transversely isotropic properties on the cylinder surface of the single-walled nanotube is also confirmed by numerical calculations.
Figure 3.3 $E_z$ and $E_\theta$ distribution versus radius of armchair single-walled carbon nanotubes in energy and force approaches
Figure 3.4 Poisson’s ratios $v_{\theta z}$ and $v_{z\theta}$ versus radius of armchair single-walled carbon nanotubes

Fig. 3.5 Shear modulus $G_{\theta z}$ versus radius of armchair single-walled nanotubes
Fig. 3.6 $C_{33}$ versus radius of armchair single-walled carbon nanotubes

Fig. 3.7 $C_{23}$ versus radius of armchair single-walled carbon nanotubes
Table 3.4  Elastic moduli of single-walled carbon nanotubes

(a) Elastic moduli obtained from energy approach

<table>
<thead>
<tr>
<th>(n,n)</th>
<th>$E_z$</th>
<th>$E_\theta$</th>
<th>$C_{33}$</th>
<th>$G_{\theta\zeta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6,6)</td>
<td>0.704</td>
<td>0.693</td>
<td>1.069</td>
<td>0.235</td>
</tr>
<tr>
<td>(7,7)</td>
<td>0.706</td>
<td>0.702</td>
<td>1.069</td>
<td>0.233</td>
</tr>
<tr>
<td>(8,8)</td>
<td>0.707</td>
<td>0.710</td>
<td>1.070</td>
<td>0.238</td>
</tr>
<tr>
<td>(9,9)</td>
<td>0.708</td>
<td>0.708</td>
<td>1.070</td>
<td>0.242</td>
</tr>
<tr>
<td>(10,10)</td>
<td>0.711</td>
<td>0.707</td>
<td>1.073</td>
<td>0.233</td>
</tr>
<tr>
<td>(11,11)</td>
<td>0.711</td>
<td>0.704</td>
<td>1.074</td>
<td>0.234</td>
</tr>
<tr>
<td>(12,12)</td>
<td>0.710</td>
<td>0.695</td>
<td>1.062</td>
<td>0.235</td>
</tr>
<tr>
<td>(13,13)</td>
<td>0.709</td>
<td>0.699</td>
<td>1.062</td>
<td>0.235</td>
</tr>
<tr>
<td>(14,14)</td>
<td>0.709</td>
<td>0.690</td>
<td>1.061</td>
<td>0.238</td>
</tr>
<tr>
<td>(15,15)</td>
<td>0.709</td>
<td>0.688</td>
<td>1.060</td>
<td>0.238</td>
</tr>
<tr>
<td>(16,16)</td>
<td>0.709</td>
<td>0.689</td>
<td>1.061</td>
<td>0.239</td>
</tr>
<tr>
<td>(17,17)</td>
<td>0.709</td>
<td>0.691</td>
<td>1.062</td>
<td>0.240</td>
</tr>
<tr>
<td>(18,18)</td>
<td>0.708</td>
<td>0.697</td>
<td>1.062</td>
<td>0.241</td>
</tr>
<tr>
<td>(19,19)</td>
<td>0.709</td>
<td>0.695</td>
<td>1.062</td>
<td>0.241</td>
</tr>
<tr>
<td>(20,20)</td>
<td>0.708</td>
<td>0.696</td>
<td>1.062</td>
<td>0.241</td>
</tr>
<tr>
<td>Average</td>
<td>0.708 ±0.001</td>
<td>0.697 ±0.002</td>
<td>1.065 ±0.001</td>
<td>0.239 ±0.001</td>
</tr>
</tbody>
</table>
(b) Elastic moduli obtained from force approach

<table>
<thead>
<tr>
<th>(n,n)</th>
<th>$E_z$</th>
<th>$E_\theta$</th>
<th>$C_{33}$</th>
<th>$C_{23}$</th>
<th>$G_{R\theta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6,6)</td>
<td>0.705</td>
<td>0.685</td>
<td>1.065</td>
<td>0.222</td>
<td>0.237</td>
</tr>
<tr>
<td>(7,7)</td>
<td>0.707</td>
<td>0.684</td>
<td>1.064</td>
<td>0.220</td>
<td>0.239</td>
</tr>
<tr>
<td>(8,8)</td>
<td>0.708</td>
<td>0.686</td>
<td>1.063</td>
<td>0.219</td>
<td>0.241</td>
</tr>
<tr>
<td>(9,9)</td>
<td>0.709</td>
<td>0.686</td>
<td>1.063</td>
<td>0.218</td>
<td>0.242</td>
</tr>
<tr>
<td>(10,10)</td>
<td>0.710</td>
<td>0.686</td>
<td>1.064</td>
<td>0.218</td>
<td>0.243</td>
</tr>
<tr>
<td>(11,11)</td>
<td>0.710</td>
<td>0.684</td>
<td>1.064</td>
<td>0.217</td>
<td>0.243</td>
</tr>
<tr>
<td>(12,12)</td>
<td>0.710</td>
<td>0.685</td>
<td>1.062</td>
<td>0.216</td>
<td>0.244</td>
</tr>
<tr>
<td>(13,13)</td>
<td>0.710</td>
<td>0.686</td>
<td>1.062</td>
<td>0.216</td>
<td>0.244</td>
</tr>
<tr>
<td>(14,14)</td>
<td>0.710</td>
<td>0.685</td>
<td>1.061</td>
<td>0.215</td>
<td>0.244</td>
</tr>
<tr>
<td>(15,15)</td>
<td>0.710</td>
<td>0.683</td>
<td>1.061</td>
<td>0.215</td>
<td>0.245</td>
</tr>
<tr>
<td>(16,16)</td>
<td>0.710</td>
<td>0.682</td>
<td>1.062</td>
<td>0.215</td>
<td>0.245</td>
</tr>
<tr>
<td>(17,17)</td>
<td>0.710</td>
<td>0.680</td>
<td>1.061</td>
<td>0.215</td>
<td>0.245</td>
</tr>
<tr>
<td>(18,18)</td>
<td>0.709</td>
<td>0.677</td>
<td>1.061</td>
<td>0.214</td>
<td>0.245</td>
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<tr>
<td>(19,19)</td>
<td>0.708</td>
<td>0.677</td>
<td>1.061</td>
<td>0.214</td>
<td>0.246</td>
</tr>
<tr>
<td>(20,20)</td>
<td>0.709</td>
<td>0.678</td>
<td>1.061</td>
<td>0.214</td>
<td>0.246</td>
</tr>
</tbody>
</table>

Average 0.708 ± 0.001  0.682 ± 0.001  1.062 ± 0.001  0.217 ± 0.001  0.243 ± 0.001
<table>
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<tr>
<th>(n,n)</th>
<th>$v_{z\theta}$</th>
<th>$v_{\theta z}$</th>
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<td>(7,7)</td>
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<td>(10,10)</td>
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<td>(11,11)</td>
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<tr>
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<td>(18,18)</td>
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<td>(19,19)</td>
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<tr>
<td>(20,20)</td>
<td>0.396</td>
<td>0.408</td>
</tr>
</tbody>
</table>

Average $0.404 \pm 0.002$  $0.414 \pm 0.001$

* The elastic constants are in the units of TPa.
* $z$-direction is the axis direction of the nanotube.
4 ENERGY RELEASE RATE AND STRESS FIELD IN ATOMIC SYSTEM

In this chapter, macroscopic fracture parameters are examined from both atomic-scale and macroscopic continuum model. An atomic model near a crack tip in a semi-infinite graphene sheet is proposed. The energy release rates and atomic stress are investigated by applying remote Mode I and Mode II displacement field that is obtained from the linear elastic fracture mechanics (LEFM) with an initially specified stress intensity factor. Also a sample made of graphite that represents cracks in a plane with finite width is used to calculate the elastic energy release rates under Mode I and II small deformation. In the direct atomistic simulation, Tersoff-Brenner interatomic potential is used to describe the atomic force interactions among carbons. Two methods, global energy approach and local force approach are both adopted to compute the energy release rates. The energy release rates and deformed crack surface profile are also calculated from linear elastic fracture mechanics through homogenized material properties for comparison.

4.1 Atomic Configurations

4.1.1 Case I: Crack in Semi-infinite Domain

First we consider the case that a crack is in a semi-infinite domain. The atomic system which consists of 728 carbon atoms represents a small zone near crack tip, as shown in Figure 4.1. The quadrangle region with the dimension of 5.274 nm × 6.279 nm can be
regarded as being cut from an infinite graphene sheet. The crack is modeled by removing the interatomic chemical bond to eliminate the interaction between atom pairs across the crack surface. The atomic displacement field obtained from LEFM with an initially specified stress intensity factor is applied to the atoms in the model. Energy release rates and the atomic stress field near crack tip will be investigated through atomistic simulation. Our primary interest here is to use atomistic simulation to obtain the macroscopic fracture parameters and to examine the extent to which the atomic numerical results are consistent with those obtained from the linear elastic solution. Only through these comparisons can we prove the reliability of atomistic simulation, and the capability of characterizing the atomic fracture by macroscopic parameters.

In fracture mechanics there are three basic deformation modes: Mode I, II, and III. Mode I is the opening or tensile mode where the relative displacements between
corresponding pairs separate symmetrically normal to the crack surface. Mode II, the sliding mode, denotes antisymmetric separation through relative tangential displacements to the crack surface, as shown in Figure 4.2. Because the graphene sheet studied here has only one single layer, there is no Mode III in this situation.

![Fig. 4.2 Two basic fracture modes.](image)

It is well established that the linear elastic solution of the stress and displacement field in the vicinity of the crack tip can be expressed as

\[ u_1 = \frac{K_I}{\mu} \sqrt{\frac{r}{2\pi}} \left( \cos \frac{\theta}{2} \left( \kappa - 1 \right) + \sin^2 \frac{\theta}{2} \right) + \frac{K_{II}}{\mu} \sqrt{\frac{r}{2\pi}} \left( \sin \frac{\theta}{2} \left( \kappa + 1 \right) + \cos^2 \frac{\theta}{2} \right) \]  \hspace{1cm} (4.1)

\[ u_2 = \frac{K_I}{\mu} \sqrt{\frac{r}{2\pi}} \left( \sin \frac{\theta}{2} \left( \kappa + 1 \right) - \cos^2 \frac{\theta}{2} \right) + \frac{K_{II}}{\mu} \sqrt{\frac{r}{2\pi}} \left( \cos \frac{\theta}{2} \left( 1 - \kappa \right) + \sin^2 \frac{\theta}{2} \right) \]  \hspace{1cm} (4.2)

\[ \sigma_{11} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[ 1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] - \frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \left[ 2 + \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \right] \]  \hspace{1cm} (4.3)
\[ \sigma_{22} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[ 1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] + \frac{K_{II}}{\sqrt{2\pi r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} \] (4.4)

\[ \tau_{12} = \frac{K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \sin \frac{\theta}{2} \cos \frac{3\theta}{2} + \frac{K_{II}}{\sqrt{2\pi r}} \cos \frac{\theta}{2} \left[ 1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] \] (4.5)

Where \( \mu \) is the elastic shear modulus of the material, \( \kappa = (3-\nu)/(1+\nu) \) for plane stress, \( \nu \) is the Poisson’s ratio. \( K_I \) and \( K_{II} \) are the stress intensity factors for mode I and II respectively.

4.1.2 Case II: Crack in the graphene sheet with finite width

Case II we proposed in this chapter is a sample of a graphene sheet in a zigzag form with dimensions \( 15.068 \text{ nm} \times 17.255 \text{ nm} \) containing a system of 9840 carbon atoms. Figure 4.3 is a schematic diagram of the sample. A crack is located in the middle of the graphene sheet and is perpendicular to some of the covalent bonds. Due to the discrete nature of atomistic modeling, the crack length is evaluated as the length measured from number of broken bonds. During the simulation, the centered crack of length \( 2a \) varying from 1.006 to 6.530 nm of the graphene sheet is examined. In the linear elastic fracture mechanics, the Young’s modulus \( (E = 0.68 \text{ TPa}) \) is calculated from an energy approach (Jin and Yuan, 2003).
4.1.3 Simulation Technique

In the direct atomistic simulation, each and every atomistic degree of freedom is explicitly accounted for, and the minimum energy configuration is determined on the basis of interatomic interactions. At the beginning, the initial state of the atomic system without applied deformation reaches equilibrium for approximately 100 ps with a time step of 1.5 fs. After equilibrium is reached, a small deformation is applied to the sample by scaling atomic positions and boundary conditions along the appropriate coordinate. In case I the atomic displacement field obtained from equation (4.1) and (4.2) with the initially specified stress intensity factor is applied to each atom. In case II three deformation modes are applied to the graphene sheet separately: 1) the fixed-grip displacement $u_z = \varepsilon_0 x_1$, $\varepsilon_0 = 0.005$, is applied...
on the top and bottom surfaces of the sample in mode I; 2) mode II, \( u_1 = \varepsilon_0 x_2 \) and \( u_2 = \varepsilon_0 x_1 \) is prescribed on these surfaces. 3) An simple shear mode, which is also widely used to study the fracture behavior, especially in the experiment investigation, is applied to the system as \( u_1 = \varepsilon_0 x_2 \) and \( u_2 = 0 \). An illustration of simple shear deformation and pure shear deformation, which is mode II, is shown in Figure 4.4. After applying the designated deformation, roughly another 100 ps period is required to reach a minimum potential energy of the system. All molecular mechanics simulations are carried out at temperature 0 K.

Fig. 4.4 Illustration of simple shear and pure shear.

4.2 Atomic Stress

Based on the description of atomic stress in chapter 2, in this discrete atomic system the atomic stress at atom \( i \) can be derived from the atom coordinates and interatomic forces. This method provides a continuum measure of the internal mechanical interactions between atoms. Similarly the expression is given by:

\[
\sigma^\alpha_\beta = \frac{1}{2V_0} \sum_{j \neq i} \epsilon^\alpha_j F^\beta_j
\]  

(4.6)
Where $\sigma^{\alpha\beta}_i$ is the atomic stress tensor in the Cartesian coordinates at atom $i$. $V_0$ is the volume per atom. $r^{\alpha}_{ij} = |r^\alpha_i - r^\alpha_j|$ is the distance between atom $i$ and $j$ projected on $\alpha$ direction. $F^{\beta}_{ij}$ is the $\beta$ component of the interatomic force exerted on atom $i$ by atom $j$.

### 4.3 Energy Release Rate in Atomic System

#### 4.3.1 Global Energy Method

Elastic strain energy release rates are calculated from the atomistic simulations by realistic crack extension models. It is assumed that the crack extension would not cause the bond reconfiguration. Two methods are proposed to calculate the energy release rate. The first method, global energy method, is based on the change of total potential energy of two self-similar graphene sheets with same dimensions but two slightly different central crack lengths, $2a$ and $2a + 2\Delta a$, as given by

$$G = -\frac{U_{2a+2\Delta a} - U_{2a}}{2\Delta a t}$$  \hspace{1cm} (4.7)

where $U_{2a}$ and $U_{2a+2\Delta a}$ are the total potential energy of the two graphene sheets under a given deformation mode obtained from Tersoff-Brenner potential. $\Delta a$ is the equilibrium interatomic distance in the $x$ direction which is equal to 0.251 nm ($0.145 \times \sqrt{3}$ nm). $t$ is the thickness of the graphene sheet. In this study an interlayer separation distance of graphite, which is 0.34 nm, is defined as the effective thickness. Figure 4.5 is the illustration of how to calculate the energy release rate.
4.3.2 Local Force Method

Another means of evaluating the energy release rates is the local force method by determining the virtual work that is required to close the crack extension. In this method, it is not required to calculate the total potential energy. Therefore it leads to less computational time, especially for those multi-million atomic systems, since only those neighboring atoms near the crack tip need to be evaluated; while the change of total potential energy requires all the atoms in the system have to be investigated.

Based on the principle of virtual work (PVW), the virtual work is illustrated in Figures 4.6 and 4.7 to close the crack extension in a graphene sheet for mode I and II small deformation respectively. The energy release rates for mode I and II, denoted by $G_I$ and $G_{II}$, are expressed by:

Fig. 4.5 Illustration of the method of calculating the energy release rate.
\[ G_I = \frac{1}{2\Delta a t} F_y (v^+ - v^-) \]  
(4.8)

\[ G_{II} = \frac{1}{2\Delta a t} [F_x (u^+ - u^-) + F_y (v^+ - v^-)] \]  
(4.9)

where \( F_x \) and \( F_y \) are the interatomic forces exerted on atom \( i \) in the \( x \) and \( y \) directions respectively by atom \( j \) and its neighboring atoms at the crack length \( 2a \). \( u^+ \), \( u^- \), \( v^+ \), \( v^- \) are the crack opening displacements of atom \( i \) and \( j \) in the \( x \) and \( y \) directions at crack length \( 2a + 2\Delta a \). Therefore two configurations have been used to obtain the value of virtual work. Note that in the discrete atomistic simulation the crack extension implies the bond broken in the immediate vicinity of the crack tip with length \( \Delta a \).

![Crack Surface](image)

Fig. 4.6 A general illustration of virtual work under Mode I.
4.4 Results and Discussions

4.4.1. Numerical Results of Case I

In the simulation, a remote $K_I$ displacement field obtained by assigning $K_I = 0.3 \text{ MPa} \cdot \text{m}^{1/2}$ and $K_{II} = 0$ in Equation 4.1 and 4.2 is applied to the above system. The energy release rate is calculated by the local force method introduced in the previous section. The numerical result is then compared with continuum theoretical solution which is $G_{\text{theory}} = K^2 / E$. Similarly, a remote $K_{II}$ displacement field can be obtained by assigning $K_I = 0$ and $K_{II} = 0.1 \text{ MPa} \cdot \text{m}^{1/2}$. Table 4.1 is the comparison of the energy release rate obtained by atomistic simulation and continuum theoretical solution. The relative errors of
the two results are very small, 0.08% and 2.10% for Mode I and Mode II respectively. The results demonstrated the capability of using macroscopic fracture parameter to describe the atomic fracture via atomistic simulation.

Table 4.1 Comparison of the energy release rate obtained by atomistic simulation and continuum theoretical solution.

<table>
<thead>
<tr>
<th></th>
<th>( K_I = 0.3 \text{ MPa} \cdot \text{m}^{1/2} )</th>
<th>( K_{II} = 0.1 \text{ MPa} \cdot \text{m}^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_{\text{simulation}} )</td>
<td>0.1325</td>
<td>0.01502</td>
</tr>
<tr>
<td>( G_{\text{LEFM}} )</td>
<td>0.1324</td>
<td>0.01471</td>
</tr>
<tr>
<td>Relative Error</td>
<td>0.08%</td>
<td>2.10%</td>
</tr>
</tbody>
</table>

Figure 4.8 gives the distribution of atomic stress \( \sigma_{22} \) in front of a crack in Mode I with the comparison of continuum stress from linear elastic solution. Figure 4.9 is the comparison between atomic stress and continuum stress of \( \tau_{12} \) in Mode II. In these two figures the atomic stress agrees remarkably well with the continuum stress. At the crack tip the atomic stress distribution yields more reasonable description than the spurious singularity of the stress field by LEFM. Therefore, the macroscopic fracture parameters that characterized the fracture phenomenon are consistent with each other under small deformation both in atomic-scale and macroscopic continuum model. Thus, the description on the atomistic aspect of fracture can be linked to the description of macroscopic fracture.
Fig. 4.8 Stress distribution of $\sigma_{22}$ in front of a crack under remote $K_I$ field.

Fig. 4.9 Stress distribution of $\tau_{12}$ in front of a crack under remote $K_{II}$ field.
4.4.2 Numerical Results of Case II

Figures 4.10, 4.11, and 4.12 are the close-up views of the deformation configuration near the crack tip under the three kinds of external applied fields described before. All the atoms coordinates in the figures are based on the numerical results but with proper enlarging ratios for the convenience of view. The crack tip is located at the center between atom $i$ and $j$. The solid line and broken line refer to the deformed and undeformed configurations respectively. For mode I the deformation of the surface of a crack obtained by LEFM is displayed as bold-dotted line in Figure 4.10. Note that in comparison with the deformed shape of the crack surfaces from atomistic simulation the deformed crack surfaces obtained from LEFM are formed by adding the equilibrium atomic separation to the resulting crack opening displacements.

Fig. 4.10 Close-up view of undeformed and deformed configurations near the crack tip in mode I. (Bold-dotted line is the deformed crack surface from LEFM)
Fig. 4.11 Close-up view of undeformed and deformed configurations near the crack tip in mode II.

Fig. 4.12 Close-up view of undeformed and deformed configurations near the crack tip in simple shear mode.
Figures 4.13, 4.14 and 4.15 show the normalized strain energy release rates $G/\sigma_0^2$ and $G/\tau_0^2$ versus crack length by three approaches, which are global energy approach, local force approach and LEFM respectively. $\sigma_0$ (or $\tau_0$) = $F_0 / A$, where $F_0$ is the external force applied on the system resulting from the fixed-grip prescribed displacements and $A$ is the area of the cross-section of graphene sheet. From the figures, a good agreement is reached between the results from atomistic simulation and those from LEFM. In Figure 4.13, the values of energy release rate obtained by local force method is slightly less than the other two curves, which implies a possible local rigid body rotation occurs around the crack tip to make considerable numerical error when calculating the relative displacements of atoms. The detailed fracture parameters are also tabulated in the following tables. In Figure 4.16, the deformed crack surface profile in mode I from atomistic simulation and LEFM is shown for the initial crack length $2a = 6.53$ nm. As expected they also match well. These results indicate that the fracture parameters calculated from LEFM can be also predicted from atomistic simulation. The atomistic simulation is not involved with the unphysical singularities of the stress field near crack tip as LEFM. Moreover, it also shed light on the proper theoretical description of both the nonlinearities in the vicinity of the crack and the bond breaking mechanism between atom pairs through atomistic simulation while the conventional continuum approach would be ultimately limited.
Fig. 4.13 \( \frac{G}{\sigma_0^2} \) versus crack length in mode I.

Fig. 4.14 \( \frac{G}{\tau_0^2} \) versus crack length in mode II.
Fig. 4.15 $G/\tau_0^2$ versus crack length in simple shear mode.

Fig. 4.16 Crack surface profile under Mode I from atomistic simulation and LEFM. (The crack length is 6.530 nm.)
Table 4.2 The numerical results of $G / \sigma_0^2$ in mode I.

<table>
<thead>
<tr>
<th>Crack Length (nm)</th>
<th>Atomistic Simulation</th>
<th>LEFM</th>
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<tbody>
<tr>
<td></td>
<td>Global Energy Method</td>
<td>Local Force Method</td>
</tr>
<tr>
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<td></td>
<td></td>
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<tr>
<td>1.005</td>
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<tr>
<td>6.530</td>
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Table 4.3 The numerical results of $G / \tau_0^2$ in mode II.

<table>
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<th>Crack Length (nm)</th>
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<td>Global Energy Method</td>
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<tr>
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<td></td>
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</tr>
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<td>6.530</td>
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Table 4.4 The numerical results of $G/\tau_0^2$ in simple shear mode.

<table>
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<th>Atomistic Simulation</th>
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5 J-INTEGRAL IN ATOMIC SYSTEM

In this chapter, the approach of calculating $J$-integral in a specified domain is developed. By mechanical molecular simulation the values of $J$-integral for both crack in a semi-finite graphene sheet and crack in the sheet with finite width are obtained under linear elastic condition. The nonlinear stress and stress relationship of a graphene sheet is evaluated and fitted with a power law curve. After modified the cut-off function in the Tersoff-Brenner potential, a series of the critical value of $J$-integral, $J_c$, is calculated. The results is briefly compared with the related references.

5.1 $J$-Integral

Energy release rate and stress intensity factor are normally only used in linear elastic material. For the nonlinear material, alternative fracture parameters are required to characterize the fracture behavior. $J$-integral, which is equivalent to the strain energy release rate under linear elastic condition, is one of the most representative parameters to evaluate the crack properties in the nonlinear continuum media (Rice and Rosengren, 1968; Hutchinson, 1968). As shown in Figure 5.1, $J$-integral is a closed contour integral of the strain energy density and work done by tractions on the contour, as following,

$$ J = \int_\Gamma (W \delta_{ij} - \sigma_{ij} \frac{\partial u_j}{\partial x}) n_j \, d\Gamma $$

(5.1)
where $W$ is the strain energy density, $\sigma_{ij}$ and $u_i$ are the stress and displacement respectively.

Subscription 1 in the above equation denotes the direction paralleling to the crack, which is the $x$ direction here.

Fig. 5.1 Typical contour for the path-independent $J$-integral.

Fig. 5.2 Contour for the $J$-integral in atomic system.
Due to the inconvenience of computing the line integral in finite element analysis (FEA), alternate ways of calculating this integral have been proposed to convert it to equivalent domain integrals in the continuum materials, which is called equivalent domain integral (EDI) method (Li, Shih and Needleman, 1985; Nikishkov, 1987; Raju and Shivakumar, 1990;

In the discrete atomic system, it would be cumbersome to directly evaluate the contour integral since most possibly the atom won’t be exactly on the contour line, as shown in Figure 5.2. Thus applied the EDI method to the atomic system is a prerequisite for calculating the atomic $J$-integral (Naktani et al., 2000). By introducing an arbitrary but continuous function $q$ which has such property:

\[ q(r, \theta) = 1 \quad \text{on } \Gamma_2 \]

\[ q(r, \theta) = 0 \quad \text{on } \Gamma_1 \quad (5.2) \]

In our paper the form of function $q$ is:

\[ q(r, \theta) = \frac{r - r_1}{r_2 - r_1} \quad (5.3) \]

where $r_1$ and $r_2$ are the radius of contour $\Gamma_1$ and $\Gamma_2$ respectively.

As the line integrals on $\Gamma_3$ and $\Gamma_4$ are zero due to the crack’s traction free properties, the $J$-integral can be written as

\[ J = \int_{\Gamma_1} (W \delta_{ij} - \sigma_{ij} \frac{\partial u_j}{\partial x_1}) n_j \, d\Gamma = \int_{\Gamma_1} (W \delta_{ij} - \sigma_{ij} \frac{\partial u_j}{\partial x_1}) q n_j \, d\Gamma \quad (5.4) \]
where $\Gamma^* = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$. Hence, based on divergence theorem, the line integral can be converted to the domain integral

$$J = \iint_{\Gamma} (W\delta_{ij} - \sigma_{ij} \frac{\partial u_i}{\partial x_j}) \frac{\partial q}{\partial x_j} \, ds \quad (5.5)$$

The discrete form of the domain integral for the atomic model will be

$$J = \frac{1}{t} \sum_{\alpha \in S} [(W^{\alpha} \delta_{ij} - \sigma_{ij}^{\alpha} \frac{\partial u_i^{\alpha}}{\partial x_j}) \frac{\partial q^{\alpha}}{\partial x_j} V^{\alpha}] \quad (5.6)$$

Where $W^{\alpha}$ is the local potential energy density of atom $\alpha$; $\sigma_{ij}^{\alpha}$ and $u_i^{\alpha}$ are the atomic stress and displacement of atom $\alpha$ respectively. $V^{\alpha}$ is the volume occupied by the atom $\alpha$. $t$ is the thickness of graphen sheet.

### 5.2 Displacement Gradient

The macroscopic description of the deformations of a continuum body begins with the consideration of the change in distance between any two arbitrary points of the body. The quantitative evaluation of the deformation is always denoted by the displacement gradients and strains. In atomic system, in spite of its discrete nature such concepts are still needed to quantitatively describe the extent of structure deformation. In previous atomistic simulations, generally only external strain, such as tensile and shear strain for the whole structure, is calculated by the global coordinate. This method is only effective in the uniform deformation. For the investigation in the vicinity of crack tip, displacement gradients vary a lot. Therefore, the local deformation information is necessary to be known.
Based on the continuum mechanics, for two arbitrary points, there exist:

\[
\frac{\partial u_1}{\partial x_1} = \frac{dX_1 - dX_1^0}{dx_1^0} \quad (5.7)
\]

\[
\frac{\partial u_2}{\partial x_2} = \frac{dX_2 - dX_2^0}{dx_2^0} \quad (5.8)
\]

where \( dX_1^0 \) and \( dX_2^0 \) are the original distance between the two points in \( x_1 \) and \( x_2 \) direction respectively. \( dX_1 \) and \( dX_2 \) are the distances after deformation.

The shear components, \( \frac{\partial u_1}{\partial x_2} \) and \( \frac{\partial u_2}{\partial x_1} \), represent the change of angle of \( x_1, o x_2 \) which was originally a right angle, as shown in Figure 5.3a. In the graphene sheet which consists of hexagonal units, we proposed the calculation of \( \frac{\partial u_1}{\partial x_2} \) and \( \frac{\partial u_2}{\partial x_1} \) as the angle change of the atom with proper atoms at vertical and horizontal direction respectively, as shown in Figure 5.3b.
In the graphene sheet each atom has three neighboring atoms except for those atoms on the boundary and crack surface. Unlike the infinitesimal properties of the element of volume selected around the points, the dimension of hexagonal units is fixed. This leads to the problems that the results of displacement gradients are different with different neighboring atoms. Let us consider a one-dimensional spring model as shown in Figure 5.4. The strain of the spring between \( i \) and \( j \) is \( \Delta L_i / L_i \), the strain of the strain between \( j \) and \( k \) is \( (\Delta L_j - \Delta L_i) / L_j \). The two strains are not necessarily equal to each other. To characterize the deformation around \( j \), a proper way should be average all the strains around that designated points, which is

\[
\varepsilon_j = \frac{1}{2} \left( \frac{\Delta L_i}{L_i} + \frac{\Delta L_j - \Delta L_i}{L_j} \right)
\]  

(5.9)
Similarly, in the 2-dimensional atomic system the displacement gradient at an atom can be obtained by taking an average over its neighboring atoms, which is given by:

\[
\frac{\partial u_i}{\partial x_j} = \frac{1}{N} \sum_{\alpha=1,N} (\frac{dX_i - dX_{i0}}{dX_j})_{\alpha}
\]

(5.10)

where \( \alpha \) is the identity of the neighboring atoms around.

5.3 J-integral in Linearity

5.3.1 Case I: Crack in Semi-infinite Domain

The atomic system investigated in this section is the same as the case in section 4.1.1. Remote \( K_j \) and \( K_n \) displacement fields are applied to the region around crack tip in an infinite graphene sheet respectively. During the calculation several different values of \( r_1 \) and \( r_2 \) are selected to verify the path independent property of the J-integral. The results shown in Figure 5.5 and 5.6 clearly demonstrate the path independence. This ensured the validity of using atomistic simulation to evaluate the J-integral.
Fig. 5.5 $J$-integral with different $r_1$ and $r_2$ in mode I.

Fig. 5.6 $J$-integral with different $r_1$ and $r_2$ in mode II.
Table 5.1 Comparison of $J$-integral with energy release rate.

<table>
<thead>
<tr>
<th></th>
<th>$J_{\text{simulation}}$</th>
<th>$G_{\text{simulation}}$</th>
<th>$G_{\text{theory}}$ ($J_{\text{theory}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_j = 0.3$ MPa·m$^{1/2}$</td>
<td>0.1305</td>
<td>0.1325</td>
<td>0.1324</td>
</tr>
<tr>
<td>$K_H = 0.1$ MPa·m$^{1/2}$</td>
<td>0.01451</td>
<td>0.01502</td>
<td>0.01471</td>
</tr>
</tbody>
</table>

Table 5.1 is the comparison of the atomistic simulation results of $J$-integral with the theoretical ones, and also with the numerical results of energy release rate obtained in the previous computations. As listed in the table there is a good agreement with a relative error 1.4% in both deformation modes.

5.3.2 Case II: Crack in the graphene sheet with finite width

In LEFM $J$-integral is equivalent to the energy release rate. For a graphene sheet with finite width, the distributions of $J$-integral with regard to different crack lengths in different deformation modes are shown in Figure 5.7, 5.8, and 5.9. Due to the relatively small scale of the cracks, the selection of $r_1$ and $r_2$ should be very careful to assure sufficient numbers of atoms located in that integral zone. Hence, crack length less than 0.3 nm is not evaluated. Figure 5.7 and 5.9 shows good agreements between the $J$-integral and energy release rate obtained from both global energy method and local force method in mode I and simple shear mode. In Figure 5.8 there is a clear trend that the longer the crack length is, the better $J$-
integral matches with the energy release rate obtained from global energy method. As discussed in chapter 4, a slight difference exists between the values of energy release rate from global energy method and local force method.

![Graph](image)

**Fig. 5.7** $J$-integral versus crack length in mode I. GEM represents global energy method; LFM represents Local force method.
Fig. 5.8 $J$-integral versus crack length in mode II.

Fig. 5.9 $J$-integral versus crack length in simple shear mode.
5.4 J-Integral in Nonlinearity

5.4.1 Nonlinear Stress-Strain Relationship

In the nonlinear materials the relationship of the elastic-plastic stress and strain is normally described in a power law function as given by:

\[
\frac{\varepsilon}{\varepsilon_0} = \left(\frac{\sigma}{\sigma_0}\right) + \alpha \left(\frac{\sigma}{\sigma_0}\right)^n
\]

(5.11)

where \(\sigma_0\) is a reference stress value which is 23.8 GPa in this simulation; the corresponding strain, \(\varepsilon_0\), is 3.5%; \(\alpha\) is a constant and \(n\) is the strain hardening exponent. The above equation is called as the Ramberg-Osgood equation which has been widely used for the curve-fitting stress-strain data in elastic-plastic materials. In our simulation the stress-strain curve of graphene sheet is shown in Figure 5.10. Analytical curve is fitted using the least-square algorithm. The parameters are:

\[
\alpha = 0.009091
\]

\[
n = 3.7155
\]

(5.12)

The strain and stress at tensile failure, which denoted as \(\varepsilon_c\) and \(\sigma_c\), is 30% and 109.4 GPa respectively. A related research by Yakobson et al. (1997) in which they studied the carbon nanotube under simple tension, which has the same hexagonal unit as graphene sheet, showed the breaking strain in the range of 30-40% in MD simulation.
5.4.2 $J_c$ as a measure of fracture toughness

Based on the discussions in the previous sections, $J$-integral is able to uniquely characterize the mechanical behavior around the crack tip in nonlinear materials. In the analysis of the failure of material it is always a major concern on when the crack in the material began to propagate. Thus, the critical value of $J$-integral at the onset of crack growth, normally denoted as $J_c$, is one of the most important criteria to represent the fracture toughness in elastic-plastic materials.
Before evaluation of $J_c$ for the 2-dimensional graphene sheet, a modification on the many-body empirical potential used in our simulation is required. As shown in Fig. 2.5, the cut-off function in Tersoff-Brenner potential significantly influences the interatomic forces between the two cut-off distance 0.17 and 0.20 nm. To avoid this unphysical phenomenon Shenderova et al. (2000) extended the cut-off distance much beyond the 0.17 nm while the neighboring atoms list remained unchanged using the original cut-off distance when they studied the fracture of polycrystalline diamond. Such modification is only valid to the investigation of bond breaking and rehybridization, but not new bond formation.

![Graph showing critical values of $J$-integral in different crack length.](image)

Fig. 5.11 The critical values of $J$-integral in different crack length.

The atomic system we studied here is the same as shown in Figure 4.3, which is a sample of a graphene sheet in a zigzag form with dimensions 15.068 nm × 17.255 nm.
containing a system of 9840 carbon atoms. Displacements were applied to the graphene sheet with different center crack length from zero to the strain where the crack begun to extend. Then, a series of $J_c$ can be obtained from the atomic configurations at the initiation of crack growth, as shown in Figure 5.11. In the figure the value of $J_c$ decreases with the increase of crack length, this indicates that the graphene sheet has brittle fracture behavior. The prediction is also proven by direct observations of the fracture phenomena in graphene sheet during simulations.

Here we will have a brief comparison of the fracture toughness to some related references. Omeltchenko et al. (1997) investigated the crack front propagation in a graphene sheet and obtained the value of the fracture toughness as 4.7 MPa m$^{1/2}$, which should be the value of $K_c$ since the definition of the fracture toughness in their paper is $\sigma_f \sqrt{c}$ where $\sigma_f$ is the critical stress at which the crack starts propagating and $c$ is the length of the notch inserted in the graphene sheet. $\sigma_f$ equals 66 GPa in the paper. Shenderova et al. (2000) obtained the $K_c$ of polycrystalline diamond in the range of 2-6 MPa m$^{1/2}$ with different crystal orientations by a similar approach. The applied critical stresses in their investigation are mostly in the range of 30-50 GPa. Let us consider a case in which crack length equals 4.018 nm in our simulation, the external fracture stress at the onset of crack extension is 35.5 GPa. Then we can obtain the value of $K_c$ as 4.0 MPa m$^{1/2}$ if adopting the similar calculation method, $K_c = \sigma_{\infty} \sqrt{\pi a}$, which is actually only valid in LEFM. In one hand these brief comparisons show the consistence of our simulation results with the previous research. On the other hand, such relationship as $K_c = \sigma_{\infty} \sqrt{\pi a}$ is no longer valid in the elastic-plastic
condition, even the parameter $K_c$ is not able to characterize the fracture toughness any more. From this point of view $J_c$ uniquely characterizes the fracture toughness in the nonlinear materials.

Table 5.2 The numerical results of $J$-integral and $G$ in mode I.

<table>
<thead>
<tr>
<th>Crack Length (nm)</th>
<th>$J$-integral</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Global Energy Method</td>
</tr>
<tr>
<td>3.014</td>
<td>0.081</td>
<td>0.078</td>
</tr>
<tr>
<td>3.516</td>
<td>0.091</td>
<td>0.089</td>
</tr>
<tr>
<td>4.018</td>
<td>0.100</td>
<td>0.099</td>
</tr>
<tr>
<td>4.521</td>
<td>0.109</td>
<td>0.108</td>
</tr>
<tr>
<td>5.023</td>
<td>0.116</td>
<td>0.116</td>
</tr>
<tr>
<td>5.525</td>
<td>0.124</td>
<td>0.124</td>
</tr>
<tr>
<td>6.027</td>
<td>0.130</td>
<td>0.130</td>
</tr>
<tr>
<td>6.530</td>
<td>0.136</td>
<td>0.136</td>
</tr>
</tbody>
</table>

Table 5.3 The numerical results of $J$-integral and $G$ in mode II.

<table>
<thead>
<tr>
<th>Crack Length (nm)</th>
<th>$J$-integral</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Global Energy Method</td>
</tr>
<tr>
<td>3.014</td>
<td>0.0395</td>
<td>0.0431</td>
</tr>
<tr>
<td>3.516</td>
<td>0.0458</td>
<td>0.0489</td>
</tr>
<tr>
<td>4.018</td>
<td>0.0518</td>
<td>0.0544</td>
</tr>
<tr>
<td>4.521</td>
<td>0.0575</td>
<td>0.0596</td>
</tr>
<tr>
<td>5.023</td>
<td>0.0628</td>
<td>0.0643</td>
</tr>
<tr>
<td>5.525</td>
<td>0.0677</td>
<td>0.0687</td>
</tr>
<tr>
<td>6.027</td>
<td>0.0722</td>
<td>0.0729</td>
</tr>
<tr>
<td>6.530</td>
<td>0.0762</td>
<td>0.0762</td>
</tr>
</tbody>
</table>
Table 5.4 The numerical results of $J$-integral and $G$ in simple shear mode.

<table>
<thead>
<tr>
<th>Crack Length (nm)</th>
<th>$J$-integral Global Energy Method</th>
<th>Local Force Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.014</td>
<td>0.0090</td>
<td>0.0095</td>
</tr>
<tr>
<td>3.516</td>
<td>0.0104</td>
<td>0.0109</td>
</tr>
<tr>
<td>4.018</td>
<td>0.0117</td>
<td>0.0121</td>
</tr>
<tr>
<td>4.521</td>
<td>0.0130</td>
<td>0.0133</td>
</tr>
<tr>
<td>5.023</td>
<td>0.0143</td>
<td>0.0144</td>
</tr>
<tr>
<td>5.525</td>
<td>0.0155</td>
<td>0.0155</td>
</tr>
<tr>
<td>6.027</td>
<td>0.0167</td>
<td>0.0165</td>
</tr>
<tr>
<td>6.530</td>
<td>0.0178</td>
<td>0.0175</td>
</tr>
</tbody>
</table>
6 SUMMARY AND FUTURE WORK

6.1 Summary

This dissertation has two major parts: 1) the atomistic simulations of fracture of 2-dimensional graphene systems; 2) the atomistic simulations of the elastic properties of carbon nanotubes. In the first part the fracture mechanism of a nanostructure material are investigated by molecular mechanics simulations. The macroscopic fracture parameters, energy release rate and $J$-integral, are evaluated through atomistic simulations and continuum approaches. Stress fields and crack profiles in the atomic systems are also obtained. These simulations establish solid connections between microscopic and macroscopic description of fracture, and would be able to lead to a further insight into the fracture mechanism of nano-structured materials. Specific contributions of this study to the field of the research can be summarized as follows:

(1) The basic framework of analyzing the atomic aspect of fracture in a nanostructure material is systematically developed. The feasibility of utilizing atomistic simulations to describe the fracture phenomena in the system is demonstrated.

(2) Energy release rates are investigated in both a semi-infinite graphene sheet containing cracks and a center-cracked graphene sheet with finite width by atomistic simulation and continuum method. There is a very good agreement between the results of discrete simulations and continuum analyses. Two approaches, global energy approach and local force approach, are developed to compute the energy release rates in the atomic system.
(3) The atomic descriptions of the stress fields around crack tip are obtained. The distributions of stress in a semi-infinite graphene sheet containing cracks match very well with the linear elastic solutions.

(4) A method to calculate $J$-integral in the atomic system is successfully developed. The numerical results of $J$-integral agree very well with the energy release rate in linear elastic material. After a necessary modification on the Tersoff-Brenner potential, the critical value of $J$-integral, denoted by $J_c$, is eventually reached as the measure of the fracture toughness of graphene sheet.

In the second part the mechanical properties of SWNT are evaluated by MD simulations. Several elastic moduli of SWNTs using the MD simulations were obtained at the atomic scale. Since the single-walled nanotube has a single carbon atom in the thickness direction, the engineering constants that are related to the radial direction, $E_r$, $v_{rz}$, and $G_r$ (or $G_{rr}$), are yet to be clearly defined. The major contributions in this field are:

(1) The Young’s modulus, rotational shear modulus, and in-plane Poisson’s ratio are obtained. The values are in the range of existing theoretical and experimental results.

(2) It is shown from simulations that the elastic constants of SWNTs are insensitive to the morphology pattern such as nanotube radius. Thus the effect of curvature on the elastic constants can be neglected.

(3) Assumption of the transversely isotropic properties on the cylinder surface of the single-walled nanotube is confirmed by numerical calculations.
(4) Besides the conventional energy approach, a new method, which denoted as force approach in the dissertation, is developed to analyze the elastic properties of carbon nanotubes. The advantage of the force approach is that it can provide more accurate prediction than the energy approach since the energy approach is required to calculate several total potential energy values under different strain levels and then uses a least-square fit to obtain the elastic moduli. Furthermore, the force approach can predict the nonlinear behavior without assumption of assumed total potential energy in quadratic form described for small-strain deformation in the energy approach.

6.2 Future Work

The research on the atomistic simulation of fracture in graphene sheet may be extended in the future according to the following aspects. One is that the investigation on the thermal effect on the fracture behavior may be the primary interests. How to link the thermal strain with current local atomic strain with proper thermal coefficient would be the first concern. Also, the kinetic energy may bring the fluctuation of the total energy which leads to the less accuracy of the energy release rate and atomic stress. The second is that the fracture parameters in different orientation of the graphene sheet may be another upcoming issue. Unlike the zigzag structure where the crack is perpendicular to some of the chemical bond, in arm chair structure the crack would be parallel to the bonds and detailed consideration of the possible crack bifurcation would be necessary. And the dynamic properties of the crack propagation, such as the stress wave transmitted in the system, may also be an interesting field to consider.
REFERENCES


method for computing crack-tip integral parameters in non-elastic, thermo-

graphite sheet: a molecular-dynamics study on parallel computers”, Physical

nanotubes in novel ceramic matrix nanocomposites”, Ceramics International,

and deformation mechanisms in carbon nanotube-polystyrene composites”,

continuum modeling of crack propagation in a two-dimensional maroscopic

method in the two-dimensional analysis of mixed mode crack problems”,

tip in a power-law hardening material”, Journal of Mechanics and Physics of

brittle materials: multimillion atom molecular dynamics simulations”, Annual

3842-3844.


diamond-structure crystals”, Proceedings of the Royal Society of London. A.,

[61] Sinclair, J. E., (1972c), "Atomistic computer simulation of brittle-fracture

647-656.

geometric effects in atomic dislocation modeling”, Journal of Applied Physics,
Vol. 49, pp. 3890-3897.


APPENDIX

THE INTERATOMIC FORCES DERIVED FROM TERSOFF-BRENNER POTENTIAL

The Tersoff-Brenner potential is expressed by

\[
U = \sum_i \sum_{j\neq i} [V_K(r_{ij}) - \overline{B}_{ij}V_A(r_{ij})]
\]  

(1)

where \( r_i = (x_i, y_i, z_i) \) denotes positions of the atoms, \( I = i, j, k; r_{ij} = |r_i| = |r_j - r_i| \) is the separation distance between atom \( i \) and \( j \).

The function \( \overline{B}_{ij} \) is given by:

\[
\overline{B}_{ij} = \frac{1}{2}(B_{ij} + B_{ji})
\]  

(2)

Where

\[
B_{ij} = \left[ 1 + \sum_{k \neq i, j} G(\theta_{ijk})f(r_{ik}) \right]^{-\delta}
\]  

(3)

\( f(r_{ik}) \) is the cut-off function given in equation (4), \( \delta \) is the constant, \( G(\theta_{ijk}) \), which is the function of the angle \( \theta_{ijk} \) between bonds \( i-j \) and \( i-k \), is given by
\[ G(\theta) = a_0 \left[ 1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + (1 + \cos \theta)^2} \right] \]  

(4)

Where \( a_0 \), \( c_0 \), \( d_0 \) are constants.

The interatomic forces on atom \( i \) are obtained by

\[ F_i = -\frac{\partial U}{\partial r_i} = \sum_{j(i)} \left[ -\frac{\partial V_k(r_{ij})}{\partial r_i} + \frac{\partial B_j}{\partial r_i} V_A(r_{ij}) + B_j \frac{\partial V_A(r_{ij})}{\partial r_i} \right] \]  

(5)

In equation (5), the three terms involving derivations in the right side of the equation is expressed as:

\[ \frac{\partial V_k(r_{ij})}{\partial r_i} = f(r_{ij}) \frac{D_k}{S-1} \frac{\partial}{\partial r_i} \left( e^{-\sqrt{2S} \beta (r_{ij})} + \frac{D_k}{S-1} e^{-\sqrt{2S} \beta (r_{ij})} \right) \frac{\partial f(r_{ij})}{\partial r_i} \]

\[ = -f(r_{ij}) \frac{\sqrt{2S} \beta D_k}{S-1} e^{-\sqrt{2S} \beta (r_{ij})} \frac{\partial r_{ij}}{\partial r_i} + f'(r_{ij}) \frac{D_k}{S-1} e^{-\sqrt{2S} \beta (r_{ij})} \frac{\partial r_{ij}}{\partial r_i} \]  

(6)

\[ \frac{\partial V_A(r_{ij})}{\partial r_i} = f(r_{ij}) \frac{D_A}{S-1} \frac{\partial}{\partial r_i} \left( e^{-\sqrt{2S} \beta (r_{ij})} + \frac{D_A}{S-1} e^{-\sqrt{2S} \beta (r_{ij})} \right) \frac{\partial f(r_{ij})}{\partial r_i} \]

\[ = -f(r_{ij}) \frac{\sqrt{2S} \beta D_A}{S-1} e^{-\sqrt{2S} \beta (r_{ij})} \frac{\partial r_{ij}}{\partial r_i} + f'(r_{ij}) \frac{D_A}{S-1} e^{-\sqrt{2S} \beta (r_{ij})} \frac{\partial r_{ij}}{\partial r_i} \]  

(7)

In equation (6) and (7), \( f(r_{ij}) \) and \( f'(r_{ij}) \) are given by

\[ f(r_{ij}) = \begin{cases} 
1 & \text{if } r_1 < r_{ij} \\
\frac{1}{2} \left[ 1 + \cos \left( \frac{\pi (r_{ij} - r_1)}{r_2 - r_1} \right) \right] & \text{if } r_1 \leq r_{ij} \leq r_2 \\
0 & \text{if } r_{ij} > r_2
\end{cases} \]  

(8)
\[
C_t'(r_{ij}) = \begin{cases} 
0 & \text{if } r_{ij} < r_1 \\
- \frac{\pi}{2(r_2 - r_1)} \sin \left( \frac{\pi(r_{ij} - r_i)}{r_2 - r_1} \right) & \text{if } r_1 \leq r_{ij} \leq r_2 \\
0 & \text{if } r_{ij} > r_2 
\end{cases}
\]

In equation (5), \( \frac{\partial B_y}{\partial r_i} = \frac{1}{2} \left( \frac{\partial B_y}{\partial r_i} + \frac{\partial B_y}{\partial r_j} \right) \)

where

\[
\frac{\partial B_{ij}}{\partial r_i} = -\delta \left[ 1 + \sum_{k(ai,j)} G(\theta_{ik}) f(r_{ik}) \right]^{\frac{k-1}{2}} \cdot \left( \sum_{k(ai,j)} \frac{\partial G(\theta)}{\partial r_i} f(r_{ik}) + \sum_{k(ai,j)} G(\theta) f'(r_{ik}) \frac{\partial r_k}{\partial r_i} \right)
\]

(10)

where the expression of \( f(r_{ik}) \) and \( f'(r_{ik}) \) in the above equation is given in equation (8) and (9).

\[
\frac{\partial G(\theta)}{\partial r_i} = -\frac{\partial}{\partial r_i} \left( \frac{a_i c_0^2}{d_0^2 + (1 + \cos \theta)^2} \right)
\]

\[
= -\frac{2a_i c_0^2 \sin \theta (1 + \cos \theta)}{d_0^2 + (1 + \cos \theta)^2} \cdot \frac{\partial \theta}{\partial r_i}
\]

(11)

As \( \theta = \cos^{-1} \left( \frac{r_i \cdot r_{ik}}{r_i r_{ik}} \right) \), then

\[
\frac{\partial \theta}{\partial r_j} = -\frac{1}{r_j \sin \theta} \left( \frac{r_j \cos \theta}{r_j} - \frac{r_{ik}}{r_{ik}} \right) - \frac{1}{r_{ik} \sin \theta} \left( \frac{r_{ik} \cos \theta}{r_{ik}} - \frac{r_{ij}}{r_{ij}} \right)
\]

(12)

\[
\frac{\partial \theta}{\partial r_j} = \frac{1}{r_j \sin \theta} \left( \frac{r_j \cos \theta}{r_j} - \frac{r_{ik}}{r_{ik}} \right)
\]

(13)
\[
\frac{\partial \theta}{\partial r_k} = \frac{1}{r_k \sin \theta} \left( \frac{r_k \cos \theta}{r_i} - \frac{r_i}{r_j} \right)
\]  

(14)

Replace equation (6-14) in the right side of equation (5), we can obtain the force on atom \( i \) exerted by all its neighboring atoms.