MOLECULAR SIMULATION OF COMPOSITE INTERFACES

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To my wife and parents
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# TABLE OF CONTENTS

ACKNOWLEDGEMENT i

TABLE OF CONTENTS ii

SUMMARY v

NOMENCLATURE viii

LIST OF FIGURES x

LIST OF TABLES xiv

CHAPTER I  INTRODUCTION 1

I.1 Polymers: An Introduction 1

I.2 Molecular Simulation of Polymer 3

I.3 Motivation and Scope of Thesis 5

CHAPTER II  THEORY AND MODELS OF POLYMER AND POLYMER INTERFACES 7

II.1 Basic structure of polymer chains 7

II.2 Models for Polymer Chains 9

II.2.1 Ideal polymer chains 9

II.2.2 The Rotational Isomeric State (RIS) Model 12

II.2.3 The Rouse Model and Equations of Motion for Polymer 14

II.2.4 The Reptation Model 16

II.3 Models and Properties of Polymer Interfaces 19

II.3.1 Models of polymer interfaces 19

II.3.2 Dynamics of polymer interfaces 21
CHAPTER III  THEORY FOR MOLECULAR SIMULATION OF POLYMER AND POLYMER INTERFACES

III.1 Statistical Mechanics of Macromolecules
   III.1.1 Classical Statistical Mechanics
   III.1.2 Equations of Motion for Molecular System
   III.1.3 Construction of Polymer Chains in Molecular Simulation
   III.1.4 Numerical Integration Methods
   III.1.5 Control Ensembles in Molecular Dynamics (MD)

III.2 Models in Polymer Molecular Simulation
   III.2.1 Amorphous Cell Model in Atomistic Molecular Dynamics
   III.2.2 Multi Time Scale and Length Scale of Polymer
   III.2.3 Coarse-grained Bead-spring Model (CG)
   III.2.4 Comparison of the Amorphous cell and CG Models
   III.2.5 Mapping between the Multi-scale Models

III.3 Computation of Mechanical Properties
   III.3.1 Stress/Pressure Control in Molecular Modelling
   III.3.2 Mechanical Properties of Polymer Obtained by MD

III.4 Conclusions

CHAPTER IV  ATOMIC MD OF POLYMER AND COMPOSITE INTERFACES

IV.1 Introduction

IV.2 Molecular Modeling of Polymer Bulks
   IV.2.1 One-chain Bulk Simulation of Polymer Bulks
   IV.2.2 Mechanical Properties of Amorphous poly(ε-caprolactone) (PCL)
   IV.2.3 Mechanical Properties of 100% Crystalline PCL
   IV.2.4 Molecular Modeling of Polycrystalline PCL
IV.2.5 Comparison of MD and Experimental Results 84

IV.3 Multi-chain Simulation of Polymer 87

IV.4 Polymer Surface and Interface Simulation 89

IV.5 Molecular Modeling of Composite Interfaces 92
   IV.5.1 Molecular Models 92
   IV.5.2 Molecular Modeling of Bulk Materials 95
   IV.5.3 Molecular Modeling of Surfaces and Interfaces 97
   IV.5.4 Work of Adhesion of Polycarbonate/Silane Interfaces 100
   IV.5.5 Mechanical Properties of Polycarbonate/Silane Interfaces 102

IV.6 Conclusions 109

CHAPTER V EXPLORING NEW FORCE FIELD FOR COMPOSITE INTERFACES 112
   V.1 Basic Paradigm of Force Fields in MD 112
   V.2 Construction of Force Fields for Coarse-grained MD 117
   V.3 Parameterization of the Force Fields 121

CHAPTER VI COARSE GRAINED MODELING OF CROSSLINKED COMPOSITE INTERFACE 126
   VI.1 Introduction 126
   VI.2 Molecular Modeling of the Composite Interface 129
   VI.3 Parameterization of the CG force field 135
   VI.4 Coarse-grained Molecular Dynamic Simulation 141
   VI.5 Conclusion 146

CHAPTER VII CONCLUSIONS AND FUTURE WORK 148
   VII.1 Conclusions 148
   VII.2 Future work 151

REFERENCES 153
SUMMARY

The determination and characterization of the mechanical properties of material interfaces have always been an area of interest because the integrity of material interfaces plays a key role in the robustness of devices and material systems. However, theoretical analyses based on continuum mechanics approach and experimental investigation have seen limited success because the effects of molecular and chemical interactions at material interfaces are not accounted for in many analytical models and are difficult to ascertain experimentally. Molecular dynamics (MD) simulation can show detailed molecular motions in interfaces and has become increasingly popular because of significant improvements in computer speed. MD simulations can provide information on interfacial strength and mechanical properties of the interfacial constituents at a more fundamental level.

Molecular dynamics simulation together with first principle DFT calculations were used to model and explain experimental observations of the response of PCL nanofibers subjected to tensile loading. By restraining some parts of a PCL molecular chain model to represent the polycrystalline nature of PCL fibers, atomistic simulations of the PCL polymer under tensile strain replicated the transition from a multiple neck fiber to a uniform fiber as the strain increases from 60% to 200%. The simulations show that this phenomenon is result of stiff crystalline phases thinning out at a higher strain than the compliant amorphous phases of the fiber.

Using a commercial code with a novel algorithm controlling the strain increments during NVT thermodynamics, the diffusing interfaces of a matrix and coupling agents are
modeled. The matrix used is polycarbonate (PC) and the coupling agents studied are gamma amino-propyl-triethoxysilane (AMPTES) and stearic-propyl-triethoxysilane (SPTES). Two atomistic models of SPTES-PC and AMPTES-PC interfaces were constructed. A new algorithm is proposed to investigate the mechanical properties of polymer interfaces. The mechanical properties of PC-AMPTES and PC-SPTES composite interfaces were investigated through atomistic simulation using a combination of conjugate gradient energy minimization and molecular dynamics. The surface energies of PC, AMPTES and SPTES, as well as the work of adhesion of the interfaces of PC-AMPTES and PC-SPTES, were obtained from the simulations. It is interesting to find that the work of adhesion may not necessarily be an indication of the toughness of bi-material systems under mechanical loading.

To model highly crosslinked composite interfacial systems, a coarse-grained bead-spring molecular dynamics model was formulated and implemented into a code developed in the project for the simulations. In the model, a set of new force fields combining inter-beads potential with LJ nonbond potential to control the motions of the polymer monomers were developed. The force field is derived from Morse equation and parameterized by \textit{ab initio} molecular dynamics calculation. The model is demonstrated through the simulation of a composite interface comprising a glass/epoxy interface with AMPTES coupling agents being pulled apart. The calculations show that the interfacial crosslinking system demonstrates different mechanical properties above and below the glass transition temperature. Also the influence of strain rate is small for the yield stress. The interfacial failure is mainly cohesive failure in the present models because the silane is fully crosslinked with the fiber surface and epoxy matrix. Current work shows the
trend of molecular dynamics – development of multi-scaled algorithms with the ability to
model large polymer systems to enable the use of MD to scale up to experimental results.
The main issue to be addressed in coarse grained MD is the formulation of proper force
fields to deal with the motion of beads from the same and/or different chains.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_i )</td>
<td>atom ( i )</td>
</tr>
<tr>
<td>( b )</td>
<td>mean square root of particle position vector</td>
</tr>
<tr>
<td>( D )</td>
<td>diffusion constant</td>
</tr>
<tr>
<td>( d_i )</td>
<td>bond vector for bond ( i )</td>
</tr>
<tr>
<td>( E_H )</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>( f )</td>
<td>force</td>
</tr>
<tr>
<td>( G(t) )</td>
<td>mean square displacement (MSD)</td>
</tr>
<tr>
<td>( H )</td>
<td>Hamilton operator</td>
</tr>
<tr>
<td>( J_c )</td>
<td>Transfer of one component per unit area in the interfaces</td>
</tr>
<tr>
<td>( K )</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>( k_B )</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>( l_d )</td>
<td>fixed bond length on a polymer chain</td>
</tr>
<tr>
<td>( P_i )</td>
<td>Boltzman distribution</td>
</tr>
<tr>
<td>( p )</td>
<td>moment</td>
</tr>
<tr>
<td>( q )</td>
<td>coordinate</td>
</tr>
<tr>
<td>( R_{cm} )</td>
<td>center mass vector of a polymer chain</td>
</tr>
<tr>
<td>( R_e )</td>
<td>end-to-end vector of a polymer chain</td>
</tr>
<tr>
<td>( R_{gyr} )</td>
<td>radius of gyration of a polymer chain</td>
</tr>
<tr>
<td>( R_i )</td>
<td>position vector of atom ( i ) on a polymer chain</td>
</tr>
<tr>
<td>( R_{ij} )</td>
<td>the distance between the atom ( i ) and ( j ) along a polymer chain</td>
</tr>
<tr>
<td>( R_{max} )</td>
<td>the length of the fully extended chain</td>
</tr>
<tr>
<td>( r_i )</td>
<td>position vector of atom ( i )</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature</td>
</tr>
<tr>
<td>( U )</td>
<td>potential</td>
</tr>
<tr>
<td>( V )</td>
<td>volume</td>
</tr>
<tr>
<td>( v_i )</td>
<td>velocity vector</td>
</tr>
<tr>
<td>( Z )</td>
<td>Partition function</td>
</tr>
<tr>
<td>( \mu )</td>
<td>exchange chemical potential</td>
</tr>
</tbody>
</table>
\( \vartheta \) microscopic frictional coefficient for monomers i-j
\( \Theta \) Volume fraction in the polymer interfaces
\( \Omega \) the number of eigenstates with energy \( E \) of the system
\( \Psi \) wave function
\( \hbar \) Planck's constant divided by \( 2\pi \)
LIST OF FIGURES

Fig. 1.1  A polypropylene monomer  

Fig. 1.2  Length scales, associated time scales and computational methods in polymer simulation  

Fig. 1.3  Computational path to get information from Molecular Mechanics.  

Fig. 2.1  A chain conformation of N bonds, connecting N+1 beads.  

Fig. 2.2  Polyethylene configuration with bond length $d_i$, bending angle $\theta_i$, and tortional angle $\varphi_i$, along the backbone chain.  

Fig. 2.3  Dihedral angle energy of n-butane at room temperature.  

Fig. 2.4  The polymer chain moves back and forth along the tube.  

Fig. 2.5  Double-logarithmic plot of the mean square displacement, in case of the reptation model.  

Fig. 2.6  Some examples of polymer interfaces.  

Fig. 2.7  The formation of polymer-polymer interfaces.  

Fig. 2.8  Transfer of polymer monomers per unit area in the interface.  

Fig. 3.1  A polymer chain.  

Fig. 3.2  Two-dimensional projection of a Single Polymer Molecule within a System with Periodic Boundaries.  

Fig. 3.3  Cross-sectional View of a 2D Periodic System.  

Fig. 3.4  Multi time scale and length scale of Polymers.  

Fig. 3.5  a) A typical fcc atomistic structure (111), b) RDF of Ar at 103K.  

Fig. 3.6  Five bonds combining into one new vector along a polymer chain.  

Fig. 3.7  Coarse-grained Bead-spring Model.  

Fig. 3.8  Cross-linkers.  

Fig. 3.9  Different systems under tensile strain.
Fig. 3.10  
Chain configurations at three different times during a tensile pull.
52

Fig. 3.11  
The ParRot movement
54

Fig. 3.12  
Scheme of three steps in the mapping procedures (solid arrows) that replace a fully atomistic classical MD
55

Fig. 3.13  
Coarse-graining of bisphenol-A polycarbonate
56

Fig. 3.14  
Coarse-graining diphenyl carbonate
56

Fig. 3.15  
Axial extension and pure shear ensemble-averaged von Mises tensile stress against system work equivalent strain extension for tension applied at (a) 5 and (b) 1 bar/ps
61

Fig. 3.16  
Measured tension at PE as a function of percentage
62

Fig. 4.1  
A PC monomer
69

Fig. 4.2  
A PP parent chain with 76 monomers in an amorphous cell
70

Fig. 4.3  
PCL amorphous cell of 18-monomer-chain
70

Fig. 4.4  
A pure PCL amorphous cell of 18-monomer chain bulk cell under 70% tensile strain.
72

Fig. 4.5  
Stress-strain curve of an 18-monomer-chain amorphous bulk.
73

Fig. 4.6  
Diameter dependency of PCL nano fiber under tensile loading
74

Fig. 4.7  
100% crystalline PCL bulk
75

Fig. 4.8  
Schematic representation of the electrospinning process
78

Fig. 4.9  
Schematic representation of crystallization process of different polymers
78

Fig. 4.10  
AFM image of PCL nano fiber surface
79

Fig. 4.11  
SEM image of PCL nano fiber under tensile loading: Multiple necks (left), smooth surface 200% strain
79

Fig. 4.12  
Stress-strain curve of 0% and 20% crystalline PCL polymer
81

Fig. 4.13  
Stress-strain curve of different crystalline percentages of PCL polymer
82

Fig. 4.14  
Stress-strain curve of 40% 60% and 80% crystalline of PCL polymer
83

Fig. 4.15  
Stress-strain curve of 60% crystalline of PCL polymer
84

Fig. 4.16  
Configurations of 60% crystalline of PCL polymer under tensile loading
86

Fig. 4.17  
Density change of PP-PP interface, of 16-chain/4-chain and 16-chain/8-chain, under tensile stress
88
Fig. 4.18  Stress relaxation of polymer interfaces of multi-chain system  
Fig. 4.19  Building of PC-PP interfaces  
Fig. 4.20  Stress relaxation of polymer interfaces  
Fig. 4.21  Model of fiber/matrix interfaces  
Fig. 4.22  Structures of the matrix and silanes  
Fig. 4.23  Molecular structures of glass-PC interface with AMPTES present  
Fig. 4.24  Amorphous cell models of bulk materials  
Fig. 4.25  AMPTES surface thin films padded with vacuum in one cell  
Fig. 4.26  PC-AMPTES interface  
Fig. 4.27  Thickness of the interface cells vs the equilibrium time  
Fig. 4.28  Density profile of PC-AMPTES interface before tensile deformation  
Fig. 4.29  Density profile of PC-SPTES interface before tensile deformation  
Fig. 4.30  Density profile of PC-AMPTES interface at 53% tensile strain  
Fig. 4.31  Density profile of PC-SPTES interface at 53% tensile strain  
Fig. 4.32  Stress-Strain curve of Silane-PC interfaces under tensile loading  
Fig. 4.33  A PC-AMPTES interface being pulled apart  
Fig. 4.34  Effect of relaxation time on stress-strain relationship of AMPTES-PC cell  
Fig. 5.1  Pairwise potential vs pair distance  
Fig. 5.2  Schematic of molecular force field interaction  
Fig. 5.3  Equilibrated configuration of bond pair  
Fig. 5.4  Relationships of valence potential and distance of bead pair in Fig. 5.3  
Fig. 5.5  Least square fitting results for the valence potential of bead pair in Fig. 5.3  
Fig. 6.1  Model of fiber/matrix interfaces with silane present.  
Fig. 6.2  Structures of the matrix and silanes.
| Fig. 6.3 | Molecular structures of glass-epoxy interface with AMPTES crosslinked | 130 |
| Fig. 6.4 | Crosslinker chains | 132 |
| Fig. 6.5 | Uncrosslinked structure used to form the network system | 133 |
| Fig. 6.6 | Valence energy vs bead distance for the pairs in Fig 6.3 | 137 |
| Fig. 6.7 | The least square fitting of the force field parameters for the network system | 139 |
| Fig. 6.8 | Valence force versus bead distance | 140 |
| Fig. 6.9 | Dynamically bonded crosslinking system used as the initial configuration for the coarse grained MD | 141 |
| Fig. 6.10 | The snapshot of the crosslink system at strain of a) 0.2, b) 0.4 and c) 0.8 under tensile loading of upper wall at velocity of 0.02$\tau$. | 141 |
| Fig. 6.11 | Tensile stress-strain curve for the crosslinked system under constant temperature | 142 |
| Fig. 6.12 | Snapshots of the crosslink system at strain of 0.8 at temperature of a) 0.3, b) 0.7 and c) 1.1 under tensile loading of upper wall at velocity of 0.02$\tau$. | 143 |
| Fig. 6.13 | Tensile stress-strain curve for the crosslinked system under constant temperature | 144 |
| Fig. 6.14 | Stress distribution of a slab of the interfacial system at the yield strain | 145 |
LIST OF TABLES

Table 3.1  Several commonly used ensembles in statistical ensembles in MD  36
Table 4.1  Mechanical properties of PP, PC and PCL bulks  72
Table 4.2  Average energies (kJ/mol) for five bulk cells and surface cells of PP  90
Table 4.3  Average energies (kJ/mol) for five bulk cells and surface cells of PC, and the contributions to the surface free energies  90
Table 4.4  Cell properties of bulk materials using Amorphous cell model.  95
Table 4.5  Mechanical properties of bulk materials using Amorphous cell model  96
Table 4.6  Energy components (kJ/mol) of bulk cells and surface cells of AMPTES, and their contributions to free surface  98
Table 4.7  Energy components (kJ/mol) of bulk cells and surface cells of SPTES, and their contributions to free surface energy  99
Table 4.8  Energy components (kJ/mol) of PC-silane interface cells, and their contribution to work of adhesion  101
Table 4.9  Summary of surface tension, work of adhesion (mJ/m²) and interfacial tensions(mJ/m²) of PC(γA)-silane(γB) interfaces  102
Table 6.1  Bead mapping strategy  131
Table 6.2  Equilibrium distance between the beads  137
Table 6.3  Parameters for the force field  139
Table 6.4  Equilibrium distance between the beads  140
Molecular modeling and simulation, in recent years, have attracted more and more interest of researchers in material science, chemical engineering, physical science, life science, electrical engineering, mechanical engineering and bio-engineering, in the analysis of material properties, new material design, nanotechnology, protein synthesis and analysis, and drug design, etc. because of the fast development of computer technology in the last two decades.

In polymer research, experiments in the measurement of polymer properties and the synthesis of new polymers are time-consuming and expensive. Therefore, molecular modeling and simulation techniques are widely used in the study of polymer properties such as self-diffusion coefficient, thermal pressure coefficient, heat capacity and dielectric constant. However, there is a lack of research related to the mechanical properties of polymers and polymer interfaces in molecular modeling and simulation.

§I.1 Polymers: An Introduction

*Polymers*, also referred to *macromolecules* or *plastics*, are typically long-chain molecules composed of thousands to millions of monomers along individual polymer chains (Fig.1.1). The chain architecture can be linear, branched, or cross-linked to form the polymer bulk and/or interfaces. Polymers are made by either chain reaction or
condensation polymerization mechanisms. For instance, the vinyl family, which consists of the monomer \(-(\text{CH}_2\text{–CHX})_n\)-, is an important kind of polymer formed by chain reaction kinetics. The side group \(-\text{X}\) determines the properties of the polymer. When the side group \(-\text{X}\) is \(-\text{CH}_3\), the polymer is polypropylene (PP) (Fig.1.1). Typically the monomer number \(n\) in one chain of polymer is in the range of \(10^3\)–\(10^5\).

![Fig.1.1 A polypropylene monomer (a) and chain (b). The small spheres denote hydrogen atoms and the large spheres denote carbon atoms.](image)

Polymers usually exhibit isomerism due to different locations of atomic side groups and double bonds in 3D space giving rise to different molecular architecture although the chemical formula is the same. On crystallization, the polymer chains can configure themselves into a crystalline, semicrystalline or amorphous state. Crystallinity affects the properties of polymers. Generally, an increase in crystallinity increases the stiffness, hardness, yield strength, resistance to wear and chemical attack but decreases the impact strength.
§1.2 Molecular Simulation of Polymer

The simulation methods to study polymer and polymer interfaces are usually based on microscopic models, which vary widely in the level of detail ascribed to the monomers, the intermolecular potentials, and the realism of the molecular dynamics. The most commonly used techniques for polymer simulation are Monte Carlo (MC), molecular simulation (MS), and Brownian dynamics. Within molecular simulation, depending on time and length scales of the studied system, there are usually three approaches (Fig.1.2): quantum mechanics (QM), atomistic classical molecular dynamics (MD) and coarse-grained molecular dynamics (CG), which respectively describe the motion of electrons, atoms and monomers of the polymer systems being studied.

![Fig 1.2 Length scales, associated time scales and computational methods in polymer simulation](Muller-Plathe 2002).

Molecular simulation is used to determine macroscopic properties by evaluating the molecular behavior in a system with statistical mechanical methods. From the analysis of polymer molecular structure, the polymer molecular properties and bulk properties can be obtained (Fig. 1.3).
In comparison with relatively simple metal crystal lattices, the molecular modeling and simulation of polymers is complicated due to their complex morphologies and chemical characteristics, which include partial crystallinity in the polymer and chain orientation induced by processing conditions [Theodorou 1992] such as:

1) the complex topology of polymer chains,

2) the chemical and energetic heterogeneity of the solid surface,

3) the presence of functional groups on the polymer or surface that can react chemically, and,

4) the presence of coupling agents (crosslinkers) or adhesion promoters for polymer interface.
§I.3 Motivation and Scope of this Thesis

The determination and characterization of the mechanical properties of polymer or polymer related interfaces has long been an area of interest because the integrity of polymer interfaces plays a key role in the robustness of devices and material systems. However, the understanding of interfacial properties continually poses a challenge because material interfaces are usually of the nanometer length scale. At this scale, continuum mechanics break down and techniques for sub-micron experiments are still not fully developed. The effects of molecular and chemical interactions at material interfaces are not accounted for in many analytical models and are difficult to ascertain experimentally. With significant improvements in computer speed, molecular simulation can show detailed molecular motions in interfaces and provide information on interfacial strength and mechanical properties of the interfacial constituents at a more fundamental level.

There are still many aspects in the molecular simulation of polymer and polymer interfaces that can be improved. Quantum Mechanics is able to analyze the properties of polymers from \textit{ab initio} calculations but it is limited in the size of the system that can be modeled - usually no more than one hundred atoms even on the most powerful computers. Classical MD has the capability to simulate larger atomistic systems with tens of thousands of atoms. However, the current available sets of MD force field are not sufficient for calculating the atomistic motion of network polymer system let alone bond formation and breakage. Moreover, the systems in MD simulation are still extremely small, about \(~10\text{nm}\). Coarse-grained Molecular Simulation can simulate systems closer to
the length scale in laboratory testing, about \( \sim 1\mu m \), but existing force fields are available for only some materials.

The objective of this research project is to explore the methodology of molecular simulation for the mechanical properties of polymer interfaces, especially for composite interfaces. Atomistic classical molecular dynamics (MD), using a commercial software package with a novel algorithm combining temperature effect into strain-controlled-loading, and coarse-grained molecular dynamics (CG) with a code developed in-house, were used for studying diffusion and crosslinking at composite interfacial systems. The force field for the present CG simulation was developed and parameterized by quantum mechanics (QM). The mechanical properties of the two composite interfacial systems were also obtained and analyzed.

Each chapter in this thesis addresses a different topic and the outline is as follows:

Chapter II introduces theories and several models currently used in the molecular simulation of polymers and polymer interfaces. The algorithms of molecular dynamics (QM, MD and CG) for polymers are introduced in Chapter III. In Chapter IV, the atomistic classical MD modeling and simulations of several polymer bulks were carried out and the mechanical properties of glass/PC interfaces were studied using a new algorithm combining temperature effect with strain rate loading. A novel force field designed for polymer is explored and parameterized by QM in Chapter V.

In Chapter VI, a CG simulation was carried out by an in-house code incorporating a novel force field to study the crosslink structure of the glass/epoxy interface with silanes. Chapter VII summarizes all the work presented in this thesis and possibilities for future work are suggested.
Polymers usually consist of many different chemical components and a huge variety of structures. Chain molecules are the most simple polymer macromolecules, in which each chain contains thousands of repeat units or segments. There are several models describing the static and dynamics of polymer chains. The conformational statistics of unperturbed chains are well described by the rotational isomorphic state model (RIS), while the Rouse and the reptation models are two of the most successful dynamical models for polymer melts.

§2.1 Basic Structure of Polymer Chains

In the most ideal model of polymer chains, the monomers are simply connected and the conformation of the chain can be pictured as a succession of $N$ step (bonds) $d_i (i=1\sim N)$, in which $N+1$ beads ($A_0, A_1, \ldots, A_N$) join together as depicted in Fig.2.1.

![Fig.2.1 A chain conformation of $N$ bonds, connecting $N+1$ beads.](image)
In the model shown in Fig 2.1, the origin is assumed to be at one end of the chain, \( A_0 \). Each bead \( A_i \) can be mapped onto one or more real monomers to match the length scale of the real polymer chains, which performs a random walk in the three dimensional space. The end-to-end vector \( \mathbf{R}_e \) of the chain is

\[
\mathbf{R}_e = \sum_{i=1}^{N} \mathbf{d}_i
\]  

(2.1)

The square of the length of \( \mathbf{R}_e \) is then:

\[
\mathbf{R}_e^2 \equiv \mathbf{R}_e \cdot \mathbf{R}_e \equiv \mathbf{R}_e^T \mathbf{R}_e = \left( \sum_i \mathbf{d}_i \right) \cdot \left( \sum_j \mathbf{d}_j \right) = \sum_i \mathbf{d}_i \cdot \mathbf{d}_i + \sum_{i<j} \mathbf{d}_i \cdot \mathbf{d}_j
\]  

(2.2)

The gyration radius \( R_{gyr} \) defines the domain of motion of a polymer chain --- it can be obtained by small angle neutron scattering or light scattering in experimental measurements. The squared radius of gyration \( R_{gyr} \) is the mean of all \( \mathbf{R}_e - \mathbf{R}_{cm} \):

\[
R_{gyr}^2 = \frac{1}{N+1} \sum_{i=0}^{N-1} ( \mathbf{R}_i - \mathbf{R}_{cm} ) \cdot ( \mathbf{R}_i - \mathbf{R}_{cm} )
\]  

(2.3)

Where \( \mathbf{R}_{cm} \) is the center mass vector given by \( \mathbf{R}_{cm} = (N+1)^{-1} \sum \mathbf{R}_i \). It is also can be shown that [Flory 1969]:

\[
R_{gyr}^2 = \frac{1}{(N+1)^2} \sum_{i=0}^{N-1} \sum_{j=i+1}^{N} R_{ij}^2
\]  

(2.4)

where \( R_{ij} \) is the distance between the atom \( i \) and \( j \), and the double sum is over all pairs \( i<j \).

The relationships in eqs. 2.1~2.4 are independent of any chain model for the conformational ensemble and thus are the basis of the different polymer models.
§ 2.2 Models for Polymer Chain

§ 2.2.1 Ideal polymer chains

The central subject of modeling polymer and polymer interfaces is to simulate the movement of polymer chains. For an ideal polymer chain model, all atoms are connected by flexible bonds, which means each bond can rotate or bend at any angle. The different angular degrees of freedom can be modeled as random walk chains freely jointed chains or freely rotating chains.

The Random Walk Chain:

From Eq. 2.2, the second sum equals to \( d_i d_j \cos \theta \) where \( d_i \) is the length of bond \( d_i \) and \( \theta \) is the angle between \( d_i \) and \( d_j \). Bond orientations in which \( \cos \theta = x \) are of the same probability as bond orientations where \( \cos \theta = -x \) and \( d_i \) is independent of all other bond lengths in the chain and is also uncorrelated with \( \theta \). Thus, \( \sum d_i \cdot d_j \) will be zero along the whole chain. Then the unperturbed mean square end-to-end distances \(< R_e^2 >_0 \) is:

\[
< R_e^2 >_0 = < R_e \cdot R_e >_0 = \sum_i d_i \cdot d_i + \sum_{i \neq j} d_i \cdot d_j
\]

\[
= N<d^2> + \sum_{i \neq j} d_i \cdot d_j = N<d^2> \tag{2.5}
\]

where \(< d^2 > \) signifies the mean square length of all bonds.

From Eq. 2.4, the mean square radius of gyration can be obtained:

\[
< R_{gr}^2 >= \frac{1}{(N+1)^2} \sum_{i=0}^{N+1} \sum_{j=i+1}^{N} < R_{ij}^2 >
\]

\[
(2.6)
\]

For unperturbed chains, and fully free random walk chains (Gaussian chain), Eq. 2.5 reduces to [Flory 1969]:

[Flory 1969]
This relationship is true for most polymer chains unless they are well aligned. With the random walk model, the movement of single polymer chain can easily be calculated. However, in polymer bulks, chains are not able to move freely because the motion of each chain and each monomer is constrained by other chains and monomers. Therefore, the motion of each polymer chain in the bulk should be considered in a restrained environment.

The Freely Jointed Chain

The freely jointed chain is a random-walk chain with fixed bond length \( l_d \). Thus Eq. 2.5 becomes:

\[
\langle R^2 \rangle_0 = N\langle d^2 \rangle = Nl_d^2
\]

The mean square radius of gyration is:

\[
\langle R_{gyr}^2 \rangle_0 = \left( \frac{N+2}{N+1} \right) \frac{\langle R^2 \rangle_0}{6}
\]

With the freely jointed chain, which only involves one structural parameter, \( l_d \) (besides the chain length parameter \( N \)), it is possible to model a real linear polymer chain with \( n \) skeletal bonds of length \( l_d \). It can be obtained that:

\[
l_d = \frac{\langle R^2 \rangle_0}{R_{max}}
\]

\[
N = \frac{R_{max}^2}{\langle R^2 \rangle_0}
\]
where $R_{\text{max}}$ is the length of the fully extended chain, or the maximum possible length without unphysical distortion of the macromolecules, $Nl_d$. For random walk extensions, all local intra-chain interactions lead to a prefactor:

$$R_e^2 = C_N (N-1)l_d^2$$  \hspace{1cm} (2.12)

The characteristic ratio $C_N$ depends on the chain length and is a measure of the difference between the actual chain dimensions and the equivalent freely jointed one with the same bond length. When the chain is long enough, it becomes independent of the chain length and all local features become irrelevant:

$$R_e^2 = C_\infty (N-1)l_d^2$$  \hspace{1cm} (2.13)

The value of $C_\infty$ is also the ratio of the lengths of the step length in the freely jointed chain and the real chemical bond.

**The Freely Rotating Chain**

The freely rotating chain model is similar to the freely jointed chain model except that the angles of two adjoining bonds are held fixed at a predefined value while the torsion angles can change freely. Within the freely rotating chain model, the characteristic ratio $C_N$ then becomes:

$$C_N = \frac{1 - \cos \theta}{1 + \cos \theta} + \frac{2 \cos \theta (1 - \cos \theta)^N}{N(1 + \cos \theta)^2}$$  \hspace{1cm} (2.14)

$$C_\infty = \frac{1 - \cos \theta}{1 + \cos \theta}$$  \hspace{1cm} (2.15)

Compared to the random walk chain and freely jointed chain, this model is introduced with the chemical reality that the bond angles of real polymer chains are always confined to certain values due to the very high bending potential. Thus, the dominant degree of
freedom controlling the motion of real polymer chains is the rotation of bonds. Based on the freely rotating chain model, the Rotation Isomeric State (RIS) Model, Rouse and reptation model are developed and used for molecular modeling and simulation of polymer chains.

§ 2.2.2 The Rotational Isomeric State (RIS) Model

The concept of rotational isometric state (RIS) [Flory 1969, Mattice and Suter 1994] is widely used for the study of conformation-dependent physical properties of polymer chains. The idea of RIS comes from the fact that the motion of polymer chains are mainly controlled by the rotation of the bonds rather than bond stretching or bond bending, because compared to the bond rotation potential energy, the bond stretching and bend potential energies are very high.

Consider a simple polyethylene model with all-trans configuration (Fig.2.2), with $N+1$ monomers. There are $N-2$ dihedral angles ($\varphi_i$) between the planes of $N$ bond vectors ($d_i$)
and \( N+1 \) planes of the position vectors \( (R_i) \). With this model the case of n-butane can be considered, in which it has but one dihedral angle and the energy as a function of this angle can be calculated using quantum mechanics.

Figure 2.3 shows the relative energy as a function of dihedral angle calculated using models of butane created using InsightII [Accelrys Inc., 1998].

![Fig.2.3 Dihedral angle energy of n-butane at room temperature.](image)

From Fig. 2.3, it is shown that at room temperature there are three minima which make it possible to restrict interest to three configurations at the dihedral angles \( \phi \) of 120°, 180° and 240° respectively. The energy of the polymer, \( V \), can then be built as a function of the angles \( \phi_i \):

\[
V = \sum_{i=2}^{N-1} E(\phi_i)
\]

(2.16)

Where \( E(\phi_i) \) is the torsional potential energy of the bonds \( d_i, d_{i+1} \) and \( d_{i+2} \). With Eq. 2.16, the motion of the whole chain can be well described using the RIS model.
§2.2.3 The Rouse Model and Equations of Motion for Polymer

The RIS model works well for the determination of the static properties of polymers and initial conformation for the modeling of polymer chains. However, the motion of atoms in real polymer chains is not completely free but should instead feel a certain resistance to random forces.

In the Rouse Model [Rouse 1953], a polymer chain consists of a number of freely jointed beads connected by harmonic springs within a background of homogeneous friction. With these assumptions, each monomer along the chain acts like a colloidal particle suspended in a liquid and continuously collides with the molecules in the neighboring environment. The equation of motion can be described by [Lee 1983]:

\[
\frac{d^2 R_i}{dt^2} = \nabla \sum_{j \neq i} U_{ij} - \Gamma R_i + \mathbf{W}_i
\]

where \( t \) is time, \( \nabla = \left( \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right) \), \( R_i \) is the position of the \( i \)th monomer, \( U_{ij} \) is the interaction potential between each monomer, \( \Gamma \) is the friction constant which couples the monomer weakly to a heat bath, and is given by [Doi and Edwards 1990]:

\[
\Gamma = \frac{6 \pi \eta a}{m}
\]

where \( \eta \) is the viscosity of the solvent, \( m \) and \( a \) are the mass and radius of the monomer, respectively.

Equation 2.17 is called the Langevin equation, which was derived by Lee [1983] as a useful description of many-body Hermitian systems. In the equation, a stochastic force, \( \mathbf{W}_i^T(t) = \{ W_1(t), \ldots, W_N(t) \} \), was introduced to describe deviations from an average motion due to nonlinear effects, the initial transient process and fluctuations. Usually, the
stochastic force has zero mean, \(< \mathbf{W}(t) > = 0\), and the covariance of the force is imposed by the fluctuation-dissipation theorem [Srokowski 2000, Stevens 2001b]:

\[
\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6 \frac{k_B T}{m} \Gamma \delta(t-t')
\]  

(2.19)

where \(k_B\) is Boltzmann constant, \(T\) the temperature, and \(\delta(t)\) the Dirac delta function. The averaging \(<…>\) is carried out in the distribution function to filter out noise. In statistical physics, the fluctuation dissipation theorem states that any perturbation in a system will be dissipated as the system returns to equilibrium. For a small perturbation the response is linear.

For a long time scale during which the system configuration can change, the average velocity is zero, or constant in the case when an external force is applied. The Langevin equation 2.18 can be solved as:

\[
\frac{d \mathbf{R}_i}{dt} = -k \Gamma (\mathbf{R}_i - \mathbf{R}_{i-1}) + \mathbf{W}_i,
\]

(2.20)

For the freely jointed polymer chains, in which the atoms are connected by harmonic springs with a force constant \(k = 3k_B T / b\) where \(b\) is the root mean-square separation of adjoining atoms, the Langevin equation, Eq. 2.17 becomes (neglecting inertia forces) [Kremer and Grest, 1986]:

\[
\Gamma \frac{d \mathbf{R}_i}{dt} = -k \left[ 2 \mathbf{R}_i - \mathbf{R}_{i+1} - \mathbf{R}_{i-1} \right] + \mathbf{W}_i, \quad 1 \leq i \leq N+1
\]

(2.21)

Except for interactions due to the chain connectivity, the drawback of Rouse model is that any specific interactions between monomers cannot be described and it is limited to short polymer chains.
§ 2.2.4 The Reptation Model

For chains longer than a characteristic length, $N_c$, the motion of the chain slows down drastically and the Rouse model no longer reproduces experimental observations. One of the clearest evidence is that the viscosity $\eta$ is observed to scale with $N^{3.4}$ from the experiment data for chains longer than $N_c$, rather than with $N^2$, as predicted by the Rouse model [Berry and Fox 1968]. Another is that the diffusion constant $D$ scales with $N^{-1}$ in the Rouse model, while for chains longer than $N_c$, $D$ scales with $N^{-2}$ in experiment [Hess 1986].

The problem of the Rouse model is that it does not consider the entanglement of the chains when they are long, because it originates from excluded volume interaction. Doi and Edwards [1986] successfully used the reptation model to model the viscoelastic properties of long polymer chains, in which the topology of the surrounding suppresses the transverse motion of the atoms along the chains.

Viscoelasticity is one unique property of polymers with long chains. A polymer ball dropped onto to a floor will show good elastic property and bounces back quickly. However, if it is placed on the floor, the polymer ball will continue to stretch out slowly to the floor like a drop of water. This feature is due to the different relaxation time of the long entangled polymer chains. When the relaxation time is very short, the entangled chains are not able to response and continue to hold each other together. The polymer can thus present good elastic property. On the other hand, if the relaxation time is long enough and the chains can be unentangled due to external forces (gravity, in this case), the polymer performs as a fluid.
To account for the entanglement of the chains, the Reptation model introduces the concept of a tube, which has only a statistical meaning. This can be imagined as a bunch of cooked spaghetti, in which the chains are not able to cross each other but they move more easily along their contour than perpendicular to it. Because the chains cannot move into spaces occupied by neighboring chains, their motion is confined to a tube-like region [Fig. 2.4].

![Fig. 2.4 Motion of polymer chain in a fictitious tube. When the chain leaves a part of the tube this part vanishes and a new part of the tube is defined by the chain entering in a new space.](image)

In the Reptation model, the chain fluctuates around the primitive chain as in a tube [Fig. 2.4a]. After some fluctuation [Fig. 2.4b] it may store some excess mass, which may diffuse along the primitive chain and finally leave the tube [Fig. 2.4c]. The chain thus creates a new piece of tube while part of the original tube vanishes [Fig. 2.4d].
From the reptative motion, the long time motion of the chain can be determined. The main concept of the model is the primitive chain. To describe the motion of the chains, the mean square displacement (MSD), \( g(t) = \langle [R(t) - R(0)]^2 \rangle \), of whole chains versus diffusion as indicated by the MSD of atoms or monomers can be demonstrated as shown in Fig. 2.5.

For a Rouse model, there are two regimes for the inner-monomer-MSD while for the reptation model, there are four regimes for MSD [Fig. 2.5].
§ 2.3 Models and Properties of Polymer Interfaces

§ 2.3.1 Models of polymer interfaces

The strength of polymer interfaces is largely related with the surface energy of each polymer. Surface energy, or surface tension, is the energy barrier preventing bulk molecules from crossing the phase boundary, or surface films. Generally, the lower the surface energy, the higher the diffusion mobility of the bulk molecules. All polymers are low surface energy materials. Their surface energy, $\gamma$, ranges between 10 and 50 mJ/m$^2$. Polymers can also be divided into three classes according to their wettabilities [Shafrin 1975]:

i) Low wettability ($30 \text{mJ/m}^2 > \gamma > 10 \text{mJ/m}^2$):

Most fluoropolymers, polysiloxanes and polyolefins, etc.

ii) Medium wettability ($40 \text{mJ/m}^2 > \gamma > 30 \text{mJ/m}^2$):

Most vinylpolymers, e.g., polystyrene, PVC, PMMA, etc.

iii) High wettability ($\gamma > 40 \text{mJ/m}^2$):

Most condensation polymers, e.g., polycarbonate, nylons, epoxy resins, etc.

Polymer interfaces play an important role in the process of wetting, adsorption, and adhesion and many other applications. Polymer interfaces can be categorized into four broad groups as follows [Wool 1995]:

1) Symmetric, or chemically identical, polymer-polymer interfaces,

2) Asymmetric, or chemically different, polymer-polymer interfaces

3) Polymer-nonpolymer interfaces, and

4) Multi-component polymer interface.
In contrast with other material interfaces, polymer chains can be entangled or bonded in the interface region, resulting in physical and chemical complexity in their study. Figure 2.6 shows some examples of polymer interfaces, including interfaces between incompatible or partially incompatible homopolymer [Fig. 2.6a] and polymer-nonpolymer interfaces [Fig. 2.6b], where a grafted layer or polymer “brush” is formed by the adsorption of end-functionalized polymers on the surface and an adsorbed layer is produced when the functional groups are distributed uniformly along the polymer backbone, or if every monomer is a potential adsorber. In other words, the grafted layer, or brush, is formed like trees with one end bonded to the substrate while in the adsorbed layer, each polymer chain has more than one group bonded to the substrate. In the
composite interface, the layer attached on the fiber surface is a kind of grafted layer. For the grafted layer, only one functional site contributes to the adhesion for each chain, the wetting area (or wetting density) thus dominates the interfacial tension and adhesive failure, instead of cohesive failure, will be the main cause of damage in the interfacial system.

§ 2.3.2 Dynamics of polymer interfaces

The procedure of building polymer-polymer interfaces is shown in Fig. 2.7. Two polymer bulks are brought into contact [Fig. 2.7a] and maintained above the glass transition temperature [Fig. 2.7b] for a certain time $t$ for the junction to develop mechanical strength [Fig. 2.7c]. As mentioned, there are mainly two cases of polymer interfaces A/B:

1. A and B are chemically identical, but $N_A \gg N_B$, and
2. A and B are chemically different.

![Fig. 2.7 The formation of polymer-polymer interfaces. (a) Two surfaces are put into contact, (b) just at the start of heating no chain crosses the boundary. (c) After some time $t$ of the heating, a chain, with one head $A$, may have reptated by a curvilinear length and established some bridging.](image)
The main parameter controlling the dynamics of polymer interfaces is the mutual diffusion coefficient $D_M$. Equation 2.21 can also be written as [Doi and Edwards 1990]:

$$
\langle (R_i(t) - R_i(t_0))^2 \rangle = 6D_M t
$$

(2.22)

where

$$
D_M = \frac{k_BT}{m\Gamma}
$$

(2.23)

In the polymer interfacial system, the mutual diffusion coefficient control the mobility of the polymer chain diffusing into the other polymer, while the surface energy controls the surface stability of the polymer.

Consider the polymer interface A/B as constructed in Fig. 2.7. The diffusion of polymer A (bottom part) into polymer B (upper part) can be characterized by the concentration $c(R,t)$ in polymer A, which means $c$ will be the number of A monomers per unit volume in the A-B mixture region.

Assuming $x$ is the direction perpendicular to the AB interface plane, the diffusion process is interpreted in Figure 2.8. The reference plane is a plane assumed to be located in the contact surface just before heating (Fig.2.7b). The diffusion of polymers A and B through
the interfacial space can be described by the concentration of monomers $c(x,t)$. Thus the transfer of A monomers per unit area, $J_c = cv_A$, is proportional to the concentration gradient (Brochard-Wyart 1991):

$$J_c = -D_M(\Theta)\nabla c$$  \hspace{1cm} (2.24)

where $v_A$ is the velocity of component A and $\Theta$ is volume fraction with $\Theta = cV_A$, and $V_A$ is the volume per monomer. Also the volume transfer $J_A$ of A, $J_A = \Theta v_A$, called $J$, can be used:

$$J = -D_M(\Theta)\nabla \Theta$$  \hspace{1cm} (2.25)

Assuming that there is no overall change of volume of the two polymers upon mixing, according to the constant density, the volume transfer of B per unit time across unit area is therefore [Crank 1975]:

$$J_B = -J_A = -J$$  \hspace{1cm} (2.26)

which means:

$$(1-\Theta)v_B = -\Theta v_A$$  \hspace{1cm} (2.27)

For self diffusion $D_s$, in which A and B are chemically identical polymers, the atomic motion follows the Brownian motion:

$$<x^2> = 2D_s t$$  \hspace{1cm} (2.28)

where $x$ is the displacement along one of three Cartesian coordinates. For a A-B interfaces, there should be two self-diffusion coefficients $D_{sA}$ and $D_{sB}$.

Combining Eq.2.25 and 2.26, Fick’s law, can be obtained:

$$J_B = -J_A = -J = D_M(\Theta)\nabla \Theta$$  \hspace{1cm} (2.29)

Using the mass conservation law, it can be obtained:
\[
\frac{\partial \Theta}{\partial t} + \text{div } J = 0 \quad (2.30)
\]

With above two equations, the concentration profile, \(\Theta(x)\), of the polymer interface A-B results in

\[
\frac{\partial \Theta}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial (\Theta)}{\partial x} \quad (2.31)
\]

If two compositions of a specimen, \(\Theta_1\) and \(\Theta_2\), at two moments are specified, with constant D, the concentration profile, or thickness of diffusion through the interface, can then be obtained. The interdiffusion coefficient \(D\) can be obtained by plotting different profile \(\Theta(x)\), at different times [Crank 1975].

Assuming A and B consist of flexible polymer chains with \(N-1\) bonds, there are two different mechanisms according to the Rouse and reptation model.

For Rouse chains, where \(N < N_c\) \((N_c \sim 200)\), in the A/B interfaces, the frictional forces on each A and B monomers can be written as

\[
F_A = \vartheta_{AB} (1 - \Theta)(v_A - v_B) \quad (2.32)
\]

\[
F_B = \vartheta_{AB} \Theta(v_B - v_A) \quad (2.33)
\]

where \(\vartheta_{AB}\) is microscopic frictional coefficient for monomers A-B and \(\vartheta_i \sim a \eta_0\), where \(\eta_0\) is a microscopic viscosity. Using Einstein’s relation between mobility and diffusion coefficient, Eq. 2.23 becomes:

\[
D_{ji} = \frac{k_B T}{N_i \vartheta_i}, \quad i = A, B \quad (2.34)
\]

If \(N > N_c\), the polymer should be modeled using the reptation model, in which the chains in the interfaces are entangled. In the reptation model, the chains are trapped in a matrix.
of tubes formed by other chains and the tubes move with velocity $v_T$ when the chains move in the mobile matrix (Fig. 2.4).

By setting $F_i = \vartheta_i \Theta N_i/ N_A(v_i - v_T)$, $i = A,B$, $F_i$ becomes the frictional force per unit volume acting on the matrix. Then the tube velocity $v_T$ can be deduced from the balance between frictional forces acting on the chains and those acting on the matrix [Brochard-Wyart 1991]:

$$v_T = J \frac{\vartheta_A N_A - \vartheta_B N_B}{\vartheta_A N_A \Theta + \vartheta_B N_B (1 - \Theta)} \quad (2.35)$$

The equation of $v_T$ shows that the matrix is immobile in the symmetrical case ($\vartheta_A N_A = \vartheta_B N_B$), on the other hand the matrix moves at the velocity of the longer chains, say, A, if $\vartheta_A N_A >> \vartheta_B N_B$. The diffusion coefficient $D_M$ in the reptation model can be obtained [Crank 1975]:

$$D_M = N_e \frac{\Theta^2 (1 - \Theta)^2}{\vartheta} \left[ \frac{1}{N_A \Theta} + \frac{1}{N_B (1 - \Theta)} \right]^2 \quad (2.36)$$

Equation 2.36 works for long reptation times, and it describes that, for asymmetrical polymer interfaces, a rapid interdiffusion is controlled by the fast (short) chains and independent of slow (long) chains, which was also observed experimentally by Jordan et al [1988] using infrared microdensitometry for the diffusion of polybutadienes (PBD).
CHAPTER III

THEORY FOR MOLECULAR SIMULATION
OF POLYMER AND POLYMER INTERFACES

In recent decades, computer simulation has become a useful tool for the analysis of the interfacial polymer structures and properties in coating, lubricants, and adhesives. Full atomistic level simulation using quantum mechanics (QM) derived interatomic potentials presents an attractive and robust approach to study polymer interfaces.

§ 3.1 Statistical Mechanics of Macromolecules

§ 3.1.1 Classical Statistical Mechanics

Molecular simulation typically involves the implementation of ensemble analysis. An ensemble can be regarded as an imaginary collection of a very large number of systems in different quantum states with common macroscopic attributes [Sadus 1999]. One example is the canonical ensemble \((N,V,T)\), in which the system has constant temperature, volume and number of molecules.

With the ergodic hypothesis [Haile 1992], the equivalence of the time-average and ensemble-average properties, say, \(A\), can be established:

\[
A_{\text{time}} = \langle A \rangle \quad (3.1)
\]

Consider a system of \(N\) molecules occupying a container of volume \(V\) with coordinate \(q\) and momenta \(p\) as:

\[
q = (q_1, q_2, \cdots, q_N) \quad (3.2a)
\]
\[ \mathbf{p} = (p_1, p_2, \cdots, p_N) \]  

(3.2b)

where \( \mathbf{q}_i \) and \( p_i \) are coordinates and momenta of each molecule \( i \) (\( i = 1, 2, \cdots, N \)), and \( \mathbf{p} = m\mathbf{v} \). Denote \( \Omega(N,V,E) \) as the number of eigenstates with energy \( E \) of the system, then the average energy \( \langle E \rangle \) of the system at a given temperature \( T \) is given by:

\[ \langle E \rangle = \sum_i E_i P_i \]  

(3.3)

where \( P_i \) is the Boltzmann distribution for a system at temperature \( T \):

\[ P_i = \frac{\exp(-E_i/k_BT)}{\sum_j \exp(-E_j/k_BT)} \]  

(3.4)

The average energy \( \langle E \rangle \) becomes:

\[ \langle E \rangle = \frac{\sum_i E_i \exp(-E_i/k_BT)}{\sum_j \exp(-E_j/k_BT)} = -\frac{\partial \ln Z}{\partial 1/k_BT} \]  

(3.5)

where \( Z \) is the partition function and \( k_B \) the Boltzmann constant, a sum over all quantum states \( i \) of the Boltzmann factor \( \exp(-E_i/k_BT) \):

\[ Z = \sum_i \exp(-E_i/k_BT) \]  

(3.6)

When equilibrium is reached, \( \ln Z \) of the total \( N \)-molecule system is at a maximum, which means that \( \ln Z \) is related to the thermodynamic entropy \( S \) of the system. For a microcanonical ensemble \( (NVE) \), in which the systems have the same number of molecules \( N \), system volume \( V \) and free energy \( E \), the relationship between the entropy and \( \ln Z \) is \([Frenkel and Smit 2002]\):

\[ S(N,V,E) = k_B \ln Z(N,V,E). \]

The Helmholtz free energy, \( E_H \), of the system is:

\[ E_H = -k_BT \ln Z = -k_BT \ln \left[ \sum \exp(-E_i/k_BT) \right] \]  

(3.7)
Comparing Eqs 3.5 and 3.7, the free energy can be expressed with the thermodynamic relation:

\[ E = \frac{\partial (E_p / T)}{\partial (1/T)} \]  \hspace{1cm} (3.8)

With Eqs 3.7 and 3.8, the relation between the *Helmholtz* free energy and the partition function is more convenient to use than the relation between the entropy and \( \ln Z \). Moreover, Eq. 3.7 is the workhorse of equilibrium statistical mechanics [Frenkel and Smit 2002]. Thus far, ensemble-average properties of the system can be computed as:

\[ \langle A \rangle = \frac{\sum_{i} \exp\left(-E_i / k_B T\right) <i|A|i>}{\sum_{j} \exp\left(-E_j / k_B T\right)} \]  \hspace{1cm} (3.9)

where \(<i|A|i>\) denotes the expectation value of the operator \( A \) in quantum state \( i \). Equation 3.9 shows how the thermal averages of the system are calculated:

Firstly, the *Schrodinger* equation is solved, which for the many body system is:

\[ H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \]  \hspace{1cm} (3.10)

where \( H \) is *Hamilton* operator, \( \Psi \) is wave function and \( \hbar \) is Planck's constant divided by \( 2\pi \).

The second step is to compute the expectation value of the operator \( A \) for all the quantum states that have a non-negligible statistical weight [Frenkel and Smit 2002]. Thus the properties of the system can be obtained and studied. For instance, the force on each molecule is related to the energy gradient and the harmonic vibrational frequencies can be obtained from the second derivatives of the energy.
§ 3.1.2 Equations of Motion for Molecular System

Usually, it is extremely difficult to solve the Schrodinger Eq. 3.10 explicitly for most systems. If the Hamilton operator is independent of time and the nuclei mass is much higher than electron mass, within the Born-Oppenheimer approximation [Leach 2001], it is possible to express Eq. 3.10 as two separate equations. The first one describes the electronic motion with \( r \), the electron position:

\[
H\Psi(r) = E(R)\Psi(r) \tag{3.11a}
\]

which depends only parametrically on the determination of nuclei \( R \), the positions. Equation 3.11a also defines the energy \( E(R) \), which is a function of only the coordinates of the nuclei.

The energy \( E(R) \) is usually called the potential energy surface. Then the second equation describes the motion of the nuclei on this potential energy surface:

\[
H\Phi(R) = E(R)\Phi(R) \tag{3.11b}
\]

In Eq.3.11 the Hamiltonian \( H \) of the system is a sum of kinetic energy \( K \) and potential energy \( E \) functions:

\[
H(q, p) = K(p) + U(q) \tag{3.12}
\]

where the kinetic energy \( K \) can be obtained as:

\[
K = \sum_{i=1}^{N} \sum_{\alpha} p_{i\alpha}^2 / 2m_i \tag{3.13}
\]

where \( m_i \) is the molecular mass, and the index \( \alpha \) runs over the different \( (x, y, z) \) components of the momentum of molecule \( i \). The Hamiltonian \( H \) of the system can also be defined as:

\[
H(q, p) = \sum_{i} \dot{q}_i p_i - L(q, \dot{q}, t) \tag{3.14}
\]
where $L$ is the Lagrangian of the system and defined as:

$$L = K - U$$  \hspace{1cm} (3.15)

Combining Eq. 3.14 and 3.15 leads to the Euler-Lagrange equation of motion:

$$\frac{d}{dt}\left( \frac{\partial L(q, \dot{q})}{\partial \dot{q}} \right) - \frac{\partial L(q, \dot{q})}{\partial q} = 0$$  \hspace{1cm} (3.16a)

The generalized momentum $p$ can be associated with the generalized coordinate $q$ [Calkin 1996]:

$$p = \frac{\partial L(q, \dot{q})}{\partial \dot{q}}$$  \hspace{1cm} (3.16b)

Replacing $\frac{\partial L(q, \dot{q})}{\partial \dot{q}}$ in 3.16a with 3.16b gives:

$$\dot{p} = \frac{\partial L(q, \dot{q})}{\partial q}$$  \hspace{1cm} (3.16c)

Eqs 3.12 to 3.16 show that for the system [Allen and Tildesley 1987]:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$  \hspace{1cm} (3.17a)

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$  \hspace{1cm} (3.17b)

$$\frac{\partial L}{\partial t} = -\frac{\partial H}{\partial t_i}$$  \hspace{1cm} (3.17c)

Equations 3.17 define the Hamilton equation of motion of the system. Comparing the difference between the formulations of Hamiltonian 3.17 and Lagrangian 3.16 shows that they can lead to identical results. However, the Lagrangian technique is more useful to derive the equation of motion of a system with constraints and it is exclusively used in most of the ab initio molecular dynamics literature. On the other hand, the Hamiltonian
expressions are dominant when connected with statistical mechanics \cite{Frenkel2002}.

Combining Eqs 3.12 and 3.17, the force on the particle of the system can be obtained as:

\[ f_i = \dot{p}_i = -\frac{\partial H}{\partial q_i} = -\frac{\partial U}{\partial q_i} \]  

(3.18)

That means the force on the molecules can be derived from the potential of the system.

\section*{§ 3.1.3 Construction of Polymer Chains in Molecular Simulation}

The potential energy \( U \) of the system (Eq.3.11 and 3.12) is commonly called a force field, and takes the form:

\[ U = E_{\text{valence}} + E_{\text{cross-term}} + E_{\text{nonbond}} \]  

(3.19)

Where the cross-term potential, \( E_{\text{cross-term}} \), accounts for factors such as bond or angle distortions caused by nearby atoms while the energy of interactions between nonbonded atoms, \( E_{\text{nonbond}} \), consists of van der Waals interactions \( E_{\text{vdW}} \), electronstatic \( E_{\text{Coulomb}} \), and hydrogen bond \( E_{\text{hbond}} \) terms:

\[ E_{\text{nonbond}} = E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{hbond}} \]  

(3.20)

For a system containing polymer chains, the energy of valence interactions \( E_{\text{valence}} \) generally accounts for bond stretching \( E_{\text{bond}} \), valence angle bending \( E_{\text{angle}} \), dihedral angle torsion \( E_{\text{torsion}} \), and out-of-plane interactions \( E_{\text{inversion}} \), i.e.:

\[ E_{\text{valence}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{inversion}} \]  

(3.21)

The bond stretching potential \( E_{\text{bond}} \) is usually expressed as a harmonic spring:

\[ E_{\text{bond}} = k (\Delta R)^2 \]  

(3.22)

Or in the form of the Morse potential \cite{Jensen1999}:
\[ E_{\text{Morse}} = D \left[ 1 - e^{\lambda R_{\text{eq}} / 2D} \right]^2 \]  
\hspace{2cm} (3.23)

where \( D \) is the dissociation energy.

Defining \( d_a \) as the length of bond \( a \), \( \theta_a \) as the angle between bond \( a \) and \( a-1 \), \( \phi_a \) as the dihedral angle of bond \( a \), \( a-1 \) and \( a-2 \) as shown in Fig.3.1, the bond angle bending potential \( E_\theta \) and torsional potential \( E_\phi \) (Fig.3.1), can be expressed as follows:

\[ E_\theta(\theta_a) = \frac{1}{2} k_\theta (\theta_a - \theta_a^0)^2 \]  
\hspace{2cm} (3.24)

and

\[ E_\phi(\phi_a) = \sum_k c_k \cos^k \phi_a \]  
\hspace{2cm} (3.25)

where \( \theta_a^0 \) is the equilibrium value, the coefficients \( c_k \) defines the potential, and:

\[ \cos \theta_a = \frac{d_a \cdot d_{a-1}}{|d_a| |d_{a-1}|} \]  
\hspace{2cm} (3.26)

\[ \cos \phi_a = -\frac{(d_a \times d_{a-1}) \cdot (d_{a-1} \times d_{a-2})}{|d_a \times d_{a-1}| |d_{a-1} \times d_{a-2}|} \]  
\hspace{2cm} (3.27)

\[ \text{Fig. 3.1 A polymer chain. The bending angle } \theta_a \text{ is the angle between the bond vectors } d_a \text{ and } d_{a-1}, \text{ the angle } \phi_a \text{ is the angle between the plane defined by } d_a \text{ and } d_{a-1} \text{ and that defined by } d_{a-1} \text{ and } d_{a-2} [\text{Allen and Tildesley 1987}]. \]
With the building of a backbone configuration as shown in Fig. 3.1, the molecular simulation can be started with random atomic velocities with a \textit{Maxwellian} distribution for a given temperature. The equilibrating of the structure can converge rapidly and the equilibrated system can then be used as the initial structure for molecular dynamic simulation \cite{Allen1987}. However, due to the complexity of the polymer structure, the requirements of computational resource and time to get full atomistic details are very great. Hence, only several polymer molecular chain models, according to the theory of RIS, Rouse and reptation model as described in Chapter 2.2, have been used in the last two decades to save computational effort.

\section*{§ 3.1.4 Numerical Integration Methods}

In molecular dynamics, the motion of the atoms (Eq.3.1 and 3.2) are evolved through time by integrating the equations of motion, which represent a set of differential equations and can be solved by using any standard finite-difference algorithm (FDA). The FDA used in MD can be mainly classified as predictor method (the site coordinates are updated from quantities obtained in the current or previous time steps) and predictor-corrector method (the algorithm firstly predicts new site coordinates and get the value of some variables and then reversely use those data to correct those predictions) \cite{Allen1987}. Depending on the order of the derivatives, the \textit{Verlet} \cite{Verlet1967} algorithm and its modifications and \textit{Gear} \cite{Gear1971} algorithm are two widely used examples for each method. The two methods are both derived from the Taylor series expansion of the atom or molecular coordinates, but with different order of derivatives.
From equations of the Hamiltonian (3.17) and Lagrangian (3.16), the Newton’s second law for the system of \( N \) particles can be obtained:

\[
\frac{d^2 r_i}{dt^2} = \frac{f_i}{m_i} \quad (3.28)
\]

Integrating Eq.3.28 with respect to time yields:

\[
\frac{dr_i}{dt} = \left( \frac{f_i}{m_i} \right)t + C_i = a_i t + v_i \quad (3.29a)
\]

\[
r_i = r_i t + \frac{1}{2} a_i t^2 + C_2 \quad (3.29b)
\]

where \( C_2 \) is the current position of the particle \( i \). The Verlet algorithm is a Taylor series expansion about \( r(t) \).

\[
r(t + \Delta t) = r(t) + \frac{dr}{dt} \Delta t + \frac{1}{2!} \frac{d^2 r}{dt^2} \Delta t^2 + \ldots \quad (3.30a)
\]

\[
r(t - \Delta t) = r(t) - \frac{dr}{dt} \Delta t + \frac{1}{2!} \frac{d^2 r}{dt^2} \Delta t^2 - \ldots \quad (3.30b)
\]

Adding eqs.3.30a and 3.30b, and omitting higher order terms:

\[
r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \frac{d^2 r}{dt^2} \Delta t^2 \quad (3.31)
\]

Equation 3.31 is the Verlet’s algorithm, from which the velocity is easily obtained:

\[
v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t} \quad (3.32)
\]

From the Verlet algorithm, there are many other modified methods, like Leap-Frog Verlet [Hocknet 1970] and Velocity-Verlet [Swope et al 1982] etc., which improve the performance of MD in different applications.
The Gear algorithm was also derived from the Taylor series expansion of the molecular coordinate as in Eq.3.30a, but with higher order terms:

\[
r(t + \Delta t) = r(t) + \frac{dr}{dt} \Delta t + \frac{1}{2!} \frac{d^2r}{dt^2} \Delta t^2 + \frac{1}{3!} \frac{d^3r}{dt^3} \Delta t^3 + \frac{1}{4!} \frac{d^4r}{dt^4} \Delta t^4 \ldots
\] (3.33)

With Eq.3.33, the velocities and accelerations can be obtained as:

\[
v(t + \Delta t) = v(t) + \frac{d^2v}{dt^2} \Delta t + \frac{1}{2!} \frac{d^3r}{dt^3} \Delta t^2 + \ldots
\] (3.34a)

\[
a(t + \Delta t) = a(t) + \frac{d^3r}{dt^3} \Delta t + \ldots
\] (3.34b)

which is then corrected to yield the actual trajectory by calculating the accelerations \(a_c\) from the new coordinate and getting the difference \(\Delta a\) between these values and the predicted \(a_p\) values:

\[
\Delta a(t + \Delta t) = a_c(t + \Delta t) - a_p(t + \Delta t)
\] (3.35)

Then the predicted value of \(r_p\), obtained by Eq.3.33, can be corrected:

\[
r_c(t + \Delta t) = r_p(t + \Delta t) - k_d \Delta a(t + \Delta t)
\] (3.36)

where \(k_d\) is a constant that depends on the order of time derivative [Gear 1971].

The speeds of execution for the MD are very close for all the different integrators because, in the simulation, most of the computational resources are consumed by the calculation of force field. However, it is worth to note that, with small time step \(\Delta t\), the Gear algorithm of 4 or 5 terms is more accurate than the Verlet algorithms, but the later are easier to implement [Sadus 1999].

§ 3.1.5 Control Ensembles in Molecular Dynamics (MD)
As shown in Eq.3.9, the simulation of the \( N \)-particle system is determined by the choice of the ensemble, which is a collection over all quantum states \( i \) with common macroscopic properties, like pressure \( P \), temperature \( T \), volume \( V \), and number of molecules \( N \), etc. A summary of four commonly used ensembles are listed in Table 3.1.

**Tab.3.1 Several commonly used ensembles in statistical ensembles in MD [Sadus 1999]**

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Constraints</th>
<th>Partition function ( Z )</th>
<th>Probability ( P_i )</th>
<th>Thermodynamic feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcanonical</td>
<td>( N, V, E )</td>
<td>( \sum_i \delta(E_i - E) ) ( \delta(E_i - E) / Z_{NVE} )</td>
<td>( S = k_B \ln Z_{NVE} )</td>
<td></td>
</tr>
<tr>
<td>Canonical</td>
<td>( N, V, T )</td>
<td>( \sum_i e^{-E_i(NV)/k_B T} ) ( \sum_i e^{-E_i(NVT)/k_B T} / Z_{NVT} )</td>
<td>( E_F = -k_B T \ln Z_{NVT} )</td>
<td></td>
</tr>
<tr>
<td>Isothermal-Isobaric</td>
<td>( N, P, T )</td>
<td>( \sum_i e^{P(NP)/k_B T} ) ( \sum_i e^{P(NPT)/k_B T} / Z_{NPT} )</td>
<td>( G = -k_B T \ln Z_{NPT} )</td>
<td></td>
</tr>
</tbody>
</table>

In table 3.1, \( S, E_F, G \) are entropy, Helmholtz function and Gibbs function of the system, respectively. In a microcanonical system, or a \( NVE \) ensemble, the control of the total energy is achieved by the contribution of kinetic energy \( K \):

\[
E_A = K_A + U
\]

\[
K_D = E_D + U
\]

(3.37a)

(3.37b)

where the index \( A \) and \( D \) represent the actual and desired value of the energy, \( U \) is the potential energy of the NVE system. The desired energy can be obtained by scaling the initial velocities of each particle with the desired and actual kinetic energies respectively:

\[
v_{ik}^{new} = v_{ik} \sqrt{K_B / K_A}  \\ k = x, y, z
\]

(3.38)

In practice, the scaling procedure needs to be performed during the equilibration state of the molecular simulation to make sure the NVE system is statistically stable. For a \( NVT \) ensemble, the velocity scaling method can also be used but with the evaluation of desired and actual temperature. The kinetic energy of the system can be obtained from:
\[ K = \frac{1}{2N} \left( \sum m_i \mathbf{v}_i \cdot \mathbf{v}_i \right) = \frac{3}{2} k_B T \]  
(3.39)

Then the temperature can be expressed as:

\[ T = \frac{1}{3k_B N} \left( \sum m_i \mathbf{v}_i \cdot \mathbf{v}_i \right) \]  
(3.40)

Thus the scaling equation can be obtained:

\[ v_{ik}^{\text{new}} = v_{ik} \sqrt{\frac{T_D}{T_A}} \quad k = x, y, z \]  
(3.41)

Here, “new” means the final value according to the desired temperature.

In a NVT ensemble, the scaling of velocity should be performed periodically to compensate for the drift of energy, which is exchanged between the potential and kinetic energy during the equilibration.

The essential issue of the heat bath coupling method is to control the fluctuation of temperature around the desired value. Thus another way of implementing a thermostat, or temperature control, in NVT is to couple the system to an external heat-bath corresponding to the desired temperature:

\[ \frac{dT_A}{dt} = \frac{\Delta t}{\tau} (T_D - T_A) \]  
(3.42)

where \( \tau \) is a constant determining how tightly the coupling of the bath and system is.

Equation 3.42 can be also written as:

\[ \Delta T = \frac{\Delta t}{\tau} (T_D - T_A) \]  
(3.43)

Then the scaling algorithm will be as follows:

\[ v_{ik}^{\text{new}} = v_{ik} \sqrt{1 + \frac{\Delta t}{\tau} \left( \frac{T_D}{T_A} - 1 \right)} \quad k = x, y, z \]  
(3.44)
which is identical to the velocity scaling when $\tau = \Delta t$.

Andersen [1980] carried out an algorithm to combine MD with stochastic process to guarantee a NVT distribution by introducing stochastic collision at the outset of the simulation. In the method, the probability of a particle of the system involved in a stochastic collision is $\kappa \Delta t$, where $\kappa = v_c / N^{2/3}$ and $v_c$ is the collision frequency and $N$ is the number of atoms of the system.

By introducing an additional degree of freedom $s$, Nose [1984] implemented an approach to integrate a thermal reservoir to the system, in which the potential and kinetic energy of the reservoir, denoted by subscripted “res”, are as follow:

$$U_{\text{res}} = g K T_D \ln s$$  \hspace{1cm} (3.45a)

$$K_{\text{res}} = \frac{Q}{2} \left( \frac{ds}{dt} \right)^2 = \frac{p_i^2}{2Q}$$  \hspace{1cm} (3.45b)

Here, $Q$ is a parameter which couples the reservoir to the real system and affects the temperature fluctuation. In Nose’s algorithm, “$s$” can be regarded as a virtual dimension through which the heat is flowing. The velocities of the atoms in the real system are then given by:

$$v = s \frac{dr}{dt} = \frac{p}{ms}$$  \hspace{1cm} (3.46)

The kinetic energy of the real system is:

$$K_{\text{real}} = \frac{p^2}{2ms^2} = \frac{1}{2} m s^2 \cdot \left( \frac{dr}{dt} \right)^2$$  \hspace{1cm} (3.47)

Thus, the Hamiltonian for the extended system becomes:

$$H_s = \sum_i \frac{p_i^2}{2m_i s^2} + U(q) + \frac{p_s^2}{2Q} + g k_B T_D \ln s$$  \hspace{1cm} (3.48)
which is the essential feature and can lead to the equation of motion for the system:

\[
\dot{q} = \frac{p}{ms^2} \quad (3.49a)
\]

\[
\dot{p} = F(q) \quad (3.49b)
\]

\[
\dot{s} = \frac{p_s}{Q} \quad (3.49c)
\]

\[
\dot{p}_s = \sum_i \frac{p_i^2}{m_is^2} - \frac{gk_bT_d}{s} \quad (3.49d)
\]

To remove the extra degree of freedom \( s \) in the Nose method, Hoover [1985] revised the equation of motion 3.49 by introducing a friction coefficient \( \zeta \) which evolves with time:

\[
\dot{q} = \frac{p}{m} \quad (3.50a)
\]

\[
\dot{p} = F(q) - p\zeta \quad (3.50b)
\]

\[
\dot{\zeta} = \frac{\sum_i \frac{p_i^2}{m_i} - gk_bT_d}{Q} \quad (3.50c)
\]

Equations 3.50 are usually called Nose-Hoover algorithm, in which the value of \( \zeta \) was determined by 3.50c as a feedback equation. This method was further modified later by replacing a single thermostat with a chain of variables \( \zeta_i \) (\( i=1,2,\ldots,m \)), to adapt it in small or stiff (non-ergodic) system [Martyna et al 1992].

The Nose-Hoover algorithm can also be used in a \( NPT \) ensemble [Hoover 1985], or isothermal-isobaric system by reduced coordinate \( x \equiv q/(V^{d/d}) \) (\( d \) is the number of dimensions):

\[
\dot{x} = \frac{p}{mV^{d/d}} \quad (3.51a)
\]
\[ \dot{p} = F(q) - p(\dot{\varepsilon} + \zeta) \quad (3.51b) \]

\[ \zeta = \frac{\sum P_i^2 - g k_B T_D}{Q} \quad (3.51c) \]

\[ \dot{\varepsilon} = \frac{\dot{V}}{dV} \quad (3.51d) \]

\[ \ddot{\varepsilon} = \frac{P_A - P_D}{\tau^2 k_B T_D} \quad (3.51e) \]

where \( \tau \) is the relaxation time, \( P_A \) and \( P_D \) are the actual and desired pressures respectively.

\section*{§3.2 Models in Polymer Molecular Simulation}

\subsection*{§ 3.2.1 Amorphous Cell Model in Atomistic MD}

In molecular simulation, the bulk system is generally modeled as enclosed in a cell box with periodic boundary conditions, in which the system is considered to be surrounded on all sides by replicas of itself to form an infinite macro-lattice. In any periodic system of polymer, however, the atoms from the same macromolecule may lie in different cells, due to its long polymer chains.

To solve this problem, the amorphous cell model of polymer [Theodorou and Suter 1985] was constructed. In the amorphous cell model, only the parent molecular chains are modeled and all others are treated as image molecules, which are image replicas of parent molecules. All the atoms, which do not belong to the parent molecules but lie in the central cell, are images of the atoms of parent molecules outside the central cell (Fig.3.2).
During a molecular simulation, only the atoms in the central cell are simulated and are referred to as parent atoms, other atoms are image atoms. With the periodic boundary conditions, all image atoms move exactly the same way as their parent atoms except for a fixed translational difference. When an atom leaves the central cell through one side, its image enters through the opposite side (Fig. 3.2).

The generation of the initial configuration of the parent molecules is based on Rotational Isomeric State (RIS) theory [Flory 1989], in which the configurational statistics of a macromolecular chain in the bulk is well represented by an independent rotational isomeric state as described in chapter 2.2.2. In the RIS approach, all degrees of freedom except the torsion of the backbone are neglected due to the fact that the force constants for bond stretching and bending are so large that changes in bond lengths and angles are
very small, compared with changes in backbone torsional angles, during equilibration. The statistical weight for a bond pair in a given conformation, with Eq.3.5, is given by:

\[
w_a(\phi_{a-1},\phi_a) = \exp\left[-E(\phi_{a-1},\phi_a)/RT\right]
\]

(3.52)

where \(E(\phi_{a-1},\phi_a)\) is a bond pair energy and \(\phi_{a-1}, \phi_a\) are two consecutive dihedral angles forming the bond pair, as shown in Fig.3.1. In the Amorphous Cell scheme, a polymer chain conformation can then be generated by setting backbone rotational states one by one from the tail to reach the head of the chain. The normalized a priori probability of occurrence \(P_{\xi,i}\), for bond \(i\) in state \(\xi\), for a given chain conformation in the RIS scheme is [Yarovskiy 1997]:

\[
P(\phi_1,\ldots,\phi_n) = Z^{-1} \prod_i E(\phi_{i-1},\phi_i)
\]

(3.53)

A chain conformation can be constructed by (starting from the tail of the chain) setting backbone rotational state one by one according to the a priori probabilities \(P_{\xi,i}\) until the head of the chain is reached [Theodorou and Suter 1985,1986a,b]. The three backbone atoms, at the tail of the chain, are placed in the cell with random orientation. Then the chain is constructed stepwise in a backbone bond by bond as in Eq.3.53. For each step in choosing the rotational state of bond \(i\), a conditional probability \(P''\) is used as:

\[
P''_{i-1,i}(\phi',\phi) = \frac{P'_{i-1,i}(\phi',\phi) \exp\left[-\Delta E_i(\phi)/RT\right]}{\sum_{\phi'} P'_{i-1,i}(\phi',\phi') \exp\left[-\Delta E_i(\phi')/RT\right]}
\]

(3.54)

where \(\Delta E_i(\phi)\) denotes the increase in nonbond interaction energy by newly adding the \(i+1\) atom on the constructed backbone atom \(i\). The factor \(P'_{i-1,i}(\phi',\phi)\) denotes the conditional probability of finding \(i\) in state \(\phi\) when \(i-1\) is known to be in state \(\phi'\). Thus,
with Eq.3.53, \( P'_{i-1,i} \) may be defined in terms of bond and bond pair a priori probabilities \( P_i \) [Yarovsky 1997]:

\[
P'_{i-1,i}(\phi',\phi) = \frac{P_{i+1,i}(\phi',\phi)}{P_{i-1,i}(\phi')}
\]

(3.55)

Then the state of bond \( i \) can be chosen according to the modified conditional probabilities \( P' \). After building the initial conformation, the Amorphous Cell can then be minimized to reach equilibrium with the assumption that the backbone carbon atoms and pendant hydrogen atoms are treated explicitly, but the side groups are lumped in to single “quasi-atoms” of appropriate size. However, in the Amorphous Cell method, the thermal motion is not considered, instead, the temperature factor is incorporated through specification of the density [Theodorou and Suter 1985].

In the simulation of polymer interfaces, similar considerations can be applied between two phases, in which case the periodicity extend in only two of the three principal directions (Fig.3.3).

The non-periodic direction is perpendicular to the interface and is usually used for modeling thin films with thickness greater than the cutoff of the bulk molecules.
[Mansfield and Theodorou 1990]. The thickness of the thin films can be calculated as [Polymer, Accelrys Inc., 1997]:

\[ c_2 = c_1 \left( \frac{m_2}{m_1} \right) \left( \frac{d_1}{d_2} \right) \]  (3.56)

where \(c_1\) and \(c_2\), \(m_1\) and \(m_2\), \(d_1\) and \(d_2\) are, respectively, thickness, mass and density of the two parts to be built. Compared to the building of bulk models, there are two additional procedures in polymer interface amorphous cell:

1) the two sides of the thin films should be initially treated as surfaces, which means no bond is allowed to cross the two sides, and

2) in the building of polymer interface cell, some strain is imposed, which should be removed by relaxing the system to equilibrium state [Yarovsky 1997]

By replacing one of the polymer parts with non-polymer substrate, the molecular model of polymer-non-polymer interface can also be built with the amorphous cell method.

§3.2.2 Multi Time Scale and Length Scale of Polymer

Polymer simulations, due to its hierarchy of length scales and associated time scales, can be and are being done on different levels.

Figure 3.4 shows the scale ranges of polymer simulation. The length scale ranges from several Angstroms to millimeters and the time ranges from sub-picoseconds to seconds. According to different degrees of freedom from the motion of electrons to atom groups or monomers, polymer simulation uses different methods such as quantum mechanics (QM), atomistic molecular dynamics (MD), coarse-grained molecular dynamics (CG), or Finite Element Methods (FEM). In Molecular Simulation, treating several neighboring atoms or even monomers as a “meso atom”, or bead gives rise to a coarse-grained model of
polymer which is very computationally efficient if the time and length scale of the interested polymer properties are independent of the motions of the atoms inside those beads.

\[ \rho(r) = \rho \cdot g_r(r) \]  \hspace{1cm} (3.57)

where \( \rho \) is the average density of the system, and the \( g_r(r) \) is called the radial distribution function (RDF). A typical plot of the RDF is shown in Fig. 3.5.

Figure 3.5b shows that \( g_r(r) \) of Ar converges to 1 for large \( r \), which is implied by its definition in Eq. 3.57. The RDF is usually evaluated in MD because it can be easily measured by scattering experiments like X-ray or neutron scattering.
From the determination of the RDF, several quantities of interest for the system, like thermodynamic energy $E$ and pressure $P$, etc, can be obtained as:

$$E = \frac{3}{2} k_B N T + \frac{1}{2} N \int d^3 r \rho g_s(r) U(r)$$ (3.58)

$$P = \frac{k_B N T}{V} - \frac{1}{6 \rho^2} \int d^3 r \rho g_s(r) r \frac{dU}{dr}$$ (3.59)

where $U$ is the inter-particle potential of the system.

For a polymer chain system of $N$ bonds with bond vector $d_i$, as described in Chapter 2.2, the distribution of the end-to-end vector $R_e$ of the polymer chains can be written as [Doi and Edwards 1986]:

$$\Omega(\vec{R}) = \left\{ \frac{3}{2\pi Nb^2} \right\}^{3/2} \exp\left\{ -\frac{3R^2}{2Nb^2} \right\}$$ (3.60)

Equation 3.60 is called central limit theorem, which means the end-to-end vector $R_e$ of the system has a Gaussian distribution. Applying the result to a general RIS chain, i.e. Eq. 2.1 described in Chapter 2.2, gives $R$ as:
That means \( \lambda \) bond vectors can be combined into one new vector. In other words, for a polymer chain of \( N \) bonds connecting \( N+1 \) monomers, it is a Gaussian Chain. When several neighboring monomers, with \( \lambda \) bonds, are treated as one bead, the modified chain, with \( N/\lambda \) bonds, is also a Gaussian Chain. Figure 3.6 describes the transfer of bonds, one example of which is bond \( d_i-4, d_i-3, d_i-2, d_i-1, \) and \( d_i \) are combined as one bond \( d'_i \) in the new polymer chain model.

If \( \lambda = 5 \), as shown in Fig.3.6, then Eq. 2.6 approximates to:

\[
\langle x^2 \rangle \approx \lambda b^2
\]  

Equations 3.60~3.62 lead to the theoretical support for the coarse-grained model CG, in which several neighboring atoms or monomers are grouped as one bead to save computer resources. The CG polymer chains can then be treated by the Rouse and reptation model discussed in Chapter 2.2.

§ 3.2.3 Coarse-grained Bead-spring Model (CG)

To simplify the molecular modeling of polyethylene (PE) chains, Rigby and Roe [1987,1988], used a spring potential between carbon atoms, a bond-bending potential,
and a torsional potential to account for the backbone structure of the molecule chain. With the simplification, the relaxation time of the particle systems was greatly decreased. In many polymer interfaces, the polymer blends do not mix, i.e., the two systems can be separated easily by a weak repulsive force. The interfacial adhesive strength is not due to weak van der Waal forces alone, large numbers of polymer entanglements result in significant interfacial strength. This is especially true for polymer-nonpolymer (substrate) interfaces: the interfacial strength depends on the number of chemical bonds between monomers of the polymers and sites on the substrate (Fig. 2.6b).

**Fig. 3.7 Coarse-grained Bead-spring Model [Sides et al 2002].**

Based on the spring potential proposed by Rigby and Roe, a coarse-grained bead-spring model [Kremer and Grest 1995] was proposed to treat bulk polymer and cross-linked networks. Figure 3.7 shows a schematic for the bending potential in the bead-spring model. The three labeled monomers define the triplet used in calculating the bending force associated with angle θ.
The monomers of the molecules are represented by beads bonded together using a potential in the coarse grained bead-spring model [Kremer-Grest 1995] to prevent chain crossing. The potential is the sum of the purely repulsive Lennard-Jones (LJ) interaction with a cutoff distance of $2^{1/6}\sigma^*$ ($\sigma^*$ represents the LJ diameter) and a finite-extensible nonlinear elastic (FENE) attractive potential. However, a drawback of the Kremer-Grest model is that the FENE bonds are not allowed to break. To allow bond breakage and preserve the continuity of the bond force, the model was modified [Stevens 2001a,b] using a Lennard-Jones (LJ) potential, $U_{LJ}$, with a cutoff of $2.5\sigma^*$ and a quartic bond potential, $U_4$, to replace the FENE potential:

$$U_{LJ}(r) = 4u_0\left[\left(\frac{\sigma^*}{r}\right)^{12} - \left(\frac{\sigma^*}{r}\right)^6\right]$$

$$U_4(r) = \begin{cases} 
  k_4 (y - b_1)(y - b_2)y^2 + U_0 & r < r_c \\
  U_0 & r \geq r_c 
\end{cases}$$

where $u_0$ represents the LJ energy, $U_0$ is a prescribed energy, and $y = r - \Delta r$ shifts the quartic center from the origin. The value of $b_1$ is set to match the FENE bond minimum and the potential cutoff is $r_c$. When a bond stretch is larger than $r_c$, the bond would be broken and the bond potential between the pair is turned off to prevent the bond from re-forming.

Figure 3.8 shows three systems of polymer-nonpolymer interfaces where a polymer network lies between two solid walls. Each wall is composed of two layers of particles in an fcc lattice. The (111) direction (z-direction) is perpendicular to the walls. The wall particles, which interact with the beads via LJ potential in Eq. 3.63, are bound to the
lattice sites by a harmonic spring. The wall dimensions give the simulation cell lateral lengths and periodic boundary conditions are applied in the lateral direction.

Using the modeling algorithm above, three systems under the tensile pulling of the two walls are simulated [Stevens 2001a]. In systems $b$ and $c$ there is one bond per cross-linker and three bonds per cross-linker to the surface, respectively. In system $a$, a network with some strands connect next nearest neighbor planes of cross-linkers. From the different constructions of network connection, in which the beads are connected orderly and randomly respectively, adhesive failure (Fig. 3.9a) and cohesive failure (Fig. 3.9b) are observed (Fig. 3.9).

*Fig. 3.8 (a) Cross-linkers A and B. (c) Dark circles represent the strands in O$_2$ that connect next nearest cross-linkers, the dangling ends are labeled D. (b&d) Projections of O$_1$ and O$_3$ with cross-linkers (gray), walls (black), and strand beads (circles) O$_1$, O$_2$ and O$_3$ refer to Fig.3.9. [Stevens 2001a].*
§ 3.2.4 Comparison of the Amorphous cell and CG Models

The development of the Amorphous Cell model and the Coarse-grained Bead-spring model represent two different aspects in the molecular simulation of polymer and polymer interfaces. The latter focuses on the movement of the monomers on the polymer chain to save computer resources while the former emphasizes the motion of molecule backbone chains and needs relatively more computational effort.

In the Coarse-grained Bead-spring model, a bead represents a group of monomers and the number of beads depends on the particular polymer. The stiffer the polymer, the more monomers per bead. Because of the large savings in computer time, this model is able to treat entanglement dynamics for time scales of at least one microsecond. With the

Fig.3.9 Different systems under tensile strain. (a) the randomly formed network at failure, (b) the ordered network O₁ at the same strain, and (c) the ordered network O₃ during failure. [Stevens 2001a].
introduction of the potential for breakable bonds, chain breakage can be obtained in the polymer interface simulation [Fig.3.10].

Figure 3.10 shows chain configurations at three times during a tensile pull simulation for tethered chains of length $N_t = 250$ at temperature $T = 0.3 \varepsilon/k_B$, pull velocity $v = 0.167 \sigma \tau^{-1}$ (where $\tau = \sigma (m \varepsilon)^{1/2}$, $\sigma$ and $\varepsilon$ are the LJ length and energy scales respectively) and chain bending energy $U_\theta = 0.0$ (fully flexible). Elapsed times shown are (a) $300 \tau$ (b) $900 \tau$ and (c) $1200 \tau$. The broken monomers belong to the tethered chains before pulling. The upper part of the polymer bulk belongs to sections of tethered chains that are no longer attached to the bottom substrate. In this CG model, the system contained nearly 0.5 million atoms [Sides et al 2002].

In Amorphous Cell methods, considerable attention is paid to the construction of “reasonable” amorphous packing starting from atomistic models of single polymer chains (Eq. 3.52). Four approaches in the last two decades can be identified:
1) growing chains into dense phases by adding new segments to reach the target chain properties using appropriate criteria \cite{Theodorou and Suter 1985},

2) guessing a coarse initial molecule structure generated on a lattice \cite{Brostow and Kubat 1993},

3) using experimental densities of specified polymer to condense an initially low density of polymer system \cite{Gusev et al 1994},

4) generating the polymer chain with initially liquid monomers in the periodic box \cite{Kotelyanskii et al 1996}.

All the above methods start with an “initial guess” structures and relax the structure by potential energy minimization or annealing molecular dynamics in which the temperature is annealed gradually to that of interest \cite{Brown et al 1994}. In practice, only relatively simple systems, consisting of purely amorphous polymers formed by monodisperse, flexible, linear chains, and of molecularly smooth solid surfaces interacting with the polymers via London dispersion force, may be simulated at the molecular level using the Amorphous Cell model \cite{Theodorou 1992}.

To make the initial guess structures obey the proper chain statistics while avoiding atomic overlap, a Parallel-Rotation algorithm (ParRot) is carried out \cite{Muller et al, Santos et al 2001} to efficiently relax the torsion angles that are deep inside long chains in dense systems.

In the Parallel-Rotation algorithm, the bond length and the bond angles are assumed as rigid constraint bonds. As shown in Fig. 3.11, the ParPot move consists of a concerted change in the torsion angles $\{\phi_1, \phi_2, \phi_3\}$ driven by a change in $\phi_0$. The direction vectors $\mathbf{u}$
and \( u_\perp \) remain unchanged after the ParRot move. The direction vector \( u \) is determined by dihedral angles \( \phi_0 \), \( \phi_1 \), and \( \phi_2 \), while \( \phi_3 \) only causes the vector \( u_\perp \) to rotate around \( u \).

By improving the Amorphous Cell model, in which the initial guess starts from the tail of one chain and thus could only treat linear chains, the ParRot method emphasizes four consecutive dihedral angles without considering the molecular structure between the joint sites and can be applied to molecules with side groups, or branched chains, and even to systems with arbitrary bond lengths, angles and monomer-unit sizes.

§ 3.2.5 Mapping between the Multi-scale Models

Polymer systems can be simulated at different length and time scales with different numbers of degrees of freedom. In recent years, a combination of the features of both atomistic and coarse-grained models of polymer have been used by more researchers in order to save computer resources without losing the structure details of polymer chains [Baschnagel et al 2000]. One of the most attractive ideas is the mapping of conformation...
between two models at different levels [Muller-Plathe 2002], in which an atomistic polymer model is built first with the RIS method and then mapped onto a coarse-grained model. The CG simulation is performed in order to obtain the properties of interest, and the results can be reversed mapped back onto the atomistic conformation. The final atomistic detailed polymer conformation can then be used for more atomic-related property analysis, like bond orientation and concentration profile etc. The procedures are shown in Fig. 3.12.

![Fig. 3.12 Scheme of three steps in the mapping procedures (solid arrows) that replace a fully atomistic classical MD [Baschnagel et al 2000].](image)

Before the first step of mapping, the mapping criteria must first be decided upon, i.e. the number of atoms, or bonds, that needs to be contained in one bead [Fig. 3.13].

From Fig. 3.13, it is apparent that if more atoms are lumped together into one bead, the more efficient the computation becomes but at the expense of less atomistic detail. In the mapping algorithm, the radial distribution function between the centers of mass of
different molecules is calculated and used as the structural feature to be reproduced. One comparison between different mapping schemes is shown in Fig. 3.14.

![Fig. 3.13 Coarse-graining of bisphenol-A polycarbonate as a) a 2:1 scheme (two super-atoms per chemical repeat unit) and b) a 4:1 scheme [Muller-Plathe 2002].](image1)

![Fig. 3.14 Coarse-graining of diphenyl carbonate (393 K, 1 bar): a) Three-site model, b) two-site model. Shown is the centre of mass radial distribution function and, where useful, the corresponding coarse-grained potential [Meyer et al 2000].](image2)

After the generation of the initial conformation with the mapping, the coarse grained system is then simulated with a force field obtained from optimizing atomistic classical
force field by means of a simplex technique [Faller 2000]. It is shown that this automatic simplex optimization algorithm works well for Methylpentane [Faller et al 1999], diphenyl carbonate [Meyer et al 2000], poly(acrylic acid) [Reith et al 2001] and polyisoprene [Reith et al 2003].

§3.3 Computation of Mechanical Properties

§3.3.1 Stress/Pressure Control in Molecular Modelling

With the building of the polymer molecular model, mechanical properties, like, stress vs strain curves etc., can then be obtained from the simulation. Considering again the N-particle-system described by Eq. 3.2, the temperature and pressure may be calculated using the virial theorem with the form of generalized partition [Munster 1969]:

\[
\langle p_i \partial H / \partial p_i \rangle = k_B T \quad (3.65a)
\]

\[
\langle q_k \partial H / \partial q_k \rangle = k_B T \quad (3.65b)
\]

The pressure can then be calculated via eq 3.65b or from the following:

\[
P V = N k_B T + \frac{2}{3} \langle W \rangle \quad (3.66)
\]

where \( W \) is the internal virial of the N-particle-system with periodic boundary conditions enclosed in a container of volume \( V \):

\[
W = \frac{1}{2} \sum_{i=1}^{N} r_i f_i \quad (3.67)
\]
here \( r_i \) is the site position in Cartesian coordinates and \( f_i \) is the force on the site. Then the atomic level stresses can be written as [Gao and Weiner 1987]:

\[
\frac{V t_y}{k_B T} = \sum_a \langle \sigma_y (a) \rangle \tag{3.68}
\]

where \( t_{ij} \) is the macroscopic stress tensor in the system (force per current area) and \( \sigma_{ij}(a) \) is the instantaneous atomic level stress associated with atom \( a \). In the simulation of polymer chain, the molecular virial stress [Theodorou et al 1993] can be used:

\[
\tau^{\alpha\beta} = \langle \sigma_{m.v.}^{\alpha\beta} \rangle = \left\langle -\frac{1}{V} \sum_c \frac{P_{cm,c}^{\alpha} \cdot P_{cm,c}^{\beta}}{m_c} \right\rangle
\]

\[
-\frac{1}{2V} \sum_{j-in-box} \sum_{j-in-box} \left( r_{cm,c(i)}^{\alpha} - r_{cm,c(jmin(l))}^{\alpha} \right) F_{ij}^{N_{ij}min,fl} + \tau_{tail}^{\alpha\beta} \tag{3.69}
\]

Here, \( \tau^{\alpha\beta} \) is the \( \alpha\beta \)-component of the stress tensor \( \tau \), while \( m_c, r_{cm,c}, p_{cm} \) and \( F_{cm,c} \) denote the mass, center of mass position, center of mass momentum, and total force on each molecule \( c \) in the system, and \( i,j_{min}(l) \) describes the different images of same parent chain or of different parent chains (Fig.3.2).

In molecular systems, there are mainly three methods of pressure/stress control: the Anderson method [Anderson 1980], the Berendsen loose-coupling method [Berendsen et al 1984] and the Rahman-Parrinello (PR) technique [Parrinello and Rahman, 1981] in conjunction with the Nose-Hoover thermostat [Nose 1984ab, Hoover 1985]. Under external pressure, the first two methods allow volume changes, but not shape changes, which means only the pressure is controlled. With the PR method, the cell’s shape can change, and thus both pressure and stress can be controlled.
To model the fluctuation of a system at constant pressure, Anderson [1980] assumed a system in a container of variable volume which can be compressed by a piston. Then a change in volume causes an isotropic expansion or contraction. With the Anderson method of pressure control, the shape of the cell is preserved while its volume can change isotropically. The cell box can become elongated in the absence of restoring forces if the shape of the cell were allowed to change. Thus, the method is useful for simulating liquids at a constant shape to make the dynamics analysis easier. It is not very useful, however, for studying materials under nonisotropic stress or phase transitions, which involve changes in both cell lengths and cell angles.

By changing the coordinates of the particles and the size of the unit cell in periodic boundary conditions, the Berendsen method couples the system to a pressure “bath” to maintain the pressure at a certain target. The strength of coupling is determined both by the compressibility of the system (using a user-defined variable $\gamma$) and by a relaxation time constant (a user-defined variable $\tau$). At each step, the $x$, $y$, and $z$ coordinates of each atom are scaled by the factor [Berendsen et al 1984]:

$$\mu = \left(1 + \frac{\Delta t}{\tau} \gamma (P - P_0) \right)^{1/3}$$  \hspace{1cm} (3.70)

where $\Delta t$ is the time step, $P$ is the instantaneous pressure, and $P_0$ is the target pressure. The Cartesian components of the unit cell vectors are scaled by the same factor $\mu$. For polymer systems, the Berendsen method, in practice, has been found to predict first order properties similar to those obtained by more rigorous approaches [Evans and Holian 1985].
In the Parrinello-Rahman (PR) method \cite{1981} of pressure and stress control, the Lagrangians of the system, provided by Anderson \cite{1980}, are modified such that a term representing the kinetic energy of the cell depends on a user-defined inertia-like parameter $W_0$, which determines the rate of change of the volume/shape matrix. A large $W_0$ means a heavy, slow cell, while a small $W_0$ means fast motion of the cell. An elastic energy term is related to the pressure and volume or the stress and strain of the system. The equation of motion for the atoms and cell vectors can be derived from this Lagrangian. The motion of the cell vectors, which determines the cell shape and size, is driven by the difference between the target and internal stress.

The PR method can allow simulation of a model under externally applied stress, in which both the shape and the volume of the cell can change. So it is useful for studying the stress-strain relationship for materials.

§ 3.3.2 Mechanical Properties of Polymer Obtained by MD

When an external force is applied to a material, and if the force is small in comparison to the displacement between the atomic spacing, the relation of the potential energy and strain can be expressed as a Taylor series:

\[
U = U_0 + \sum_i \frac{\partial U}{\partial \varepsilon_i} \varepsilon_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j + \text{higher order terms} \tag{3.71}
\]

where $U_0$ is the Equilibrium energy. The stiffness matrix can then be obtained as:

\[
C_{ij} = \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \tag{3.72}
\]
With Eq.3.72, Theodorou and Suter [1986ab] used a static method, in which only energy minimization was applied for the polymer system and the temperature was not considered, to estimate the elastic moduli of glassy PP and studied the effects generated by changes in configurational entropy on polymer deformation. In their study, [Mott et al 1993] the constant-strain minimization method was carried out using the strain increment tensor to obtain the stress-strain behaviour of the amorphous polypropylene (Fig.3.15). The system stress and strain of the polymer model was first obtained along six coordinates and then weighted by volume average of the atomic stress tensor $\sigma$ and strain increment tensor $\varepsilon$:

\[
d\varepsilon^{SYS} = \sum_n v^n d\varepsilon^n \\
\sigma^{SYS} = \sum_n v^n \sigma^n
\]

where $v^n$ is the volume fraction of each of the $N$ Voronoi polyhedra of the periodic cell.

Fig. 3.15 Axial extension and pure shear ensemble averaged von Mises tensile stress against system work equivalent strain [Mott et al 1993].
Figure 3.15 shows the von Mises equivalent tensile stress response to deformation. Elastic response was observed and followed by yielding at about 7% strain.

Brown and Clarke [1991ab] applied a tensile stress at constant rates of 1 bar/ps and 5 bar/ps, with a modified Berendsen pressure-control approach [Berendsen et al 1984], using the constant stress minimization method, in which the system is minimized at every interval of stress increment. The plastic properties as well as the elastic response of the Polyethylene (PE) were obtained under extremely rapid loading (Fig.3.16).

![Graph showing tension vs. extension for PE under different stress applied rates.](image)

*Fig. 3.16 Measured tension at PE as a function of percentage extension for tension applied at (a) 5 and (b) 1 bar/ps. [Brown and Clarke 1991b].*
The third approach uses the fluctuation formulae applied to molecular simulations in different ensembles. Parrinello and Rahman [1982] used a simple formula to perform a constant stress ensemble in a simulation:

$$ C_{ik} = \frac{kT}{\langle V \rangle} \langle \varepsilon, \varepsilon_k \rangle^{-1} \quad (3.74) $$

Also, Gusev et al [1996] presented an alternative fluctuation expression as:

$$ C_{ik} = \langle \varepsilon, \sigma_i \rangle \langle \varepsilon, \varepsilon_k \rangle^{-1} \quad (3.75) $$

When Eq. 3.75 was used to get the elastic constants of the nearest neighbor FCC argon crystal between 1K and 36K and, compared to Eq. 3.74, an improved convergence was obtained [Gusev et al 1996].

§3.4 Conclusions

Despite rapid developments in the past few decades, the bottleneck of polymer molecular simulation is still computational resources. For instance, it takes about 15 days to simulate 1ns of molecular dynamic simulation of the interface between PMMA (polymerization of 125 and molecular weight of 12,500) and PTFE (polymerization of 145 and molecular weight of 14,500) interfaces with a total of 10,488 interaction sites on a SUN SS20 (SPARC 40 MHz) + MD Engine (16 chips) system. This system is 1.5 times faster than a high-end Alpha Station (DEC 21164A 500 MHz) [Okada et al 2000].
The time scale is also an important issue in the study of mechanical properties using molecular dynamic simulation, in which the computational experiment time are usually no more than the order of 100 ps. The result is that the loading rates are usually too high compared with actual experiments. One example is that the simulation performed by Brown and Clarke [1991ab], where the loading rate was in the order of 1 bar/ps, or $1\times10^{11}$ MPa/s.

On the other hand, with coarse grained algorithm, it is possible to calculate a system containing about one million atoms in the order of micro seconds, which is closer to the experimental situations [Baschnagel et al 2000]. Recently developed algorithms of mapping between the coarse-grained and atomistic models make it more efficient to obtain the polymer properties with as much details as possible polymer chain structures. However, the accuracy of the mapping method is mainly based on vigorous atomistic classic MD. For some systems containing crosslink structures or changes of chemical bonding, for instance, atomistic classical MD cannot work properly, due to the unavailability of suitable force fields.

Therefore, the molecular modeling and simulation of polymer and polymer interfaces is still far from developed. More effort is needed to develop simplifying algorithms for molecular modeling, while retaining sufficient atomistic details. The present study is an attempt to explore the application of molecular simulation to polymeric interfaces, especially for composite interfaces with silane coupling. Both atomistic classical and coarse grained MD are implemented and a novel force field, used in CG, is carried out for the crosslinked structures of glass/epoxy interface with silane present.
This chapter reports on a study of composite interfaces using atomistic classical molecular dynamics with the Amorphous Cell model. The mechanical properties of polypropylene (PP) and polycarbonate (PC) bulks as well as PP/PP and PP/PC interfaces were studied and compared with experimental data. The composite interfaces of glass/PC with silanes present were also modeled and the interfacial adhesion was studied. An algorithm is proposed and developed in this project to study the mechanical properties of the bulk and interface cells. With the new method, the mechanical properties of poly(ε-caprolactone) (PCL) fiber, a degradable biopolymer of various percentage of crystallinity, was calculated and analyzed. Some interesting results were obtained and comparisons with a recent experiment on PCL nano-fibers are made.

§ 4.1 Introduction

In material systems, interfaces of different materials or different phases of materials usually play a key role in the determination and characterization of their mechanical properties. However, continuum mechanics break down and techniques for sub-micron experiments are still not fully developed for the understanding of interfacial properties which are usually of the nanometer length scale. For instance, some researchers believe
interfacial strength is best described as adhesion [Di Landro and Pegoraro, 1996; Drzal et al 1997], while others believe that the strength of interfaces is better described by the energy required to separate the constituents [Wu and Claypool 1991; Beckert and Lauke 1997]. Theoretical analyses based on continuum mechanics approach and experimental investigation have seen limited success because the effects of molecular and chemical interactions at material interfaces are not accounted for in many analytical models and are difficult to ascertain experimentally [Pisanova et al 2001; Nairn et al 1996]. Molecular dynamics (MD) simulations can provide information on interfacial strength and mechanical properties of the interfacial constituents by providing detailed molecular motions in interfaces at a more fundamental level and has become increasingly popular with the rapid development of computer power.

While there have been reports of MD simulations of polymer-polymer interfaces, very little is reported on MD simulations in determining the mechanical strength of such material systems. One reason for the lack of literature is the prohibitively large numbers of molecules that need to be included in the model in order to relate to practical applications. With the huge computational task of force-field calculation, high-performance computer resource becomes necessary. Another reason is that, unlike the crystal lattice models of metals which have regular atomistic arrangements, there is still no well established methodology for building the initial conformation of polymers. In fact, the construction of a “reasonable” amorphous packing of polymer bulk for the initial structure is by itself an active area of research.

Very often the amorphous conformation is obtained, as described in Chapter 3.2.4, by relaxing an initial “guess” structure through energy minimization or simulated annealing.
with incremental changes in temperature and/or pressure [Muller et al 2001] until the final state is achieved. The Amorphous Cell model [Theodorou and Suter 1985] is commonly used to create initial structures and has been used as the starting point for many MD simulations in the study of polymers and polymer interfaces.

Reiter et al [1990] studied interfaces between polymer melts through MD simulation and found that thicker and more stable interfaces than predicted by theory can be obtained with anti-periodic boundary conditions. Similar studies on the interfacial thickness and interactions of several kinds of polymers obtained from MD simulations have also been reported by Yao et al [1997]. Mansfield and Theodorou [1991] proposed a method to predict the internal energy contribution to the adhesion of materials. Although their implementation focused on interfaces of polymer and graphite, the method is sufficiently general and can be applied to polymer-polymer interfaces as well. A short review of the development of MD simulation for predicting bulk and interfacial properties of organic coatings can be found in a report by Yarovsky [1997], in which another method was used to study the interfacial stability, degree of curing in polymers and permeability to small molecules. The same methodology was applied to investigate a system of an inorganic substrate with a layer of cured epoxy coating [Yarovsky and Evans 2002]. The study reported on the barrier properties and shrinkage of the resin. A similar method was also developed independently by Natarajan et al [1998] and Clancy and Mattice [1999] to study the interfacial region and the work of adhesion of Polypropylene (PP)-PP, PP-Poly(1,4-cis-butadiene) (PBD), PBD-PBD, and polyolefin interfaces. Okada et al [2000] used the same method to study the interfacial properties and the separation of a large amorphous poly(methyl methacrylate) (PMMA)-poly(tetrafluoroethylene) (PTFE) system.
using non-equilibrium MD calculation [Gao J and Weiner 1995]. Interestingly, when PMMA was separated from the PTFE, some chains of PTFE remained attached to the PMMA and were pulled out of the bulk PTFE even though the surface energy of PTFE is larger than that of PMMA.

Despite the interest in material interfaces, the mechanical properties of polymer-polymer interfaces, specifically, the fiber-matrix interfaces of fiber-reinforced composites and the mixture of amorphous-crystalline in bio-polymer fibers, by MD simulation have yet to be reported.

§ 4.2 Molecular Modeling of Polymer Bulks

§ 4.2.1 One-chain Bulk Simulation of Polymer Bulks

In the present modeling of one-chain polymer bulks, polycarbonate (PC), polypropylene (PP) and poly(ε-caprolactone) (PCL) were chosen for the modeling and simulation. Using the Amorphous Cell Method, the modeling of PC, PP and PCL samples follows the assumptions of Cohen and Turnbull’s [Uhlmann and Kreidl 1983] concept of glasses:

1) The model does not incorporate thermal motion and the temperature effects are incorporated through specification of the density,

2) The polymer is represented as an ensemble of microscopic structures,

3) Bond lengths and bond angles are fixed, according to RIS theory, and the molecular chains move through bond rotations,

4) Backbone carbon atoms and pendant hydrogen atoms are treated explicitly but side groups are lumped into single “quasi-atoms” of specified size.
A PC chain comprising 17 monomers is prepared and packaged in an amorphous cell using the above theories and shown in Fig. 4.1. In the study of this chapter, unless indicated, the periodic boundary condition is used for all the three dimensions.

The density of the bulk PC is 1.2 g/cm$^3$, which was specified for PC at 300K [Mark 1996]. The amorphous cell length, with the parent chain of 17 monomers, is 1.816 nm (Fig. 4.1b), about two times of the energy cutoff distance 0.85 nm (based on neutral groups of atoms) for the nonbonded interactions. If the cell length is shorter than two times of the cutoff, atoms may interact with the periodic image of themselves. The energy of the sample was first minimized to achieve equilibrium. Then the amorphous cell was relaxed by NPT molecular dynamics under tensile stress at increments of 0.02 GPa in the $z$-direction with 5 ps relaxation.

To get the statistical mean values, five samples were modeled. In the sampling, Parrinello-Rahman constant-stress molecular dynamics [Parrinello and Rahman 1981] with a Nose-Hoover thermostat [Nose 1984ab and Hoover 1985] was employed as the
simulation technique. The *cvff* forcefield [Sun et al 1994] was used. The equations of motion were integrated with the velocity version of the Verlet algorithm [Allen and Tildesley 1987] at 300K with a time step of 1.0fs. The PC bulk properties of the mean values by the five samples are listed in Table 4.1 and shown in Fig. 4.4 respectively.

![Fig. 4.2 (a) A PP parent chain with 76 monomers in an amorphous cell, where the dashed cubic represents the main cell, the gray balls represent hydrogen atoms and the darks represent carbon atoms. (b) Strain-Stress Curve of PP and PC bulk under tensile stress](image)

Using the same sampling strategies, the PP and PCL bulks were also modeled. The densities of PP and PCL of 300K are 0.892g/cm³ and 1.145g/cm³. The amorphous cell length of PP is 1.814nm using 76 monomers (Fig. 1.1) in the parent chain, as shown in Fig. 4.2a. The stress-strain curves of PP and PC are shown in Fig. 4.2b.

![Fig. 4.3 PCL amorphous cell of 18-monomer-chain. Red sphere: oxygen atom.](image)
The parent chain of the 18-monomer PCL in the amorphous cell, with cell length of 1.439nm, is shown in Fig. 4.3.

§ 4.2.2 Mechanical Properties of Amorphous poly(ε-caprolactone)

(PCL)

After preparing the PP, PC and PCL bulks, the mechanical properties of both static and dynamics were studied using the methods described in Chapter 3.3.2. Table 4.1 lists the static elastic properties for PP, PC and PCL using equation 3.73, which was obtained by energy minimization of the amorphous cells. The kinetic energy and temperature were not accounted for. Table 4.1 shows that the results for tensile modulus from molecular simulation are close to the experimental data range, with PP at 0.9–1.5 GPa, PC at 2.3–2.5 GPa and PCL at 0.5–1.5GPa [Mark 1996].

The resulting amorphous cell is then analyzed with molecular dynamics in which the temperature is considered by adding atomistic velocities. In the present study, the mechanical properties of PCL fiber with its degradable biopolymer polycrystalline structure, was obtained from MD analysis and the numerical results are compared with a recent experiment on PCL nanofibers. The PCL fiber consists of a mixture of co-existing phases of both amorphous and crystalline polymer chains. Although the simulation methodology also involves the use of the Amorphous Cell algorithm, very few MD studies into the mechanical properties of polymer amorphous-crystalline interfaces have been reported.

Using a controlled incremental strain rate [Deng et al 2004] with relaxation time of 4000 fs between strain increments, the stress strain curve can be obtained. One of the bulk
configurations of the 18-monomer-chain PCL with pure amorphous cell at 70% strain is shown in Fig. 4.4. In the simulation, the COMPASS forcefield [Sun 1998] combined with CDiscover [Cerius2, Accelrys Inc. 2001] was used.

Table 4.1 Mechanical properties of PP, PC and PCL bulks.

<table>
<thead>
<tr>
<th>Property</th>
<th>PC</th>
<th>PP</th>
<th>PCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile modulus (GPa)</td>
<td>3.07</td>
<td>1.64</td>
<td>2.015</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.39</td>
<td>0.36</td>
<td>0.45</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>4.80</td>
<td>1.92</td>
<td>6.695</td>
</tr>
<tr>
<td>Shear modulus (GPa)</td>
<td>1.10</td>
<td>0.60</td>
<td>0.695</td>
</tr>
<tr>
<td>Lame Const. $\lambda$ (GPa)</td>
<td>4.07</td>
<td>1.52</td>
<td>6.23</td>
</tr>
<tr>
<td>Lame Const. $\mu$ (GPa)</td>
<td>1.10</td>
<td>0.60</td>
<td>0.69</td>
</tr>
</tbody>
</table>

![Fig. 4.4 A pure PCL amorphous cell of 18-monomer chain bulk cell under 70% tensile strain.](image)

Figure 4.5 shows a typical stress-strain curve of the molecular dynamics calculation for the 18-monomer-chain PCL amorphous cell. In the tensile loading of the 100% amorphous PCL bulk, three stages of the tensile deformation are clearly shown. Initially, under tensile loading, the amorphous PCL bulk undergoes elastic deformation in which the monomers slide under the resistance of van der Vaals forces. In the second stage, or
the yielding plateau, the polymer chains start to overcome the torsional energy barrier, which is much lower than the bond stretch and bond angle potential. During this stage of chain deformation, the backbone bonds rotate, instead of stretch, along the loading direction to sustain the strain increment.

When all the bonds of the backbone have rotated and are aligned to the external loading direction, they start to stretch to overcome bonding potential until breakage. The last stage is also called strain hardening in which the stress increases very fast because the bonding potential barrier is very high.

The tensile deformation of the 18-monomer-chain PCL bulk, however, is an ideal case and cannot compare quantitatively with real PCL fibers. The main reason is that at room temperature, the polymer chains of fibers usually form a polycrystalline structure because the chain is very long and entangled (§ 4.2.4). Another important factor influencing the strength of the real fiber is that many defects form during the manufacturing process.

---

Fig. 4.5 Stress-strain curve of an 18-monomer-chain amorphous bulk.
These defects often initiate void growth leading to stress concentration under tensile loading. The voids will propagate with strain increment and the fiber fails before or during the early strain hardening stage. For nanofibers, the thinner the fibers are, the less the number of defects; and thus the higher the failure stress. This is also observed in the experiments by Ng et al. [2005] [Fig. 4.6]. Thus, the MD calculation is compared to actual tensile testing of the thinnest nanofiber.

Fig. 4.6 Diameter dependency of PCL nano fiber under tensile loading [Ng et al 2005].

§ 4.2.3 Mechanical Properties of 100% Crystalline PCL

In the Amorphous Cell algorithm, the interaction of polymer atoms consists of bonding potentials for polymer chains in amorphous state and is not able to treat 100% crystalline polymers. Thus the PCL crystalline bulk is modeled and analyzed using the CAMbridge
Serial Total Energy Package (CASTEP), an *ab initio* molecular simulation code [Accelrys Inc. 2001]. The PCL crystalline configuration that was obtained is shown in Fig. 4.7.

![Fig. 4.7 100% crystalline PCL bulk.](image)

In Fig. 4.7, the periodic boundary condition is used on all three dimensional directions. Geometry optimization is first performed with CASTEP to obtain the ground state of the PCL crystalline conformation. The mechanical properties of the 100% crystalline bulk were then determined by prescribing an axial extension on the cell, one direction at a time. The incremental strain applied to the periodic cells at each step of the simulation was,

\[
de_x = \begin{bmatrix}
1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix} \times 10^{-3}
\]  

(4.1)

If \(L_i\) (i=1~3) are the cell lattice constants, then the new cell lengths \(L'_i\) after the strain increment are

\[
L'_i = L_i + u_i (L)
\]  

(4.2)
where \( u_i \) is the displacement of the cell lattice. Equation 4.2 can be written as:

\[
L_i' = \sum_{j=1}^{3} \left( \delta_{ij} + \frac{\partial u_i(L)}{\partial L_j} \right) L_j
\]  
(4.3)

where the total energy \( U = \frac{\partial u_i(L)}{\partial L_j} \) is unchanged under rotations of the crystal cell.

Thus the strain tensor \( \varepsilon \) of the cell is:

\[
\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i(L)}{\partial L_j} + \frac{\partial u_j(L)}{\partial L_i} \right)
\]  
(4.4)

Using Voigt notation, with 1~6 representing, respectively, \( xx \), \( yy \), \( zz \), \( yz \), \( xz \) and \( xy \), the total internal energy \( U(V,\{e_i\}) \) can be expressed as:

\[
U(V,\{e_i\}) = U(V) + V \sum_{i=1}^{6} \sigma_i e_i + \frac{V}{2} \sum_{i,j=1}^{6} c_{ij} e_i e_j + \ldots
\]  
(4.5)

where \( V \) corresponds to the cell volume with unstrained energy and the strain tensor is:

\[
C = \begin{pmatrix}
  e_1 & \frac{1}{2} e_6 & \frac{1}{2} e_5 \\
  \frac{1}{2} e_6 & e_2 & \frac{1}{2} e_3 \\
  \frac{1}{2} e_5 & \frac{1}{2} e_3 & e_3
\end{pmatrix}
\]  
(4.6)

The potential energies of each deformed cell were obtained by CASTEP for every strain increment. By applying equations 4.4~4.6 with the potentials from CASTEP, the elastic stiffness matrix of the 100% PCL crystalline [Fig. 4.7] is obtained [GPa]:

\[
C = \begin{pmatrix}
  1.279082 & 0.000482 & -0.000441 \\
  0.000482 & 1.282138 & -0.001332 \\
 -0.000441 & -0.001332 & 1.130346
\end{pmatrix}
\]
§ 4.2.4 Molecular Modeling of Polycrystalline PCL

During the last two decades, significant advances have been made in the development of biodegradable materials for biomedical applications as well as industrial applications. Generally, conventional polymers such as polycarbonate (PC) and polypropylene (PP) take a long time to degrade and are therefore not suitable for applications in which plastics are used for short time periods and then quickly disposed of. Biodegradable polymers with hydrolyzable chemical bonds are being researched extensively for agricultural, biomedical, packaging, and pharmaceutical applications. Biodegradable polymers are designed to degrade upon disposal by the action of living organisms. Extraordinary progress has been made in the development of practical processes and products from polymers such as starch, cellulose, and lactic acid [Gross and Kalra 2002]. A variety of natural, synthetic, and biosynthetic polymers are bio- and environmentally degradable. A polymer with C-C backbone tends to be nonbiodegradable, whereas heteroatom-containing polymer backbones confer biodegradability. Biodegradability can therefore be engineered into polymers by the judicious addition of chemical linkages such as anhydride, ester, or amide bonds, among others. The mechanism for degradation is by hydrolysis or enzymatic cleavage resulting in a scission of the polymer backbone.

The degradation products often define the biocompatibility of a polymer, not necessarily the polymer itself. Poly(esters) based on polylactide (PLA), polyglycolide (PGA), polycaprolactone (PCL), and their copolymers have been extensively employed as biomaterials. Nano-fibers from the above biodegradable polymers can be produced by electrospinning [Fig. 4.8].
In the manufacturing of fibers like electrospinning, different crystallizations results from different polymer chain lengths in different environments [Fig. 4.9]. For entangled long polymer chains, a polycrystalline structure is generally formed with the presence of both amorphous and microcrystalline domains/phases. The polymer chain participates simultaneously in both types of domains. A polymer chain may even participate in more than one crystalline and/or more than one amorphous domain [Fig. 4.9].
Recently, an interesting experiment was carried out to study the mechanical properties of PCL nano-fiber [Ng et al 2005]. The polycrystalline structures of the PCL nanofiber were studied by using atomic force microscopy (AFM). Figure 4.10 is a typical AFM image of the PCL nanofiber surface from which interlamellar fragmentation re clearly shown. From their AFM experimental results, it is shown that the deformation behavior of single nanofiber can be elucidated by a series of microstructural rearrangements during critical stages of tensile loading, namely linear elastic deformation, yielding, plateau and strain hardening [Ng et al 2005].
However, an interesting phenomenon that was observed was the formation of many necked regions along the PCL nanofiber under tensile loading before the fiber smoothed out again at larger strains [Fig. 4.11]. MD modeling and simulation was performed to compare and explain the experimental results.

As shown in Figs. 4.8 and 4.9, physical PCL nanofibers have polycrystalline structures at room temperature. Thus, the strength of the fiber is mainly controlled by the interfaces of crystalline and amorphous phases. Figure 4.11 shows the failure phenomena of the polycrystalline structure is different from the failure of metals under tensile loading in which usually only one necked region is formed and broken consequently.

The multiple necks formed in the PCL nanofiber is due to the chain folded lamellas which are connected by chains in amorphous states. The amorphous parts, under tensile loading, will slide and stretch first while the crystalline lamellas remain rigid. The failure difference between the polycrystalline and pure amorphous regions is that before strain hardening of the former, the crystalline lamellas are relaxed before the bond stretching of amorphous chains. The strain hardening stage of the polycrystalline structure will start until full relaxation of the crystalline lamella, in which all the backbone bonds are relaxed and aligned to the direction of external loading as in the amorphous part.

To model the polycrystalline structure with the Amorphous Cell algorithm, bond restraints were introduced to “freeze” part of the parent chain to simulate the crystalline lamella. The restraints are released after the amorphous bonds are fully stretched and aligned to simulate the relaxation of the crystalline lamella. By changing the different
numbers of monomers to restrain along the parent chain, the relationship of mechanical properties between polycrystalline structures with different crystalline percentage were obtained. In the present study, the torsional degree of freedom was restrained to simulate the rigid crystalline lamella.

To model the polycrystalline structure of PCL nanofibers with Amorphous Cell, a larger PCL bulk than the 18-monomer-chain bulk used previously was required. A 54-monomer-chain bulk cell was built and analyzed. Then 20% of the monomer along the parent chain backbone was restrained and MD simulation was undertaken to obtain the mechanical properties. The stress strain curve was obtained using the same algorithm as for the 18-monomer-chain bulk. The two stress-strain curves are plotted in Fig. 4.12.

![Stress-strain curve of 0% and 20% crystalline PCL polymer](image)

**Fig. 4.12 Stress-strain curve of 0% and 20% crystalline PCL polymer.**

Figure 4.12 clearly shows that the existence of crystalline lamella influences the mechanical behavior of the polymer. For instance, 20% crystalline PCL polymer has a shorter yield strain plateau than that of pure amorphous bulk, i.e., the pure amorphous
polymer can sustain larger strain compared with the 20% crystalline polymer before reaching the strain hardening stage. However, the differences between the stress values in the yield strain plateau are not significant.

To get a systemic comparison of the influence of percentage crystallinity, the PCL polymer bulk were modeled and simulated with 20%, 40%, 60% and 80% of the 54 monomers along the chain backbone restrained. The stress strain relationships are then obtained and plotted with the pure amorphous (0% crystalline) PCL [Fig. 4.13].

![Stress-strain curve of different crystalline percentages of PCL polymer.](image)

Fig. 4.13 Stress-strain curve of different crystalline percentages of PCL polymer.

It is seen that in the elastic stage, the tensile modulus, or the trendline of the curve, increases as the crystalline concentration increases. This is because a high crystalline concentration means there are less amorphous state monomers, which with their higher mobility than the crystalline part, can sustain the stress at the van der Vaals scale. It is also apparent that the yield stresses, which correspond to the yield strain plateau, increases with the increase of crystalline percentages of PCL polymer. Moreover, there is
no clear yield strain plateau in the curve of 80% crystalline PCL polymer. The phenomenon is close to the behavior of actual crystal materials. The relationship can be clearly observed by comparing the mechanical properties of 40% and 60% crystalline concentration PCL polymer, by the releasing the restrained monomers after the yield strain plateau stage [Fig. 4.14].

From Fig. 4.14, it is shown that 40% crystalline concentration can sustain larger failure strain albeit a lower yield stress for the yield strain plateau stage. On the other hand, 80% crystalline concentration PCL polymer has the highest yield stress and lowest yield strain. At room temperature, the crystalline concentration of PCL fiber is usually around 60%. Thus, the 60% crystalline PCL polymer model was studied in greater detail to compare with the experimental results by Ng et al.
§ 4.2.5 Comparison of MD and Experimental Results

The results of molecular dynamics and AFM experiment for elastic deformation of 60% crystalline concentration PCL nanofiber are plotted in Fig. 4.15.

It is seen that the elastic responses (<0.05 strain in the study) are very similar for the results from molecular dynamics and experimental data, although the MD results predicts a stress value an order of magnitude larger than that of the experiment. This difference is expected because in the MD simulation the PCL chain is perfect without defect.

Figure 4.15 shows that the trend predicted by MD is reasonable and comparable with that of experimental data. However, it should be noted that the strain rate used in MD is 0.1%/5ps. This is very high compared to the actual experiments. An unrealistically high strain rate is needed for MD simulation to keep computational time reasonable. Even with such high strain rates, it usually takes several months on a high performance workstation for just one nano-second relaxation.
To explain the multiple necked regions along the PCL nanofibers under tensile loading in the experiment, several snapshots of the 60% crystalline concentration PCL polymer under tensile loading in the MD simulation are plotted in Fig. 4.16.

Figure 4.16-a shows the initial configuration of 60% crystalline concentration PCL polymer. The monomers within the yellow circles were restrained to simulate the crystalline lamella. It shows that the crystalline part (in yellow circles) remain crystalline while the backbone bonds in amorphous status are aligned to the loading direction under tensile loading at 70% strain [Fig. 4.16-b]. The restrained parts correspond to the crystalline lamella in experiment [Fig. 4.10-11]. The configuration can explain that the multiple necks in Fig. 4.11 are formed due to the stretching of the amorphous part in the inter-lamella region along the PCL nanofiber. Figure 4.16-c shows the 60% crystalline PCL under 160% strain. At this strain, the crystal lamella begins to slide and the
deformation becomes more uniform along the fibers. In Fig. 4.16-d, the PCL polymer is under 200% strain; all parts of the chain backbone are stretched uniformly.

From the molecular simulations of the different crystalline concentrations of the PCL polymer, it is shown that the present MD algorithm is capable of simulating and explaining the macro experimental results for the polycrystalline structures, which are seldom explored by computer simulations. Using MD modeling and simulation, the trend of mechanical property changes due to crystalline concentration can be reasonably predicted and are comparable to AFM experimental results. However, it should be noted that the above algorithm to simulate the crystalline lamella in the polymer chain is relatively simple because the relaxation of the crystal lamella was controlled manually and somewhat arbitrary during the tensile loading.

§ 4.3 Multi-chain Simulation of Polymer

To compare the above results of one-chain amorphous cell, multi-chain simulation was also carried out. Three kinds of PP samples, with (38-monomer × 16-chain), (76-monomer × 8-chain), (152-monomer × 4-chain), and one 17-monomer × 8-chain PC sample were prepared. Due to the limitation of the computer resources, only one sample was prepared for each of the bulk. Using the above multi-chain bulk, five interfaces were built, 8-chain PP/PC, 4-chain PP/PC, 16-chain PP/PC, 16-chain PP/8-chain PP and 16-chain PP/4-chain PP. An external tensile stress of 1.1GPa was added perpendicular to the interfaces of the five samples. Figure 4.17 shows the density profile of the 16-chain/4-chain and 16-chain/8-chain PP/PP interface under tension.
Fig. 4.17 Density change of PP-PP interface, of 16-chain/4-chain and 16-chain/8-chain, under tensile stress.

From Fig. 4.17, it can be seen that the interface density increases with the stretching of the chains. This is because as the chains were pulled apart, the interface column decreased. Figure 4.18 shows the stress relaxation of the five interface samples under 1.1GPa tensile stress. From Figs. 4.17 and 4.18, it can be seen that in the Amorphous Cell
algorithm, the results for different chains are similar. It shows that one chain interface system can obtain results close to those from much larger multi-chain systems.

§ 4.4 Polymer Surface and Interface Simulation

To study the physical and mechanical properties of polymer surface and interfacial systems, a vacuum is introduced into the cell to simulate the surface interface. The surface films of the PP and PC were formed by extending in $z$ dimension of the periodic box to 10nm so that the parent chains no longer interacts with its image along $z$ dimension, which is the coordinate normal to the surface of the films [Misra et al 1995]. To reach equilibrium state, the surface films were then subjected to molecular mechanic (MM) energy minimization followed by 50ps of NVT molecular dynamic simulation at 300K. During the 50ps simulation, the snapshots with the lowest energy of the NVT ensembles were chosen and minimized using MM energy minimization techniques to create the thin film structures.

The energies of the bulk and surface cells of PP and PC are presented in the second and third columns of Table 4.2 and Table 4.3, respectively. The contributions of the potential energy to the mean surface energy are presented in the last column of Table 4.2 and Table 4.3. The surface energy $\gamma$ are obtained as [Clancy and Matice 1999]:

$$\gamma = \frac{<E_{surface} - E_{bulk}>}{2A}$$

(4.7)

where $A$ is the area of one of the two surfaces of the thin film, and $E_{surface}$ and $E_{bulk}$ are the energies of the bulk and surface cells. The calculated values are very close to the
experimental result of surface energy with 25.7 mJ/m² for PP and 45 mJ/m² for PC [Mark 1996]. The COMPASS force field [Sun 1998] was used for all the polymers, except PP.

Table 4.2 Average energies (kJ/mol) for five bulk cells and surface cells of PP, and the contributions to the surface free energies (mJ/m²) deduced from their differences.

<table>
<thead>
<tr>
<th>Component</th>
<th>PP bulk cells</th>
<th>Surface cells</th>
<th>Surface energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond stretching</td>
<td>111.04</td>
<td>98.57</td>
<td>-3.14</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>832.06</td>
<td>807.36</td>
<td>-6.22</td>
</tr>
<tr>
<td>Torsions</td>
<td>-2084.09</td>
<td>-2125.82</td>
<td>-10.51</td>
</tr>
<tr>
<td>Nonbond</td>
<td>216.73</td>
<td>440.79</td>
<td>56.43</td>
</tr>
<tr>
<td>Total</td>
<td>-924.27</td>
<td>-779.1</td>
<td>36.56</td>
</tr>
</tbody>
</table>

Table 4.3 Average energies (kJ/mol) for five bulk cells and surface cells of PC, and the contributions to the surface free energies (mJ/m²) deduced from their differences.

<table>
<thead>
<tr>
<th>Component</th>
<th>PC bulk cells</th>
<th>Surface cells</th>
<th>Surface energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond stretching</td>
<td>249.38</td>
<td>244.82</td>
<td>-1.15</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>392.12</td>
<td>382.01</td>
<td>-2.55</td>
</tr>
<tr>
<td>Torsions</td>
<td>-728.94</td>
<td>-705.71</td>
<td>5.85</td>
</tr>
<tr>
<td>Nonbond</td>
<td>-1078.71</td>
<td>-970.27</td>
<td>27.32</td>
</tr>
<tr>
<td>Cross terms</td>
<td>-392.07</td>
<td>-383.51</td>
<td>2.16</td>
</tr>
<tr>
<td>Restraint</td>
<td>-98.49</td>
<td>-54.76</td>
<td>11.02</td>
</tr>
<tr>
<td>Total</td>
<td>-1649.64</td>
<td>-1481.21</td>
<td>42.44</td>
</tr>
</tbody>
</table>

The interfaces were constructed by putting the two thin films of polymers together with surfaces contacting but without overlapping (Fig. 4.19). The PP and PC surface films were used to build the PP-PP and PP-PC interfaces. For the later case, in which the periodic boundary conditions are different, the smaller periodic box (PP) was chosen. The potential energy of the interface cell was minimized using MM energy minimization.
techniques and then subjected to 300ps of \textit{NVT} MD simulations at 300K. During the 300ps simulation, the snapshots with the lowest energy of the \textit{NVT} ensembles were chosen and minimized using MM energy minimization techniques to create the thin film structures.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{building.png}
\caption{Building of PC-PP interfaces (left: PP, right PC)}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{stress.png}
\caption{Stress relaxation of polymer interfaces.}
\end{figure}
The mechanical properties of the PP-PC and PP-PP interfaces were also investigated. An external stress of 1.1GPa was applied to the PP-PC and PP-PP interface cells normal to the interface plane (Fig. 4.20).

§ 4.5 Molecular Modeling of Composite Interfaces

In the present study, the interfaces of a matrix and coupling agents are modeled. The matrix used is polycarbonate (PC) and the coupling agents studied are gamma amino-propyl-triethoxysilane (AMPTES) and stearic-propyl-triethoxysilane (SPTES). Two atomistic models of SPTES-PC and AMPTES-PC interfaces were constructed and an algorithm is proposed to investigate the mechanical properties of polymer interfaces.

§ 4.5.1 Molecular Models

Figure 4.21 shows a fiber embedded in matrix with silanes present, as typically found in fiber-reinforced composites. The interface comprises a glass fiber and PC matrix with a coupling agent - AMPTES or SPTES. The chemical structures of PC, AMPTES and SPTES are shown in Fig. 4.22.

*Fig 4.21 Model of fiber/matrix interfaces.*
In the fabrication of fiber-reinforced composites, the fiber is first cured with some coupling agents. The reactions give rise to a crosslinking process, which in the present case (glass fiber cured with silanes) is

\[
3E\uparrow{\text{OH(\textit{excess})}} + \begin{array}{c} \text{OH(\textit{excess})} \\ \text{OH(\textit{excess})} \end{array} \xrightarrow{\text{CH}_3\text{CH}_2\text{OH}} 3E\uparrow{\text{OH(\textit{excess})}} + \begin{array}{c} \text{O} \\ \text{O} \end{array} \text{Si-R}
\]

Fig. 4.22 Structures of the matrix and silanes.

(a) Polycarbonate (PC) monomer.

(b) Gamma amino-propyl-triethoxysilane (AMPTES)

(c) stearic-propyl-triethoxysilane (SPTES)

In the fabrication of fiber-reinforced composites, the fiber is first cured with some coupling agents. The reactions give rise to a crosslinking process, which in the present case (glass fiber cured with silanes) is
Here, $R-$ is *stearie-propyl* or *amino-propyl* and $E$ is $-\text{CH}_2\text{CH}_3$ in the present models.

Figure 4.23 shows the molecular structure at the glass-PC interface together with AMPTES after the crosslinking reaction given in equation 4.8. Due to the strong $-\text{Si-O-Si}-$ bonds between the glass fiber and silanes, the “weakest site” of the composite interfaces would be at either the interface of the silane-matrix or inside the bulk of silanes and/or matrix (Fig. 4.23). Hence, it is sufficient to model just the PC and silane and the interfaces between them to study the mechanical properties of fiber-matrix interfaces.

In the MD calculations, the Parrinello-Rahman constant-stress molecular dynamics [1981] with a Nose-Hoover thermostat [Nose 1984a,b; Hoover 1985] was employed. COMPASS [Sun 1998], a Class II force field [Hwang et al 1994], was chosen for the MD calculation because it was developed from cvff [Sun et al 1994] to accommodate most organic molecules, including silanes and rings.

---

**Fig. 4.23** Molecular structures of glass-PC interface with AMPTES present.
§ 4.5.2 Molecular Modeling of Bulk Materials

The Amorphous Cell procedure was used to build atomistic models of the PC and silane bulk systems. The main cells have one main chain with 17 monomers for PC, 16 molecules for AMPTES and seven molecules for SPTES (Fig. 4.24). To obtain a statistical average, five amorphous cell samples of each material were built. The bulk densities [Mark 1996] and cell constants of the amorphous cells are listed in Table 4.4. The energies of the cells are first minimized using the conjugate gradient method with a convergence criterion of RMS atomic force cutoff of 0.1 kcal/mol·Å. The molecules in each amorphous cell are set to vibrate by NVT molecular dynamics for 50ps at 300K. The configuration with the minimum potential energy is then selected and minimized to a convergence of 0.01 kcal/mol·Å with the conjugate gradient method. The resulting amorphous cells are then analyzed for their mechanical properties.

Table 4.4 Cell properties of bulk materials using Amorphous cell model.

<table>
<thead>
<tr>
<th></th>
<th>PC</th>
<th>AMPTES</th>
<th>SPTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/cm³)</td>
<td>1.20</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>Cell constants(Å)</td>
<td>18.16</td>
<td>18.36</td>
<td>18.66</td>
</tr>
</tbody>
</table>
In the simulations, the equations of motion were integrated with the velocity version of the Verlet algorithm [Allen and Tildesley 1987] at 300K with a time step of 1.0fs. A cutoff distance of 8.5 Å (based on neutral groups of atoms) was used for the nonbond interactions. The static mechanical properties are listed in Table 4.5. For completeness, information on PC is also listed with AMPTES and SPTES.

Table 4.5 Mechanical properties of bulk materials using Amorphous cell model (GPa).

<table>
<thead>
<tr>
<th></th>
<th>PC</th>
<th>AMPTES</th>
<th>SPTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile modulus</td>
<td>3.07</td>
<td>1.64</td>
<td>3.45</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.39</td>
<td>0.36</td>
<td>0.34</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>4.80</td>
<td>1.92</td>
<td>3.57</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>1.10</td>
<td>0.60</td>
<td>1.29</td>
</tr>
<tr>
<td>Lame Const. Lamda</td>
<td>4.07</td>
<td>1.52</td>
<td>2.72</td>
</tr>
<tr>
<td>Lame Const. mu</td>
<td>1.10</td>
<td>0.60</td>
<td>1.29</td>
</tr>
</tbody>
</table>
§ 4.5.3 Molecular Modeling of Surfaces and Interfaces

The thin surface films of PC and silanes are constructed from the amorphous cells by extending the periodic box of the cells in the z-direction to about 60 Å and then padding the end of the box with a vacuum of about 50 Å in length as in the previous simulation. The resultant cells are representative of thin films with the z-axis being the thickness direction.

The thin films are then subjected to molecular energy minimization followed by 50 ps of NVT MD simulation at about 300K. To excite the thin films, the cells are heated to about 600K for 100 ps followed by 100 ps MD at about 300K. The snapshots with lowest potential energy were chosen to construct the final surface thin film conformations through energy minimizations to a convergence of 0.1 kcal/mol·Å with the conjugate gradient method.

![Fig. 4.25 AMPTES surface thin films padded with vacuum in one cell.](image)

Figure 4.25 shows the amorphous cell of the thin surface film of AMPTES, in which the vacuum length is about 50 Å. The energies of the bulk and surface cells of the AMPTES
and SPTES are presented in the second and third columns of Tables 4.6 and 4.7, respectively. The values are the averages of five samples for each amorphous cell.

*Table 4.6 Energy components (kJ/mol) of bulk cells and surface cells of AMPTES, and their contributions to free surface energy (mJ/m²).*

<table>
<thead>
<tr>
<th></th>
<th>AMPTES bulk</th>
<th>Surface cells</th>
<th>Surface energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Potential Energy</td>
<td>-3792.35</td>
<td>-3718.96</td>
<td>18.08</td>
</tr>
<tr>
<td>Restraint</td>
<td>-91.53</td>
<td>-59.43</td>
<td>7.9</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>12.59</td>
<td>11.89</td>
<td>-0.17</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>162.95</td>
<td>162.74</td>
<td>-0.05</td>
</tr>
<tr>
<td>Torsion</td>
<td>-1506.23</td>
<td>-1500.15</td>
<td>1.50</td>
</tr>
<tr>
<td>Cross terms</td>
<td>-71.01</td>
<td>-70.17</td>
<td>0.21</td>
</tr>
<tr>
<td>Nonbond</td>
<td>-2299.08</td>
<td>-2263.83</td>
<td>8.69</td>
</tr>
</tbody>
</table>

In Tables 4.6 and 4.7, the total energies listed on the top of each column are the sum of interactions for internal bonding, cross terms and nonbonding energies. The internal bonding energy is the sum of harmonic and anharmonic terms for bond stretching, angle bending and bond torsion. The cross term includes the coupling influence of bond-bond, bond-angle, angle-angle, angle-angle-torsion, bond-torsion and angle-torsion terms. The nonbonding energy is the sum of repulsive and dispersive van der Waal forces and electrostatic interactions. The contributions of the potential energy to the mean surface energy are presented in the last column of Tables 4.6 and 4.7. The results of PC are already shown in Table 4.3. The magnitudes of the energy components show that nonbonding energy has a more dominant contribution to the free surface energy than the internal bonding interaction energy. The result is consistent with other reports [Natarajan

98
et al 1998; Clancy and Mattice 1999]. It shows that SPTES has higher surface tension than AMPTES.

Table 4.7 Energy components (kJ/mol) of bulk cells and surface cells of SPTES, and their contributions to free surface energy (mJ/m²).

<table>
<thead>
<tr>
<th>Energy Component</th>
<th>SPTES bulk</th>
<th>Surface cells</th>
<th>Surface energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Potential Energy</td>
<td>-2603.67</td>
<td>-2522.98</td>
<td>19.25</td>
</tr>
<tr>
<td>Restrains</td>
<td>-95.83</td>
<td>-44.83</td>
<td>12.41</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>26.81</td>
<td>26.29</td>
<td>-0.12</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>290.24</td>
<td>287.97</td>
<td>-0.54</td>
</tr>
<tr>
<td>Torsion</td>
<td>-1585.45</td>
<td>-1585.20</td>
<td>0.06</td>
</tr>
<tr>
<td>Cross terms</td>
<td>-98.12</td>
<td>-96.46</td>
<td>0.40</td>
</tr>
<tr>
<td>Nonbond</td>
<td>-1141.27</td>
<td>-1111.55</td>
<td>7.09</td>
</tr>
</tbody>
</table>

Fig. 4.26 PC-AMPTES interface. (left: PC, right: AMPTES).
Material interface cells were created by putting two thin films together with the surfaces in contact without overlapping. The potential energy of the contacting films was minimized followed by 100ps of MD simulations at about 300K. The cells are then heated at about 600K for 100ps to facilitate the diffusion of the two materials across the interface. This is followed by 100ps of NVT MD calculations at 300K to simulate annealing. The snapshots with lowest potential energy were chosen and subjected to energy minimization again to a convergence of 0.1 kcal/mol·Å with the conjugate gradient method to obtain the final interface conformations. Two material interfaces, PC-AMPTES (Fig. 4.26) and PC-SPTES, were constructed in this manner.

§ 4.5.4 Work of Adhesion of Polycarbonate/Silane Interfaces

The work of adhesion $W_{AB}$ per unit area is obtained from the difference in energy between the interfacial system and the energy of the two individual thin films which were used to build the interface.

$$W_{AB} = \frac{(E_{film\ A} + E_{film\ B} - E_{interface})}{A}$$

Then, with the relationship of the Dupre equation [Dupre 1869], the interfacial tension $\gamma_{AB}$ can be obtained from,

$$\gamma_{AB} = \gamma_A + \gamma_B - W_{AB}$$

where the free surface energies $\gamma_A$ and $\gamma_B$ are obtained from equation 4.1.

Figure 4.26 shows the interface cell of PC-AMPTES and Table 4.8 shows the work of adhesion calculations of the two interfacial systems using equation 4.3. The equilibration process of the PC-silane interfacial cells is shown in Fig. 4.27, in which the thickness of the interfaces is shown to approach a constant value. The energy of the PC-AMPTES and
PC-SPTES interfaces are listed in the second and fourth columns of Table 4.8 and the work of adhesion are listed in the fourth and seventh columns, respectively. Each component of the energy contributions is also listed. Here, the work of adhesion are obtained by equation 4.9, in which the energy of the two surface films is calculated using the thin films in each of the final cells separated by 200 Å.

Table 4.8. Energy components (kJ/mol) of PC-silane interface cells, and their contribution to work of adhesion (mJ/m\(^2\)).

<table>
<thead>
<tr>
<th></th>
<th>PC-AMPTES interface</th>
<th>PC-SPTES interface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_{\text{interface}})</td>
<td>(E_{s1}+E_{s2})</td>
</tr>
<tr>
<td>Total Potential Energy</td>
<td>-5285.94</td>
<td>-5173.77</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>259.98</td>
<td>254.78</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>563</td>
<td>540.84</td>
</tr>
<tr>
<td>Torsion</td>
<td>-2206.37</td>
<td>-2205.91</td>
</tr>
<tr>
<td>Cross terms</td>
<td>-458.59</td>
<td>-453.16</td>
</tr>
<tr>
<td>Nonbond</td>
<td>-3284.86</td>
<td>-3299.56</td>
</tr>
</tbody>
</table>

Fig. 4.27 Thickness of the interface cells vs the equilibrium time.
Table 4.9. Summary of surface tension, work of adhesion (mJ/m²) and interfacial tensions (mJ/m²) of PC(γₐ)-silane(γₖ) interfaces.

<table>
<thead>
<tr>
<th>Interfaces</th>
<th>γₐ</th>
<th>γₖ</th>
<th>Wₐₖ</th>
<th>γₐₖ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/AMPTES</td>
<td>42.44</td>
<td>18.08</td>
<td>55.89</td>
<td>4.63</td>
</tr>
<tr>
<td>PC/SPTES</td>
<td>42.44</td>
<td>19.25</td>
<td>58.51</td>
<td>3.18</td>
</tr>
</tbody>
</table>

Table 4.9 is a summary of the surface tension γₐ and γₖ, work of adhesion Wₐₖ and interfacial tension γₐₖ for the two PC-silane interfaces calculated from equations 4.1, 4.3 and 4.4 respectively. The predicted surface tension, work of adhesion and interfacial tension of the polymers and polymer interfaces are all within the range of reported experimental results on polymers [Lee 1991; Brandup et al 1999]. Table 4.9 also shows that the work of adhesion for PC-SPTES is higher than the work of adhesion for PC-AMPTES. This is expected because SPTES has a higher surface tension than that of AMPTES and the greater the interfacial attraction, the greater the work of adhesion.

§ 4.5.5 Mechanical Properties of Polycarbonate/Silane Interfaces

The mechanical properties of the interfaces were studied by prescribing an axial extension on the interface cells in the z-direction (i.e. thickness direction). The incremental strain applied to the periodic cells at each step of the simulation was,

\[
d\varepsilon_z = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \times 10^{-3}
\]  

(4.11)

This same strain increment was also used by Mott et al [1993] to study the plastic deformation of bulk polypropylene cells. They used energy minimization through conjugate gradient minimization which, however, does not allow for temperature effects to be included. In fact, the stress-strain relationship of polymer interfaces has never been
reported before. In the present simulation, the strain increment was applied perpendicularly to the interface with 1ps NVT MD equilibration at 300K for each increment. The force and displacement histories were recorded to obtain the stress-strain curves at room temperature. With this approach, it is possible to investigate the polymer interface at any temperature and thus attach more practical applications to the simulation.

In the MD calculations, the non-bond energy cutoff used is 5.5 Å. For an interface cell of 55 residues with 3687 atoms, it took an IBM PC, with a 2.3GHz Pentium 4 CPU, 75 minutes for 1000 steps of simulation.

Figures 4.28 and 4.29 show the density profiles of the interfaces of PC-AMPTES and PC-SPTES. The density is plotted as a function of position in the thickness direction (i.e. along the z-coordinate) on the central axial mass of the interfacial cell. From the depth of diffusion of the chains of the two constituents, the thickness of the PC-AMPTES and PC-SPTES interfaces can be determined to be about 18 Å and 8 Å, respectively. These values
are of the same order of magnitude as other reported values of immiscible polymer-polymer interfaces thickness - 10~15 Å for PP-PBD [Natarajan et al 1998], 15~20 Å for PP-PP [Clancy and Mattice 1999], 15~25 Å for PS-PMMA [Fernandez et al 1988] and 22~38 Å for PS-PE [45], and 20 Å for PMMA-PTFE [Hermes et al 1997].

It should be noted from the figures that the thickness of the PC-AMPTES interface is twice as large as that of the PC-SPTES interface even though they were formed under the same heating and annealing process and both silanes have similar free surface energies as shown in Table 4.9. This is because there are only four bonds on the backbone of tails for AMPTES chains whereas the SPTES chains have 22 bonds on the backbone of tails. It is therefore much easier for the shorter AMPTES chains to diffuse into the PC compared to the longer SPTES chains.

To study the mechanical properties of the silane-PC interfaces, the two interface cells are pulled apart by imposing incremental strains in the thickness direction according to...
equation 4.11. In the NVT simulation, the strain was added incrementally, and MD was used to equilibrate the structure for 1ps after every strain increment with time step of 1fs. The density profile of the interfaces and the stress-strain curve were obtained and are shown in Figs 4.30 ~ 4.32.

![Density profile of PC-AMPTES interface at 53% tensile strain.]

![Density profile of PC-SPTES interface at 53% tensile strain.]

Fig. 4.30 Density profile of PC-AMPTES interface at 53% tensile strain.

Fig. 4.31 Density profile of PC-SPTES interface at 53% tensile strain.
Figures 4.30 and 4.31 show the density profiles of the interfaces after 53% deformation. For each strain increment, 1000 steps of NVT MD equilibrium at 300K with a time step of 1.0fs are performed. The component of stress in the thickness direction plotted against the strain of the cell is shown in Fig. 4.32. From the stress-strain curves, the elastic-plastic properties of the interface cells can be deduced. It is interesting to note that at 53% strain, the PC-AMPTES interface can still continue to sustain tensile loads whereas the interaction in the interfacial cell of PC-SPTES has reduced significantly and is no longer able to sustain any tensile stress beyond 53% strain. This is despite the fact that the work of adhesion of PC-SPTES is larger than that of PC-AMPTES (Table 4.9). The results can be explained by comparing the density thickness changes of the interface cells from Figs. 4.28 and 4.29. The figures show that over two thirds of the PC chains were pulled out of SPTES whereas in PC-AMPTES interface, no more than half of the PC chains were
pulled out. The deeper diffusion of PC chains inside the surface of AMPTES resulted in improved ductility and enabled the AMPTES-PC interface to sustain higher strains than the SPTES/PC interface. The results can also be deduced from the equation of diffusion coefficient 2.89,

\[
D_M = N_e \frac{\Theta^2(1-\Theta)^2}{\mathcal{G}} \left[ \frac{1}{N_{\alpha}\Theta} + \frac{1}{N_{\beta}(1-\Theta)} \right]^2
\]

From the equation, it is shown that the interdiffusion of polymer-polymer interfaces is mainly controlled by the fast (short) chains and less dependent on the slow (long) chains [Brochard-Wyart 1991]. Similar observations were reported by Zhang Newby et al [1995] in which it was concluded that higher surface tension does not necessarily imply higher adhesion. The presented results also prove that the adhesion should be correlated strongly with the physical components of the interfacial systems.

Table 4.9 shows that the surface tension of PC is much larger than that of the two silanes. Thus, the PC bulk should have more attractive forces in the interface films. This was also proved by the present simulation. After pulling the interfacial system apart, some silane molecules were also found to depart and attached onto the PC film (Fig 4.33).
During the stretching of the interface cells, 1ps of NVT MD relaxation time was carried out for each strain increment. The relaxation time is kept short to keep computational

Fig. 4.34 Effect of relaxation time on stress-strain relationship of AMPTES-PC cell.

During the stretching of the interface cells, 1ps of NVT MD relaxation time was carried out for each strain increment. The relaxation time is kept short to keep computational
time manageable although it is noted that longer relaxation times of MD calculation may be needed to bring the system to equilibrium. To study the effects of relaxation time, the stretching of PC-AMPTES interface was also performed with a range of relaxation times for elongation up to 10% strain. The stress-strain curve of PC-AMPTES obtained with relaxation times of 1 ps to 20 ps between strain increments are plotted in Fig. 4.34. It shows that longer relaxation time produces a smoother curve stress-strain curve. From the stress-strain curves shown in Fig. 4.32 and Fig. 4.34, it shows that the yield stress occur at the strain of 1. This is because when the interface system is under tensile loading, the van der Vaals force reaches a maximum and the interface starts to yield. Following the yield stress, there is a plateau with the value equal to around the yield stress. This marks when the chains in the interfaces begin to stretch. The van der Vaals forces can still sustain the external tensile forces until the PC chain was totally pulled out.

§ 4.6 Conclusions

Using Amorphous Cell methods, polymer interfaces were modeled and simulated with one parent chain and multiple parent chains in the main cell, respectively. With one-parent chain, it was shown that nearly all the mechanical properties of the polymer properties can be obtained. The polycrystalline structure in the PCL fiber was modeled and calculated. The MD simulations showed the crystalline concentration dependent mechanical properties of the PCL nanofiber. The predicted stress-strain relationships were found to be reasonable and
comparable to the experimental data. The present MD simulation is able to explain the multiple necking phenomena observed during the tensile loading of the PCL nanofibers. The mechanical properties of PC-AMPTES and PC-SPTES composite interfaces were also investigated through atomistic simulation using a combination of conjugate gradient energy minimization and molecular dynamics. AMPTES and SPTES are coupling agents commonly used at the fiber-matrix interfaces of fiber-reinforced composites. The surface energies of PC, AMPTES and SPTES were obtained from atomistic simulations by considering the difference in the potential energies of amorphous cells of bulk materials and amorphous cells of materials with a free surface. The work of adhesion of the interfaces of PC-AMPTES and PC-SPTES were also determined by considering the energies of PC, AMPTES and SPTES individually and the energies of PC-AMPTES and PC-AMPTES systems. It was found that SPTES has a higher surface energy than AMPTES and, similarly, the work of adhesion of PC-SPTES was also found to be higher than that of PC-AMPTES. However, in MD simulations of PC-SPTES and PC-AMPTES systems under tension perpendicular to the interface, both systems were found to have similar flow stress but the PC-SPTES system was found to separate at a much lower strain than the PC-AMPTES system. Hence, the work of adhesion may not necessarily be an indication of the toughness of bi-material systems under mechanical loading.

However, in the application of molecular simulations, focus is usually on some features of the systems. Often, complete detailed atomic information calculations which take up large computing resources are not needed. Thus, the relatively simpler Coarse-grained Bead-spring method, with the development of relative algorithms and combination with
some specific force fields, is desirable for more realistic application of molecular simulations of composite interfaces, which is the content of the next two chapters.
Chapter V

Coarse Grain Force Fields for Composite Interfaces

The inter-atomic force field is the most important aspect in the molecular dynamics simulations. It describes the interactions between the atoms and molecules in the molecular system. Depending on the properties of interest, the construction of force fields should include the influence of electron movement, atomic vibration and van der Waals forces, etc. This chapter discusses procedures for deriving force fields for clusters of atoms in the present crosslinked system by using *ab initio* Molecular Dynamics method for the parameterization.

§ 5.1 Basic Paradigm of Force Fields in MD

The main goals of molecular mechanics are the prediction of equilibrium molecular structures and the stabilities of molecular conformations at and away from equilibrium and reproduction of the dynamics of molecular motion [Dinur and Haggler 1991]. To achieve these goals, one needs to select an appropriate force field to describe the potential energy surface. The potential controls the motions of the polymer chains because forces for molecular motion are derived from the first spatial derivatives of the potential. In general, the force fields of polymer systems are derived from the sum of bond, cross-term and nonbond interactions. In general, force fields are classified into two groups [Hwang
et al 1994]. The classical force fields (Class I), like MM2 [Allinger 1977], AMBER [Weiner et al 1984] and CHARMm [Brooks et al 1983, Smith JC and Karplus 1992], etc, consider only harmonic bond and nonbond terms, reflecting electrostatic and van der Waals interactions etc. To improve on modeling accuracy, Class II force fields, such as CFF [Maple et al 1988, 1994], which was designed specially for alkane molecules, and MM3 [Allinger 1989], include anharmonic bond and cross terms. They can therefore be used directly for isolated molecules, condensed phases, and macromolecular systems without modification [Hwang et al 1994].

\[ U = \sum \sum \sum \sum \sum \sum U_{i,jk} R_{i,j,k} + \ldots \] (5.1)

where \( \sum \sum \) notation indicates a summation over all distinct \( i \) and \( j \) pairs, \( R_{i} \) is the position of the \( i \)th monomer, \( U \) is the total potential, \( U_{m} \) is called “m-body potential”

---

Fig. 5.1 Pairwise potential vs pair distance.
The first term corresponds to an external potential for \( i \)th monomer. The second term describes pairwise interactions of the monomers, which depends only on the magnitude of the pair distance \( R_{ij} = |\mathbf{R}_i - \mathbf{R}_j| \), so it can be written as \( U_{ij}(R_{ij}) \) (Fig. 5.1).

Then the pair potential of the system can be written as:

\[
E = \sum_i E_i = \sum_{i \neq j} U_{ij}(R_{ij})
\]

(5.2)

where \( E \) is the total energy of the polymer system, \( E_i \) is the site energy for monomer \( i \) (note that \( U_{ij} \) is different for attraction and repulsion), \( U_{ij} \) and \( R_{ij} \) are the interaction energy and distance between monomers \( i \) and \( j \), respectively [Abell 1985].

\[
U_{ij}(R_{ij}) = C_i(R_{ij})\left[A \exp(-\lambda_1 R_{ij}) - B_i \exp(-\lambda_2 R_{ij})\right]
\]

(5.3)

where \( A, B_i, \lambda_1 \) and \( \lambda_2 \) are positive, for analytical convenience as well as the physical grounds that atomic orbitals decay exponentially with \( r_{ij} \) [Abell 1985]. In general, \( \lambda_1 > \lambda_2 \).

If \( \lambda_1 = 2\lambda_2 \), the Morse potential [Jensen 1999] is obtained:

\[
U_{\text{Morse}} = D \left[ 1 - e^{\alpha R_{ij}} \right]^2
\]

(5.4)

where \( D \) is the dissociation energy and \( \alpha \) is related to the force constant \( \alpha = \sqrt{k_b/2D} \).

In Eq. 5.3, \( C_i \) is an optional cutoff function to restrict the range of the potential. The first term represents the repulsive pair interaction, which is the Pauli force overlap repulsion plus interatomic electrostatic repulsion. The cutoff function \( C_i \) is used because the interatomic forces tend to zero above a certain inter-atomic distance.

Based on Eq. 5.3, an empirical pairwise potential can be constructed to describe the pairwise bonds for an atom by introducing a bond-order function [Brenner 1990]:

\[
B_y = (B_y + B_x)/2 + f_y(N_i^{(s)}, N_j, N_{ij}^{\text{conj}})
\]

(5.5)
where $f_{ij}$ is a function used to define bonding connectivity in the system. For conjugated systems and crosslinked systems, in which more than two same and/or conjugated bonds are connected to one atom, Eq. 5.5 can be well described. Furthermore, the potential was improved to allow covalent bond breaking and forming [Brenner et al 2002]. The potential Eq. 5.3, together with Eq. 5.5, have been successfully used for silicon and carbon nanotube system [Brenner et al 2002]. However, for large molecular systems like polymers and biopolymers, the molecular potentials are usually constructed by the sum of contributions from bond stretching, bond angle bending, dihedral angle and out-of-plane motion, and interactions between nonbonded atoms:

$$U = E_{\text{valence}} + E_{\text{cross-term}} + E_{\text{nonbond}}$$

(5.6)

where the cross-term potential, $E_{\text{cross-term}}$, accounts for factors such as bond or angle distortions caused by nearby atoms.

---

**Fig. 5.2 Schematic of molecular force field interactions** [Dinur and Haglar 1991].
The valence bond terms and cross terms can be interpreted as shown in Fig. 5.2. The energy of interactions between nonbonded atoms, \( E_{\text{nonbond}} \), consists of van der Waals interactions (\( E_{\text{vdW}} \)), electrostatic (\( E_{\text{Coulomb}} \)), and hydrogen bond (\( E_{\text{hbond}} \)) terms:

\[
E_{\text{nonbond}} = E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{hbond}}
\]  
(5.7)

However, the atomistic classical force field is still not used to calculate larger systems [Deng et al 2004], due to the huge computational cost of detailed bonding analysis. Using a high end workstation, Okada et al was only able to analyze \( \sim 50,000 \) atoms [2000] which is much smaller than laboratory scale of experiments.

When a polymer system is large enough, the motions and interactions of the atoms inside the function groups of the chains can be ignored and one or more function groups can be treated as one “big atom”, therefore only the motions and interactions between such “big atoms”, or beads, are considered [Baschnagel et al 2000]. Therefore, when an atomistic system is mapped to a coarse grained one, many detailed bonding interactions in Fig. 5.2 can then be hidden or omitted. It is therefore possible to simulate larger molecular systems closer to laboratory experiment with coarse grained molecular dynamics [Muller-Plathe 2002]. The principles to construct a force field of coarse grained MD for certain material should fulfill two major aspects:

1) It should be able to describe large enough systems with significantly less computer time since the coarse-grained MD simulations are several orders of magnitude faster and cheaper than atomistic classical MD. Usually, in a high performance workstation or PC cluster, material systems modeled by coarse-grained MD simulation can reach thicknesses up to 60nm, close to the small region near the surface [Stevens 2001b].
2) Sub-grain and short term phenomena should not affect macro properties significantly. Consider bond stretching for instance, the interaction of atoms inside the side groups can be omitted because the properties of interest are not sensitive to the vibration of atoms in the side groups.

§ 5.2 Construction of Force Fields for Coarse-grained MD

In molecular simulations, the motions and interactions of atoms, or beads, are controlled by force fields. With the help of quantum mechanical calculations as well as experimental results, certain empirical force fields can be constructed and parameterized accordingly for different desired molecular models [Hopfinger and Pearlstein 1984, Dinur and Hagler 1991]. Based on these approaches, several classes of force fields were developed for atomistic classical molecular dynamics simulation of polymer and biopolymer systems [Hwang et al 1994, Leach 2001]. For coarse grained molecular simulations, however, only a few force fields were reported. The original coarse-grained model used a Lennard-Jones (LJ) potential to control the interaction of monomers, or beads. Adjacent monomers along each chain are coupled through an attractive potential strong enough to prevent chain crossing with a pure repulsive LJ potential added to model the asymmetry of the pairwise bonding energy [Kremer and Grest 1990, 1995]. In the Kremer-Grest model, all the monomers interacted with a repulsive Lennard-Jones potential:

$$
U_{ij}^{LJ} = \begin{cases} 
4e \left[ \left( \frac{r_{ij}}{r_g} \right)^{12} - \left( \frac{r_0}{r_g} \right)^6 + \frac{1}{4} \right], & r_{ij} \leq 2^{1/6} r_0 \\
0, & r_{ij} > 2^{1/6} r_0 
\end{cases}
$$

(5.8)
where $r_{ij}$ is the distance between monomers $i$ and $j$. For monomers connected along each polymer chain, an attraction potential, finite-extensible nonlinear elastic (FENE) potential [Bird et al 1987], was used:

$$U_{ij}^{\text{FENE}} = \begin{cases} -0.5kR_0^2 \ln\left[1 - \left(\frac{r_{ij}}{R_0}\right)^2\right] & r_{ij} \leq R_0 \\ \infty, & r_{ij} > R_0 \end{cases} \quad (5.9)$$

To increase the degree of freedom of the chains, a chain-breakable quartic bond potential was added to describe the motions of polymer chains [Stevens 2001ab].

$$U_4(r) = \begin{cases} k_4(y-b_1)(y-b_2)y^2 + U_0 + U_{ij}^{\text{LJ}}(r) & r_{ij} \leq r_c \\ U_0, & r_{ij} > r_c \end{cases} \quad (5.10)$$

where the third term uses a repulsive LJ potential similar to Eq. 5.7. The parameters were determined by fitting the total bond force with the quartic component (first term in Eq. 5.10) to that of FENE at the first zero and minimum [Stevens 2001a]. With the breakable quartic bond potential, interfacial failure can be simulated in a large system of thickness up to 60 nm, close to the small region near the surface [Stevens 2001a].

However, the parameters of the potentials are chosen roughly, or only within the range of the magnitude of experimental data to recover the trend of the computational experiments.

Recently, several methods for parameterization of potentials were also carried out based on the atomistic classical molecular dynamics force field [Muller-Plathe 2002, Reith et al 2003]. One of the more attractive methods is an automatic parameterization of force fields which uses an optimization procedure [Sides et al 2002, 2004] with reference to physical properties that have been extensively characterized through experiments. Usually one of the properties is the radial distribution function (RDF). A merit function
was constructed using the weighted squared difference between the simulated RDF $g_s(r)$ and the target RDF $g(r)$ integrated over an appropriately chosen interval $[r_{\text{max}}, r_{\text{min}}]$.

$$f = \int_{r_{\text{min}}}^{r_{\text{max}}} w(r)(g(r) - g_s(r))^2 dr . \quad (5.11)$$

The parameters of the target coarse grained force field were adjusted according to the comparison and convergence of the properties obtained by the calculation. The potential constants obtained by this approach are close to experimental data or that of atomistic MD. However, such CG force fields are not able to describe bond forming and breakage in the simulation of polymer failure. Moreover, it is difficult for the atomistic classical molecular dynamics to simulate a crosslinking system, in which the atoms are connected as a network in space. Thus the coarse grained force field of crosslinked system cannot be generated from atomistic-based force field.

Usually, for the pairwise bond, the bonding stretching energy is associated with the bonding balance length and frequency. For instance, each Na and Cl atom of NaCl usually oscillate about their equilibrium length, $b_0 = 0.23609\text{nm}$, with a characteristic frequency $\omega = 365\text{cm}^{-1}$. Thus the bond stretching energy can be described by [Dinur and Hagler 1991]:

$$U_{\text{NaCl}} = \frac{1}{2} \mu \omega^2 (b - b_0)^2 = \frac{1}{2} k_b (b - b_0)^2 \quad (5.12)$$

where $b$ is the bond length and $\mu$ is the molecular reduced mass. In Eq. 5.12, the stretching force constant $k_b$, or the product $b\mu$, is the characteristic of NaCl in the gas phase. On the other hand, the bonding stretching energy can be written as a Taylor expansion [Jensen 1999]:
\[ E_{sr}(r-r_0) = E(0) + \frac{dE}{dR}(r-r_0) + \frac{1}{2} \frac{d^2E}{dr^2}(r-r_0)^2 + ... \]  
\( (5.13) \)

where \( E(0) \) is usually set to zero because the derivative are evaluated at \( r=r_0 \) at the minimum energy. Usually Eq. 5.13 is used to within the fourth order. However, polynomial expansions of the stretch energy go toward infinity for larger bond lengths, which is different from physical systems as shown in Fig. 5.1. The Morse potential, in fact, can describe the curve in Fig. 5.1 quite well. Expanding Eq. 5.4, the Morse potential can be written as [Dinur and Hagler 1991]:

\[ U_b(r) = D \alpha^2 (r-r_0)^2 \left[ 1 - \alpha (r-r_0) + \frac{7}{12} \alpha^2 (r-r_0)^2 + ... \right] \]  
\( (5.14a) \)

with \( \alpha = \sqrt{k_b/2D} \), it becomes:

\[ U_b(r) = \frac{1}{2} k_b (r-r_0)^2 \left[ 1 - \alpha (r-r_0) + \frac{7}{12} \alpha^2 (r-r_0)^2 + ... \right] \]  
\( (5.14b) \)

If Eq. 5.14b is terminated at the fourth order, we obtain:

\[ U_{bc}(r) = k_{bc} (r-r_0)^2 \left[ 1 - \alpha (r-r_0) + \frac{7}{12} \alpha^2 (r-r_0)^2 \right] \]  
\( (5.15) \)

where \( k_{bc}=0.5k_b \) and \( \alpha \) is now taken as a fitting parameter [Jensen 1999]. Thus, with Eqs 5.8 and 5.15, the present coarse grained force field can be constructed as:

\[ U_{cg}(r) = \begin{cases} 
U_{bc} + U_0 + U_{ij}^{LJ}, & r_{ij} \leq r_c \\
U_0, & r_{ij} > r_c 
\end{cases} \]  
\( (5.16) \)

where \( U_{bc} \) and \( U_{ij}^{LJ} \) take the forms of Eq. 5.8 and 5.15. \( U_0 \) is the residual potential energy after the breakage of bonds and this value will be determined by quantum mechanics calculation. At inter-bead distances larger than \( r_c \), the bond breaks and cannot be formed again.
It is noted that Eq. 5.16 has similar form with the quartic equation 5.10 by Stevens [2001a]. However, instead of an arbitrary force field, the force field used here will be fitted directly by *ab initio* molecular dynamics which is presented in the next chapter.

§ 5.3 Parameterization of the Force Fields

To parameterize the force field of certain molecules, the atomistic structure should be firstly geometrically optimized to obtain the configuration with minimized potential energy. As an example, in Fig. 5.3, an equilibrated configuration of two beads obtained by CASTEP [Accelrys Inc.] is shown. \( o_1 \) is the center of the benzene ring, \( c_1 \) and \( c_2 \) are the positions of the two carbon atoms connected by bond \( b_0 \), \( b_0' \) is the distance between \( o_1 \) and \( c_2 \), while \( c_3 \) and \( c_4 \) are other carbon atoms as shown. The two circles depict how the two beads are mapped.

![Fig. 5.3 Equilibrated configuration of bond pair \( a \), where \( o_1 \) is the center of the benzene ring, \( c_1 \) and \( c_2 \) are the position of the two carbon atoms connected by bond \( b_0 \), \( b_0' \) is the distance between \( r_1 \) and \( c_2 \).](image-url)
In the construction of atomistic classical force fields, the valence interaction between each atom should be studied in detail --- all bond stretching energies between each neighboring carbon-carbon and carbon-hydrogen bond pairs, all bond angle bending energies between each neighboring bonds along the chain, all bond torsional energies among any four consecutively neighboring atoms along one chain and all cross terms among the atoms, bonds, bond angles as well as improper bonds [Jensen 1999].

As an example, the bond stretching potential will be considered between atom pairs like \(c_1\) and \(c_2\). The bond equilibrated length of \(c_1\) and \(c_2\) is \(b_0\). Bond bending potential and bond torsional potential exist among \(c_3, c_1, c_2, c_3\), and \(c_3, c_1, c_2, c_4\), respectively. The interactions among the whole configuration were considered with full atomistic details. However, usually not all the information in atomistic details is of interest. For studying mechanical properties, for instance, the interactions between the atoms inside the benzene ring and side groups are not so important because their bonding energy do not contribute much to the bond breakage along the backbone chain, which is the main structure sustaining the external loading. With this idea, the configuration can be divided into two beads like the two circles drawn in Fig. 5.3. The new force field can be constructed by considering only the interaction between the two beads for the valence part as described by Eq. 5.16, while the valence interactions among other atoms can be hidden in the beads to save computer resources.

To obtain the valence interaction between the two beads, a series of configuration was built by moving the two beads to different distances along the line of \(c_1\)–\(c_2\). Then an ab initio MD calculation (DMol3 [Accelrys Inc.]), was performed to get the corresponding valence energy of each configuration. DMol3 was used to replace CASTEP because
CASTEP is better suited to obtained geometry optimization of molecular structures but is computationally costly for the calculation of valence potential. The valence potential of the molecular configuration in Fig. 5.3 can be plotted as a function of the distance between the two beads and the relationship is shown in Fig. 5.4. The bead distance used here is the distance between $c_1$ and $c_2$. However, in the coarse grained system, the bead distances are usually not the bond length of certain atom pairs. In the configuration of Fig. 5.3, for instance, the bond length to use should be the distance between the center of benzene ring $o_1$, and $c_2$. In other words, the bead center should be shifted according to certain mapping strategy while different bead center can be used for different properties or considerations of interest. In coarse grained MD mapping, different groups of atoms can be used as different beads.

![Graph showing the relationship between bead distance and valence potential.](image)

*Fig. 5.4 Relationships of valence potential and distance of bead pair in Fig. 5.3.*

Figure 5.4 shows the potential curve consists of repulsive and attractive parts. The asymmetry of the valence curve is because the Pauli force overlap repulsion plus inter-
atomic electrostatic repulsion always falls off much faster than the electrostatic attraction \cite{Abell1985}. Equation 5.16, with the repulsive LJ term, thus can represent the energy behavior. The LJ potential was cut off at $1.1r_0$ where $r_0$ is the equilibrium distance as shown in Fig. 5.3.

\[ E = k_2[(b-b_0)^2] \]

\[ E = k_2[(b-b_0)^2] + k_3[(b-b_0)^3] \]

\[ E = k_2[(b-b_0)^2] + k_3[(b-b_0)^3] + k_4[(b-b_0)^4] \]

\textit{Fig. 5.5 Least square fitting results for the valence potential of bead pair in Fig. 5.3.}
To interpolate the valence potential to parameterize Eq. 5.16, the least square fitting algorithm was used to fit the lower part of the curve for the second, third and fourth order terms. The fitting results for configuration bond pair a-b are plotted in Fig. 5.5.

From Fig. 5.5, it is shown that the fourth order expansion fits the curve best and thus is used in the construction of the valence force field. For a certain crosslinked system with a certain mapping strategy, only selected pairs of beads are parameterized. Thus, with the parameterization method above, the coarse grained force field can be obtained with certain crosslinking system and mapping strategies. The results of coarse grained force field parameters of the present composite interfacial system will be shown in Chapter 6.
This chapter focuses on the modeling of a glass-epoxy interface with an extensively cross-linked epoxy system and silanes by coarse grained molecular dynamics (CGMD). The force field obtained in Chapter 5 was parameterized according to the crosslinking system and mapping strategies used. The composite interfacial crosslinking system was then simulated and its mechanical properties were analyzed.

§ 6.1 Introduction

The performance and strength of many composites, hybrid and thin multi-layered material systems depend strongly upon the mechanical properties of interfaces. However, continuum mechanics approach to explore the interfacial properties has usually had limited success because it is often unable to incorporate the effects of molecular and chemical interactions into the model. There is therefore a need to understand and study the influence of these factors on the mechanical properties of interfaces, such as adhesion strength, at a more fundamental level. Molecular dynamics (MD) simulation is a popular approach to obtain detailed molecular motions in interfaces and has attracted more interest recently with the rapid development of computer technology and fast algorithms [Baschnagel et al 2000]. When a polymer system is large enough, in molecular simulation, the motions and interactions of the atoms inside the function groups of the chains can be ignored and one or more function groups can be treated as one “big atom”, therefore, only the motions and interactions between such “big atoms”, or beads, needed to be considered. The coarse-grained bead-

Baljon and Robbins [1996] simulated crosslinked chains between two rigid walls to study the energy-dissipation mechanisms during the rupture of a thin adhesive bond using coarse grained model [Kremer and Grest 1990, 1996]. By separating the walls at different velocities and at different ambient temperatures, the interfacial failure displayed different stages like cavitation, plastic yielding and bridge rupture. These have similarities to nucleation, plastic flow and crazing in commercial polymeric adhesives. By changing the wetting area between the crosslinker and the walls, adhesive failure and cohesive failure of the interfaces were also simulated [Gersappe and Robbins 1999]. The coarse grained model has also shown that different failure modes were observed as the chain length, or monomers per chain N, is increased - from polymer cavitation to complete crazing, when N is larger than the entanglement length N_e [Baljon and Robbins 2001]. Simulation with chain lengths close to those of commercial polymers gave results comparable to experimental data. To simulate the scission of polymer chains in interfacial failure, a potential for breakable bonds was added to the bead-spring model to study the different failure modes of ordered and disordered network systems [Stevens 2001a] and the effects of interfacial bond density and system size on interfacial fracture [Stevens 2001b]. Furthermore, the effects of cross-linker functionality and number of interfacial bonds on the adhesive to cohesive failure transition was also studied and the results are comparable with experimental observation [Tsige and Stevens 2004]. By adding the bond bending potential in the coarse-grained bead spring model, end-grafted polymers were also modeled to investigate the effects of temperature, tethered chain area density, tethered chain length, chain bending energy and tensile pull velocity on the adhesive failure mechanisms of pullout and/or scission of the tethered chains [Sides et al 2001, 2002, 2004]. Although coarse-grained models developed rapidly for the simulation of interfacial failure, two main problems need to be
addressed before simulation results can be realistically related to experimental data - the selection of an appropriate force field to control the motions of polymer chains and a reasonable initial configuration of the chains.

For a crosslinked epoxy adhesive, the strength of the interface is governed by the wetting percentage and the bond strength of the network system [Baljon and Robbins 1996]. Consequently, the location of the failure relates to the region of lowest initial yield stress and cannot be predicted from equilibrium interfacial free energies [Baljon and Robbins 1996]. A recent experiment of an epoxy adhesive failure on a silicon wafer [Kent et al 2004] also indicates that the failure mode is cohesive and the failure stress is constant at high wetting percentage, while at low wetting percentages, the failure is in adhesion and the failure stress is dependent only on weak van der Waals interactions [Tsige and Stevens 2004].

However, as the epoxy adhesive is fully wetted, it becomes unclear how cohesive failure initiates and how failure is related to the bond strengths. By simulating several crosslinked epoxy adhesive systems using coarse grained molecular dynamics, Stevens [2001ab] recently studied the effect of interfacial failure by varying the number of bonds across the interface. Certain relationships between the bond numbers, bond strengths and interface areas were carried out and analyzed [Stevens 2001b]. However, the bonds strength used are identical in his model and differed from the physics of epoxy chains, in which the bond strengths are different for different covalent bonds. It is expected that, in the stretching of the crosslinked network systems, bond breakage would occur initially among those bonds with weaker strength.

In the present study, a glass/epoxy interfacial system crosslinked with coupling agent was modeled and simulated with coarse grained bead-spring molecular dynamics. The coupling agent used is gamma amino-propyl-triethoxysilane (AMPTES). The bond breakage force field, developed in Chapter 5, is used and parameterized, by the calculations of ab initio molecular dynamics, to control the motion and breakage of the polymer chain network. The relationship between the yield
stress and bond strength was explored. The mechanical properties of the interfacial system were also obtained.

§ 6.2 Molecular Modeling of Composite Interface

Figure 6.1 shows a fiber embedded in a matrix, as typically found in fiber-reinforced composites. The interfacial region comprises a glass fiber and epoxy matrix with a coupling agent – AMPTES. The structures of epoxy and AMPTES are shown in Fig 6.2.

![Fig. 6.1 Model of fiber/matrix interfaces with silane present.](image)

In the fabrication of fiber-reinforced composites, the fibers are cured with some coupling agents. The reactions give rise to a crosslinking process, which in the present case (glass fiber cured by silanes) is

\[
\text{E} \rightarrow \text{OH} \ (\text{excess}) + \text{OH} \ (\text{excess}) + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{3E} \rightarrow \text{OH} \ (\text{excess}) + \text{O} \text{Si-R} \ (6.1)
\]

Here, R- is *amino-propyl* and E is –CH\_2CH\_3 in the present models.

In addition to the crosslinking reaction in Eq. 6.1, the C-O bonds of the epoxy group were broken and crosslinked with the amino function groups on the AMPTES to construct the network of the glass-epoxy composite interfaces. The molecular structure of glass-epoxy interface with crosslinked
AMPTES is constructed and shown in Fig. 6.3. In the present model, the $n$ in epoxy chain is 0 [Fig 6.2a].

Fig. 6.2. Structures of the matrix and silanes. (a) Epoxy chain. (b) Gamma amino-propyl-triethoxysilane (AMPTES)

Fig. 6.3. Molecular structures of glass-epoxy interface with AMPTES crosslinked.

A molecular structure of the crosslinked system is shown in Fig. 6.3, in which two AMPTES silane molecules were fully bonded on the glass surface while the amino-groups on the other side bonded with two epoxy groups on the two ends of an epoxy molecule chain. The atoms grouped in different circles with different colors represent different beads in the mapping strategy of the coarse grained
model and will be described in detail later. In the molecular system, with the bead map strategy shown in Fig. 6.3, eight kinds of pairwise bonds connect nine beads shown in Table 6.1.

### Table 6.1 Bead mapping strategy

<table>
<thead>
<tr>
<th>Bead</th>
<th>circle of color</th>
<th>molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td>CH$_2$-CH-CH$_3$</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>-C$_6$H$_5$</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td>-O-CH$_3$</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>-CH$_2$-OH</td>
</tr>
<tr>
<td>e</td>
<td></td>
<td>-CH$_3$</td>
</tr>
<tr>
<td>f</td>
<td></td>
<td>-NH$_2$</td>
</tr>
<tr>
<td>g</td>
<td></td>
<td>-C$_3$H$_7$</td>
</tr>
<tr>
<td>h</td>
<td></td>
<td>-SiO$_3$H$_3$</td>
</tr>
<tr>
<td>i</td>
<td></td>
<td>-Si$_3$</td>
</tr>
</tbody>
</table>

Using ab initio MD calculations, a coarse grained force field can be constructed and parameterized as discussed in Chapter 5.

In quantum mechanics calculation, Material Studio [Accelrys Inc.], with its CASTEP and DMol3 modules, was used to obtain the geometrically optimized structures and the relationships between the bonding energies and bonding distances of the bead pairs as discussed in Chapter 5. Firstly, seven pairs of the beads (beads a to h in Fig. 6.3) were modeled in atomistic detail by replacing all valence atoms bonded to the structural unit with protons [Hopfinger and Pearlstein 1984]. Then geometry optimization calculations were performed using CASTEP for the seven bead pairs to get the equilibrium conformation. Based on the optimized configurations for each pair, the bonding energies were calculated with different distance between the beads. To accelerate the computing, DMol3 was used for the plotting of bonding energy as a function of bead distance. The force field, Eq. 5.16, was then parameterized using least squares fitting methods with the results of DMol3, as...
described in Chapter 5. The bonding strength of each pair is also obtained. The bond forming and
breakage strategies are derived based on the bond strength obtained and will be discussed in detail
later.

With the schematic configuration in Fig. 6.3, the crosslinker chains can be modeled using the
constructed force field. As shown in Fig. 6.4, the crosslinker chain consists of five beads,
corresponding to five beads from the pink to purple ones shown in Fig. 6.3. The tail bead is
represented by the pink one and the head bead is represented by the purple bead in Fig. 6.3,
respectively. Beads a, b, c, d and e correspond to the beads with same color along the epoxy chain
in Fig. 6.3. The head and tail beads are the crosslinkers and are capable of bonding with two other
crosslinker beads. Based on the mapping strategy, the whole system is then constructed using the
model by Stevens [2001ab], in which the epoxy adhesive is contained between two rigid walls and
the periodic boundary condition is applied along the two directions parallel to the wall while tensile
loading is applied along the direction perpendicular to the wall. In the present model, each wall
consists of two layers of beads. The topmost layer represents the surface of the glass fiber and each
bead consists of three Si atoms (shown in grey circle in Fig. 6.3) and the other layer consists of
beads with red circle. The bonds between the two layers, bond h-i in Fig. 6.3, are Si-O bonds which
are assumed to be strong and will not break during the tensile loading. Thus the bead pair h-i is
treated as rigid. In the present simulation, full wetting of fiber curing was modeled, which means
the AMPTES are fully bonded on the glass fiber by assuming the bond h-i was considered rigid and
fixed.
In the construction of the initial configuration, the AMPTES molecules are fully pre-bonded with the inner wall beads. Each AMPTES molecule then hangs on the wall with a crosslinker bead bonded. The crosslinker chains are aligned between the two walls as shown in Fig 6.5, where the blue and white beads represent the crosslink chains as shown in Fig 6.4. The distances between each bead are obtained from the equilibrium configuration obtained by CASTEP and are listed later. There are a total of 28200 beads in this system with $L_x=30$, $L_y=19.5$ and $L_z=21.5$, where $L_x$ and $L_y$ are the two directions parallel to the wall and $L_z$ is the direction perpendicular to the wall. Periodic boundary condition is applied on $L_x$ and $L_y$ while the two outmost wall beads are free surfaces.

The present coarse grained molecular dynamics simulation is performed at constant temperature $T$ using the Rouse Model [Kremer and Grest 1990,1995]. As shown in Chapter 2, a polymer chain consists of a number of freely jointed beads connected by harmonic springs in a background of homogeneous friction. This frictional resistance represents collective reaction forces acting on a
bead due to its continuous collision with the neighboring beads. The equation of motion is described by the Langevin equation [Lee 1983]:

\[
\frac{d^2 R_i}{dt^2} = \nabla \sum_{j \neq i} U_{ij} - \Gamma R_i + W_i
\]

where \( t \) is time, \( \nabla = \left( \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right) \), \( R_i \) is the position of the \( i \)th bead, \( U_{ij} \) is the interaction potential between each bead, \( \Gamma \) is the friction constant which couples the monomer weakly to a heat bath, and is given by [3,22]:

\[
\Gamma = \frac{6\pi \eta a}{m}
\]

where \( \eta \) is the viscosity of the solvent, \( m \) and \( a \) are the mass and radius of the monomer, respectively. In Eq. 6.1, \( W_i^T(t) = \{ W_i(t), \ldots, W_N(t) \} \), was introduced as a stochastic force to describe deviation from an average motion due to nonlinear effects, the initial transient process and fluctuations. Usually, the stochastic force has zero mean, \( \langle W_i(t) \rangle = 0 \), the covariance imposed by the fluctuation-dissipation theorem [9,23] is

\[
\langle W_i \rangle^2 = \langle W_i(t) \cdot W_j(t') \rangle = 6\frac{k_B T}{m} \Gamma \delta(t-t')
\]

where \( k_B \) is Boltzmann constant, \( T \) the temperature, \( \delta(t) \) the Dirac delta function and the average \( \langle \ldots \rangle \) is carried out to reduce noise.

The thermostat integration time step is 0.003 \( \tau \). \( \tau = R(m/e)^{1/2} \) is the LJ time unit where \( R \) and \( e \) are the length and energy scales in the LJ potential respectively as shown in next chapter, and \( m \) is the mass of the bead. By fixing the position of two walls, the initial configuration is obtained by shaking the system under a Langevin thermostat with \( T=1.1e \). The crosslinker is freely bonded when their distance is less than \( R_c \), which is obtained from \textit{ab initio} MD calculations. The “shaking” process is carried out for 50k steps with the condition that the crosslinked bonds will not break once they are formed. After the initial crosslinked structure is obtained, the mechanical properties are studied by pulling up the upper wall along the \( z \) direction at a velocity of \( 0.02R_0/\tau \) with the bottom
wall fixed. The loading process is under constant temperature at $T=0.3e$, $0.7e$ and $1.1e$. The glass transition temperature is $T=0.5e$ [Baljon and Robbins 1996, Stevens 2001b]. The stretching simulation was also performed at different velocities of $0.06R_0/\tau$ and $0.002R_0/\tau$ under constant temperature at $T=0.3e$, to compare the results of different strain rates below glass transition temperature.

§ 6.3 Parameterization of the CG force field

Firstly, seven pairs of the beads (bonds $a$-$b$ to $g$-$h$ in Fig 6.3) were modeled in atomistic detail by replacing all valence atoms bonded to the structural unit with protons. Using CASTEP, the seven configurations are then geometrically optimized to get the ground states, in which the equilibrated distance and bonding energy were obtained, as shown in Chapter 5.
CG MODELING OF GLASS/EPOXY INTERFACE

(c) bond pair c

(d) bond pair d

(e) bond pair e

(f) bond pair f
Using the algorithm in Chapter 5, the relationships between valence potentials and bead distances are obtained by DMol3. Their equilibrium configuration and valence potentials are shown in Fig. 6.6. The equilibrium distances between the beads are shown in Table 6.2.

In Table 6.2, the bond length of pair a-b is the distance between the carbon atom $c_2$ and the center of benzene ring $o_1$, instead of the distance between $c_1$ and $c_2$ [Fig 6.6-a]. Other distances are shifted accordingly for balance. The least square fitting of the force field is shown in Fig 6.7, in which all the energy curves are left-shifted with the the equilibrium point moving on the Y-axis. As described in Chapter 5, only the lower part of the energy curves are used for interpolation. Then Eq. 5.15 becomes:

$$U_{bc}(r) = k_{bc} \Delta r^2 \left[ 1 - \alpha \Delta r + \frac{7}{12} \alpha^2 \Delta r^2 \right]$$  \hspace{1cm} (6.5)

where $\Delta r = r - r_0$, is the change of bond length.
\( y = 1614.93x^4 - 1888.44x^3 + 1288.16x^2 \)

(a) Pair a-b

\( y = 1708.36x^4 - 1787.93x^3 + 1091.53x^2 \)

(b) Pair b-c

\( y = 1000.996x^4 - 1219.616x^3 + 866.82x^2 \)

(c) Pair c-d

\( y = 1254.02x^4 - 1429.356x^3 + 950.37x^2 \)

(d) Pair d-e

\( y = 1628.184x^4 - 1773.29x^3 + 1126.62x^2 \)

(e) Pair e-f

\( y = 1480.392x^4 - 1663.30x^3 + 1089.81x^2 \)

(f) Pair f-g
CHAPTER VI                           CG MODELING OF GLASS/EPOXY INTERFACE

\[ y = 947.12x^4 - 1313.62x^3 + 1062.8x^2 \]

Table 6.3 lists the force field obtained by the least square fitting results in Fig. 6.7. The LJ lengths and energies are normalized and scaled by the longest bead length, pair g-h, and its energy.

**Tab 6.3 Parameters for the force field**

<table>
<thead>
<tr>
<th>Bead pair</th>
<th>(k_{bc})</th>
<th>(\alpha)</th>
<th>LJ length</th>
<th>LJ energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-b</td>
<td>1288.16</td>
<td>1.466</td>
<td>0.952876</td>
<td>1.212044</td>
</tr>
<tr>
<td>b-c</td>
<td>1091.53</td>
<td>1.638</td>
<td>0.904777</td>
<td>1.027032</td>
</tr>
<tr>
<td>c-d</td>
<td>866.82</td>
<td>1.407</td>
<td>0.954501</td>
<td>0.8156</td>
</tr>
<tr>
<td>d-e</td>
<td>950.37</td>
<td>1.504</td>
<td>0.952876</td>
<td>0.894213</td>
</tr>
<tr>
<td>e-f</td>
<td>1126.62</td>
<td>1.574</td>
<td>0.936952</td>
<td>1.060049</td>
</tr>
<tr>
<td>f-g</td>
<td>1089.81</td>
<td>1.526</td>
<td>0.935652</td>
<td>1.025414</td>
</tr>
<tr>
<td>g-h</td>
<td>1062.8</td>
<td>1.236</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Consider the bead pairs at ground state, the force to move beads along the bead distance from equilibrium position can be obtained by the differential of the curve:

\[ F = -\frac{\partial U}{\partial r} \]  \hspace{1cm} (6.6)

Thus the force required to displace a bead can be obtained. The relationships between the valence force and the bead distance are plotted in Fig. 6.8. To compare all the seven bead pairs, the bead equilibrium distance are set to zero thus the valence force required to pull the bead apart from ground state can be plotted. From Fig. 6.8, it shows that when the beads are pulled, the valence

Fig. 6.7 The least square fitting of the force field parameters for the network system.

(g) Pair g-h
forces are increased first to a maximum and then decreased. From the valence force curve, under constant external tensile loading, the bond can be assumed to be broken even when certain energies still can sustain the valence potential.

Recall the coarse grained force field obtained by Chapter 5:

\[
U_{cg}(r) = \begin{cases} 
U_{bc} + U_{0} + U_{ij}^{LJ}, & r_{ij} \leq r_{c} \\
U_{0}, & r_{ij} > r_{c}
\end{cases} \tag{6.6}
\]

We assume that the bond will break after the force reaches the maximum, the bond breakage length, \(r_{c}\) in Eq. 6.6, can thus be determined. The residual energy can also be obtained from the corresponding energy from the energy curve in Fig. 6.6. The residual energies and the corresponding bond breakage length of the seven pairs are listed in Table 6.4.

<table>
<thead>
<tr>
<th>Bead pair</th>
<th>a-b</th>
<th>b-c</th>
<th>c-d</th>
<th>d-e</th>
<th>e-f</th>
<th>f-g</th>
<th>g-h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual energy ((U_{0}))</td>
<td>38.97</td>
<td>37.72</td>
<td>30.93</td>
<td>38.57</td>
<td>37.91</td>
<td>38.08</td>
<td>33.83</td>
</tr>
<tr>
<td>Bond break length (r_{c})</td>
<td>1.339</td>
<td>1.301</td>
<td>1.305</td>
<td>1.339</td>
<td>1.316</td>
<td>1.317</td>
<td>1.305</td>
</tr>
</tbody>
</table>

Fig. 6.8 Valence force versus bead distance.
§ 6.4 Coarse-grained Molecular Dynamic Simulation

In the formation of the initial interfacial system shown in Fig. 6.5, a pre-bonding simulation was performed using Langevin thermostat at a temperature of $T=1.1e^2$, in which the crosslinker beads were bonded together when their distance is less than $r_c$. The equilibrated crosslinking configuration is shown in Fig. 6.9.

![Fig. 6.9 Dynamically bonded crosslinking system used as the initial configuration for the coarse grained MD.](image1)

![Fig. 6.10 The snapshot of the crosslink system at strain of a) 0.2, b) 0.4 and c) 0.8 under tensile loading of upper wall at velocity of 0.02 R/τ.](image2)
The crosslinked interfacial structure is then loaded by pulling up the upper wall along the z direction at a velocity of $0.02R/\tau$ with the bottom wall fixed. The loading process is under constant temperature at $T=0.3e$, $0.7e$ and $1.1e$, respectively. Fig. 10 shows snapshots of the crosslink system at strains of a) 0.2, b) 0.4 and c) 0.8 under constant temperature of $T=0.3e$. The cohesive failure from void initiation to propagation is clearly shown (Fig. 6.10). The stress-strain curve is plotted in Fig. 6.11 together with those at temperatures of $T=0.7e$ and $1.1e$.

![Graph showing tensile stress-strain curve for the crosslinked system under constant temperature at $T=0.3e$ (diamond), $0.7e$ (square) and $1.1e$ (triangle).]

**Fig. 6.11** Tensile stress-strain curve for the crosslinked system under constant temperature at $T=0.3e$ (diamond), $0.7e$ (square) and $1.1e$ (triangle).

Figure 6.11 shows that there are three stages in all the three curves. At a strain of about 0.08, there is a first peak, which corresponds to the yield stress. This yield is mainly due to the van der Vaals forces between the beads reaching a maximum. The second stage is a plateau which corresponds to plastic deformation. This is because, after the van der Vaals interaction gradually decreases beyond the cutoff distance, the entangled and folded beads begin to stretch while the stress can be still sustained by bead bonding. The third stage appears when the folded bead bonds are stretched and reach their equilibrated distance. At this stage the stress is sustained by the bond stretching strength. When bead bonds stretch to certain distance, some bonds break followed by voids generation and
propagation. Finally ruptures occur and the interfacial systems are totally failed. Similar stress-strain relationships were also reported by Stevens [2001b] for adhesive failure.

It is interesting to note that, in Fig. 6.11, the three curves present two different shapes. The stress-strain curves of the models under $T=0.7e$ and $1.1e$ are very close except that the model at $T=1.1e$ can sustain larger strain than that at $T=0.7e$. Both curves, however, differ significantly from that at $T=0.3e$. When the model was stretched at $T=0.3e$, the top of plateau is much lower than the yield stress while the difference is very small for the other two models.

The phenomenon is due to the glass transition temperature being $T=0.5e$ [Baljon and Robbins 1996, Stevens 2001b]. At the temperature of $T=0.7e$ and $1.1e$, the crosslinking system is at an amorphous state and behaves as a glassy film. While at the temperature of $T=0.3e$, more energy is needed to overcome the van der Vaals barrier and beads with lower velocities can sustain larger tensile stress. This can also be seen from snapshots of the three models at a strain of 0.8, as shown in Fig. 6.12. At a strain of 0.8 it shows that the $T=0.3e$ system is at the end of plastic deformation and bead bonds are stretched to breakage; some voids have already propagated to failure. For the other two systems with temperature above the glass transition temperature, there is still no clear void generated at a
strain of 0.8, hence, they can still sustain plastic deformation. It can be shown that, above the glass transition temperature, the interfacial crosslinking system behave like glassy state polymers. This interesting phenomena is similar to a diffusion system investigated by Baljon and Robbins, in which the entangling polymer chains exhibit similar property trends when the temperature is higher than the glass transition temperature [1996].

To study the effect of strain rates, the model was pulled again with the upper wall at different velocities of $0.06 R_0/\tau$ and $0.002 R_0/\tau$ at constant temperature of $T=0.3e$. The stress-strain curves are plotted in Fig. 6.13 together with the model with velocity of $0.02 R_0/\tau$. From Fig. 6.13, it is seen that the model, under different strain rates, has the same yield stress but different failure strain. The lower the strain rate, the larger the failure strain. It is shown that different strain rates do not influence the van der Vaals interaction, for the three curves are nearly the same in the first elastic stage. Similar results are reported recently for a calculation of a diffusing polycarbonate-silane interface, in which the yield stresses are also same under different strain rate using atomistic classical molecular dynamics [Deng et al 2004]. However the third stage of the crosslinked system

Fig. 6.13 Tensile stress-strain curve for the crosslinked system under constant temperature at $T=0.002 R_0/\tau$ (diamond), $0.02 R_0/\tau$ (square) and $0.06 R_0/\tau$ (triangle).
was influenced by the different strain rate. And the lowest strain rate can sustain largest failure strain [Fig. 6.13].

The stress distribution of the interfacial system can also be plotted, by dividing the system into several regions along x,y,z dimension. The stress distribution of a slab of the system, at the yield strain of 0.08, with a velocity of $0.02R_0/\tau$ and $T=0.3e$ is plotted in Fig. 6.14a. The corresponding snapshot of the molecular configuration of a slab of the domain is shown in Fig. 6.14b.

![Stress distribution](image1.png)

**Fig. 6.14 a)** Stress distribution of a slab of the interfacial system at the yield strain of 0.08, with a velocity of $0.02R_0/\tau$ and $T=0.3e$, corresponding snapshots of the slab region are shown at the strain of b) 0.08 and c) 0.8
To plot the stress distribution, the whole system was divided into 1000 regions (10x10x10 in each dimension). Along the y dimension, a x-z slab region (Fig. 6.14b) was selected (divided to 10x10 square regions along x and z dimensions). The stress was then calculated for each region and plotted. Fig. 6.14a shows that a stress concentration occurs at the top of left slab. The stress-strain curve, shown in Fig6.11, indicates that the slab is now at the yield stress, as the van der Vaals distances between some beads have reached the maximum. Thus, at the site of the stress concentration, the van der Vaals interaction of some beads should have reached the cutoff distance and the stress has started to decrease, resulting in the initiation of a void. This is shown by the snapshot of the same slab region at the strain of 0.8 in Fig. 6.14c.

In all the simulations, ruptures are due to cohesive failures and occur at the adhesive film of epoxy. This can be expected because in all the simulations, the amino silane were fully crosslinked with glass fiber and epoxy matrix. Thus, the adhesive completely wets the composite interfaces. The mechanics of cohesive failure have been discussed here. Literature on adhesive failure has been reported by Stevens [2001ab] who studied the relationship between wetting area and interfacial strength.

§ 6.5 Conclusion

A coarse-grained bead-spring molecular dynamics simulation model has been implemented for the simulation of a composite interface. In the model, a new force field was combined with LJ nonbond potential to control the motions of the polymer monomers. The model is demonstrated through the simulation of a composite interface being pulled apart. The calculation shows that the interfacial crosslinking system demonstrates different mechanical properties above and below the glass transition temperature. Also the influence of strain rate is small for the yield stress. The interfacial failure is mainly cohesive failure in the present model because the silane was fully crosslinked with the fiber surface and epoxy matrix. Current work shows the trend of molecular dynamics –
development of multi-scaled algorithms with the ability to model large polymer systems to enable the use of MD to scale up to experimental results. The main issue to be addressed in CGMD is the formulation of proper force fields to deal with the motion of beads from the same and/or different chains. A lot of development remains to be done in this aspect because only a few force fields for CGMD has been thoroughly examined to date [Baschnagel et al 2000].
§ 7.1 Conclusions

In this thesis, some composite interfacial systems were modeled and studied by atomistic classical and coarse grained molecular dynamics respectively. The adhesion and mechanical properties of diffusing and crosslinked interfaces were obtained.

Molecular dynamics simulation together with first principle DFT calculations were used to elucidate experimental observations of the response of PCL nanofibers subjected to tensile loads. Physical testing reveals that when PCL fibers of nominal diameters 50–250nm are stretched, multiple necked regions form at strains of up to 60%. On further loading, the fibers thin down uniformly with no discernable localized deformation. By restraining some parts of a PCL molecular chain model to represent the polycrystalline nature of PCL fibers, atomistic simulations of the chain under tensile strain replicated the transition from a multiple neck fiber to a uniform fiber as the strain increases from 60% to 200%. The simulations show that this phenomenon is the result of stiff crystalline phases thinning out at a higher strain than the compliant amorphous phases of the fiber.

Using a commercial code incorporating well developed force fields, diffusion interfaces of a matrix and coupling agents were modeled. The matrix used is polycarbonate (PC) and the coupling agents studied are gamma amino-propyl-triethoxysilane (AMPTES) and
stearic-propyl-triethoxysilane (SPTES). Two atomistic models of SPTES-PC and AMPTES-PC interfaces were constructed and an algorithm is proposed to investigate the mechanical properties of polymer interfaces. The surface energies of PC, AMPTES and SPTES, as well as the work of adhesion of the interfaces of PC-AMPTES and PC-SPTES, were obtained from atomistic simulations. It is interesting to find that the work of adhesion may not necessarily be an indication of the toughness of bi-material systems under mechanical loading.

The mechanical properties of PC-AMPTES and PC-SPTES composite interfaces were also investigated through atomistic simulation using a combination of conjugate gradient energy minimization and molecular dynamics. The stress-strain relationships of the two interfacial systems were obtained. The stress-strain curves first increase linearly followed by a plateau regime. The linearly increasing stress, or the elastic response, is due to the van der Vaals forces between the polymer atoms while the plateau regime is caused by the sliding of polymer chains. The relationship obtained by simulation has the same trend as laboratory experimental tests.

To model the highly crosslinked composite interfacial system, a coarse-grained bead-spring molecular dynamics model was implemented to carry out the simulation. In the model, a new set of force fields was constructed by combining the bead stretching potential with LJ nonbond potential to control the motions of the polymer monomers. The force field is derived from Morse equation and parameterized by \textit{ab initio} molecular dynamics calculation. The model is then used to simulate the pulling apart of a composite interface (glass/epoxy with AMPTES coupling). The mechanical properties of the crosslinked system was obtained and studied.
For the crosslinked composite interfaces, there are three stages in the stress-strain curves. Firstly, there is a linear increase in stress to a peak, which corresponds to the yield stress. This yield is mainly due to the van der Waals forces between the beads reaching a maximum. The second stage, after the yield stress, is a plateau which corresponds to plastic deformation. This is because the entangled and folded beads begin to stretch while the stress can be still sustained by bead bonding. The third stage appears after the folded bead bonds are aligned and reach their equilibrated distance. At this stage the stress is sustained by the bond stretching strength. When bead bonds stretch to certain distance, some bonds break followed by void generation and propagation. Finally ruptures occur and the interfacial systems are totally failed.

In the study of the mechanical properties of crosslinked composite interfaces, several models were simulated under different temperatures and different strain rates. The calculation shows that the interfacial crosslinking system demonstrates different mechanical properties at temperatures above and below the glass transition temperature. Also the influence of strain rate is small for the yield stress. In present study, the interfacial failure is due mainly to cohesive failure. Adhesive failure did not occur because the silane was fully crosslinked with the fiber surface and epoxy matrix in the initial configuration.

The present work shows the trend of molecular dynamics – development of multi-scale algorithms with the ability to model large polymer systems to enable the use of MD to scale up to experimental results. The main issue to be addressed in CGMD is the formulation of proper force fields to deal with the motion of beads from the same and/or different chains.
§ 7.2 Future work

The recommendations for future research are summarized below.

1. It is easy to extend the present atomistic classical molecular dynamics algorithm to other polymer diffusion interfacial systems for studying their adhesion and mechanical properties. In fact, if the interface properties of longer polymer chains can be determined, the trend of the properties should converge and approach laboratory experiment.

2. It is meaningful to improve the coarse grain mapping algorithm to model a larger molecular system closer to laboratory experimental environment. For example, the system size by current coarse grained molecular dynamics can reach thickness up to 60 nm, just close to the small region near the surface. However, the simulation would be more useful if the size can reach to \( \sim 1 \mu m \).

3. It is important to develop more powerful coarse grained force field for interfacial system, especially for highly crosslinked structures. Current CG force fields available are seldom explored and degrees of freedom are small compare with atomistic classical force field. For instance, the force field should be more reliable if the torsional potential can be added because the dihedral motion can contribute significantly to stretching of the polymer bonds.

4. The coarse grained molecular dynamics for the present crosslinking system can provide more bond connecting information with better visualization techniques. The interfacial failure mechanism can be explored more exhaustively if the bond
connection can be displayed during the failure initiation and propagation. With the changing of bond connection, a more reliable failure criterion at the molecular level can be studied.
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