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CHARACTERIZATION OF ASPHALT PROPERTIES AND

ASPHALT-AGGREGATE INTERACTION USING MOLECULAR DYNAMICS SIMULATION

By

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ABSTRACT OF THE DISSERTATION

Characterization of Asphalt Properties and Asphalt-Aggregate Interaction

Using Molecular Dynamics Simulation

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The objectives of this dissertation are to discover the chemo-mechanical relationship of asphalt binder, to investigate asphalt-aggregate interfacial mechanical behavior, and to understand moisture damage and rejuvenation mechanism using computational modeling. Molecular dynamics (MD) simulations were utilized to understand the properties of assemblies of asphalt molecules in terms of their chemical compositions, molecular structures and atomic interaction, which serve as complements to conventional laboratory experiments conducted at the macroscopic level. Molecular models of asphalt material were prepared and a series of molecular simulations were carried out. The following tasks were conducted using MD simulations: (1) identify and

validate available molecular models of asphalt binder; (2) predict physical, thermodynamic, rheological, and diffusive properties of asphalt binder; (3) build atomistic models for asphalt-aggregate interface, and study adhesion and moisture damage; (4) link asphalt chemical compositions to asphalt properties and asphalt-aggregate interfacial interaction; (5) develop molecular models for aged asphalt, and investigate how oxidative aging affect properties of asphalt binders; (6) build molecular model for asphalt rejuvenator, and investigate interaction between virgin and aged asphalt binder with rejuvenator effect.

The MD simulation results showed a reasonable agreement with experimental data and observations. MD simulation can be used as a powerful tool to study asphalt properties, giving the optimal molecular models and appropriate force field are available. Fundamental chemo-physical and chemo-mechanical relationship of asphalt binders can be studied by MD simulations. Insights into the deformation and failure mechanism of asphalt-aggregate interface at an atomistic scale provided by MD simulations enable better understand adhesion and moisture damage of asphalt mixture. The molecular interactions between virgin asphalt, aged asphalt, and rejuvenator is a sophisticated process but of great practical importance for recycling of asphalt binder. MD investigations can be further used to select the optimum type and amount of rejuvenator in an accelerated manner with less experiment effort.

Dedication

I dedicate this dissertation to my parents

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Table of Contents

ABSTRACT OF THE DISSERTATIONii
Dedication iv
Acknowledgement v
Table of Contents vi
List of Tables xi
List of Figuresxii
Chapter 1 Introduction 1
1.1 Background and Motivation1
1.2 Research Objective and Scope 4
1.3 Dissertation Outline
Chapter 2 Literature Review7
2.1 Basics of Classical MD Simulations7
2.2 Force Field 10
2.3 Calculation of MD properties
2.3.1 Ensemble
2.3.2 Single-Point Property and Time Correlation Function15
2.3.3 Calculating Continuum Property by Atomic Scale Approach 15
2.4 Asphalt Chemistry and Components17

2.4.1	Asphalt Chemistry and Components	. 17
2.4.2	Asphalt Pavement Failure Mechanism	. 19
2.5 MD \$	Studies on Asphalt	. 20
2.5.1	Chemo-Mechanical Relationship of Asphalt Binder	. 21
2.5.2	Aggregation and Aging Behavior of Asphalt Binder	. 25
2.5.3	Asphalt-Aggregate Interface Behavior	. 28
Chapter 3	MD Characterization of Asphalt Binder	. 32
3.1 Mole	cule Models for Asphalt	. 32
3.1.1	3-component Asphalt	. 32
3.1.2	12-component Asphalt	. 35
3.2 Dens	ity of Asphalt	. 39
3.3 Surfa	ace Free Energy of Asphalt	. 41
3.4 Cohe	esive Energy Density and Solubility Parameter of Asphalt	. 43
3.5 Visco	osity	. 45
3.5.1	Green-Kubo Method	. 45
3.5.2	Muller-Plathe Method	. 49
3.6 Shear	r Modulus and Phase Angle	. 54
3.7 Radia	al Distribution Function	. 57
3.8 Diffu	sion Coefficient	. 59
3.9 Force	e Field Effect	. 62

Chapter 4 MD Characterization of Asphalt-Aggregate Interface	65
4.1 Creation of Asphalt-Aggregate Interface	65
4.1.1 Construction of Confined Asphalt Layer	65
4.1.2 Molecular Models of Mineral Aggregate	66
4.1.3 Creation of Asphalt-Aggregate Interface	67
4.2 Work of Adhesion between Asphalt and Aggregate	69
4.3 Moisture Effect on Asphalt-Aggregate Adhesion	73
Chapter 5 Simulation of Pull-Off Test	78
5.1 Model Preparation	78
5.2 Interface Mechanical Behavior	80
5.2.1 Stress-Separation Responses	80
5.2.2 Loading Rate Effect	81
5.2.3 Temperature Effect	84
5.3 Cohesive Zone Model Parameters	85
5.4 Chemo-Mechanical Relationships	89
Chapter 6 MD simulations on Oxidative Asphalt Aging	93
6.1 Virgin and Aged Asphalt Models	94
6.2 Molecular Structure of SARA fractions in Aged asphalt	99
6.3 Translation Mobility of Asphalt Molecules	103
6.4 Aging Effect on Self-Healing Potential of Asphalt	106

6.5 Aging Effect on Moisture Damage Susceptibility of Asphalt	112
Chapter 7 Rejuvenator Application in Asphalt Binder	116
7.1 Model Preparation	117
7.1 Molecular Model of Rejuvenator	117
7.2 Layered Model of Virgin and Aged Binder	118
7.3 Mixture Model of Virgin and Aged Binder	120
7.2 Effect of Rejuvenator on Diffusion between Aged and Virgin Binder	122
7.2.1 Diffusion of Rejuvenating Agent	122
7.2.2 Effect of Rejuvenator on Blending between Aged and Virgin Asphalt	125
7.3 Effect of Rejuvenator on Molecular Structure of SARA Fractions	127
7.4 Effect of Rejuvenator on Translational Mobility of Asphalt Molecules	134
Chapter 8 Conclusions and Recommendations	137
8.1 Summary of Main Findings	137
8.1.1 Cohesion and Adhesion Properties of Asphalt Mixture	137
8.1.2 Asphalt-Aggregate Interfacial Mechanical Behavior	138
8.1.3 Oxidative Aging Effect on Asphalt Properties	139
8.1.4 Effectiveness of Rejuvenating Agent with Recycled Asphalt Binder	140
8.2 Conclusions	141
8.3 Recommendations and Future Works	142
Appendix A	144

A.1 Experimental Asphalt Composition	
Appendix B	145
B.1 Molecular Asphalt Composition for MD Simulation	
Appendix C	
C.1 Average Molecular Structures of SHRP Core Asphalts	
Acknowledgment of Previous Publications	150
Bibliography	151

List of Tables

Table 3.1 Molecular composition of 3-component asphalt model	33
Table 3.2 Component fractions in model and experimental AAA-1 asphalt	39
Table 3.3 Surface free energy and work of cohesion of asphalt	43
Table 3.4 Cohesive energy density and solubility parameter of bulk asphalt	45
Table 5.1 SHRP asphalt binders with different SARA ratios	89
Table 6.1 SARA mass fraction of virgin and aged simulated asphalt system (AAA-1)	97
Table 6.2 Calculated properties of virgin and aged asphalt from MD simulation	97

List of Figures

Figure 2.1 A typical MD simulation flow chart
Figure 2.2 Classification of asphalt four components
Figure 3.1 Molecular structures used in 3-component asphalt
Figure 3.2 Molecular structures of 12-components AAA-1 asphalt
Figure 3.3 Comparison of density results for two asphalt models
Figure 3.4 Density of AAA-1 asphalt in dependence of time during NPT
Figure 3.5 Normalized stress autocorrelation function as a function of time
Figure 3.6 Viscosity of AAA-1 asphalt model at 533.15K using GK method 47
Figure 3.7 Asphalt viscosity comparisons using GK method
Figure 3.8 Viscosity of AAA-1 asphalt model at 533.15K using MP method
Figure 3.9 Viscosity comparisons using MP method
Figure 3.10 Frequency dependent modulus and phase angle of asphalt model at 533.15K
Figure 3.11 Effect of asphalt compositions on rheological properties
Figure 3.12 Radial Distribution Functions for SARA molecules in AAA-1 asphalt model
Figure 3.13 Schematic of determination of diffusion coefficient
Figure 3.14 Calculated diffusion coefficients of SARA components at 298.15K
Figure 3.15 Effect of force field on the AAM asphalt density at various temperatures 64
Figure 4.1 Asphalt thin film formation for surface energy calculation
Figure 4.2 Atomistic model of SiO ₂ substrate

Figure 4.3 Asphalt-1/aggregate interface atomistic model	9
Figure 4.4 Interaction energy and its component predicted by MD simulation	1
Figure 4.5 Work of adhesion between asphalt and aggregate predicted by MD simulation	
	2
Figure 4.6 Moisture sensitivity calculated from MD simulation	б
Figure 5.1 Representative model and schematic of tensile simulation in MD	9
Figure 5.2 Stress-separation response in tensile simulation by MD	1
Figure 5.3 Effect of strain rates on stress-strains relationship	3
Figure 5.4 Development of cohesive damage at small loading rate	3
Figure 5.5 Effects of temperatures on predicted adhesive stress	4
Figure 5.6 Cohesive zone law from the MD-derived stress-separation response	б
Figure 5.7 Stress-time relationships during loading and unloading conditions	8
Figure 5.8 Relationship between asphalting index and CZM parameters	1
Figure 6.1 Molecular structures of SARA fractions before and after oxidation aging90	б
Figure 6.2 Effect of aging on rheological properties of AAA-1 asphalt	8
Figure 6.3 Illustraion of asphalt molecular structures at 298.15K 100	0
Figure 6.4 RDFs of SARA pairs in aged AAA-1 asphalt models	2
Figure 6.5 Comparison of the MSD of SARA fractions in virgin and aged asphalt 105	5
Figure 6.6 Self-healing process of layered asphalt models	7
Figure 6.7 Effect of healing on asphalt density 109	9
Figure 6.8 Diffusion coefficients versus temperatures for virgin and aged binder 11	1
Figure 6.9 Effect of aging on asphalt-aggregate adhesion	2
Figure 6.10 Asphalt-aggregate interface model with moisture	4

Figure 6.11 Effect of asphalt aging on moisture damage under three different scenarios
Figure 7.1 Molecular model of asphalt rejuvenator117
Figure 7.2 Layered model for rejuvenator penetration and asphalt diffusion 119
Figure 7.3 Mixture model of virgin and aged asphalt with rejuvenator 121
Figure 7.4 Diffusion coefficients of rejuvenator in layered model
Figure 7.5 Relative concentration profiles of rejuvenator in layered model 125
Figure 7.6 Effects of rejuvenator and temperatures on inter-diffusion coefficients 126
Figure 7.7 Effect of rejuvenator on SARA radial distribution functions
Figure 7.8 Illustration of self-aggregation of asphaltenes in the mixture model of virgin-
aged asphalt132
Figure 7.9 Illustration of self-aggregation of saturates
Figure 7.10 Effect of rejuvenator on diffusion coefficients of SARA fractions
Figure 7.11 Effect of temperature on SARA diffusivity in rejuvenated asphalt system 135

Chapter 1 Introduction

1.1 Background and Motivation

Asphalt concrete has been widely used for roadway pavements due to its ability to provide structural capacity and smooth surface. In asphalt concrete, aggregate forms the skeleton of mixture; while asphalt binder serves as the primary binding material. However, several types of pavement distresses, such as premature rutting, raveling, and cracking are commonly observed during the early life of asphalt pavements.

A huge number of experimental studies have been carried out to study the asphalt material and asphalt mixture properties. It has been found that three factors are responsible for the failure of asphalt concrete, including cohesion loss within asphalt, strength reduction of aggregate particles, and breakdown of adhesive bonding between aggregate and asphalt [1]. Cohesion properties of asphalt binder and adhesion properties of asphalt to aggregate (i.e. bonding strength) are largely dependent on chemical compositions of asphalt and aggregate. Besides, due to the hydrophobic nature of asphalt binder, moisture effect has been found being the major driving force causing the loss of adhesion between asphalt and aggregate and further deterioration [2].

Asphalt cohesion loss and adhesion property belong to the mechanical behavior, which are largely dependent on the chemical components of asphalt. To find the link between the chemical components and mechanical properties of asphalt is challenging. Asphalt is a very complex mixture and the complexity of its chemistry lies in the fact that many different chemicals are present, about 10^5 - 10^6 different molecules according to Wiehe and Liang (1996) [3]. As a result of this, approaching detailed asphalt chemistry is impossible. The asphalt molecules are generally separated into different chemical families and divided into fractions, depending on their sizes, solubility and mobility. One separation method to be mentioned here is to divide asphalt into four SARA fractions which are saturate, aromatic, resin, and asphaltene, respectively, and thus the composition of asphalt is usually given in terms of the relative quantity nowadays [4]. These four fractions present different properties and they interact with each other, determining complicated behaviors of asphalt binder.

Aging of asphalt and asphalt mixture has been recognized as a contributing factor to fatigue distress of asphalt concrete pavement. The detailed mechanism for asphalt aging is still uncertain due to the complexity of chemical compositions of asphalt. Aging changes chemical compositions of asphalt and leads to an increase of the overall stiffness and brittleness. Although the hardening of asphalt could be beneficial by enhancing rutting resistance of pavement, aging could be detrimental for accelerating pavement distresses and causing premature failure. Therefore, understanding asphalt aging effect is important for asphalt material design to achieve longevity and durability.

Experimental studies have been and being carried out, and methods were proposed to relate asphalt chemical composition to mechanical properties. For instance, surface energy was used as an index to find their relationships, and acceptable and reasonable results were obtained [5]. However, it has to be noted that only limited pure asphalts were used, and more samples are still needed to validate the findings, due to the complex nature of asphalt as mentioned before. A clear relationship between the chemical components of asphalt and rheological and mechanical properties is still not fully understood despite of half a century's intensive experimental study and research work. To this end, it is necessary to discuss asphalt chemistry and get insights of this relationship from the more fundamental micro and nano scale based on bottom-up perspective, the information of which cannot obtained by traditional techniques. In addition, the successful mapping of human genome has revolutionized the treatment of human diseases such as cancer and disorders. It is possible to use the same concept in civil engineering materials such as asphalt in terms of its chemical composition, microstructure and inherent infect.

Recently, asphalt is popularly studied by means of molecule simulations, and many interesting properties and behaviors were understood. Atomistic modeling is proved to be is a powerful and feasible approach for material design and performance prediction, because the atomistic structures and components of materials determine the behavior at the continuum scale. To this end, this promising method can be employed to study the asphalt chemical composition and structure and mechanical properties; besides, since information of the initiation and evolution of material damage at the nanoscale can be obtained, the interface and interaction between asphalt and aggregate, as well as moisture sensitivity, can also be investigated. This necessitates investigation of the fundamental and better understanding of asphalt and asphalt concrete using a systematic atomistic modeling approach.

1.2 Research Objective and Scope

The objectives of this work are to discover the chemo-mechanical relationship of asphalt binder, to investigate asphalt-aggregate interaction, and to understand moisture damage and rejuvenation mechanism using computational modeling. Asphalt is comprised of molecular species that vary widely in polarity and molecular weight, and thus asphalt chemistry at the molecular and intermolecular levels is discussed herein, in order to find how chemical composition may explain performance characteristics in roadways. Computer simulations will be adopted in the hope of understanding the properties of assemblies of molecules in terms of their chemical compositions, molecular structures and atomic interactions, which serves as complements to conventional experiments that are usually conducted at the macroscopic level. Molecular models of asphalt material will be prepared and a series of molecular simulations will be carried out. The research results in this dissertation can be used for performance prediction and modification of asphalt material. In this dissertation, the following tasks will be conducted using molecular dynamics (MD) simulations:

1) Identify and validate available molecular models of asphalt binder;

2) Predict physical, thermodynamic, rheological, and diffusive properties of asphalt binder;

3) Build atomistic models for asphalt-aggregate interface, and study adhesion and moisture damage;

4) Link asphalt chemical compositions to asphalt properties and asphalt-aggregate interfacial interaction;

5) Develop molecular models for aged asphalt, and investigate how oxidative aging affect properties of asphalt binders.

6) Build molecular mode for asphalt rejuvenator, and investigate interaction between virgin and aged asphalt binder with rejuvenator effect.

1.3 Dissertation Outline

This dissertation studied related properties of asphalt binder as well as asphaltaggregate interface by means of molecular dynamics simulations. The dissertation is composed of eight chapters as described below.

Chapter 1 provided an introduction and an overview of the dissertation.

Chapter 2 of this dissertation presented literature review on the principles of molecular dynamics simulation, and an overview of MD application relating to engineering materials, especially asphalt material.

Chapter 3 introduced the selection and verification of available molecular models and force fields for asphalt materials. Related properties were studied and compared with experimental data, including thermodynamic, rheological and diffusive properties. Reasonable simulation results were obtained, and thus molecular model and force field selection were verified.

Chapter 4 and Chapter 5 described the model building of two-layer asphaltaggregate interface, and investigated the interfacial adhesion properties and mechanical behaviors. The susceptibility of asphalt-aggregate interface to moisture damage was discussed, and the interfacial chemo-mechanic relations were explored. In Chapter 6, mechanism of asphalt oxidative aging process was studied, and possible molecular models were prepared for the aged asphalt. Based on the proposed models, aged asphalt's thermodynamic, diffusive, and healing potential properties were investigated, as well as the adhesion properties to the mineral aggregate.

In Chapter 7, rejuvenating agent was used in aged asphalt to simulate the current engineering practice of reclaimed asphalt pavement, and simulation results of the molecular interaction and diffusion between rejuvenating agent and asphalt molecules were provided.

Chapter 8 concluded the whole dissertation by providing summary of main findings, conclusions and recommendations for future works.

Chapter 2 Literature Review

2.1 Basics of Classical MD Simulations

Molecular dynamics simulations can be characterized as a technique for calculating the equilibrium and transport properties of a classic many-body system, in which the word classic means that particles motion obeys the laws of classical mechanics. It computes the motions of a number of atoms and molecules in a system as a function of time. The basis of MD simulation is Newton's law of motions and statistical mechanics, where statistical ensemble averages are equal to time averages of a system. Molecular dynamics simulations require the definition of a potential function, or a description of the terms by which the particles in the simulations will interact. Particle in the simulation system has the kinetic (K) and potential (U) energies, and the sum of two together constitute total energy E.

Newton's equations of motion in mechanics are used to describe how particles in the system evolve in a period of time from a given initial state. For a system of N particles, the potential energy, U, with respect to the coordinate ri, the equation is described as

$$-\nabla_{\mathbf{r}_{j}}\mathbf{U}(\mathbf{r}) = \mathbf{m}_{i}\frac{\partial^{2}\mathbf{r}_{i}}{\partial t^{2}}$$
(2.1)

Where, m_i is the mass of atom i, r_i is a vector representing 3 coordinates of atom i, and j =1, 2,...N. Eq.(2.1) may look simple in the first glance, however it is as complicated when N is greater than 2. This can be solved numerically carried out in MD simulation, which is explained below.

The particles evolve as a sequence of time steps proceed in the MD simulation, and the process can be characterized by

$$\mathbf{r}(t_0) \rightarrow \mathbf{r}(t_0 + \Delta t) \rightarrow \mathbf{r}(t_0 + 2\Delta t) \rightarrow \dots \rightarrow \mathbf{r}(t_0 + k\Delta t)$$
(2.1)

where, **r** is a vector representing 3 coordinates of an atom and Δt is time step of MD simulation. **r**_i can be written in a Taylor series expansion,

$$\mathbf{r}(t_0 + \Delta t) = \mathbf{r}(t_0) + \mathbf{v}(t_0) \Delta t + 1/2 \mathbf{a}(t) (\Delta t)^2 + \dots$$
(2.3)

$$\mathbf{r}(t_0 - \Delta t) = \mathbf{r}(t_0) - \mathbf{v}(t_0) \Delta t + 1/2 \mathbf{a}(t) (\Delta t)^2 + \dots$$
(2.4)

Adding these two expression gives

$$\mathbf{r}(t_0 + \Delta t) = -\mathbf{r}(t_0 - \Delta t) + 2\mathbf{r}(t_0) + \mathbf{a}(t_0)(\Delta t)^2 + \dots$$
(2.5)

where, in Eq. (2.5), $r(t_0+\Delta t)$ is the particle position of the next time step $(t_0+\Delta t)$. Because particles positions at t_0 and the time step are already given, so what we need is acceleration of particle at time t_0 . For this purpose, F(r)/m is used, which is calculated in Eq. (2.1). Therefore the integration of the Newton's equations of motion is accomplished in successive time increments.

Like real experiment, molecular scale simulations are usually accomplished in the following procedures. At first it is sample preparation. The appropriate molecular models are developed, and the number of particles is specified. An optimized interatomic potential (or force field), together with reasonable initial and boundary conditions are required. A following equilibrium process is performed until the system properties no longer change with time. Newton's equation (i.e., $\mathbf{F}=\mathbf{ma}$) was applied and solved, and molecular positions, velocities and trajectories will be updated. Finally we perform the measurement and collect the desired properties from the molecular trajectories. Basically, four critical components are included in a classical MD simulation: (1) the potential

function (also force field), which is used to calculate forces among the atoms; (2) classical mechanics (i.e., $\mathbf{F}=m\mathbf{a}$), to determine the atoms acceleration and instantaneous velocity; (3) integration algorithm, to update energy and generate trajectories; (4) statistical mechanics/thermodynamics, the link between atomistic-scale and macro-scale could be interpreted. A typical MD simulation flow chart is shown in Fig. 1-1.



Figure 2.1 A typical MD simulation flow chart

Among these steps listed in Figure 2.1, the force calculation part is critical and is directly related to the efficiency and accuracy of simulation results. On one hand, the force calculation should be as simply as possible in order to increase efficiency; on the

other hand, physical description should not be comprised during the calculation. Since the force is calculated by taking the gradient of the potential U as described in Eq. (2.1), the specification of U is of vital importance.

2.2 Force Field

In the field of molecular simulation, a force field refers to a mathematical functional form and parameter sets used to describe the interatomic potential and calculate the potential energy of a system of atoms or coarse-grained particles in molecular mechanics and molecular dynamics simulations. It is clear that interaction potential is the most critical quantity in MD simulation and the goal of a force field is to describe entire classes of molecules with reasonable accuracy.

Some force fields were developed for high accuracy while only limited set of element types were included. This enables accurate prediction of many molecular properties. On the other hand, some force fields aimed for the broadest coverage of elements in the periodic table at a cost of lower accuracy. Therefore, during a MD simulation process, accuracy, transferability and computational speed are considered in all to determine the selection of a force field. In general, the total potential energy U can be comprised of a number of bonded and non-bonded interaction terms as shown in Eq. (2.6).

$$U_{\text{total}} = E_{\text{bond}} + E_{\text{non-bond}} \tag{2.6}$$

In Eq. (2.6), bonding potentials mainly include the following terms,

Bond stretch potential. Bond length is described as a harmonic potential based on Hooke's law inside a molecule. This potential is computed as the force needed to stretch a particular bond between atoms i and j with respect to its equilibrium length.

$$E_{bsp} = \frac{1}{2} \sum_{bonds} k_{i,j}^{r} (r_{ij} - r_{eq})^{2}$$
(2.7)

where $k_{i,j}^r$ is force constant of bond length, and r_{eq} is the equilibrium length.

Bend angles potential. The bend angle potential also has a harmonic form,

$$E_{\text{bap}} = \frac{1}{2} \sum_{\text{angles}} k_{i,j,k}^{\theta} (\theta_{ijk} - \theta_{eq})^2$$
(2.8)

where θ_{ijk} is the actual bond angle between atoms i, j and k, and θ_{eq} is the equilibrium value of the bond angle.

Torsion potential. Torsion angle are defined in terms of three connected bonds, hence four atoms are included, and the potential form is described by,

$$E_{tp} = \frac{1}{2} \sum_{\substack{\text{torsion} \\ \text{angles}}} k_{ijkl} (1 + \cos(m \emptyset_{ijkl} - \emptyset_{ijkl}^0))$$
(2.9)

where, k is torsional barrier, m is number of minima over 360°, and ϕ_{ijkl} and ϕ_{ijkl}^0 are actual and reference value of torsion angle between atoms i, j, k and l.

Non-bonded Interactions

In terms of the potential energy $E_{non-bonded}$, it characterizes the non-bonded interactions between atoms. Basically, non-bonded interactions between atoms are often divided into 1-body, 2-body, 3-body... terms. Three-body (and higher order) interactions are often neglected, and one-body term represents and external applied potential field or effect of walls. For a qualitative understanding of MD essentials it is sufficient to adopt the assumption that the interatomic potential U can be represented as the sum of twobody interactions. Therefore, a long range attraction and short range repulsion between two-body terms is described in van der Waals energy terms, which is always expressed as Lennard-Jones 12-6 potential.

$$E_{vdW} = \sum_{i < j} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$
(2.10)

where σ is the diameter, ε the well depth, and r is the distance between atoms.

If electrostatic charges are present, and then the appropriate Coulomb potentials are added.

$$E_{\rm cou} = \sum_{i < j} \frac{Q_1 Q_2}{\epsilon_r r}$$
(2.11)

where Q_1 , Q_2 are the charges of atoms i and j respectively, and ϵ_r is dielectric constant of the medium.

A similar form of force field as stated above is the OPLS (Optimized Potentials for Liquid Simulations) all-atom optimized potentials which is a popular force field for simulating biomolecules and polymers. Its functional form is simple and their parameters are typically determined by quantum chemical calculations combined with thermophysical and phase coexistence data. Meanwhile, some force fields will also include many cross terms such as COMPASS II (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field, which is the first parameterized and validated ab initio-based force field [6]. It has a broad coverage in covalent molecules including most common organics, small inorganic molecules, and polymers.

$$\begin{split} E_{\text{total}} &= \sum_{b} [k_{2}(b - b_{0})^{2} + k_{3}(b - b_{0})^{3} + k_{4}(b - b_{0})^{4}] + \sum_{\theta} [H_{2}(\theta - \theta_{0})^{2} + \\ H_{3}(\theta - \theta_{0})^{3} + H_{4}(\theta - \theta_{0})^{4}] + \sum_{\phi} [V_{1}(1 - \cos \phi) + V_{2}(1 - \cos 2\phi) + V_{3}(1 - \cos 3\phi)] + \\ \sum_{\chi} k_{\chi} \chi^{2} + \sum_{b,b'} F_{bb'}(b - b_{0})(b' - b_{0}') + \sum_{b,\theta} F_{b\theta}(b - b_{0})(\theta - \theta_{0}) + \sum_{\theta,\theta'} F_{\theta\theta'}(\theta - \\ \theta_{0})(\theta' - \theta_{0}') + \sum_{b,\phi} (b - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \sum_{b',\phi} (\theta - b_{0})(\theta - \theta_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi + V_{2} \cos 2\phi + V_{3} \cos 3\phi) + \\ \sum_{b',\phi} (\theta - b_{0})(V \cos \phi +$$

 θ_0)(V cos ϕ + V₂ cos 2 ϕ + V₃ cos 3 ϕ) + $\sum_{\theta,\phi} (\theta - \theta_0)$ (V cos ϕ + V₂ cos 2 ϕ +

$$V_{3}\cos 3\phi) + \sum_{\phi} \sum_{\theta'} \sum_{\theta'} K_{\phi\theta\theta'} \cos \phi(\theta - \theta_{0})(\theta' - \theta'_{0}) + \sum_{i>j} \frac{q_{i}q_{j}}{\varepsilon r_{ij}} + \sum_{i>j} \left[\frac{A_{ij}}{r_{ij}^{9}} - \frac{B_{ij}}{r_{ij}^{6}} \right] (2.12)$$

where the first four terms represent bond stretching (term 1), angle bending (term 2), a three-term Fourier expansion for torsions (term 3) and the out-of-plane (also called inversion) coordinate (term 4). Terms 5-11 describes the coupling between different degrees of freedom of bond deformation for cross terms. Terms 12 and 13 represent non-bond terms, in which term 12 is the Coulombic interaction between the atomic charges, and term 13 represents the van der Waals interactions, in which an inverse 9th-power term for the repulsive part rather than the more customary 12th-power term was adopted.

2.3 Calculation of MD properties

2.3.1 Ensemble

The output of any MD simulation is thus simply the positions and velocities of the particles of the system, that is, at every time step of the simulation. However, we cannot compare this kind of information to the experimental data, since no experiment so far provide such detailed measurements. In a typical experiment, an averaged property is averaged over a large number of particles and over short and/or long time range. Statistical mechanics can guide us what kind of averages we should aim to compute, in which it is assumed that every quantum statement of a many-body system with energy is equally likely to be occupied, and an average over all possible quantum states of a system is called an ensemble average. The truth of MD simulation is we can investigate the

average behavior of a many-particles system simply by computing the nature time evolution of the system numerically and averaging the quantity of interest over a sufficient long time.

An ensemble is a collection of all possible systems which have different microscopic states but have an identical macroscopic or thermodynamic state. Statistical ensembles can be generated by fixing state variables (for example, the energy E, volume V, temperature T, pressure P, and number of particles N). Structural, energetic, and dynamic properties can then be calculated from the averages or the fluctuations of these quantities over the ensemble generated. Three common ensembles are introduced here.

NVE ensemble, also known as microcanonical ensemble. In this case, system is isolated from changes in moles (N), volume (V) and energy (E), and corresponds to an adiabatic process with no heat exchange. A microcanonical molecular dynamics trajectory may be seen as an exchange of potential and kinetic energy, with total energy being conserved. The desired temperature cannot be achieved because there is no energy flow facilitated by the temperature control methods.

NVT ensemble, or canonical ensemble. In this ensemble, amount of particle (N), volume (V) and temperature (T) are conserved, and the energy of endothermic and exothermic processes is exchanged with a thermostat.

Isothermal-isobaric ensemble, also called constant-temperature, constant-pressure ensemble (NPT) allows control over both the temperature and pressure. Amount of particle (N), pressure (P) and temperature (T) are conserved. In addition to a thermostat, a barostat is added.

2.3.2 Single-Point Property and Time Correlation Function

Using output of any MD simulation is thus simply the positions and velocities of the particles, quantities that are of physical interest can be computed. Consider <A> as a time average over the trajectory generated by MD, where A is a dynamical variable, A(t). Two kinds of calculations are of common interest based on the MD simulation, and they are equilibrium single-point properties and time correlation functions.

The equilibrium single-point properties are running time average over the MD trajectories, where time t can be taken as long as possible.

$$\langle A \rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' A(t')$$
 (2.13)

When discrete timesteps are chosen, Equation (2.13) changes to

$$\langle \mathbf{A} \rangle = \frac{1}{L} \sum_{k=1}^{L} A(t_k) \tag{2.14}$$

The other one is time correlation function, and a correlation function of two dynamical variables has the form of,

$$< A(0)B(t) >= \frac{1}{L'} \sum_{k=1}^{L'} A(t_k) B(t_k + t)$$
 (2.15)

where B refers to another dynamical variable in general, and L' denotes the number of time origins. Eq. (2.15) shows a clear time-dependent relation, and it can describe dynamical information of the system.

2.3.3 Calculating Continuum Property by Atomic Scale Approach

One of the most important issues when considering multiscale modeling is how to define the continuum variables that are calculable within an atomic system. Both statistical mechanics approach and continuum theory can be related to thermodynamical concepts, and in this sense thermodynamics can be recognized as the bridge between atomistic methods and continuum theories, linking microscopic states with a macroscale system. On the basis of ensembles, accurate paths are defined mathematically connecting collective atomic behavior to thermodynamic equilibrium. For instance, calculation of temperature can be seen as a good way to explain this relationship as shown in Eq. (2.16), and several thermodynamic properties are to be studied and explored in later following chapter.

$$T = \frac{1}{3Nk_B} \langle \sum_{i=1}^N m_i \boldsymbol{v}_i \cdot \boldsymbol{v}_i \rangle$$
(2.16)

where N is particle numbers, v_i is velocity and k_B is Boltzmann constant.

Mechanical property is an interesting and important topic in both continuum and atomistic scale, and it is challenging to define an atomistic-based stress measure related to the continuum stress. Since continuum properties are valid at any random material point, and this is not true for atomistic quantities due to the discrete nature of atomic microstructure, in which the virial stress needs to be averaged over space and time to converge to the Cauchy stress tensor. In mechanics, the virial theorem (VT) elaborates a connection with the potential energy between particles. Although originally derived for classical mechanics, the virial theorem also holds for mechanics at atomistic scale, and in a fixed volume V containing interacting particles, the stress field can be determined by the virial theorem (VT). Extension of VT to MD simulations provides the instantaneous ensemble stress. For atomistic calculation, the internal stress tensor can be obtained using the so-called virial expression:

$$\boldsymbol{\sigma} = -\frac{1}{V_0} \left[\left(\sum_{i=1}^N m_i(\boldsymbol{v}_i \boldsymbol{v}_i^T) \right) + \left(\sum_{i < j} \boldsymbol{r}_{ij} \boldsymbol{f}_{ij}^T \right) \right]$$
(2.17)

where index N is particle number; i was summed over all the atoms occupying the total volume; m_i and v_i represent the mass and velocity of particle i; \mathbf{r}_{ij} denote distance vector from j to I; \mathbf{f}_{ij} is the interatomic force applied on atom i by atom j; and V_0 means the (undeformed) system volume. In a static model, the stress tensor is calculated with the first term on the right hand side omitted.

In summary, a system of particles which can be studied in a solid, liquid, or gas through MD simulations, and thermodynamic, structural, mechanical, dynamic and transport properties can be calculated from the outputs. Besides, detailed atomic trajectories were collected from MD simulations can help us clearly observe and calculate diffusion mechanisms which otherwise may only be indirectly deducted from experimental studies instead.

2.4 Asphalt Chemistry and Components

2.4.1 Asphalt Chemistry and Components

Amongst the earliest of construction materials, asphalt was used aplenty in all the early civilizations. In ASTM D 8-97, asphalt (or bitumen) is defined as a class of black or dark-colored (solid, semi-solid, or viscous) cementitious substances, natural or manufactured, composed principally of high molecular weight hydrocarbons, of which asphalts, tars, pitches, and asphaltites are typical. Asphalt is produced through the refining of petroleum, and its chemistry is very complicated because many different chemicals are present. As an overall descriptor, the chemical nature of the crude oil is generally described as paraffinic, naphthenic or aromatic if a majority of saturate, cyclic or aromatic structures are present, respectively. The elemental composition of asphalt is largely dependent on its crude source and it is difficult to give geographical generalization. Basically, asphalt consists in carbon (typically 80-88 wt.%) and hydrogen atoms (8-12 wt.%), which gives a hydrocarbon content generally superior to 90 wt.%. In addition, heteroatoms such as sulphur (0-9 wt.%), nitrogen (0-2 wt.%) and oxygen (0-2 wt.%) are generally present [7].



Figure 2.2 Classification of asphalt four components

Since asphalt material contains about 10^5 - 10^6 different molecules and has such a complex chemical mixture, it is totally torturous and impossible to obtain the detailed information on its chemical components. Therefore, modern separation techniques were used to divide asphalt into different fractions, which had similar polar and molecular characterization. It is noted that different separation methods used can cause different fractions of asphalt. From solubility point of view, asphalt materials are composed of

three main constituents, i.e., asphaltene that is the most viscous and polar components, saturates, consisting of aliphatic molecules and are least viscous and non-polar, and resin whose properties are in between of above two. Meanwhile, a four components method was proposed by American Society for Testing and Materials (ASTM) D4124-09, in which asphalt is divided into saturate, aromatics, resins and asphaltenes four components. Methods can be briefly described in Figure 2.2 [4].

2.4.2 Asphalt Pavement Failure Mechanism

Failure of typical civil engineering structures is defined as break or fracture, and this usually happens when applied load exceeds the maximum allowable value. Different types of distress can occur in asphalt pavement, and these distress could developed due to repeat of traffic load, temperature, moisture, aging, construction, or combinations. Common pavement distress includes fatigue cracking, rutting, roughness, thermal cracking, shoving, etc. All these distress can result in decrease of serviceability of pavement and deterioration of pavement performance [8].

Using appropriate preventive maintenance has been proved to be an efficient way to make sure that asphalt paving project will last long. However, it is necessary to be clear the factors and the mechanism for the pavement failure. Other than the insufficient design and poor construction issues, two most important mechanisms can be accounted for this problem. The first one is he sun and the air. To be specific, thin layer of mastic on the asphalt pavement surface ages (oxidizes) from exposure due to the air (oxygen) and the sun (ultraviolet light). In the aging process, the chemistry of the asphalt changes, turning it more brittle, less sticky (adhesive) and less elastic, and thus cracking can begin in cold weather. Besides, water plays the enemy part for the pavement. Once surface water can't get away in time, it works on debonding the asphalt binder from the aggregates, making the loose, unbound rocks easily raveling off the road. If water goes into the base layers, it can wash away the underlying pavement structure. Once moisture is trapped underneath the pavement, the water vapor creates pressure, forcing the asphalt to bleed to the surface, leaving the aggregates unbound and the pavement unstable. Modified asphalt and porous asphalt structure were proposed and used successfully and many years in the Netherland.

2.5 MD Studies on Asphalt

Molecular simulation techniques have been developed over many years, with the improvement of computer performance and computational technology, molecular simulation can be used to study more complex systems, and provide more accurate results and predictions. One example is using MD in the field of asphalt materials MD also has been proved to be a powerful and useful tool. Asphalt, widely used as a binder, is a highly complex material that comes mainly from the byproduct of crude oil distillation. This kind of old materials throws an interesting while challenging problem of modeling, since no single pure compound dominates their properties based on physical and chemistry viewpoints. By better understanding this important and necessary civil engineering material, efforts have been being made during past year, and important improvements have been achieved especially in recent years by using molecular

dynamics, which is recognized as a powerful method and has been commonly used for multiple purposes so far.

2.5.1 Chemo-Mechanical Relationship of Asphalt Binder

The chemical composition and molecular structure of asphalts are known to affect their rheological and mechanical properties. Zhang and Greenfield made an assumption that analyzing the microstructure of asphalt components and understanding molecular interactions among them can supply guidance on how to modify asphalt compositions, which could eventually make asphalt work better as road pavement [9]. A threecomponent mixture was chosen to represent the chemical families found in paving asphalt, two different asphaltenes model structures were considered, and a polymermodified model asphalt was also studied. OPLS-aa (all-atom optimized parameters for liquid simulations) force field was employed and two simulations programs Towhee and Lammps were used. Especially in this stud, both MD and MC were carried out, while MC was used to initiate each ternary system at five different temperatures, with a different random number seed chosen to ensure independent simulations, and MD was used to continue running the simulations for at least 1500 ps to reach a better equilibrated and lower energy state. It is suggested that the ultimate model mixtures displayed properties in simulations that were qualitatively similar to those of real asphalts but not quantitatively the same. The properties calculated from MD simulations of the mixtures include density and isothermal compressibility (inverse of bulk modulus). The thermodynamic properties suggest a high-frequency glass transition above 25 °C for both
model mixtures, and the mixture based on the more aromatic asphaltene shows a more pronounced transition and has a higher bulk modulus. Another conclusion was that the physical properties discrepancy between real asphalts and model asphalts was observed and this may due to the short time scales accessible in molecular simulations.

In another Zhang and Greenfield's work, the same experiment conditions were selected, and the viscosity and local dynamics in asphalts were studied at constant temperature and volume to two three-component model asphalt systems, based on two different asphaltenes which were stated above [10]. Local dynamics (decay in rotational correlation function and single-molecule diffusion coefficient) were studied at four different temperatures. The Green-Kubo and Einstein methods were applied to calculate viscosity at high temperatures and the Debye-Stokes-Einstein equation and Rouse model were used to inter-relate these results. Semiquantitative accuracy of such equivalent temperature dependence was found for naphthalene, and the results also showed diffusion coefficient had much smaller temperature dependence for all components in the model asphalt systems. Dimethylnaphthalene diffused the fastest while asphaltene molecules diffused the slowest. Neat naphthalene diffused faster than any component in model asphalts.

In Greenfield and Zhang's report, computer based MD simulations have been used towards developing simple mixture compositions whose physical properties resemble those of real asphalts [11]. MC simulations with the OPLS all-atom force field were first used to predict the density, heat capacity, thermal expansion coefficient, and isothermal compressibility for small molecules similar to compounds found in asphalts. Similar calculations were then performed on a 3-component mixture for which detailed property measurements were available in the literature. Good agreement between simulations predictions and experiment (literature values) was found in all cases. After that, MD simulations were used to estimate the same properties for two asphalt-like mixtures. Different density, glass transition, and bulk modulus properties were found for the mixtures, indicating the effects of different asphaltenes structures. Distributions in molecular orientation between molecules were also calculated to learn the extent of predicted parallel vs. perpendicular ordering in the mixture. A key finding was that molecules tend to order randomly over 3 nm length scales.

Ramamohan conducted MD simulations on MS using a COMPASS force field in NVT (MD conducted at constant volume and constant temperature) to investigate surface free energy and molecular diffusion coefficients of SHRP binders, as well as a hypothetical asphalt binder, which comprising of 20% asphaltenes (by weight), 40% napthene aromatics and 40% of saturate [12]. He concluded that the exact molecular structure and composition of asphalt binders could not be determined, and it was not possible to determine the exact molecular structure and composition of asphalt binders tructure and composition of asphalt binders tructure and composition of asphalt binders with the present available technology. However, instead of trying to determine the absolute values of surface energy or diffusion coefficients, he focused on the trends in these values based on changes in the chemical makeup of asphalt binders. The interfacial diffusion coefficient was proposed to be a better parameter than self- diffusion coefficient for estimating the healing in asphalt binders, in which higher percentage of saturates (longer chains) in the chemical structure resulting into higher diffusion coefficients.

Amit Bhasin, et al. used MD simulations to study self-healing properties of asphalt binder [13]. Their finding, based on MD simulations, explored the relationship

between molecular morphology and rates of self-healing and further reinforced the relationship of chain length and branching to self-diffusivity of molecules at the interface. It is also concluded that the accuracy of the results from MD simulation is dependent on the accuracy of molecular structures used as an input for the analysis. In all, this study illustrates the utility of using molecular simulations to better understand the interrelationship among molecular properties, healing mechanism, and experimental parameters that may be used to quantify these properties.

More recently, one four-component united-atom molecular model of bitumen of "Cooee-bitumen" model based on the Hubbard-Stanfield classification was proposed by Hansen et al [14]. This four-component model contains realistic chemical constituents, and a coarse graining level that suppresses the highest frequency was introduced. To understand the dynamical heterogeneity of bitumen, relaxation processes was studied, mean-square displacement, the stress autocorrelation function, and rotational relaxation were studied, the shear viscosity and shear modulus were also evaluated and compared to the experimental data, and results were in reasonable agreement.

New chemical compositions of model asphalts to represent the AAA-1, AAK-1 and AAM-1 asphalts of the Strategic Highway Research Program are proposed by Li and Greenfield, in order to enable molecular simulations that can further an understanding of asphalt physical, rheological and mechanical properties [15]. Larger molecules than before were used, and classical molecular dynamics simulations were performed. Physical properties for one of the model asphalt systems such as densities was calculated and results were closer to experimental data compared to previous model systems, with good agreement for thermal expansion coefficient. In Li and Greenfield's following study, viscosity, relaxation time and dynamics were also computed and results provide an improved tool for relating asphalt chemical compositions to rheological and mechanical properties [16].

Besides using MD, experimental study was also carried out to find the chemomechanical relation. Wei et al. adopted the statistical methods of a single regression and multiple regression analysis to correlate the relationships between chemical composition and surface free energy of asphalt binders, and twenty-three asphalt binders were used in a Strategic Highway Research Program (SHRP) [5]. Results showed that concentrations of saturates, aromatics, wax or asphaltenes can lower the value of the surface free energy of the asphalt binder; while the resins, ratio of resins/asphaltenes, and the colloid index positively correlate the value of the surface free energy. Four proposed regression models were developed, but they also pointed out that more asphalt binders are suggested to validate the models.

2.5.2 Aggregation and Aging Behavior of Asphalt Binder

Asphalt was described as a colloidal dispersion of asphaltenes micelles in the maltenes. The resins, which are the polar components of the maltenes, were thought to stabilize the asphaltene micelles [17]. Based on this structure, agglomeration behavior of asphalt is of vital interest since it will influence the asphalt chemical structure which is the foundation of materials physical properties. To this end, the aggregation behavior of asphaltenes in asphaltene-resin mixtures within different host media was studied by Ortega et al. in order to predict the effect of the intermolecular interactions on the

aggregation process as a function of composition and embedding medium [18]. MM/MD simulations were shown as a complementary tool to understand the behavior of asphaltene-resin mixtures. Ding et al. studied agglomeration behavior of asphalt by means of MD, and investigated effects of addition of three types of Styrene-butadiene-styrene (SBS) to see how they affect chemical structure of asphalt binders [19]. Radial Distribution Function Statistical Analysis (RDF) was performed to find molecular agglomeration behavior between asphaltene-resin and asphaltene-maltene. Results of simulation show that SBS affected the molecular agglomeration behavior of asphalt binders, and the impact of modifiers is largely dependent on the molecular structure of asphaltenes. The agglomeration structure of asphalt molecules is more susceptible to SBS when the asphaltene alkane side branches are longer.

Wang et al. conducted molecular dynamics study interactions of the saturate, aromatic, resin, and asphaltene (SARA) four fractions, as well as the correlation between fractions and the "bee-like structures" observed by atomic force microscopy in asphalts [20]. It was found confirmed that the arrangement of SARA fractions largely conformed to the modern colloid theory, and long-chain alkanes were inserted into layers of asphaltenes, and small sulfides without long alkyl chains were adhered to large sulfides or asphaltenes. "Bee structures" were formed by strong interactions between the dispersed phase and continuous phase, and affected by long-chain paraffin. Asphaltenes played as a core in the whole mixture.

Asphalt binders, during production, construction and in the field, are subject to oxidative aging that involves the reactions between oxygen molecules and the component species of bulk asphalt. As a result, significant alterations can occur to the desired physical and/or mechanical properties of asphalt. Aging effect on the thermodynamic properties of asphalt binder components were investigated by Tarefder and Arisa [21]. A Culgi software and Dreiding forcefield were employed to start the MD simulations. For oxidative aging of asphaltenes, the percentage of oxygen considered in MD simulations is 0.1, 1, 12, 23, and 46.5% of asphaltenes. For oxidative aging of resins, the percentage of oxygen used in MD simulations is 5, 15, and 25% of resins. MD simulations were run on a system at a fixed NPT ensemble to predict internal energy, structure, and density as function of the temperature. Density, glass-transition temperature, and potential and kinetic energies of the system were analyzed as output. Changes in potential and kinetic energies of asphaltene and resin due to oxidative aging were discussed in the paper, and the results showed that the glass-transition temperatures of asphaltene and resin were determined from density versus temperature relationships. The density decreased with the increasing temperature due to the expansion of the free volume, and the glass-transition temperature was affected by the percentage of oxygen while in resin, no definite relationship between them could be established.

Asphalt aging could cause long-term deterioration of asphalt binders during the service life. It was concluded that the generation of oxygen-containing polar chemical functionalities can result in asphalt molecules oxidative hardening, which in turn causes agglomeration among molecules due to increased chemophysical associations [22]. In addition, oxidation can also cause aromatization of certain asphalt molecules, and as a result, further agglomeration of asphalt components are to be expected in ambient conditions. In practice, a common way to alleviate asphalt aging is to addition of chemical additives or modifiers as antioxidants, and two physical properties including

viscosity and ductility were always tested for oxidation and antioxidant evaluation. While from a microscale point of view, molecular interactions among the polar molecules of asphalt are the primary mechanism of agglomerations that strongly influence the physical properties and macroscopic performance of asphalt [23]. To this end, an investigation was carried out by Pan et al. [24]. They developed an atomistic-based chemophysical environment to evaluate asphalt oxidation and antioxidants. In their study, molecule models of asphalt and anti-aging additives (lignin) were proposed, a reaction force field (ReaxFF) was employed. Generation of light-molecular-weight saturate molecules tends to leave the bulk asphalt, and agglomeration of asphaltenes and aromatics were also observed during aging. Chain breaking of saturates, sulfoxidation, and ketonization at benzylic carbons are the major mechanisms for the oxidative hardening of asphalt in typical service conditions. Besides, lignins can slow down the aging speed of asphalt, and increase asphalt stiffness as well.

2.5.3 Asphalt-Aggregate Interface Behavior

Asphalt concrete consists of mineral aggregate bound together with asphalt, laid in layers, and compacted. Asphalt-aggregate interactions are important in the adhesion of asphalt cement to aggregate because the asphalt must adhere to the aggregate for the adhesive binding action of asphalt to occur, and the strength of the adhesion bond between aggregates and asphalts determines the performance of pavement. For acceptable performance, this adhesion bond must withstand the presence of water for prolonged periods of time. Pavement failure at the aggregate-asphalt interface due to water is termed "water stripping" [1]. The asphalt-aggregate interaction is a thin-film phenomenon, their bad interaction relates to pavement distresses such as moisture damage, tender mix, permanent deformation, fatigue cracking, and low temperature cracking. The thickness of the films or layers often is in the range of 2 nm up to 1 μ m and more in layered pavement materials, and by studying atomic motion in this region could investigate the deformation and ductile failure process and help us better understand interface failure mechanism.

Headen and Boek described a method for the calculation of the free energy of aggregation of an asphaltene molecule on a calcite surface, and, for the first time, calculated the potential of mean force (PMF) between an asphaltene molecule and the calcite surface directly by a constraint force method, and the preliminary calculations of were presented in his paper [25]. The free energy of adsorption was calculated to be -110 kJ/mol, which was a reasonable value for simulations in vacuo corresponding to an effective solvent [18]. He suggested that a further effect of using an explicit solvent, instead of an effective dielectric medium, be investigated to give more precise values for binding forces and energies between asphaltene molecules and calcite surfaces, which would allow for a comparison to atomic force microscopy (AFM) and surface force apparatus (SFA) data to help interpret the nature of asphaltene aggregation on the calcite surface.

Bulk mechanical properties of asphalt and mineral aggregate, as well as asphaltaggregate interface properties under tensile or confined shear loading were studied [26]. The moisture sensitivity properties of the interface are also evaluated. In this paper, he first reviewed the advances of nano-mechanics modeling method and then introduced the recent advances of our research on the molecular origin of deformation and failure processes of asphalt-aggregate interfaces. MD simulations were carried out by Lammps using a CVFF-aug force field, asphalt-aggregate interfacial atomistic deformation and failure behaviors, as well as moisture effects on asphalt mixture strength were evaluated. The simulations results, which showed a satisfactory agreement between the theoretical and pavement industry observations, provided valuable insights into mechanistic details of nanoscale interactions, particularly under conditions of various deformation rates and different temperatures. Lu and Wang employed MD to investigate the elastic constants of a quartz structure, tensile stress-strain state and adhesion failure behavior of asphalt-rock interfaces, and an interfacial debonding characteristics or the adhesive failure were implemented with a large-scale MD simulations technology [27]. The results showed that molecular mechanics method gave an efficient way of calculating elastic properties of crystal structures, and highly anisotropic elastic properties of a quartz structure would appear from atomistic scale and tensile strength of the asphalt-quartz interface system was controlled by the stress state at the asphalt-rock interface layer. Asphalt-rock interface adhesive failure appears to be ductile at freezing environmental temperature and low strain rate.

MD simulation can help gain insights into the molecular behavior of different asphalt fractions on aggregate surface. With a purpose to analyze oil fractions distribution on soil and the influences of solvent extraction conditions, Wu et al. used MD to study the molecular scale sorption, diffusion and distribution of asphaltene, resin, aromatic and saturate (SARA) fractions of heavy crude oil on quartz surface [28]. Temperature effect was also considered. Results showed that when oil adheres to the quartz surface, aromatics and saturates transported randomly into and out of the complex consisting of asphaltenes surrounded by resins, and this distribution pattern could be rearranged by temperature increase. Temperature plays a pivotal role in the microstructure changes of oil fractions at the surface which was ultimately responsible for the sorption, diffusion and distribution of oil molecules. Besides, among molecular interactions, Van der Wall energy accounts for the major contribution.

Chapter 3 MD Characterization of Asphalt Binder

This chapter developed an atomistic modeling approach for studying related properties of asphalt materials and evaluated the accuracy of modeling through comparisons with experimental data. In order to achieve this objective, fully atomistic models were built for MD simulation considering representative 3-component asphalt models, as well as the most recent 12-component asphalt models. Bulk asphalt models were used to derive material properties of asphalt binder in terms of thermodynamic, rheological, structural, and diffusive behaviors. The MD simulation data were compared with laboratory results, and the force field effects were also discussed.

3.1 Molecule Models for Asphalt

3.1.1 3-component Asphalt

Asphalt material is a complex chemical mixture of molecules that are predominantly hydrocarbons with a small amount of structurally analogous heterocyclic species and functional groups containing sulphur, nitrogen and oxygen atoms. From solubility point of view, asphalt materials are composed of three main constituents, i.e., asphaltene that is the most viscous and polar components, saturates, consisting of aliphatic molecules and are least viscous and non-polar, and resin whose properties are in between of above two. Due to the complex mixture nature of asphalt, many efforts were made to construct model asphalt mixtures with reasonable compositions. The average molecular structures for different asphalt binders were proposed based on Nuclear Magnetic Resonance (NMR) spectra [29]. These average asphalt molecular models can achieve proper element concentrations and aromatic/aliphatic ratios, but it cannot reflect the molecular packing between different molecular phases and thus accurately capture the complexity of asphalt composition.

In order to build a model more similar to the real asphalt, the diversity of chemistries and polarities are required. Since the focus of this study is not to determine the representation of molecular structure for asphalt binder, an existing three-component model asphalt system was used [9]. In the three-component model, n-C22 molecules were used to represent saturates and 1,7-dimethylnaphthalene was used to represent resin (naphthene aromatics). Two different asphaltene molecules were proposed, one is a moderate-size aromatic core with very small branches, and the other is smaller aromatic core and much longer alkane side branches. This relative simple model has been proved acceptable to predict physical and rheological properties of asphalt binder in a general sense [10]. Figure 3.1 shows the molecular structures of two different asphaltene models. Table 3.1 shows the molecular compositions of asphalt mixtures with two different asphaltene models. The mass fraction was selected to resemble the total carbon/hydrogen ratio reported by previous researchers [30].

Asphalt	Asphaltene		1, 7-dimethyl naphthalene		n-C ₂₂	
Model	Molecule	Mass	Molecule	Mass	Molecule	Mass
	number	fraction	number	fraction	number	fraction
Asphalt-1	5	20.7	27	19.7	41	59.6
Asphalt-2	5	21.1	30	19.8	45	59.1

Table 3.1 Molecular composition of 3-component asphalt model



(c) 1,7-dimethylnaphthalene (d) n-C22

Figure 3.1 Molecular structures used in 3-component asphalt (Carbon atoms are shown in grey, sulfur atoms in yellow, and hydrogen atoms in white)

3.1.2 12-component Asphalt

Recently, with the development of computer simulation and material characterization method, three 12-component asphalt models were proposed by Li and Greenfield [15] to represent three of SHRP core asphalt, namely are AAA-1, AAK-1 and AAM-1 asphalts, in order to better understand asphalt physical, rheological and mechanical properties. Larger molecules than three-component asphalt systems in the past can improve agreement with size characterization data, and by using molecular simulations, it is supposed to provide us a better understanding of asphalt physical, rheological and mechanical properties. For this study, these newly developed models were used as they are. Each separate molecule structure is illustrated in Figure 3.2. The numbers of each component in the asphalt model were chosen by the comparison between model and experimental values for all three asphalt systems, as shown in Table 3.2.

The 12-component asphalt model, first proposed to represent SHRP core asphalt AAA-1, was used to represent the virgin asphalt binder [15]. Figure 3.2 shows asphalt molecular models following SARA classification system (S for saturates, first A for asphaltenes, R for resins and the second A for aromatics). The details of asphalt molecular system composition and the number of atoms are listed in Table 3.2. From solubility point of view, and the four components concept proposed by American Society for Testing and Materials (ASTM) D4124-09, the asphalt is divided into saturate, aromatics, resins and asphaltenes four components. It can be observed that resins in the

three components of asphalt were further divided into resins and aromatics in the four components of asphalt.

Three different molecular structures are used to represent asphaltene fraction, which is the most polar component with biggest size in the asphalt system, as shown in Figure 3.2(a). These asphaltene structures are originally proposed by Mullins, and they are asphaltene-phenol, asphaltene-pyrrole and asphaltene-thiophene, respectively [31]. Slight modifications, such as side group locations, were made to optimize molecular configuration, and these structures are used as asphaltene molecules in our asphalt system, following the suggestions in the literature [15]. Resins, also called polar aromatics, are composed of polar aromatic rings and non-polar paraffinic groups. Heteroatoms such as oxygen, sulphur and nitrogen are found in rein molecules and it is the second polar fraction in asphalt. Resin acts as a stabilizer for the asphaltene and thus plays an important role in asphalt stability [17].

Figure 3.2(b) illustrates the five molecules used in this study to represent resin fraction. namely quinolinohopane, thio-isorenieratane, and they are benzobisbenzothiophene, pyridinohopane and trimethylbenzene-oxane. The aromatics, sometimes referred as naphthene aromatics, are hydrocarbons structures with light molecular weights as well as minimal polarity in asphalt system. Two molecular models, perhydrophenanthrene-naphthalene (PHPN) dioctyl-cyclohexane-naphthalene and (DOCHN), are selected as representative aromatic fraction, as shown in Figure 3.2(c). Resins, together with resins, are the most abundant fractions within an asphalt. Saturates contain aliphatic chain structures with branching and cyclic alkanes. Saturates are the least sensitive to oxidative aging and rarely change with time due to lack of polar atoms

or aromatic rings. Squalane and hopane, which are shown in Figure 3.2(d), are adopted as saturates molecules.



(a) Asphaltene molecules



(b) Aromatic molecules

ž.



(c) Resin molecules



(d) Saturate molecules

Figure 3.2 Molecular structures of 12-components AAA-1 asphalt

(Carbon atoms are grey, sulfur are yellow, hydrogen are white, and red is oxygen)

A sphalt composition molecule		No. of	Mass	Fractions by
Aspiration	composition molecule	molecules	fraction	exp. solubility
Saturate	Squalane	4	10.7	10.6
	Hopane	4	10.7	10.0
Aromatic	PHPN	11	30.6	31.8
	DOCHN	13	50.0	
Resin	Quinolinohopane	4		
	Thioisorenieratane	4		
	Trimethylbenzeneoxane	5	38.1	37.3
	pyridinohopane	4		
	Benzobisbenzothiophene	15		
Asphaltene	Asphaltene-phenol	3		
	Asphaltene-pyrrole	2	16.5	16.2
	Asphaltene-thiophene	3		

Table 3.2 Component fractions in model and experimental AAA-1 asphalt

3.2 Density of Asphalt

Density is an important thermodynamic property and it is a direct indicator to see whether the model size and force field could yield reasonable and accurate simulation results. Therefore, density values at different temperatures were calculated for asphalt-1 and asphalt-2 models, respectively. With the simulation process stated above, the density results of asphalt models are shown in Figure 3.3. The results show that the highest predicted density is $0.92g/\text{cm}^3$ at -10 °C and the densities reduces to $0.85-0.88g/\text{cm}^3$ at 60 °C. As expected, a steady increase of density with decreasing temperature was observed. The density predictions are slightly smaller than the reported experiment data from 0.99 to 1.33 g/cm³ at 60 °C [32]. This is properly because the higher hydrogen, more carbon, and less sulfur were used in the molecular model of asphalt, together with a lack of heteroatoms besides sulfur [9]. An improved model asphalt system with 12 chemical components has been proposed recently to provide more accurate density predictions [15], which will be used in future study.



Figure 3.3 Comparison of density results for two asphalt models

The density of asphalt was calculated using molecular dynamics at each temperature and 1 atm pressure, and the detailed method is described in [33]. As shown in Figure 3.4, the AAA-1 density at 300K was 1.003g/cm³. Literature data for experimental SHRP AAA-1 asphalt at 333.15K is 1.03-1.04 g/cm³, and around 1.0g/cm³ at 300K for simulated results by Li and Greenfield [15]. It can be found that the later asphalt model showed higher accuracy of asphalt density results than the earlier asphalt models with three components.



Figure 3.4 Density of AAA-1 asphalt in dependence of time during NPT

3.3 Surface Free Energy of Asphalt

Surface free energy is theoretically defined as the magnitude of work required to create a unit area of a new surface of the material under vacuum conditions. From an atomistic point of view, molecules in the bulk material are surrounded by other molecules from all sides; the surface free energy equals the work needed to extract the molecules from the bulk and create a new area of surface molecules. Therefore, surface free energy can be used to measure the disruption of intermolecular interaction that occurs when a surface is created. Surface free energy has been proposed for selecting the combination of asphalt binders and aggregate types that have the necessary compatibility to form strong bonds and resist moisture damage [34]and it was found related to the cohesive bond energy of asphalt materials [35].

In this study, the surface free energy was calculated as the difference between the potential energies of the thin asphalt layer and its corresponding bulk asphalt divided by the surface area created upon formation of the thin layer, as shown in Eq. (3.1) [36] [37]. This definition calculates the contribution of internal potential energy to the surface free energy but cannot consider the entropic contribution due to deformation and segregation of molecular chains to the surface energy. The Connolly surface area was used to consider the surface unevenness due to molecular agglomeration in asphalt models. The Connolly surface area consist of all the points of the van der Walls surface at which a solvent sphere can touch and it is also known as accessible surface area [38].

The work of cohesion (W_{aa}) can be calculated from the surface free energy (γ_a) using Eq. (3.2), which is defined as the work required to separate a unit area of a liquid or solid into two unite areas. The work of cohesion is used as an indicator for cohesion properties of asphalt when the failure within the asphalt is concerned.

$$\gamma_a = (E_{\text{film}} - E_{\text{bulk}})/2A \tag{3.1}$$

$$W_{aa}=2\gamma_a \tag{3.2}$$

Where, γ_a is surface free energy; W_{aa} is work of cohesion; E_{film} and E_{bulk} are the potential energy of the confined asphalt layer and bulk asphalt, respectively; and A is area of the new surface to be created.

Table 3.3 summarizes the calculated surface free energy and work of cohesion for two asphalt models. The difference between the dimensional area and the real surface area of asphalt model can be clearly observed. It can be seen that in general the calculated results agree well with the measured values reported in the literature, although the simulation results were slightly greater than most experimental results. The discrepancies could be caused by the approximation of asphalt molecular models. Previous experimental measurements have shown that the concentration of saturates or asphaltene could lower the value of surface free energy, while the resins and the ratio of resin/asphaltene could increase the value of surface free energy [5]. This indicates that further study is needed to evaluate sensitivity of surface free energy of asphalt with different chemical compositions and elemental contents.

Asphalt-1	Asphalt-2	AAA-1	Expt. values
34.11^3	35.64^3	38.08^3	N/A
2258	2604	2655	N/A
29.91	37.01	35.49	13-47.6
30.01			[5] [39]
77 60	74.02	70.98	27-65
//.02	74.02		[40] [41]
	Asphalt-1 34.11^3 2258 38.81 77.62	Asphalt-1 Asphalt-2 34.11^3 35.64^3 2258 2604 38.81 37.01 77.62 74.02	Asphalt-1Asphalt-2AAA-134.11^335.64^338.08^322582604265538.8137.0135.4977.6274.0270.98

Table 3.3 Surface free energy and work of cohesion of asphalt

3.4 Cohesive Energy Density and Solubility Parameter of Asphalt

Cohesive energy density (CED) is used as a measure of the mutual attractiveness of molecules to assess intermolecular interaction inside an asphalt molecule model [42]. A solubility parameter can be further defined from the CED using Eq. (3.3). The solubility parameter quantifies the solvent-solute interactions to separate solvent-solvent and solute-solute molecules as a means of minimizing the Gibbs free energy of the entire system [43]. It has been used to study molecular attractions properties in the asphalt system and new asphalt models and evaluate colloidal stability in asphalt [44] [45]. Since the intermolecular interaction within asphalt is evaluated via van der Waals and electrostatic (including hydrogen bond) interactions, solubility parameter can be expressed in two components, as shown in Eq. (3.4).

$$\delta = \sqrt{\text{CED}} \tag{3.3}$$

$$\delta = \sqrt{\delta_{\rm vdw}^2 + \delta_{\rm ele}^2} \tag{3.4}$$

where, δ is solubility parameter; CED is cohesive energy density; and δ_{vdw} and δ_{ele} are representing the contributions from van der Waals forces and electrostatic interactions, respectively.

Table 3.4 shows the calculated CED and solubility parameter of bulk asphalt model. The values of CED and solubility parameter were found in good agreement between simulation results and previous results from experiments or simulations. It was found that for solubility parameter values, van der Waals component was much greater than electrostatic component. This means that cohesion is largely dependent on van der Waals forces which held the molecules of asphalt binder together. On the other hand, the results show that the asphalt-1 model has slightly greater values of CED and solubility parameter than those of the asphalt-2 model. It indicates that asphalt-1 has stronger mutual attractive interactions among its molecules fractions, and presents better cohesion properties as compared to asphalt-2. This finding is consistent with the work of cohesion of two asphalt models that is derived from surface free energy as shown in Table 3.3.

Properties	Asphalt-1	Asphalt-2	AAA-1 asphalt	Expt. and previous simulation values
CED (10^8 J/m^3)	3.22	3.08	3.10	3.19-3.22 [20]
Solubility δ ((J/cm ³) ^{1/2})	17.95	17.56	17.58	13.30-22.50 [20] [46]
Electrostatic δ ((J/cm ³) ^{1/2})	1.11	0.90	1.42	N/A
Van der Waals δ ((J/cm3) ^{1/2})	17.92	17.54	17.29	N/A

Table 3.4 Cohesive energy density and solubility parameter of bulk asphalt

3.5 Viscosity

Fluid viscosity measures its resistance to gradual deformations caused by shear or tensile stress. Asphalt viscosity is an important engineering property because it is closely related to the mixing and compaction temperatures used in the construction of hot mix asphalt (HMA). The required fluidity of asphalt binder will facilitate its use in pumping for delivery, plant operations, aggregate coating, etc. In this section, two simulation methods were employed here to evaluate the viscosity of asphalt binder.

3.5.1 Green-Kubo Method

In Green and Kubo's series of studies, it was showed that shear viscosity can be related to the correlation functions of tensor in thermal equilibrium [47], and this approach was used widely by many researchers in MD simulations [10] [16] [48]. In order to calculate the asphalt viscosity from MD simulation, the shear stress autocorrelation function was calculated by Eq. (3.5) and the corresponding Green-Kubo equation was used and given in Eq. (3.6).

$$C_{p}(t) = \frac{1}{3} \sum_{ab} \langle P_{ab}(0) P_{ab}(t) \rangle$$
(3.5)

$$\eta = \frac{V}{K_{\rm B}T} \int_0^\infty C_{\rm p}(t) dt \tag{3.6}$$

where, **P** is atom stress tensor, ab indicates the off-diagonal stress elements in xy, yz and xz direction were used, and <...> shows ensemble average was performed. T is the simulation temperature; V is the volume of simulated system; k_B is the Boltzmann constant.

The Green-Kubo (GK) method was used to calculate the model asphalt viscosity at 533.15 K as a function of integration time. The correlation function results are shown in Figure 3.5, and the calculated viscosity result is illustrated in Figure 3.6.



Figure 3.5 Normalized stress autocorrelation function as a function of time



Figure 3.6 Viscosity of AAA-1 asphalt model at 533.15K using GK method

In Figure 3.5, the stress autocorrelation function was averaged over the xy, yz and xz direction, and was fully decayed. The relaxation process was quantified by a nonexponential function and fitting result was also presented. A higher temperature of 533.15K was used in order to obtain viscosity result at shorter time period integration. Using the fitting function and integrate with time the viscosity result was obtained. An estimated viscosity result based on the plateau of integrated function is approximately 1.24cP (1cP= 0.001Pa·s), as shown in Figure 3.6. The estimated viscosity result of model AAA-1 asphalt is in good agreement with previous research result by Greenfield, which was 2.2cP at 533.15K [16]. Using the same method, viscosity of AAA-1 asphalt at different temperatures, and asphalt models containing different chemical compositions, such as AAK and AAM asphalt models, were also compared. Their estimate results are summarized in Figure 3.7.



(a) asphalt composition effect





Figure 3.7 Asphalt viscosity comparisons using GK method

From Figure 3.7 it can be seen that the asphalt viscosity varied with its chemical compositions, and all are in a reasonable range of viscosity values. This is in accordance with the fact that asphalts obtained from different crude oil show different viscoelastic behaviors. Besides, the temperature-viscosity relations presented in Figure 3.7 agreed well with the facts that asphalt is a type of temperature sensitive material, and its viscosity increased with the decrease of temperature. However, the present viscosity estimations have uncertainties. This is because molecules at low temperature are difficult to fully relax, and this is especially true when large molecules such as asphaltene molecules are considered. Longer simulation times are required to ensure the molecules are fully relaxed. This explained our observation that the asphalt viscosity values were far from experimental values, especially at low temperatures such as 333.15K. It is expected that longer time simulation performed by computers with higher computation ability will improve the viscosity simulation results at low temperatures. Besides, the Debye-Stokes-Einstein equations can predict the asphalt low temperature viscosities by relating the high temperature viscosities and molecular relaxation times.

3.5.2 Muller-Plathe Method

Unlike the equilibrium Green-Kubo method, Muller-Plathe method is a type of non-equilibrium method to calculate the shear viscosity. Besides, as a reverse nonequilibrium MD (rNEMD) method, the cause and effect are reversed compared with usual non-equilibrium MD (NEMD) simulations in which the shear velocity is imposed and the stress response is measured. The advantage of Muller-Plathe method lays in the following facts. For one thing, flux is hard to define or converge slowly microscopically. For another, the method can be used in microcanonical ensemble in MD simulation where no thermostat is used and the total energy and linear momentum is conserved [49].

Specifically, the Muller-Plathe (MP) method imposes a momentum flux on the system and then records the shear velocity at selected time steps, and the calculation process is followed by Eq. (3.7) and (3.8).

$$j_{z}(p_{x}) = -\eta \frac{\partial v_{x}}{\partial z}$$
(3.7)

$$j(p_x) = \frac{p_x}{2tA}$$
(3.8)

Where η is shear viscosity, $j_z(p_x)$ is momentum flux (x momentum flows in z direction), and $\frac{\partial v_x}{\partial z}$ denotes shear rate with respect to xz direction. A is area which equals box length $L_x \ge L_y$; t is simulation length. The factor 2 is used because the periodical condition of simulated system. The response of the shear velocity was recorded every 10000 steps. The viscosity unit was changed from gram/mol/angstrom/femtosecond in MD system to cP (0.001Pa s) in the experimental asphalt testing specification, by using Avogadro's constant and unit conversion coefficient. The viscosity results as a function of simulation time are illustrated in Figure 3.8.

Figure 3.8 shows the viscosities at the temperature of 533.15 K in the unit of centipoise (0.001Pa·s). From Figure 3.8(a) it can be found that the temperature fluctuated during the simulation when we set our target temperature at 533.15K. Before generating results, the system was equilibrated in NPT and NVT ensemble for 5ns and 5ns, respectively. The temperature once decreased to 520K or even went up to 550K, but stayed at 533.15 +/- 5 K most of the time, and this is a normal phenomenon often

observed in MD simulation. A fluctuation was observed for the first 500ps and then kept consistent at a certain magnitude, as shown in Figure 3.8(b). This is acceptable considering the size of simulated system used in our MD simulations. The average of estimated viscosity result for AAA-1 asphalt was 15.1cP, which is larger than that of GK method (1.2cP). The calculated viscosity was in the same range as Yao's research result of 54.16cP at 443.15K, in which a four-component asphalt model as well as Amber force field was employed [50]. At the same time, the experimental value of AAA-1 asphalt at such a high temperature was not available, and the only viscosity value at a higher temperature is 283 Centistokes (kinematic viscosity unit, around 250cp after unit transfer) at 408.15K [51]. However, we found the viscosity result agreed well with the experiments values of PG 58-34 asphalt, in which a viscosity of around 100cP was reported at the temperature of 463.15K [52].



(a) Muller-Plathe viscosity calculation as a function of temperature



(b) Muller-Plathe viscosity calculations as a function of time Figure 3.8 Viscosity of AAA-1 asphalt model at 533.15K using MP method

Figure 3.9 presents the MP viscosity results for AAA, AAM and AAK asphalt. All the simulation and calculation process are the same and thus it is not repeated here. Different values and trends were observed when compared with GK viscosity results, and this is probably due to the different simulation methods employed. However, it can be found that the trends between asphalt viscosity and asphalt composition were the same for both methods. Specifically, the AAM asphalt showed highest viscosity value while AAK exhibited lowest viscosity. The MP method predicted higher viscosity than that of GK method. It has to be noted that as a non-equilibrium MD method, the simulation time needed for viscosity calculation may be not as long as that required by equilibrium MD such as GK method. We did observe the large viscosity values at the first 1ns and then became stable, and the appropriate time needed is still to be determined. The difference between the simulation and laboratory data could be due to model accuracy as well as force field selection. Further works are needed to narrow the difference.



(b) temperature effect

Figure 3.9 Viscosity comparisons using MP method

3.6 Shear Modulus and Phase Angle

Asphalt is a thermoplastic material showing viscoelastic behaviors in most pavement service conditions [53]. These behaviors are often measured under linear viscoelastic (LVE) condition, in which factors affecting the material stresses and strains relations are temperature and loading time rather than their magnitudes. The rheological properties under LVE conditions are of critical importance to the asphalt performance in the field. Normally, the parameters well indicating asphalt rheological properties are always described with respect to the complex modulus (G*) and phase angle (δ). G* is defined as a ratio which equals maximum shear stress divided by maximum strain when the asphalt is subjected to shearing loading condition; while the δ means the lag (or phase difference) between applied stress and strain in the situation of harmonic oscillation. In laboratory testing process, these two parameters are recorded and calculated automatically by Dynamic Shear Rheometer (DSR) followed by American Association of State Highway and Transportation Officials (AASHTO) specification T315-10.

In the traditional approach, the G* and phase angle were measured over a range of temperature and frequency conditions, and then materials response and performance were determined. Recently, many research works found the asphalt performance at macro scale is largely dependent on the individual components properties and their interactions at the micro scale [26] [54]. In a recent Hansen's study, the G* is related to the frequency dependent viscosity which was calculated in GK method. Recall the GK viscosity equation shown in Eq. (3.6), and frequency dependent viscosity is defined in Eq. (3.9) and the following G* and θ can be calculated by Eq. (3.10) and (3.11) [14].

$$\eta^*(\omega) = \frac{V}{K_B T} \int_0^\infty C_p(t) \exp(-i\omega t) dt$$
(3.9)

$$G^*(\omega) = G'_{\omega} + iG''_{\omega} = i\omega\eta^*(\omega)$$
(3.10)

$$tan\theta = \frac{G''}{G'} \tag{3.11}$$

where ω is frequency, $G^*(\omega)$ is frequency-dependent shear modulus, θ is phase angle.

Figure 3.10 shows the frequency dependent viscosity, shear modulus, as well as phase angle results at 533.15K. According to time-temperature superposition principle, high frequencies are equivalent to low temperatures. Asphalt shows elastic behavior at smaller viscosity values, higher shear modulus as well as smaller phase angles. However, when the low frequency was applied indicating higher temperature conditions, asphalt response was observed to be viscous with greater viscosity values, smaller modulus and higher phase angles. It also can be found that asphalt exhibited a pure vicious behavior when frequency is lower than 100 GHz. Figure 3.11 compared three asphalt rheological properties by means of complex modulus and phase angle.



(a) Frequency-dependent viscosity



(c) Frequency dependent phase angles

Figure 3.10 Frequency dependent modulus and phase angle of asphalt model at 533.15K



Figure 3.11 Effect of asphalt compositions on rheological properties

3.7 Radial Distribution Function

The molecular structure properties were evaluated using the molecule-molecule radial distribution functions (RDFs) in model asphalt systems. The RDFs reflect the relative concentrations of molecules as a function of distance with respect to a given molecule, as shown in Eq. (3.12) [55].

$$x_{\alpha} x_{\beta} \rho g_{\alpha\beta}(\mathbf{r}) = \frac{1}{N} \langle \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \delta\left(\mathbf{r} - \mathbf{r}_{i} + \mathbf{r}_{j}\right) \rangle$$
(3.12)

Where, x_{α} and x_{β} are mole fraction of chemical types of α and β , respectively; N_{α} and N_{β} are the number of atoms of chemical type α and β ; N is the total number of atoms; $\rho=N/V$ is the atoms overall number density; V is system volume; $\delta(r)$ indicates the Dirac delta function; and $\langle \cdot \rangle$ means the ensemble average. It is supposed that atom i and atom j are of different chemical types, and i = j are excluded when the chemical types are the same. When RDF is equal to one, the particles in the local structure are uniformly
distributed. Values greater than or less than one imply an enhanced or reduced probability relative to a uniform distribution.

In this study, molecular structures inside asphalt were evaluated by computing RDF of molecules pairs for each SARA fraction. The distances were based on atoms positions rather than center of mass positions to observe the aggregation behavior at atomistic level. The results of different molecules in the same SARA fraction were calculated together and averaged. Figure 3.12 shows RDF results of the intra- and inter-SARA pairs in AAA-1 asphalt at 298.15K. Compared with other pairs, the RDF for asphaltene-asphaltene pair in virgin asphalt shows a strong first peak around 6-7Å, which means asphaltene molecules have a highly tendency for aggregation. A second peak around 13-14Å indicates an extension of the stacked structure, and after that, the RDF had a value around utility suggesting the layered structure disappeared.



(a) Intra RDFs of SARA molecules



(b) Inter RDFs of SARA molecules

Figure 3.12 Radial Distribution Functions for SARA molecules in AAA-1 asphalt model

3.8 Diffusion Coefficient

Information on asphalt materials diffusion is usually obtained through the analysis of mean square displacement (MSD), as identified in Eq. (3.13). MSD is a measure of variability of the atomic positions as a function of time, and a greater MSD curve slope indicates larger molecules diffusivity. Therefore, the slope of MSD curve is used here to calculate the diffusion coefficient (D) of specified molecules according to Einstein equation by Eq. (3.14), and to evaluate the translational mobility of asphalt SARA components and rejuvenator in this study.

$$MSD(t) = \langle |r_i(t) - r_i(0)|^2 \rangle$$
(3.13)

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} < |r_i(t) - r_i(0)|^2 >$$
(3.14)

where, r_i (0) denotes the initial position of molecules i and r_i (t) is position of molecule i at time t. N is total number of molecules. The angular bracket indicates the ensemble average is performed over all molecules and over all simulation time.

Based on Einstein relationship, if the simulated particles experience random Brownian walk in the three-dimensional simulation matrix, the particles' self-diffusion coefficient can be determined by calculating the slope of MSD plot as a function of time [56]. However, within a crowded model systems like asphalt molecules, molecular pathway might be inevitably influenced by anomalous diffusion [57]. In this case, the slope of log (MSD) vs. log (t) plot was not always equal to 1.0, and these MD trajectories cannot be directly used to for analysis. In this study, molecular trajectories where Einstein diffusion took place (slope of log (MSD) vs. log (t) plot is 1.0) were extracted to calculate diffusion coefficient [28].

For instance, diffusion coefficient determination of asphaltene molecules at 298.15 K is shown in Figure 3.13. Asphaltene molecules began to show diffusive behavior (red line with slope equals 1.0 on log scale) at a time between $\log_{10}^{(t)}=2.0$ and $\log_{10}^{(t)}=2.40$, as shown in Figure 3.13(a), and this time period corresponds from t=100ps to t=350ps. Therefore the MD trajectories between 100 and 350 ps were extracted and analyzed, and the slope of MSD curve was 0.0055 (Figure 3.13(b)) and corresponding calculated D value was $9.17 \times 10^{-8} \text{ cm}^2 \text{s}^{-1}$. Compared with the previous experimental value of asphaltene diffusion coefficient of $3.5 \times 10^{-6} \text{ cm}^2/\text{s}$ the simulated values seems way too small. However, the environment of asphaltene could play a pivotal role in its diffusivity. In our model, asphaltene molecules are surrounded by other component molecules; while

in the experimental testing, the asphaltene molecules were in dilutions and were at extremely low concentrations (0.03-3.0 mg/L) where aggregation did not take place [58].



(b) MSD vs. time

Figure 3.13 Schematic of determination of diffusion coefficient



Figure 3.14 Calculated diffusion coefficients of SARA components at 298.15K

Figure 3.14 shows the mobility of four SARA components at room temperature. It was obviously observed that the saturate presented higher dispersive ability than the remaining components, and at room temperature the mobility of SARA components was ranked in the order of saturate > aromatic > resin > asphaltene. Besides, slight difference was observed between resin and aromatic fractions. These results may vary with the exact values of experimental findings due to different testing environment, but diffusion behaviors were observed and trends were the same as previous simulations. This suggests that MD can be used as a considerably cheaper and faster approach than experiments.

3.9 Force Field Effect

In the field of molecular simulation, a force field refers to a mathematical functional form and parameter sets used to describe the interatomic potential and calculate the potential energy of a system of atoms or coarse-grained particles in molecular mechanics and molecular dynamics simulations. It is clear that interaction potential is the most critical quantity in MD simulation and the goal of a force field is to describe entire classes of molecules with reasonable accuracy.

Some force fields aim for high accuracy for a limited set of element types, which enable good prediction of many molecular properties, while some force fields were developed for the broadest possible coverage of the periodic table, with necessarily lower accuracy. Therefore, during a MD simulation process, accuracy, transferability and computational speed are considered in all to determine the selection of a force field. During our simulations, we did find that using different force filed can generate various simulation results. A typical example can be found in Figure 3.15. Two popular force fields, COMPASS and Optimized Potential for Liquid Simulations (OPLS) force fields, were compared. The difference in the density results can further lead to glass transition temperature difference, as shown in Figure 3.15.

While the exact form of COMPASS force field is listed in Eq. (2.12), the specific form for OPLS force field is listed below in Eq. (3.15) [59]. Compared with COMPASS force field, it can be found that OPLS force field is simple and many bonded energy terms are not considered. It is reported that OPLS potential is well suited for describing intermolecular interactions. A distinctive feature of the OPLS parameters is that they were optimized to fit experimental properties of liquids, such as density and heat of vaporization, in addition to fitting gas-phase torsional profiles.

$$E_{\text{total}} = \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 + \sum_{\text{angles}} K_{\theta} (\theta - \theta_{\text{eq}})^2 + \sum_{\phi} \left[\frac{V_1 (1 + \cos \phi)}{2} + \frac{V_2 (1 - \cos 2\phi)}{2} + \frac{V_2 (1 - \cos$$

$$\frac{V_3(1+\cos 3\phi)}{2} + \frac{V_4(1-\cos 4\phi)}{2}] + \sum_{i,j} \left[\frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_{ij} \left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}}\right)\right] f_{ij}$$
(3.15)

where the first term represents bond stretching, the second term describes angle bending, term 3 represents torsions (also called dihedral angle distortion), and term 4 describes non-covalent interactions including electrostatic (Coulombic interaction between the atomic charges) and van der Waals interactions using a customary 12th-power term. K_r, K_θ, V_n, and φ are empirical parameters relating to bond length, bond angle and dihedral angle. f_{ij}=0.5 if i, j are 1,4 (i.e. inter- and intramolecular 1,4-interaction), and otherwise f_{ij}=1.0.



Figure 3.15 Effect of force field on the AAM asphalt density at various temperatures

Chapter 4 MD Characterization of Asphalt-Aggregate Interface

The fact that material failure originates from particle dislocation and bond rupture at the nanoscale necessitates the importance of atomistic modeling approach in material design. The physical and chemical compatibility of asphalt binder and aggregate affects fatigue cracking and moisture damage in asphalt concrete. Molecular dynamics simulations can provide valuable insights in understanding the interaction between asphalt and aggregate at the nanoscale and relate chemical compositions of asphalt concrete to its macroscopic behavior. Currently, understanding how asphalt concrete deforms and breaks under mechanical and environmental loading is often limited to phenomenological engineering approaches, neglecting the underlying failure mechanism in the atomistic structure. The nanoscale details of material failure are still not clear and the experiments are time-consuming and expensive. The atomistic approach developed from this study laid the ground work to predict failure potential of asphalt concrete in a computational testing environment. This will lead to better design of asphalt mixture for road pavements with longer service life and less repair.

4.1 Creation of Asphalt-Aggregate Interface

4.1.1 Construction of Confined Asphalt Layer

Confined layers of asphalt binders were built for the asphalt-aggregate interface model. The only difference between the bulk asphalt model and the confined asphalt layer lies in the periodical conditions in the z direction. In the confined layer, the box

boundary in the z direction functions as hard repulsive wall, and if asphalt atoms move close to the z boundary during model construction, the atoms will rebound back into the box. Compared to the bulk asphalt model, confined asphalt layer had a relatively flat surface in the z direction, which was used for the asphalt-aggregate interface model as described below. For the purpose of calculating surface free energy, a free surface was created by arbitrarily elongating the dimension of the cell in the z direction and equilibrating the periodic system in isometric-isothermal (NVT) conditions. The illustration of bulk asphalt and the confined asphalt layer with free surface is shown in Figure 4.1.



(b) confined asphalt layer with free surface

Figure 4.1 Asphalt thin film formation for surface energy calculation

4.1.2 Molecular Models of Mineral Aggregate

A mineral is defined as an element or chemical compound that is normally crystalline and resulted from geological processes. A crystal structure is the orderly geometric spatial arrangement of atoms in the internal structure. This crystal structure is based on regular internal atomic or ionic arrangement in the geometric form. Chemistry and crystal structure together define a mineral. Crystal structure greatly influences the physical properties of mineral. Mineral aggregates that are widely used in construction materials include sand, granite, limestone, quartz, etc. Among all the mineral aggregate materials used in asphalt concrete, silicon dioxide (or silica) and calcium carbonate (or calcite) are two most common chemical compounds. For example, limestone consists primarily of calcium carbonate, while silicon dioxide is common in sand and granite with a high percentage. Therefore, in this study, silica (SiO₂) and calcite (CaCO₃) were used to represent ideal aggregate in molecular dynamics simulation. A skematic view of SiO2 substrate construction can be seen in Figure 4.2.



(a) Unit cell of SiO₂



Figure 4.2 Atomistic model of SiO₂ substrate

(Silicon atoms are orange, red is oxygen and hydrogen atoms are white)

4.1.3 Creation of Asphalt-Aggregate Interface

The confined asphalt layer was attached to the aggregate substrate to form an asphalt-aggregate interface model. At first, a unit crystalline silica, with lattice

parameters of a=b=4.913Å, c=5.405Å, α = β =90°, and γ =120°, was imported from structures database in Materials Studio. As for the calcite, a unit cell with dimension of a=b=4.990Å, c=17.061Å, α = β =90°, and γ =120° was used. It is believed that during the simulations, the orthogonal geometry was preferred for the purposes of model construction and further calculation. Therefore, the unit silica or calcite cell were first cleaved in [0, 0, 1] direction, and then followed by geometry transformation to have an orthogonal shape with P1 space group, in which α = β = γ =90°. By repeating the unit cell in x and y directions to generate the same size as asphalt models, a 2-D bulk silica or calcite surface was created. After that, a vacuum slab was added to form silica or calcite blocks with 3D periodic boundary conditions. Confined asphalt layers were then placed over the silica or calcite blocks. A vacuum of 30Å was added above to avoid the interaction across the mirror image in the z direction. The final bi-material interface model between asphalt and aggregate was built as shown in Figure 4.3.

Once the interface model was obtained, geometry optimization for 5000 iterations was carried out followed by a dynamic equilibration run of 200ps with canonical ensemble (NVT), to make sure that the model configuration was further optimized. An additional 50ps NVT with 50 frames was performed for a product run with the subsequent calculation purposes. Trajectory files after molecular dynamic simulations were used for calculation with statistical mechanics. A modified script based on Perl language was developed to calculate the interaction energy between asphalt and aggregate.



Figure 4.3 Asphalt-1/aggregate interface atomistic model (Carbon atoms are grey, sulfur atoms are yellow, hydrogen atoms are white, red is oxygen, orange is silicon, and green is calcium)

4.2 Work of Adhesion between Asphalt and Aggregate

The work of adhesion is described as the work required to separate asphalt from aggregate at the interface. The work of adhesion between asphalt and aggregate relates significantly to the resistance of asphalt mixture to fracture-related failure behavior and durability. The work of adhesion between asphalt and aggregate can be calculated using Eq. (4.1), with the interaction energy (E_{inter}) derived from Eq. (4.2). This approach has been used in the literature to successfully calculate work of adhesion between polymer-metal, polymer-polymer and more general solid-liquid systems [60] [61], which considers the pure physicochemical interaction between two interacting materials. Based on the

definition in Eq. (4.1) and (4.2), a negative value of E_{inter} or $W_{adhesion}$ indicates attraction between these two components, while a positive value of E_{inter} or $W_{adhesion}$ indicates repulsion. The calculated E_{inter} or $W_{adhesion}$ from MD simulation are negative values and the absolute values were used in the analysis for indicating the attraction between asphalt and aggregate.

$$W_{adhesion} = \Delta E_{inter_aag} / A \tag{4.1}$$

$$\Delta E_{inter_aag} = E_{total} - (E_{asphalt} + E_{aggregate})$$
(4.2)

where, ΔE_{inter_aag} is interaction energy between asphalt and aggregate; E_{total} is total potential energy of asphalt and aggregate in contact at equilibrium; and $E_{asphalt}$ and $E_{aggregate}$ are the potential energies of asphalt and aggregate (i.e., silica and calcite) separated in vacuum at equilibrium, respectively; $W_{adhesion}$ is work of adhesion between asphalt and aggregate; and A is the interface contact area between asphalt and aggregate.

Figure 4.4 shows the calculated interaction energy between asphalt and aggregate and the contributions of non-bond components (van der Waals and electrostatic energy). The results indicate that the interaction energy between asphalt and aggregate varies depending on the combination of material types. The values of interaction energy were found equal to the summation of van der Waals and electrostatic components, which indicated that adhesion between asphalt and aggregate was mainly the non-bond interaction. This is because no chemical bond was formed during the interaction and therefore covalent components were negligible. On the other hand, it was found that van der Waals energy constituted the major contribution to the non-bond energy terms. The Coulomb interaction was found negligible in the asphalt-silica interaction and serving as a minor role in the asphalt-calcite interaction. Although different theories (physical, chemical or mechanical) have been proposed to explain the adhesion between asphalt binder and aggregate, the actual mechanism is not fully explained. The Strategic Highway Research Program (SHRP) studies found that the polar constituents in the asphalt adhere to the aggregate surface through electrostatic forces, hydrogen bonding, or Van der Waals interactions. Several different methods of measuring the energy of adsorption indicated that physisorption rather than chemisorption is occurring [1].



Figure 4.4 Interaction energy and its component predicted by MD simulation

Figure 4.5 shows the calculated work of adhesion between different types of asphalt and aggregate models. Three definitions of interface areas, including the layer dimensional area, the Connolly area of asphalt surface, and the Connolly area of aggregate surface, were used in the calculation. It was found that the selection of interface contact area could cause significant variations in calculating the work of adhesion from MD simulation. It is believed that the actual interface contact area is dependent on the morphological feature of asphalt and aggregate, which could be larger than the layer dimensional area and stay between the rough surface areas of asphalt and aggregate. In general, the range of work of adhesion values calculated using the Connolly area agree well with the experimental results reported in the literature, which range from 60 to 150 mJ/m² with different sources of asphalt and aggregate [41] [62].



Figure 4.5 Work of adhesion between asphalt and aggregate predicted by MD simulation

The work of adhesion results show that for the same type of aggregate, the difference between the work of adhesion of asphalt-1 and asphalt-2 models is small. On the other hand, the effect of aggregate mineral on the work of adhesion is much more obvious. In particular, for the same type of asphalt, the work of adhesion between asphalt and calcite is much greater than that between asphalt and silica. Therefore, calcite is more

prone to adsorb asphalt than silica at dry condition. This is in agreement with the experimental finding that a mineral with an alkaline (basic) nature such as calcite, results in a stronger adhesion with asphalt, compared to quartz (acidic) with a rather acidic nature [63].

4.3 Moisture Effect on Asphalt-Aggregate Adhesion

Due to the hydrophobic nature of asphalt binder, water has a detrimental impact on the bonding between asphalt and aggregate. The energy associated with the displacement of asphalt by water from the asphalt-aggregate interface or debonding is referred to as the work of debonding, as expressed in Eq. (4.3) [39]. The calculated values of the work of debonding were found negative that was consistent with experimental findings. This indicates that there exists a thermodynamic potential for water to disrupt the asphalt-aggregate interface. In other words, no external energy is required to be added into the system in order to separate the asphalt-aggregate interface due to the water-loving nature of aggregate.

$$W_{debonding_water} = (\Delta E_{inter_aw} + \Delta E_{inter_agw} - \Delta E_{inter_aag}) / A$$
(4.3)

Where, $W_{debonding_water}$ is work of debonding when water displaces asphalt from the asphalt-aggregate interface; ΔE_{inter_aw} is the interaction energy between asphalt and water; ΔE_{inter_agw} is the interaction energy between aggregate and water; ΔE_{inter_aag} the interaction energy between asphalt and aggregate; and A is the interface contact area.

The energy ratio (ER) has been used in previous experimental studies to evaluate moisture effect on the adhesion between asphalt and aggregate, which is based on the hypothesis that moisture sensitivity is directly proportional to the dry adhesive bond energy, and inversely proportional to the work of debonding [35] [39]. A higher value of ER is more likely indicating the less susceptibility to moisture damage. In this study, the ER was calculated using the ratio of the work of adhesion in dry condition as compared to the work of adhesion in wet condition, as shown in Eq. (4.4). It was assumed here that the introduction of water would not change the interface area between asphalt and aggregate. In other words, water molecules at the interface were assumed in full contact with asphalt and aggregate at the interface. Therefore, the selection of interface contact area would not affect the results of ER values.

$$\mathbf{ER} = |\mathbf{W}_{adhesion} / \mathbf{W}_{debonding_water}| \tag{4.4}$$

where, $W_{adhesion}$ is the work of adhesion between asphalt and aggregate in dry condition, and $W_{debonding_water}$ is work of debonding when water displaces asphalt from the asphalt-aggregate interface.

Figure 4.6 shows the calculated ER values for asphalt-silica and asphalt-calcite models with three scenarios of moisture contents. The simulation results are towards to the lower ends as compared to the range of ER values (0.3 to 30) observed from experiments [39] [62] [64]. The discrepancy is properly because the chemical composition of aggregate (such as quartz and limestone) are more complicated than the pure silica and calcite. Previous research has found that ER values higher than 1.5 indicates that asphalt mixture has relatively high resistance to moisture damage; while asphalt mixtures with high susceptibility to moisture damage are related to ER values smaller than 0.5 [65].

The results show that large differences were observed for the ER values when the same type of asphalt interacts with silicate and calcite. This indicates that moisture susceptibility is strongly dependent on aggregate chemistry. In particular, silica shows much less water susceptibility than calcite. It is noted that mixed findings have been reported for the moisture susceptibility among different mineral aggregates (such as limestone, granite, sandstone) due to differences in chemical composition, aggregate adsorption, porosity, contaminants, and surface texture [35] [62] [64]. It was found that the ER value between asphalt and silica decreased as the moisture content increased; while the ER value between asphalt and calcite were very small regardless of moisture contents. This indicates that the asphalt-calcite bond could be susceptible to moisture damage at relatively small moisture content. Previous studies have measured bond strength between asphalt binder and aggregate at different moisture conditions and found that the pull-off strength between limestone and asphalt binder dropped significantly after 6-24 hours moisture conditioning [66].

On the other hand, for the two asphalt models interacting with silica, the ER value was smaller for the asphalt-2 model at the relatively small moisture content. The ER values of two asphalt models became close when the moisture content increased. This indicates that the effect of asphalt composition on moisture susceptibility with silica may be only significant at the relatively small moisture content. However, when two asphalt models interact with calcite, the effect of asphalt on moisture susceptibility is negligible. This observation should be further studied by changing the chemical composition of asphalt in different ways, such as polymer-modified binder or the addition of anti-stripping agent.



(a) asphalt-silica system



(b) asphalt-calcite system

Figure 4.6 Moisture sensitivity calculated from MD simulation

It is noted that the classical MD simulations conducted in this study cannot account for the formation and breakage of bonds in the reaction. For example, the dissociation of water molecules at the surface of quartz can form hydrogen bonds and affect the calculation of surface energy and work of debonding. Future study with the reactive interatomic potential (such as ReaxFF) will be conducted to conquer this limitation. The MD simulations could be further improved by considering the effect of aggregate adsorption (such as hydroxylated silica or calcite surface), porosity, and surface texture.

Chapter 5 Simulation of Pull-Off Test

Experimental evaluation of interface bonding strength is mostly determined by pull-off tests due to their convenience in the test setup, and also because they can be done very quickly. The failure mode together with the adhesive strength can be determined from test results, and the weakest location in the interface can be observed. Therefore, in this study, pull-off tests were simulated by means of MD simulations to study the asphalt-aggregate interfacial separation phenomenon at the atomistic scale. It is noted that the study undertaken here focused on the opening separation process of interface. The sliding separation process which is also referred to shear failure is not included here.

5.1 Model Preparation

In the simulation of pull-off test, boundary conditions (or constraint) need to be applied in order to separate asphalt and aggregate phases from each other; otherwise, moving the silica substrate will cause all asphalt atoms to move together with the silica layer and there will be no separation. In this study, a two-layer system consisting asphalt and silica was built, as shown in Figure 5.1. During the tensile simulation, a portion of the asphalt at the top was fixed and the silica layer was separated from the asphalt at a constant velocity. The fixed portion of asphalt enables the whole system not to move downward together. In the interface separation process, traction forces were recorded during the whole simulation. Tensile stresses were calculated by normalizing the traction force by the area of silica surface layer.



(a) Atomistic view

(b) Schematic view

Figure 5.1 Representative model and schematic of tensile simulation in MD

During the tensile simulation, the deformation in silica substrate is assumed negligible and thus the silica substrate was treated as a rigid body. The equations of motion were integrated with a time step of 1fs, and a Langevin thermostat with a 10fs damping constant was used to control the system temperature. The interface adhesive stress was calculated as traction force during the tensile process divide by the contact area, and the stress-strain curves were recorded in the simulation process.

Tensile simulations were carried out to study asphalt-aggregate interface deformation and failure process. All the asphalt and silica models were built in Materials Studio 7.0 software [67], and then transferred to Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) using a self-developed Matlab code [68] [69]. All of tensile simulations were performed using LAMMPS classical MD codes. The interfacial atomistic models and separation process were viewed and recorded using the visualization software OVITO [70].

5.2 Interface Mechanical Behavior

5.2.1 Stress-Separation Responses

The results of stress-separation relationship in the tension-induced interface failure process are shown in Figure 5.2. The applied loading rate was 10m/s and the temperature was controlled at 273.15K (0 °C). The stress-displacement relationship can be described that the stress experienced an initial linear increase which continued up to a peak value at roughly 2-3 Å displacement (from point A to point B), after that the stress dropped sharply because a reduction of interaction between asphalt and silica took place when the silica layer was kept moving downwards (point C). The interfacial stress reduced to zero or a steady value in the end which indicated a final separation between asphalt and silica, depending on whether or not a portion of asphalt molecules remain attracted to the silica layer upon full separation (point D). Variations found during the stress calculation are probably due the thermal fluctuations in the system. Consequently, a consecutive 0.5 picoseconds (5 points) moving average of stress values was employed.

It can also be found that the failure modes under this scenario turned out to be adhesive failure rather than cohesive failure. When the silica layer displaces apart from the asphalt layer, the asphalt system is stretched at first and micro-voids are initiated in regions of the asphalt molecules network with lower connectivity afterwards. These micro-voids grow and coalesce with further separation of the silica layer.



A-Initial structure; B-max traction; C-voids development; D-separation Figure 5.2 Stress-separation response in tensile simulation by MD

5.2.2 Loading Rate Effect

Three loading rates were employed to see whether it has effect on the interface behavior. More specifically, velocities of 10m/s, 20m/s and 30m/s were applied to the

silica layer, which was equivalent to strain rates of $2.3 \times 10^9 \text{ s}^{-1}$, $4.6 \times 10^9 \text{ s}^{-1}$, and $6.9 \times 10^9 \text{ s}^{-1}$, respectively, with respect to the original length of asphalt model configuration.

The effects of strain rates on the stress-strain relationship are given in Figure 5.3. The different loading rates can affect the shape of stress-strain curve, together with the peak value of interfacial tensile strength. It was found that the interface deformed under the smaller strain rate had a longer separation process before complete interface failure; while the shape of stress-strain curve under the higher strain rates is narrower and sharper. Therefore, the loading rate has more significant effect on the post-peak failure process (softening stage) as compared to the pre-peak process (elastic stage). For the case with the lowest strain rate, the stress could not reach zero due to the reason that a small fraction of asphalt molecules were adhered to the silica surface The separation can be determined by the distance when the stress reached zero, while for the lowest strain rate (v=10m/s), the separation distance can be determined by the cutoff distance which is 9.5Å in this study. In general, the higher the strain rate was applied, the greater the peak stress value was obtained. These trends are consistent with the cohesive law that was obtained from the pull-off strength test of asphalt-aggregate interface conducted at the macroscopic scale [66].

When the loading velocity continues to decrease to 1m/s, which corresponding to a strain rate of 2.3×10^8 s⁻¹, cohesive damage was observed instead of interface adhesive failure, as shown in Figure 5.4. Large-size voids were observed to grow inside the bulk asphalt during the tension process, which indicated that the colloidal network of asphalt rearranged to accommodate the deformation. As the same time, it was found that increasing fractions of asphalt molecules were attached to the silica surface as the interface is fully separated. The observed cohesive damage suggests that the interface is mechanically stronger than bulk asphalt as the loading rate decrease to a certain level. When the tension is applied at a small loading rate, the bulk asphalt has the greater creep deformation, which causes more cohesive failure in the asphalt.



Figure 5.3 Effect of strain rates on stress-strains relationship



Figure 5.4 Development of cohesive damage at small loading rate

5.2.3 Temperature Effect

The effects of temperature on stress-separate curves were investigated. MD simulations were conducted at three typical field temperatures during the pavement service life, namely $0 \ C$, 25 $\ C$ and 80 $\ C$. Two extreme temperatures, -30 $\ C$ and 135 $\ C$, were also selected to better illustrate the temperature effect.



Figure 5.5 Effects of temperatures on predicted adhesive stress

The effects of temperatures on the interface failure strength are shown in Figure 5.5. It can be seen that a decreasing trend of interfacial tensile strength was observed with increasing temperature. Since the failure strength is the property of interface system, the observation of molecular configurations indicate the effect of temperature on asphalt is significant. As is known that inter-atomic forces at the interface between asphalt and silica atoms are governed by the Lennard-Jones potential and Coulomb potential, the

higher temperature increases the mobility of near-surface asphalt molecules. Therefore, the energy required to break interfacial (non-covalent) bonds is lowered, and thus the failure strength decreases.

5.3 Cohesive Zone Model Parameters

The shape of the predicted stress-displacement response by MD tensile simulation resembles the cohesive law in quasi-brittle materials [71] [72]. The cohesive law tends to behave as a system property and this gives justification to link mechanical properties derived from MD simulations to the higher-scale modeling. The cohesive zone model (CZM) describes the relationship between the traction force across two crack faces and crack opening displacement. The interfacial fracture process zone is simplified as being an initially zero-thickness zone consisting two coinciding cohesive surfaces. Under loading, the two surfaces separate and the traction between them varies in dependence of a specified traction-separation law. Therefore, the stress-separation response obtained by MD simulations can be parameterized for a higher level continuum model such as CZM.

In this study, the cohesive zone parameters, such as peak force and work of separation, were calculated using function fitting of the stress-separation curve. Different models have been used to capture the post-peak softening process in the cohesive law, such as linear, bi-linear, trapezoidal, and exponential models [73] [74]. The exponential cohesive zone model was used because it matched best with the stress-separation responses obtained from MD simulations, as shown in Eq. (5.1).

$$\sigma = \sigma_{\rm c}(\frac{\delta}{\delta_{\rm c}})\exp(1 - \frac{\delta}{\delta_{\rm c}}) \tag{5.1}$$

where, σ_c is peak normal traction value; and δ_c is critical normal separation when $\sigma = \sigma_c$.

Figure 5.6 shows the fitted stress-separation curve with an exponential model. The peak traction (adhesive tensile strength) was found being 485.57 MPa and the separation at peak traction was equal to 1.53 Angstrom. The cohesive law indicates that the interface damage is assumed to occur when the induced interface stress reaches the adhesion strength. The softening curve indicates that the interface stresses progressively drop from the peak value to zero as the interface damage increases until the full separation of interface.



Figure 5.6 Cohesive zone law from the MD-derived stress-separation response

It is noted that compared to the tensile strength measured from laboratory testing conducted at the macroscopic scale, the prediction from MD simulation is greater by about two orders of magnitude. This could be caused by the applied loading rate used in MD simulation that is much higher due to the constraint of computation time. Other reasons contributing to this include the length scale and the defect-free atomistic models used in MD simulations. It is consistent with the experimental observations that the material modulus or strength values appear to decrease in magnitude as the length scale increases.

The loading-unloading behavior of stress-separation responses at the interface was investigated. The silicate layer was subjected to tensile loading and unloaded and then reloaded again following the same loading rate that was used in the initial tension. Two different cases were simulated to see if the reloading is affected by the timing of unloading in the initial loading processes.



(a) unloading before the peak stress



(b) unloading after the peak stress

Figure 5.7 Stress-time relationships during loading and unloading conditions

Figure 5.7 shows the stress-separation curve in the loading-unloading-reloading process, respectively, when unloading was taken before and after the peak stress. The results show that if the unloading happens in the softening stage after the peak stress is achieved; the reloading process cannot reach the same failure strength. This indicates that the irreversible damage is induced in the previous tension process. On the other hand, if the unloading happens before the peak stress is achieved, reloading of the interface system attains the same failure strength as the initial tension process. This indicates that the interface system behaves elastically before the failure initiation at the peak stress. These trends are consistent with the constitutive laws describing the unloading-reloading process of CZM at the macro-scale.

5.4 Chemo-Mechanical Relationships

The effects of chemical composition of binders were studied by using molecular models that represent four types of SHRP asphalt binders with different SARA ratios. These molecule models of asphalt systems were matched to the experimental data based on elemental analyses, molecular classes, and components mass fractions specific to the crude oil sources [15] [75]. Information of SARA fractions, i.e., saturates, asphaltene, resin and aromatic, of these five asphalt binders are given in Table 5.1(After [75]).

Asphalt model Asphaltene Resins Aromatic Saturate AAA-1 16.5 38.1 30.6 10.7 AAF-1 13.1 38.7 37.4 9.7 AAK-1 19.6 40.7 30.4 6.3 AAM-1 5.0 49.9 41.1 2.1

Table 5.1 SHRP asphalt binders with different SARA ratios

Tensile simulation using MD simulations were carried out at the same loading rate and temperature for different binders. The results show that the AAK asphalt has the highest tensile strength compared to the other two asphalt binders. It indicates that the AAK asphalt has the strongest adhesion with silica layer. On the other hand, the adhesion between the AAM asphalt and silica is the weakest. The difference of adhesion properties among four asphalt binders and silica can be attributed to their chemical components. Asphaltene and resin factions contain the most polar groups. Heteroatoms and several types of metal elements are primarily found in asphaltene fraction. The adsorption of polar compounds to aggregate is much greater than the less-polar or nonpolar compounds. Besides, asphaltene and resins had the greater molecular size that may get adsorbed more on the aggregate surface than the fractions with the smaller molecular sizes, such as saturates and aromatics. These together cause asphaltenes and resins to be more attractive for aggregate surface and generate the stronger adhesion.

In order to quantify the effect of chemical compositions of asphalt binder on asphalt-silica adhesion properties, the concept of asphaltene index (I_A) was used, as shown in Equation 3 [76]. It is a colloidal stability parameter used here to assess the SARA fractions ratio.

$$I_A = (Asphaltenes + Resins)/(Saturates + Aromatics)$$
 (5.2)

The effects of asphaltene index on the interfacial adhesive properties were plotted in Figure 5.8, respectively, for tensile strength and work of separation. The work of separation is calculated by integrating force with respect to distance. Because the interface areas were not the same for all scenarios, the work of separation was normalized by the area of interface. Then the work of separation can also be calculated as the area under the curve as shown in Fig. (10). A more general calculation is presented in Eq. (5.3).

$$W = \frac{1}{s} \int_0^a \sigma S \, dx \tag{5.3}$$

where S is the interface area, a is the final separation distance, and σ is stress.

It was found that both tensile strength and work of separation has positive linear correlations with asphaltene index. This finding was consistent from the experimental results obtained by Sultana and Bhasin [77] using interfacial bonding tests. In their experimental study, the tensile strengths of asphalt binders with different polar fractions were measured and it was concluded that asphalt binders with the higher percentages of resins and asphaltenes had the higher tensile strength.



Figure 5.8 Relationship between asphalting index and CZM parameters

The results indicate that the MD derived interface properties can be used to evaluate the mechanical behavior of binders with different chemical compositions and potentially help engineering new binder materials. Although the limitations of classical MD exist in the time and length scales, it is possible that the asphalt-aggregate interface behavior at the macroscopic behavior can be captured at the atomistic scale in a consistent trend.

Chapter 6 MD simulations on Oxidative Asphalt Aging

The aging process occurs in asphalt pavements in two stages. Short-term aging occurs when asphalt is subjected to heat and air in the process of asphalt mixture production and paving, which is primarily due to oxidation and loss of volatile component at high temperatures. Long-term aging of asphalt occurs over the service life of road pavement, which is mainly progressive oxidation. Therefore, understanding asphalt aging effect is important for asphalt material design to achieve longevity and durability. The detailed mechanism for asphalt aging is still uncertain due to the complexity of chemical compositions of asphalt. One most common aging mechanism is oxidative ageing, where oxygen reacts with reactive components of asphalt and changes its physical and mechanical properties [78]. The formation of oxidation products changes chemical compositions of asphalt and leads to an increase of the overall stiffness and brittleness [79]. Although the hardening of asphalt could be beneficial by enhancing rutting resistance of pavement, aging could be detrimental for accelerating pavement distresses and causing premature failure. Asphalt chemistry links closely to thermodynamic properties and performance characteristics of asphalt. Asphalt aging, by nature, is a phenomenon caused by asphalt chemistry changes at atomic to molecular scales. Molecular dynamics (MD) simulation has been proved to be a powerful computational method for material design since it has the inherent advantage to predict manifold aspects of material properties at the molecular levels. This makes it meaningful to investigate asphalt aging effect using MD simulations.
6.1 Virgin and Aged Asphalt Models

It is difficult to obtain the detailed information on chemical components of asphalt, which is a complex chemical mixture. Thus, asphalt was divided into different fractions by modern separation techniques, according to their similar polar and molecular characteristics. At the molecular level, asphalt is a mixture of a wide variety of hydrocarbons, together with heteroatoms such as nitrogen, sulfur, oxygen, and metals. Previous research has found that asphalt materials exhibit similar kinetics during the oxidative aging, and in general there are two periods are included. The first is an initial fast reaction period, which is followed by a slower reaction period with a nearly constant rate. In the two reaction periods, the hydrocarbon chemical reactions are known to be fundamentally different. In the process of the rapid oxidation spurt, sulfoxides are the major oxidation; while for the slower reaction period, ketones are the major product. The ratio of ketones to sulfoxides formed was found dependent on oxygen concentration (pressure), temperature, and sulfur content [80].

Extensive experimental studies have been carried out to study the mechanism of asphalt aging due to oxidation. It was found that certain types of carbon and sulfur compounds in asphalt are susceptible to oxidation. The ketones and sulfoxides have been identified as major functional groups formed after oxidation [22] [81]. For example, benzyl carbon, the first carbon bonded to an aromatic ring, is a readily oxidizable site [54]. Ketone is formed when oxygen replaces the hydrogen atom attached to the benzylic carbon atom. Therefore, as illustrated in Figure 6.1, the function groups of ketone and sulfoxide were added to the possible oxidizable locations of virgin asphalt molecular models [82], representing aging effect in asphalt binder.



(a) aged asphaltene molecules



(b) aged resin molecules



(c) aged aromatic molecules



(d) saturate molecules (Virgin and aged are the same)

Figure 6.1 Molecular structures of SARA fractions before and after oxidation aging (Carbon: grey, sulfur: yellow, hydrogen: white, oxygen: red).

It is noted that the saturate fraction models were assumed the same before and after oxidation aging. The mass fraction of each molecular component was chosen to model asphalt molecular system closest to the real asphalt. The details of asphalt molecular system composition and the number of atoms are listed in Table 6.1.

Table 6.1 SARA mass fraction of virgin and aged simulated asphalt system (AAA-1)

	Asphaltene (%)	Resin (%)	Aromatic (%)	Saturate (%)	No. of atoms
Virgin	16.5	38.1	30.6	10.7	5572
Aged	17.7	39.6	32.4	10.3	5472

Table 6.2 Calculated properties of virgin and aged asphalt from MD simulation

Thormodynamic Properties	Virgin asphalt	A god asphalt	Expt.	
Thermodynamic Properties	v irgin aspirati	Ageu aspilait	measurements	
Density (298.15K, g/cm ³)	1.003	1.061	1.01-1.04 [7]	
Density (533.15K, g/cm ³)	0.867	0.943	N/A	
Surface free energy (mJ/m^2)	50.47	44.23	13-47.6 [5] [39]	
Viscosity (533.15K, cP)	15 10	15 80	N/A	
MP method	15.10	15.69		
Viscosity (533.15K, cP)	1.24	2.56	22[16]	
GK method	1.24	2.50	2.2 [10]	
Cohesive Energy Density (10^8 J/m^3)	3.32	3.59	N/A	

In addition to ketones and sulfoxides, other polar groups (such as carboxylic acids and phenols), may be also important carbonyl group products generated during asphalt aging, which should be considered in future studies. The thermodynamic properties of virgin and aged binder were calculated and summarized in Table 6.2, including density, surface free energy, viscosity, and cohesive energy density. The available experimental measurements from literature were compared and general agreements were achieved. The discrepancies between calculated and experimental results may be improved by using the more refined and accurate molecular models of asphaltene obtained using more recent advanced techniques.



Figure 6.2 Effect of aging on rheological properties of AAA-1 asphalt

It was hypothesized that the rheological response difference between virgin and aged asphalt could be demonstrated by the different master curves, as shown in Figure 6.2. On the basis of the master curves it can be found that phase angle master curves of both virgin and aged asphalt exhibited a plateau region at 88 °at low frequencies. Such a plateau indicates a large range of frequency independence and these materials appear to

demonstrate only little elastic properties at moderate frequency levels and temperature. The aged asphalt binder showed similar trend of G* development as that of virgin binder, and at the same time an increase in stiffness can also be observed compared to the virgin binder. The oxidation effect could be attributed to the G* increase for the aged asphalt binder, indicating the aging has a stiffing effect on the asphalt binder. It has to be noted that the stiffing effect could improve the rutting resistance at high temperature; however, it could have adverse effect on the low temperature properties. Based on the phase angle master curve, aged asphalt could act as hard elastic at low temperature whereas a soft viscous behavior is expected.

6.2 Molecular Structure of SARA fractions in Aged asphalt

Asphalt has been reported as a colloidal structure in prior experimental and simulation studies, where asphaltene is regarded as the dispersion phase dispersed in maltene that refers to mixture of resins, aromatics and saturates [17] [20]. Figure 6.3 illustrates the asphalt model structure by showing the SARA arrangements obtained from MD simulations, respectively, for virgin and aged asphalt. The snapshots of simulation cell were collected from the last frame of atomic trajectories after simulation, where a most possible and stable configuration is expected to be obtained. The entire bulk structure at each simulation cell consists of 8 saturate molecules, 24 aromatic molecules, 32 resin molecules and 8 asphaltene molecules, satisfying the SARA mass fraction as shown in Table 6.1.



(a) virgin asphalt



(b) aged asphalt

Figure 6.3 Illustraion of asphalt molecular structures at 298.15K (asphaltene: green, aromatic: blue, resin: orange and saturate: yellow)

It can be observed that within both the virgin and aged asphalt system, asphaltene molecules (in green color) were diluted in the dispersion medium, and they tended to form nano-aggregation structures but were unable to create a continuous network. This type of structure is also referred to asphalt sol-gel structure, that most paving asphalt binders belong to this kind of structure [83].

To further characterize molecular structure changes of asphalt because of aging, radial distribution function (RDF) was studied. The RDF describes the normalized probability of a particle radially occurs around reference particle at a given distance r in a system. In this study, the distances between molecules were calculated based on each molecule's center of mass. MD simulations were conducted for 2ns under NVT ensemble and 400 trajectories were generated for RDF analysis. The RDFs of asphaltene-asphaltene, asphaltene-resin, asphaltene-aromatic and asphaltene-saturate pairs in virgin and aged asphalt at 298.15K are compared in Figure 6.4.

As can be observed in Figure 6.4, compared with RDF for asphaltene-asphaltene pair in virgin asphalt showing a strong first peak around 6-7Å, within the aged asphalt system, the first peak value of RDF for asphaltene-asphaltene pair is seen to be shifted to a larger distance of around 10-11Å, together with a decrease of peak value. This indicates that aging weakened the asphaltene aggregation, and aged asphaltene molecules may be in non-aligned conformations rather than forming the layered structure [84].

The RDFs between asphaltene-resin and asphaltene-aromatic pairs illustrated in Figure 6.4 can also indicate the layered structure within both virgin and aged asphalt. This can be attributed to the fact that aromatic ring structures in resin and aromatic molecules tend to form π -stacking with aromatic rings in asphaltene molecules, and this

kind of aligned structure is preferred in simulations [84] [85]. The first peak positions of asphaltene-resin and asphaltene-aromatic pairs moved to shorter distances with regards to asphaltene-asphaltene pair. This is because resins and aromatic molecules are smaller molecules and served as dispersion medium in asphalt structure, and so they aligh inside or around the asphaltene-aphaltene interaction structure.



Figure 6.4 RDFs of SARA pairs in aged AAA-1 asphalt models

It was found that aging affected the way in which resin and armoatic molecues aligned to asphaltenes. This could be observed from the the changes of heights of g(r) and the positions where the peak value of g(r) took place in the asphaltene-resin pairs and asphaltene-aromatic pairs before and after aging. Due to the addition of oxygen atoms and the formation of ketones and sulfoxides function groups in the aged binder model, the center of mass of these molecules were pushed apart or pulled along from asphaltene molecules.

Saturates are highly incompatible with the asphaltenes as inferred from the relatively low peak values in RDFs of asphaltene-saturate pairs in Figure 6.4. Therefore, it can be deduced that saturate do not contribute the asphaltene nano-aggregation. The weak interaction between saturate and asphaltene could be due to the unpolar properties of saturate molecules, and also their small overall mole fraction in the whole system.

6.3 Translation Mobility of Asphalt Molecules

The translational mobility of SARA molecules in the virgin and aged asphalt structures were tracked by the mean-squared displacement (MSD) of their centers of mass. The MSD describes mobility of particles followed over time and measures the average distance a molecule travels, as shown in Eq. (3.13) and (3.14). This kind of dynamics property of asphalt components can be related to asphalt rheological property. For this purpose, MD simulations under NVT ensemble were performed, and the mobility of SARA components of asphalt was recorded as a function of time.

Figure 6.5 plots MSD as a function of time for asphaltene, aromatic, resin, and saturate components in virgin and aged asphalt, respectively, at temperatures of 298.15K and 533.15K. It can be observed that different asphalt components exhibit distinctive molecular mobility that is correlated with the molecule size. In general, molecules with lower molecular weight show faster molecular mobility. For example, asphaltene molecules have smallest MSD values and show the slowest mobility, because asphaltene has greatest molecular weight among four SARA fractions. As expected, the molecule mobility increases as the temperature increases.



(a) asphaltene



(b) aromatic



(c) resin



Figure 6.5 Comparison of the MSD of SARA fractions in virgin and aged asphalt

It was found that aging caused slowdown in the translational mobility by comparing the MSD values between virgin and aged molecules. All four SARA fractions present the greater MSD values in virgin asphalt, because the molecule sizes increase after aging. Furthermore, it was observed that the same asphalt component (saturate) performed differently in terms of molecular mobility before and after aging. The translational dynamic behavior of saturate is slowed down in aged asphalt. This is properly attributed to the difference of fraction of free volume, in which the calculated fraction of free volume (FFV) for virgin asphalt is 40.63% while for aged asphalt is 38.93%. FFV accounts for the volume which is not occupied and is available for the molecules to diffuse. Saturate molecules inside virgin asphalt possess extra spaces and thus diffuse more rapidly than that in aged asphalt.

6.4 Aging Effect on Self-Healing Potential of Asphalt

Asphalt binder is known to be degraded by environmental factors within its service life in road application. However, it is also generally known that asphalt can heal above certain temperature thresholds [86]. Phenomenologically, self-healing can be regarded as a process of disappearance of micro-cracks formatted within material and/or near the interfaces phase. Thermodynamically, it can be considered as a successive process of surface approach (rearrangement) and molecular diffusion and randomization [13].



(a) two-layer asphalt with 10Å artificial crack before healing



(b) rearrangement of crack surfaces after healingFigure 6.6 Self-healing process of layered asphalt models(asphaltene: green, aromatic: blue, resin: orange saturate: yellow)

Two models of virgin asphalt were placed in the simulation cell and a 10Å vacuum pad was added between them to create an artificial crack, as shown in Figure 6.6(a). Creating the two-layer model with vacuum space is because healing takes place across the crack interface, and thus a healing process can be simulated by the diffusion between two asphalt layers. The same model was also built for aged asphalt. After the layered models were equilibrated, MD simulation under NPT ensemble at 1atm was performed for 300ps. During this process, it was observed that asphalt molecules in opposite layers moved close to each other, showing the intrinsic self-healing potential. At the end of NPT simulation, asphalt molecules rearranged completely across the crack and came to an equilibrium, which is demonstrated in Figure 6.6(b). After that, the asphalt models were then used for NVT simulation at the controlled temperatures for 150ps to simulate the molecular diffusion across the healed crack surfaces.



(a) 298.15K



(b) 533.15K

Figure 6.7 Effect of healing on asphalt density

Figure 6.7 shows the evolution process of asphalt density as two crack surfaces approach to each other and rearrangement stages of healing process. The time period of 300ps is used in simulation to reach the stable density. It can be found that at the healed state asphalts recovers to have the same density as asphalt at the original state, regardless of virgin and aged asphalt. However, virgin asphalt shows the greater healing rate than aged asphalt at 298.15K, while both virgin and aged asphalt have the similar healing rate as the temperature increases to 533.15K.

After the crack surfaces close, the wetting stage of healing can be studied through molecular diffusion and entanglement in the approached surface. Diffusion is a process in which materials particles move from a region of high concentration to one of lower concentration. The diffusion coefficient can be related to the mean square displacement of particles based on the Einstein relation, as shown in Eq. (6.2) [87]. The relations between diffusion coefficient and temperature were studied using Arrhenius law, as shown in Eq. (6.3). The Arrhenius equation was first developed to study temperature dependence of chemical reaction rates, and it can be employed as an empirical relationship to model the temperature variation of diffusion coefficients in many processes and reactions [88].

$$D = \frac{k_{MSD}}{2d}$$
(6.2)

$$D = Aexp\left(-\frac{E_a}{RT}\right) \tag{6.3}$$

where, D is diffusion coefficient; d is the system dimensionality, and in this study d=3; K_{msd} is the slope of MSD curve with time; A is the pre-exponential factor; E_a is the activation energy; T is temperature; and R is the universal gas constant (8.314 J/mol/K).

The effect of aging on healing potential of virgin and aged asphalt was evaluated by pre-exponential factor and activation energy (as shown in Eq. (6.3)). Based on the definition of Arrhenius equation and with some adaptation, the activation energy can be recognized as the energy needed for self-healing process initialization, while the preexponential factor suggests the instantaneous healing due to wetting of crack interface and instantaneous stress gain [89] [90]. Figure 6.8 plots the relationship between diffusion coefficients and temperatures, in logarithmic and reciprocal format, respectively. Temperatures were selected at 298.15K, 358.15K, 408.15K, 453.15K and 533.15K, respectively.



Figure 6.8 Diffusion coefficients versus temperatures for virgin and aged binder

As depicted in Figure 6.8, asphalt diffusivity increases with an increase in the temperature, for both the virgin and aged asphalt. The activation energy calculated for virgin asphalt is 17.20 kJ/mol, which is a little lower than that of aged asphalt (18.02 kJ/mol). Besides, the pre-exponential factor of virgin asphalt is 3.60×10^{-4} cm²/s, which is larger than 2.72×10^{-4} cm²/s of aged binder. It can be concluded that, compared to aged asphalt, virgin asphalt has the lower activation energy barrier and thus the stronger instantaneous healing ability. This finding is in agreement with the experimental findings [91] [92]. It is believed the healing potential difference between virgin and aged asphalt depends on the level of oxidation introduced to the asphalt model. Asphalt exposed to more severe oxidation could contain structures of carboxylic acids and experience molecules loss, which are not considered here and will be studied in future work.

6.5 Aging Effect on Moisture Damage Susceptibility of Asphalt

Aging effects on the adhesion properties between asphalt and aggregate were studied. The layered asphalt and aggregate models were built following the method described by the authors' previous work. A confined asphalt layer was built with non-periodical condition in the z direction. Aggregate is represented by silica, or silicon dioxide, because silica has simple chemical composition and it is a common mineral in aggregates. Terminating hydroxyl (OH) groups with a density of 4.5 OH-group/nm² were added to represent a fully hydrated silica film, because surface silica is very reactive and will be hydroxylated in presence of water in practice [93]. Figure 6.9 showed the adhesion between asphalt and aggregate was improved due to oxidative aging at room temperature, for all three asphalt types. The improved adhesion could be attributed to the production of polar components in the middle of aging process.



Figure 6.9 Effect of aging on asphalt-aggregate adhesion

Water molecules were added to the asphalt-aggregate interface model with different scenarios to simulate the possible phenomena of water intrusion in reality. In the first scenario, water was assumed to be present only inside the asphalt matrix, where 200 water molecules were randomly mixed with asphalt molecules. The second scenario assumed that water reached the asphalt-aggregate interface after certain transport process, where a thin layer of 200 water molecules was placed between asphalt and silica layers. In the third scenario, water molecules were equally placed inside asphalt and at the interface with a total amount of 200 water molecules. The structure of bi-material interface system between asphalt and aggregate are illustrated in Figure 6.10.

The bi-material interface was subjected to geometry optimization for 5000 iterations, followed by a dynamic equilibration run of 200ps with canonical ensemble (NVT) for further conformation optimization. An additional 100ps NVT with 100 frames was performed for a product run with the subsequent calculation purposes. It is noted that the silica layer was fixed throughout MD simulation for reducing computing cost. Trajectory files were saved for animations and a modified script based on Perl language was developed to calculate the interaction energy between asphalt and aggregate. Due to the hydrophobic nature of asphalt and the water-loving nature of aggregate, water tends to separate the asphalt-aggregate interface and thus affects adversely on the bonding between asphalt and aggregate. The work of debonding is used here to evaluate the energy required for water to displace asphalt from the asphalt-aggregate interface. The energy ratio (ER) is employed to assess moisture susceptibility of virgin and aged asphalt with aggregate, which is calculated using the ratio of work of adhesion at dry condition as

compared to work of adhesion at wet condition. A higher value of ER indicates less susceptibility to moisture damage, and vice versa.



(b) water at the asphalt-aggregate interface

Figure 6.10 Asphalt-aggregate interface model with moisture

(Carbon: grey, sulfur: yellow, hydrogen atoms: white, oxygen: red, silicon: orange)

Figure 6.11 shows the calculated ER values for virgin asphalt-silica and aged asphalt-silica models under three moisture intrusion scenarios. It was found that the ER value of scenario 2 was lower than that of scenario 1 for both virgin and aged asphalt. This indicates that asphalt mixture is more susceptible to moisture damage when the asphalt-aggregate interface is penetrated by water, as compared to the water penetration in asphalt matrix. The scenario 3 has the smallest ER value, which represent the worst condition that could be accoutered in the field. The interface system composed of aged asphalt showed the slightly smaller ER values than that of virgin asphalt for all scenarios, revealing that negative consequences can be caused by asphalt aging related to moisture damage susceptibility.



Figure 6.11 Effect of asphalt aging on moisture damage under three different scenarios

Chapter 7 Rejuvenator Application in Asphalt Binder

Rejuvenating aged asphalt to a condition that resembles that of virgin binder is necessary when reclaimed asphalt pavement (RAP) is used. In practice, this is usually achieved by adding soft asphalt binder or rejuvenator, in order to soften the aged binder and minimize the negative impact of aging on pavement performance. When the amount of RAP is small, softer virgin binder can be used. For the high RAP content, the extremely soft virgin binder is necessary while it is expensive and unavailable, and thus rejuvenators are considered. It has been recognized that the mixing between aged binder and virgin binder is achieved by a combination of mechanical mixing and molecular diffusion. In the diffusion process, the virgin and aged asphalt binder diffuses into each other and become homogeneous at molecular level [94].

In the field practice, applying rejuvenator is a common procedure to improve the blending efficiency of virgin and RAP binders. Rejuvenators have the potential to restore the rheology and chemical components of aged RAP binder, and make asphalt binder effectively "available" for blending with virgin materials, thus providing the required binder performance for longer service period. Understanding the diffusion process between virgin asphalt, aged asphalt, and rejuvenator is important since it can help guide mixture design in terms of RAP content and rejuvenator selection. However, this diffusion process is essentially governed by molecular mobility and thus it is difficult to quantify by traditional experiments of construction materials at the micro or macroscale. Therefore, the inherent advantage of computational simulation at the atomistic scale, such

as molecular dynamics (MD), is beneficial to study manifold aspects of asphalt recycling at the molecular levels.

7.1 Model Preparation

7.1 Molecular Model of Rejuvenator

A rejuvenator is often employed in recycling high RAP content mixture with high RAP content. Rejuvenators were obtained from various sources, which could be plant oils, oils derived from wastes, engineered products, or traditional and non-traditional refinery base oils. Rejuvenator can be a single component or a composite consisting of different mainly aromatic and resin components. The single-component rejuvenator is used to restore the rheological properties of aged asphalt binder; while the composite rejuvenator is more often used for rejuvenating the severely aged binder and has the greater effect than single counterpart [95] [96].



Figure 7.1 Molecular model of asphalt rejuvenator

In this study, a single-component rejuvenating agent was selected for simplicity and its molecular structure is shown in Figure 7.1. The rejuvenator model has a relative low molecular size and weight, which has the potential advantage of a higher diffusion rate within the virgin and aged asphalt binder. The polar aromatic ring structure agrees well with the facts that common rejuvenators used in practice are light weight oil with high aromatic content [97]. The rejuvenator content was selected as 10% of binder weight following the recommendation based on the laboratory performance testing using different typical content of rejuvenator contents used in the laboratory study [98].

7.2 Layered Model of Virgin and Aged Binder

In reality, the recycling of RAP is usually achieved by adding rejuvenators into the aged pavement mixture. Ideally, the rejuvenator should diffuse into the RAP binder and mobilize the aged asphalt. The blending efficiency between virgin and aged binder determines if a homogeneous mix of asphalt binder can be formed and accordingly the material properties of asphalt binder. In this study, a layered model system was built to study the effect of rejuvenator on the blending efficiency between virgin and asphalt binder. The inter-layer diffusion process was simulated under the controlled pressure and temperature. The model system was built following a sequential rejuvenating process in which rejuvenator was in contact with aged asphalt first and then virgin asphalt.

In the simulation process, the initial layer structures of asphalt (virgin and aged) and rejuvenator were both prepared following the method described in the authors' previous work [33]. The rejuvenator layer was attached to the aged asphalt layer to form a bi-layer structure, followed by a geometry optimization procedure. An isothermalisobaric (NPT) simulation of 300ps was performed to model the rejuvenator penetration process, and an additional constant volume and temperature (NVT) simulation of 300ps to fully equilibrate the structure. Figure 7.2(a) illustrates the penetration of rejuvenator molecules into the aged asphalt model after molecular diffusion process.



(a) diffusion of rejuvenator into aged asphalt (Red color refers to rejuvenator)



(b) diffusion of virgin asphalt and rejuvenated aged asphalt

Figure 7.2 Layered model for rejuvenator penetration and asphalt diffusion

After that, a layered model between virgin asphalt and the aged asphalt with rejuvenator was built. The same simulation procedures, i.e., geometry optimization, NPT simulation followed by NVT simulation, were performed. Considering the increase of system size, the simulation time increased from 300ps to 500ps. Figure 7.2(b) illustrates the layered model between virgin asphalt and the aged asphalt with rejuvenator after diffusion process. In both figures, it is noted that several rejuvenator molecules were observed in the other direction of aged asphalt binder model, which is due to the periodic boundary condition applied in the MD simulation. For all MD simulations, the pressure was set as constant pressure of one atmosphere. In order to evaluate the effect of temperature on rejuvenating effects, a series of temperatures were used including 298K, 333K, 433K and 533K.

7.3 Mixture Model of Virgin and Aged Binder

An idea blending of virgin and aged binder process is that they can be finally blended together with the help of rejuvenator, and forms "new" binder, although in practice, this process may take months or even years. In order to see how the rejuvenator affects the properties of fully blended asphalt binder, a mixture model of virgin and aged asphalt (1:1 ratio) was built with addition of 10% rejuvenator, as shown in Figure 7.3. In the simulation process, a big cubic cell with an initial density of 0.1g/cm3 in 3D periodical condition was first built, with the purpose to randomly distribute asphalt molecules (with or without rejuvenators) and prevent the molecule chains twisted with each other, as shown in Figure 7.3(a).



(a) initial structure



(b) final structure after equilibrium (red color indicates rejuvenator atoms)

Figure 7.3 Mixture model of virgin and aged asphalt with rejuvenator

After a geometry optimization process, an equilibrium run with constant volume and temperature (NVT) for 200ps with a time step of 1fs was performed to preequilibrate the system, which brought the model system from an initial state to a more equilibrated state at the target temperature. In the NVT ensemble, Nose-Hoover thermostat was applied to control the temperature without pressure coupling. After that, another molecular dynamic run with isothermal-isobaric (NPT) ensemble was performed for 500ps of relaxation time to shrink the system volume and to approach a stable state of the real density, as illustrated in Figure 7.3(b). During this process, Nose-Hoover thermostat and Andersen barostat were applied for system to maintain a target temperature and pressure, respectively. The relaxation time used in the NVT and NPT processes was proved to be enough because it was observed that the temperature and density reached the stable values in the process. The last frame of trajectories were selected as a representative volume of asphalt material, and used for further analysis. Similar to the layered model, all simulations were conducted at the constant pressure of one atmosphere and a series of temperatures were used including 298K, 333K, 433K and 533K.

7.2 Effect of Rejuvenator on Diffusion between Aged and Virgin Binder7.2.1 Diffusion of Rejuvenating Agent

Diffusion is caused by random molecular motions and results in the movement of matter from one system to another system. Figure 7.4 shows the calculated diffusion coefficients of rejuvenator in the layered models at different temperatures. The calculated diffusion coefficients are consistent with the laboratory measured values reported in the literature, which proves the ability of MD simulation in discovering mechanism that is

governed by molecular interaction [94] [99]. The results indicate that temperature plays an importance role in the mobility of rejuvenator, especially as the temperature is higher than 433K. It was found that when temperature is not very high (smaller than 533K), the diffusion coefficient was greater for the rejuvenator in the three-layer model with virgin and aged asphalt as compared to in the two-layer model with aged asphalt only. This is reasonable because the diffusion rate is affected by different boundary conditions.



Figure 7.4 Diffusion coefficients of rejuvenator in layered model

Concentration profiles adopt coordinate information as input and plot relative concentrations of target atoms (or molecules) in the system along the specified direction. The concentration profile is used here to observe the rejuvenator distribution inside the virgin-aged asphalt layer diffusion system in (0 0 1) direction, or along z axis in this study. The whole system was equally divided into 50 slabs, and rejuvenator data in each slab were collected and analyzed. The relative concentration profile was calculated

according to Eq. 1, and a smoothing function (Gaussian function) was applied to obtain well-fitting results.

Relative Concentration=
$$X_{slab}/X_{bulk}$$
 (7.1)

where, $X_{slab} = (number of atoms in slab)/(volume of slab);$ and $X_{bulk} = (total number of atoms in system)/(system volume).$

Figure 7.5 presents the relative concentration profiles of rejuvenator in the twoand three- layered models at different temperatures. It was found that the concentration profiles had similar shapes but the curves became flat as the temperature increased. With the reduction of the peak relative concentration, the relative concentration profile of rejuvenator expanded in a wider region at the higher temperature, indicating more rejuvenator molecules were diffused into the virgin and aged binder and formed a larger and more uniform transition zone.



(a) rejuvenator and aged asphalt two layer system



(b) rejuvenated and virgin asphalt layer system

Figure 7.5 Relative concentration profiles of rejuvenator in layered model

It is noted that the complete penetration was not observed because the limitation of time scale used in MD simulation. In real practice, the diffusion degree of rejuvenator into asphalt and the blending between virgin and aged asphalt depends on the physical shear force and mixing time. For example, mechanical mixing for a longer mixing time could contribute to better homogeneity and fully blending in the recycling process. Previous studies found that when rejuvenator was poured into the RAP directly, it could take several days for the rejuvenator to fully diffuse into aged asphalt [94].

7.2.2 Effect of Rejuvenator on Blending between Aged and Virgin Asphalt

The pavement performance of recycled asphalt mixture is largely determined by the blending degree of virgin and RAP binder. Therefore, it is important to evaluate the effectiveness of rejuvenator on the inter-diffusion process between virgin and aged asphalt. Fig. 8 shows the change of diffusion coefficients after adding rejuvenator between virgin and aged asphalt layer, respectively, for the virgin and aged asphalt. Temperatures effects on the inter-diffusion behavior, ranging from room temperature, 298K, to mixing temperature 433K, and a higher temperature, 533K, were also evaluated.



(b) aged asphalt

Figure 7.6 Effects of rejuvenator and temperatures on inter-diffusion coefficients

It was observed that both virgin and aged asphalt showed the higher interdiffusion rates after adding rejuvenator. This effect was more significant for aged asphalt as the temperature is lower than 433K but for virgin asphalt as the temperature increases to 533K. The changing trend of inter-diffusion coefficients at different temperatures for virgin and aged asphalt is similar to the one for rejuvenator (Figure 7.4). This indicates that the penetration of rejuvenator accelerates the blending between virgin and aged asphalt. The findings are in good agreement with the blending chart developed by Shirodkar et al, in which high temperature is required for the increased blending degree between virgin and aged asphalt [100].

7.3 Effect of Rejuvenator on Molecular Structure of SARA Fractions

Figure 7.7 shows the molecular structures of different asphalt models in terms of radial distribution functions, respectively, for four SARA fractions. For virgin asphalt, the RDFs for asphaltene-asphaltene pairs presented a high peak value (much greater than one) as compared to other SARA fractions, indicating the strong self-aggregation behavior. Previous studies have reported that asphaltenes are prone to aggregate and form clusters or micelles over a wide range of concentrations and temperatures, which forms the basis of the colloidal structure of asphalt [101] [102] [103]. On the other hand, a weaker aggregation tendency was observed for resin molecules, with the peak value of RDF smaller than two. The aromatic and saturate molecules rarely showed any aggregation behavior in the virgin asphalt model.



(a) asphaltene-asphaltene pairs



(b) resin-resin pairs



(c) aromatic-aromatic pairs



(d) saturate-saturate pairs

Figure 7.7 Effect of rejuvenator on SARA radial distribution functions
When aged asphalt was mixed with virgin asphalt, the molecular structure inside the asphalt model changed. Specifically, asphaltene molecules tended to associate with each other and showed the stronger self-aggregation behavior, because a higher peak value of RDF was found for the asphaltene-asphaltene pairs in the mixture of aged-virgin asphalt binder. The same distance where the peak value of RDFs took place indicated that adding aged asphalt into virgin asphalt at the current ratio of 1:1 did not change the nature of asphaltene aggregation behavior, but induced the stronger self-aggregation. This is probably because self-aggregation of asphaltene is more likely driven by the high degree of polarity and polar interactions; while the aged asphalt has function groups of ketones and sulfoxides in asphaltene molecules due to the oxidative aging effect. As compared to the asphaltene pairs, the aggregation behavior of resin pairs and aromatic pairs was not obvious since the peak values of RDFs were close to one. However, saturate molecules show self-aggregation in the mixture of virgin-aged asphalt, as shown by the increased peak value of RDFs.

It was found that application of rejuvenator could restore the molecular structure of the mixture of virgin-aged asphalt and thus make it more similar to that of virgin asphalt. This trend was observed consistently in the RDFs of the asphaltene-asphaltene pairs, resin-resin pairs, and aromatic-aromatic pairs. In particular, rejuvenator reduced the self-association trends of asphaltene molecules in the mixture of virgin-aged asphalt. This was probably because small rejuvenator molecules could enter and break the nanoaggregation structure of asphaltene molecules, as observed from the snapshot of molecular model. As shown in Figure 7.8, the strong self-aggregation behavior of asphaltene was observed in the mixture of virgin-aged asphalt; while asphaltene molecules formed a more evenly distributed structure due to the intrusion of rejuvenator molecules, as shown in Figure 7.8(b).

An interesting phenomenon observed was the increased local concentration of saturate-saturate pairs at small separation distances, after adding the rejuvenator into the mixture of virgin-aged asphalt. Realizing that the first peak of asphaltene-asphaltene pairs and saturate-saturates pairs in the radial distribution function occurred at nearly the same distances (Figure 7.7(a) and Figure 7.7(d)), it was hypothesized that saturate molecules entered the asphaltene nanoaggregates. Since saturates are smaller molecules compared with asphaltene molecules, they tend to form local aggregation easily at small distances. Figure 7.9(a) shows that saturate molecules distributed evenly inside the virgin asphalt with low tendency to form aggregation; however, they form local aggregation in the mixture of virgin and aged asphalt with rejuvenator, as shown in Figure 7.9(b).



(b) with rejuvenator (red color refers to rejuvenator molecules)

Figure 7.8 Illustration of self-aggregation of asphaltenes in the mixture model of virgin-

aged asphalt



(a) in virgin asphalt



(b) in the mixture of virgin-aged asphalt

Figure 7.9 Illustration of self-aggregation of saturates

7.4 Effect of Rejuvenator on Translational Mobility of Asphalt

Molecules

The diffusion coefficients of SARA fractions in virgin asphalt, the mixture of aged-virgin asphalt, and the rejuvenated mixture were calculated and the results are shown in Figure 7.10. In virgin asphalt, saturate molecules are the most dispersive fraction among SARA fractions and the mobility of asphaltene molecules is the lowest. The long chains and aromatic rings of asphaltene could easily be blocked by the surrounding big and small molecules; therefore, it has the low translational mobility.



Figure 7.10 Effect of rejuvenator on diffusion coefficients of SARA fractions

The calculated diffusion coefficients of different SARA fractions were consistent with the results reported in the previous simulations [16]. It is noted that the calculated diffusion coefficients are much smaller than those of experimental measurements. This is because experimental results were based on single SARA fraction dissolved in the solution with very low concentrations, and the effects from the other components were excluded [58] [104]. However, in the MD simulation of asphalt model system, the interaction of SARA components on their diffusion behavior was considered. Besides, the temperature effect on the diffusion coefficient of SARA fractions in the Virgin+Aged+Rejuvenator system was also studied, and results are shown in Figure 7.11.



Figure 7.11 Effect of temperature on SARA diffusivity in rejuvenated asphalt system

Compared with virgin binder, asphalt molecules present smaller diffusion coefficients when virgin and aged asphalt was mixed, especially for the lighter fractions (resins, aromatics and saturates). Since aged asphalt is highly oxidized during its service period, the molecular sizes increase due to formation of function groups such as ketones and sulfoxide. This may result in the smaller fraction of free volume (FFV) that is the volume not occupied and available for the molecules to diffuse and thus slower translational mobility of asphalt molecules. However, the introduction of rejuvenator can mobilize the movement of asphaltene, resin, aromatic, and saturate molecules. Therefore, rejuvenator can restore the translational mobility of asphalt molecules due to aging and accelerate the molecular diffusion. It is noted that the diffusion coefficients of virgin and aged asphalt fractions with rejuvenator were found being greater than the ones of virgin asphalt. This is because that the diffusion of molecules is not only related to the molecular weight of component, but also influenced by the self-aggregation and the surrounding environment.

Chapter 8 Conclusions and Recommendations

In this dissertation, the application of Molecular Dynamics (MD) simulations was conducted for asphalt material and pavement engineering. The asphalt properties including thermodynamic properties, rheological properties, structure properties and mechanical properties were investigated. The adhesion behavior between asphalt and aggregate were explored, and the mechanical properties of asphalt-aggregate interface were discussed. Besides, the asphalt oxidative aging mechanism was discussed and the aged asphalt models were built. By using MD, aged asphalt properties were analyzed and the application of rejuvenator into aged binder was also discussed. The MD simulation data were compared to the experimental results, and the recommendation and future works are also provided.

8.1 Summary of Main Findings

8.1.1 Cohesion and Adhesion Properties of Asphalt Mixture

A thermodynamics-based molecular modeling approach was developed to investigate cohesion and adhesion properties of asphalt concrete for the first time. Molecular dynamic simulation was employed to derive thermodynamic properties of amorphous asphalt models (such as surface free energy and cohesive energy density) and work of adhesion between asphalt and aggregate at dry and wet conditions. The simulation results agree well with the experimental measurements reported in the literature. The main findings are listed below: (1) The results show that van der Waals force plays critical role for cohesive properties of asphalt binder;

(2) The adhesion bonding between asphalt to aggregate is largely dependent on the type of aggregate mineral (silica or calcite) in both dry and wet surface conditions.

(3) The effect of asphalt type was found significant for the adhesion between asphalt and silica at the relatively small moisture content.

8.1.2 Asphalt-Aggregate Interfacial Mechanical Behavior

The realistic system of asphalt-aggregate interface was represented by an atomistic asphalt-silica interface. MD simulations were conducted to study asphalt-silica interfacial failure behavior in a comprehensive manner. The MD models were validated by the predicted density and glass transition temperature of asphalt binder. Tensile simulations were performed and the stress-separation responses were obtained to represent the interfacial failure behavior.

(1) It was found that the interface failure was mainly adhesive failure although large air voids were formed in the bulk asphalt as the loading rate decreases to a certain level.

(2) The interface failure strength and post-peak deformation are affected by loading rate and temperature that is consistent the viscoelastic behavior of asphalt binder.

(3) The stress-separation responses match the cohesive zone model (CZM) model that are usually used in the higher-scale continuum modeling for cracking or interface failure. The exponential model was found matching the best with the simulated softening curve.

(4) The relationship between chemical compositions of asphalt binder and the mechanical properties of interface was investigated through the CZM parameters. It was found that both tensile strength and work of separation have positive linear correlations with the asphaltene index.

8.1.3 Oxidative Aging Effect on Asphalt Properties

In this work, MD simulations were used to discover the effect of oxidative aging on thermodynamic properties and performance-related indicators of asphalt. The following conclusions are concluded from the analysis:

(1) Asphalt oxidative aging can be represented by introducing oxygen atoms to replace hydrogen atoms in the chemical composition of asphalt. Oxidative aging affects thermodynamic properties of asphalt, such as increase of density, viscosity, and cohesive energy density, but reduction of surface free energy.

(2) The molecular structures of SARA fractions in asphalt is in agreement with the colloidal theory that asphaltene molecules are diluted in the dispersion medium, and tend to form nano-aggregation structures but are unable to create a continuous network. Oxidative aging weakens the nano-aggregation behavior of asphaltene molecules and reduces the translational mobility of asphalt molecules.

(3) The molecular diffusion of aged asphalt decreases due to the increase of molecular size in asphaltene, resin, and aromatic and reduction of free volume space for

saturate. This affects self-healing capability of asphalt. Compared to aged asphalt, virgin asphalt has the lower activation energy barrier and thus the stronger instantaneous healing ability.

(4) The inclusion of moisture causes adverse effects on the asphalt-aggregate interface adhesion, especially when water molecules penetrate into the interface. Aged asphalt showed less resistance to moisture damage compared to virgin asphalt.

8.1.4 Effectiveness of Rejuvenating Agent with Recycled Asphalt Binder

In this respect, MD simulations were used to study molecular interaction and diffusion between rejuvenating agent and asphalt molecules. Both layered and mixture models of asphalt system were built with virgin asphalt, aged asphalt, and rejuvenator. The following findings were derived from this study:

(1) The layered model results show that adding rejuvenator increases diffusion between virgin and aged asphalt and causes more uniform energy distribution along the diffusion path. As temperature increases, the rejuvenator distributes more evenly in the asphalt that accelerates the diffusion between virgin and aged asphalt. This proves that rejuvenator can improve the blending efficiency of virgin and aged asphalt.

(2) The radial distribution functions of asphaltene, resin, and aromatic pairs show that the application of rejuvenators into the mixture of virgin and aged asphalt could restore the molecular structure more similar to that of virgin asphalt. The rejuvenator reduces the self-association trends of asphaltene molecules because small rejuvenator molecules enter the nanoaggregate structure of asphaltnene molecules; while saturates form local aggregation inside the rejuvenated asphalt.

(3) Compared with virgin binder, asphalt molecules present smaller diffusion coefficients when virgin and aged asphalt was mixed, especially for the lighter fractions (resins, aromatics and saturates). Rejuvenator increases the diffusive mobility of four SARA fractions. The mobility of molecules does not entirely rely on the overall molecule size but also depends on its nanoaggregates and the surrounding environment.

8.2 Conclusions

Based on above summary and main findings, the conclusions can be drawn as follows:

(1) Molecular dynamics simulations can be used as a powerful tool to study asphalt properties, giving the optimal molecular models and appropriate force field are available. Accepted accuracy of modeling can be achieved with comparisons to experimental data.

(2) Fundamental chemo-physical and chemo-mechanical relationship of asphalt binders, as well as asphalt mixtures at an atomistic scale can be investigated using molecular dynamics simulations. This suggests that MD can be used as a useful tool for material design and performance prediction.

(3) In the computational testing environment, insights into the deformation and failure mechanism of asphalt-aggregate interface were obtained at the atomistic scale, which enables better understand adhesion and moisture damage of asphalt mixture.

(4) The molecular interaction between virgin asphalt, aged asphalt, and rejuvenator is a sophisticated process but of great practical importance for recycling of asphalt binder. The simulation methodology developed in this study can be further used to select the optimum type and amount of rejuvenator in a computational environment and accelerate material design process with the minimum experimental effort.

8.3 Recommendations and Future Works

MD method is a powerful analysis and computational simulation tool and is widely used to visualize and generate reasonable computed results. Analyzing material motions at the molecular and atomistic level is essential to understanding key physicochemical phenomena. It is especially beneficial to use MD method to explore mechanisms of material modification and development in an accelerated manner with less experiment effort. Based on the results obtained in this dissertation, the following recommendations are made.

(1) Currently the force field parameters were developed for polymers and biomolecules, and these are not specified for asphalt materials. It is suggested that more accurate asphalt models and force field parameters be developed to characterize asphalt materials as well as interactions with asphalt components, in the order to reduce the difference between simulation and experimental results.

(2) The limitations of the classical MD simulations have to be recognized in terms of the limitation in the time and length scale. The mechanical properties obtained from

MD simulations need be calibrated before they can be further utilized as inputs into the higher-scale simulation for bulk behavior prediction of asphalt mixture.

(3) Asphalt aging is a supplicated phenomenon consisting of both non-chemical and chemical reactions, while chemical reactions are not considered in classic molecular dynamics simulations. It is recommended further work focus on simulation of chemical reaction due to asphalt aging using the reactive force field (ReaxFF) and evaluation of rejuvenator effect on asphalt aging. This will lead to anti-aging design of asphalt material using an integrated computational and experimental approach.

Appendix A

A.1 Experimental Asphalt Composition

Element and component analysis of asphalts are provided in Table A-1, and these data were collected during the 5-year Strategic Highway Research Program (SHRP) ended in March, 1993.

Asphalt code	AAA-1	AAK-1	AAF-1	AAM-1
PG grade	PG 58-28	PG 64-22	PG 64-10	PG 64-16
Asphaltenes	16.2	20.1	13.3	4.0
Polar Aromatics	37.3	41.8	38.3	50.3
Napthene Aromatics	31.8	30.0	37.7	41.9
Saturates	10.6	5.1	9.6	1.9
Elemental Analysis				
C %	83.9	83.7	84.5	86.8
Н %	10.0	10.2	10.4	11.2
O %	0.6	0.8	1.1	0.5
N %	0.5	0.7	0.55	0.55
S %	5.5	6.4	3.40	1.2
Aromatic C %	28.1	31.9	32.8	24.7
Aromatic H %	7.63	6.83	8.66	6.51

Table A. 1 Asphalt component and element information

B.1 Molecular Asphalt Composition for MD Simulation

The specific molecular numbers used in the dissertation to represent AAK-1 and AAM-1 asphalt are provided in Table B-1 and Table B-2, respectively.

A subalt commonition male sule		No. of	Mass	Fractions by
Asphan	composition molecule	molecules	fraction	exp. solubility
Saturate	Squalane	2	6.3	5.1
	Hopane	2		
Aromatia	PHPN	10	20.4	30.0
Alomatic	DOCHN	10	50.4	50.0
	Quinolinohopane	4		
	Thioisorenieratane	4		
Resin	Trimethylbenzeneoxane	4	40.7	41.8
	pyridinohopane	4		
	Benzobisbenzothiophene	12		
Asphaltene	Asphaltene-phenol	3		
	Asphaltene-pyrrole	2	19.6	20.1
	Asphaltene-thiophene	3		

Table B. 1 Component fractions in model and experimental AAK-1 asphalt

Asphalt composition molecule		No. of	Mass	Fractions by
		molecules	fraction	exp. solubility
Saturate	Squalane	1	2.1	1.9
	Hopane	1	2.1	
Aromatic	PHPN	20	11 1	41.9
	DOCHN	21	41.1	
Resin 7	Quinolinohopane	10		
	Thioisorenieratane	10		
	Trimethylbenzeneoxane	10	49.9	50.3
	pyridinohopane	10		
	Benzobisbenzothiophene	4		
Asphaltene	Asphaltene-phenol	1		
	Asphaltene-pyrrole	1	5.0	4.0
	Asphaltene-thiophene	1		

Table B. 2 Component fractions in model and experimental AAM-1 asphalt

Asphalt composition molecule		No. of	Mass	Fractions by
		molecules	fraction	exp. solubility
Saturate	Squalane	5	9.7	9.6
	Hopane	4		
Aromatic	PHPN	18	37.4	37.7
	DOCHN	18		
Resin 7	Quinolinohopane	4		
	Thioisorenieratane	2		
	Trimethylbenzeneoxane	16	38.7	38.3
	pyridinohopane	2		
	Benzobisbenzothiophene	18		
Asphaltene	Asphaltene-phenol	4		
	Asphaltene-pyrrole	2	13.1	13.3
	Asphaltene-thiophene	2		

Table B. 3 Component fractions in model and experimental AAF-1 asphalt

Appendix C

C.1 Average Molecular Structures of SHRP Core Asphalts



(a) AAA-1 asphalt



(b) AAF-1 asphalt

Z



(c) AAK-1 asphalt



(d) AAM asphalt

Figure C. 1 Average Molecular Structures of SHRP asphalt binders

(carbon atoms are grey, sulfur atoms are yellow, red is oxygen, and hydrogen atoms

are not included in the molecule structures)

2

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Acknowledgment of Previous Publications

This dissertation consists of 3 published papers. The journal author's right to include authors' own articles in full or in part in dissertation is greatly acknowledged here.

Chapter 3 of this dissertation discussed the molecular models and simulated results by molecular dynamics simulations. This chapter has been published in the journal of "*Computational Materials Science*" in 2016, with volume number of 112 and page number 161-169. I completed this chapter with my adviser Dr. Wang.

Chapter 4 of this dissertation analyzed the asphalt-aggregate interface properties. This chapter has been also published in the journal of "*Computational Materials Science*" in 2016, with volume number of 112 and page numbers 161-169. I completed this chapter with my adviser Dr. Wang.

Chapter 5 of this dissertation investigated the mechanical properties of the asphalt-aggregate interface by MD simulations. This chapter has been also published in the journal of "*Construction and Building Materials*" in 2016, with volume number of 121 and page numbers 246-254. I completed this chapter with my adviser Dr. Wang.

Chapter 6 of this dissertation provided an understanding of the mechanism of asphalt aging via molecular scale using MD simulation. This chapter has been also published in the journal of "*Fuel*" in 2017, with volume number of 188 and page numbers 1-10. I completed this chapter with my adviser Dr. Wang.

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