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# Study of cohesion and adhesion properties of asphalt concrete with molecular dynamics simulation

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ABSTRACT

The objectives of this study is to develop a molecular modeling approach for studying cohesive and adhesive properties of asphalt concrete and evaluate the accuracy of modeling through comparisons with experimental data. Fully atomistic models were built for molecular dynamics (MD) simulation considering two representative asphalt models and two types of aggregate mineral. MD simulations were performed to study thermodynamic and cohesive properties of asphalt binder, such as density, solubility parameter, cohesive energy density, and surface free energy. The adhesion properties were investigated by calculating the interaction energy and the work of adhesion at asphalt–aggregate interface for the first time. The bond energy parameters in dry and wet conditions were used to evaluate moisture sensitivity of interface adhesion. The results show that van der Waals force plays critical role for cohesive properties of asphalt binder; while 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. The effect of asphalt type was found significant for the adhesion between asphalt and silica at the relatively small moisture content. The simulation results agree well with experimental measurements reported in the literature. This work illustrates MD can help in understanding fundamental chemo-mechanics relationship of asphalt concrete at an atomistic scale, which can be used as a useful tool for material design and performance prediction.



## 1. Introduction

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.

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. To better understand the adhesive bond between asphalt and aggregates, four fundamental theories including mechanical theory, chemical theory, weak boundary theory, and thermodynamic theory have been proposed [2]. Meanwhile, moisture effect has been found being the major driving force causing the loss of adhesion between asphalt and aggregate and further deterioration [3].

A number of studies have been conducted to evaluate adhesion properties of the asphalt–aggregate interface and moisture susceptibility of asphalt concrete using bond strength measurements from experimental and phenomenological engineering aspects [4–7]. Nanoscale experiments have also been used to measure surface free energy and adhesive/cohesive force–displacement relationships between asphalt molecular groups and aggregates at dry and wet conditions [8–11]. These experimental studies have produced acceptable and reasonable results for better understanding cohesion and adhesion properties of asphalt concrete.

Recently, atomistic modeling with molecular dynamic (MD) simulation has been employed to study the link between chemical structures and physical and mechanical behavior of asphalt concrete and durability, such as density, thermal expansion coefficient, and viscosity [12], adhesive strength [13], aging effect [14], curing [15] and self-healing [16]. Molecular dynamics simulation is a powerful and feasible approach for material design and performance

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prediction because the atomistic structures of asphalt and aggregate and their interfaces determine the behavior of asphalt concrete at the continuum scale. The significant advantage of MD simulation is to provide fundamental observations in the initiation and evolution of material damage at the nanoscale that are very difficult to obtain from the traditional experiments conducted at the laboratory.

While a number of studies have used MD simulation to study asphalt concrete from a more fundamental and nature perspective, little work has been focused on deriving cohesion and adhesion properties of asphalt concrete from the atomistic scale to the continuum scale. Limitations exist for in-depth investigation of moisture susceptibility of asphalt concrete at the nanoscale. The interaction between asphalt and aggregate is governed by various attractive intermolecular and intramolecular forces across the interface. This necessitates investigation of the fundamental cohesion and adhesion properties of asphalt concrete using a systematic atomistic modeling approach.

## 2. Objective and scope

The objectives of this study is to develop an atomistic modeling approach for studying cohesive and adhesive properties of asphalt concrete and evaluate the accuracy of modeling through comparisons with experimental data. In order to achieve this objective, fully atomistic models were built for MD simulation considering two representative asphalt models and two types of mineral aggregate. Bulk asphalt models and confined layer models were used to derive thermodynamic material properties of asphalt binder, including density, surface free energy, cohesive energy density, and solubility parameter. The work of adhesion between asphalt binder and aggregate were derived from interaction energy with different definitions of surface area. The effects of chemical structures of asphalt and aggregate and moisture contents on the adhesion between asphalt and aggregate were investigated.

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.

## 3. Molecular dynamics simulation

### 3.1. Basic principle

Molecular dynamics simulation is a technique for calculating the equilibrium and transport properties of a classic many-body system [17], in which the motion of the constituent particles 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, as shown in Eq. (1). 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. The force on an atom $i$ can be directly calculated by the derivative of the potential energy, $E$, with respect to the coordinate $r_i$.

$$-\frac{\partial \mathrm{E}}{\partial r_i} = m_i \frac{\partial^2 r_i}{\partial t^2} \tag{1}$$

where $m_i$ is the mass of atom $i$. In a system consisting of $N$ atoms, all pairs can result in $N(N-1)/2$ interactions, that is to say, even moderate numbers of atoms $N$ will generate a very large number of calculations.

### 3.2. Force field

Force field, sometimes used as potentials, refers to a mathematical function used to compute the energies of a system of atoms with various system conformations in the context of molecular modeling. In general, the force field parameters can be obtained from the experiments, together with quantum mechanical calculations. The goal of a force field is to describe entire classes of molecules with reasonable accuracy. Basically, the total potential energy $E$ can be comprised of a number of bonded and non-bonded interaction terms, as shown in Eq. (2).

$$E = E_{\text{bonded}} + E_{\text{non-bond}} \tag{2}$$

where the bonded terms, $E_{\text{bonded}}$ is for atoms interactions contributed by covalent bonds including 0062ond stretching, angle bending and dihedral and improper interaction, etc., while the non-bond interaction term describes non-covalent contributions that mainly contain van der Waals energy, Coulomb electrostatic energy, and hydrogen bond energy. A number of force fields have been developed over the years. The energy terms describing different kinds of deformations were added or changed in Eq. (2) for different force fields. In all cases using an appropriately parameterized force field is an important issue in molecular simulation.

Molecular dynamics (MD) simulations were performed using commercially available simulation software, Materials Studio [18]. COMPASS II (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field was used for describing atom-level interactions in molecular models. COMPASS is the first parameterized and validated ab initio-based force field that has a broad coverage in covalent molecules including most common organics, small inorganic molecules, and polymers. COMPASS II is a significant development extension to the COMPASS force field in terms of atom types and force field terms, which enable us to make accurate predictions material properties for a wide range of compounds in isolation and in condensed phases [19]. The more realistic the potential is, the closer the MD simulations results represent the real properties of materials. The amount of time needed for MD simulations is largely dependent on the functional complexity of potential.

### 3.3. Molecule models for 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 sulfur, 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