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Molecular dynamics simulation of physicochemical properties of the asphalt model

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HIGHLIGHTS

- The Amber Cornell Extension Force Field was used to simulate asphalt.
- The NWChem was applied to generate the ESP charges in the components.
- The Muller-Plathe method was used to calculate the viscosity of asphalt.

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ABSTRACT

The objectives of this molecular dynamics study are to simulate the asphalt model using the common components from the references, and to predict the physical properties of asphalt material. The asphalt model consists of three components: the asphaltene, aromatic, and saturate, at the ratio of 5:27:41. The docosane and 1,7-dimethylnaphthalene represents the saturate and naphthene aromatic, respectively. The Amber Cornell Extension Force Field was adopted and utilized in the asphalt model system, and the experimental parameters associated with this force field were obtained from the General Amber Force Field (GAFF). The geometry and energy optimizations of the molecular components were used to establish the stable asphalt model system. The density of the asphalt model system was calculated with the Amber Cornell Extension Force Field. The predicted densities were compared with the laboratory data to verify the model. Moreover, the glass transition temperature range of the molecular asphalt model was computed from the relationship between the specific volumes and temperatures after the molecular dynamics experimental simulation. The glass transition temperature range had a good correlation with the experimental data. The viscosity data of the molecular asphalt model was calculated using the Muller-Plathe algorithm. The predicted viscosities at specific temperatures were also compared and discussed with the laboratory data and other published results. In addition, the bulk modulus of the molecular asphalt model was determined and obtained by applying the infinitesimal strain in the model boundaries. The results of the analysis of the bulk modulus in the asphalt model were compared to the reference data, and these predicted results were better than the reference values.

1. Introduction

Asphalt is widely applied in pavement engineering due to the good performance of pavement in asphalt mixtures. Asphalt material is the byproduct of petroleum refinement, and the petroleum is naturally generated from organic matter, which forms under the ground over millions of years, subjected to various conditions of very high pressures and temperatures. About 90–95 percent (by weight) of asphalt is comprised of carbon and hydrogen, and it is called a hydrocarbon (an organic material). The rest of the asphalt consists of two types of atoms, heteroatoms and metals, such as nitrogen, oxygen, and sulfur [1–3]. These interactions of atoms determine the physical and chemical properties of asphalt. The carbon content of asphalt is around 82.9–86.8%, and the hydrogen content ranges from 9.9% to 10.9%. The contents of nitrogen, sulfur, and oxygen range from 0.2% to 1.1%, 1.0% to 5.4%, and 0.2% to 0.8%, respectively [4]. In addition, some metal atoms can be found in the asphalt, such as nickel, iron, and vanadium. However, the quantities of all metals are less than 1 percent by weight of the asphalt. The existence of these atoms that occur in small amounts depends on the locations and aging status of the asphalt. Currently, asphalt components can be separated by the Corbett and Rostler methods.

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Different absorption and desorption techniques are used in the Corbett method to separate the asphalt, and the four components are asphaltenes, saturates, naphthene aromatics, and polar aromatics. Meanwhile, sulfuric acid is used in the Rostler method to separate the asphalt, and the five components are asphaltenes, paraffins, second acidiffins, first acidiffins, and nitrogen bases [4]. In addition, three types of molecules are presented in the asphalt: aliphatics, cyclics, and aromatics. These molecules interact with each other and directly affect the physical and chemical behaviors of asphalt.

Molecular Dynamics (MD) is a computer simulation of the molecular movement of numerous N-body particles based on the physical principles of atoms and molecules. The trajectories of atoms and molecules are determined by Newton's law and the forces between the atoms and molecules, and are defined by the applied force field. A given period of time is allowed for the interaction between the atoms and molecules. Researchers have studied the asphalt material using the methods for molecular dynamics. Actually, investigations on the molecular level can increase the fundamental understanding of the properties of asphalt, as well as the modification mechanism. The asphalt binder models were recently established using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) and the Monte Carlo Method (Towhee) [5–7]. Two asphaltene structures (asphaltene1 [8] and asphaltene2 [9]) were modeled by following by the results of Artok et al. [8] and Groenzin and Mullins [9]. The *n*-docosane (n-$C_{22}H_{46}$) and 1,7-dimethylnaphthalene were adopted to model the saturate and aromatic compositions in the asphalt binder, respectively. The number of molecules, mass fraction, and mass percent by atom in the asphalt binder models were calculated to fit the parameters of the references. The OPLS-aa (all-atom optimized parameters for liquid simulations) Force Field was employed in this study to analyze the properties of asphaltene1 and asphaltene2, as well as other components in the asphalt models, such as the density and thermal expansion. The computational results showed that the OPLS-aa Force Field can efficiently supply the parameters and provide sufficient accuracy for the simulation. The temperature-density results between the simulations and experimental test data were correct. The effect of polymer modification in the asphalt binder was proven in the simulation through the property changes of the modified asphalt in the model [5]. They also studied the molecular orientations of three components in the asphalt binder models. The results showed that the orientations of the molecules near the asphaltenes were affected by the molecular structures and temperatures [7].

The tests for the relaxation time and diffusion of the asphalt components were conducted using the molecular dynamics simulation over different temperatures. The viscosity of the asphalt was computed by the Green–Kubo and Einstein methods at different temperatures [10]. A modified Kohlrausch–Williams–Watts function was employed and the results were regressed to obtain the relaxation times for the asphalt model. The Vogel–Fulcher–Tam mann and Debye–Stokes–Einstein equations were adopted to evaluate the viscosity and the diffusion of the asphalt model. The computational results revealed that the neat naphthalene diffused faster than the other components of asphalt binders and the asphaltene molecules diffused slowest in the asphalt models [6].

Recently, a new MD model was proposed to represent the Canadian/Lloydminster (AAA-1), Venezuelan (AAK-1), and USA/West Texas (AAM-1) asphalt, utilizing three kinds of asphalt molecular compositions in accordance with the element, molecular types, and composition fractions. The new model has 12 molecular components based on the common three-component model. The new model, with longer branches, contains four molecular groups: saturates, naphthene aromatics, polar aromatics, and asphaltenes [11]. In this model, the asphaltene molecules were obtained by Mullins [9,12]; the saturate fractions were represented by the squalane and hopane; the naphthene aromatic molecules were simulated by the perhydrophenanthrene-naphthalene (PHPN) and dioctyl-cyclohexane-naphthalene (DOCHN); the polar aromatic molecules were displayed by modified quinolinohopane, thio-isorenieratane, benzobisbenzothiophene, pyridinohopane, and trimethylbenzene–oxane. The new asphalt model overcame the weaknesses of previous models, such as the low density and fast relaxation time, and showed a better representation and property prediction [11].

The dynamic modulus and shift factors were also simulated in the asphalt binder model. The horizontal shift factors were fitted into the Williams–Landel–Ferry equation with parameters [13], and the dynamic modulus data was interpreted using the Maxwell models. The thermodynamic properties of asphalt binder components were analyzed by Tarefder and Arisa [13]. The results of the simulation include the density, glass transition temperature and potential energy of the systems. The results showed that the resin and asphaltene systems had a different relationship over a range of temperatures. The percentage of oxygen influenced the glass transition temperature. Oxidation levels affected the glass transition temperature of asphaltenes and did not affect the glass transition temperature of resin in the study [13]. In this study, MD was employed to calculate the physical properties of asphalt. The validated asphalt model helps us to understand the components of the asphalt and the interaction/relationship between the components from a molecular aspect.

2. Scopes and objectives

The objectives of this study are to simulate the asphalt model using the common components from the references and to predict the physical properties of asphalt material. The Amber Cornell Extension Force Field was applied to the molecular systems, and the Electrostatic Potential (ESP) charges were allocated to these components with the NWChem analysis using quantum mechanics (QM). The densities of the molecular asphalt model were used for the verification of the asphalt model. After verifying the model, the property simulations of the asphalt model were carried out, including the glass transition temperatures, viscosity, and bulk modulus. Different calculation methods were employed to simulate and predict these properties of the asphalt model. The comparisons of the predicted results with the laboratory or reference model data were conducted. In addition, these calculation and optimization methods used in this study are useful for simulating other materials, and these are also the references for generating a new asphalt model.

3. Molecular dynamics simulation theory and force field potentials

3.1. Classic MD simulation procedures

Normally, five kinds of simulations were adapted in the experimental MD simulation including the Microcanonical ensemble (NVE ensemble), Canonical ensemble (NVT ensemble), Isothermal–isobaric ensemble (NPT ensemble), Isoenthalpic–isobaric ensemble (NPH ensemble), and Generalized ensembles [14]. Energy minimization (also called geometry optimization) is another kind of MD simulation, and the geometric change in the model leads to a low energy of the system. In this research, the energy minimization, and NVT and NPT simulations have been used to bring the system to equilibrium. In addition, the procedure of the experimental MD simulation is shown in Fig. 1.