

ANALYSIS OF THE SELF-HEALING PROCESS OF ASPHALT AND ITS INFLUENCING FACTORS

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Abstract. Molecular dynamics was used in this study to understand the self-healing behavior and mechanism of asphalt. Density, solubility, and mean square displacement parameters were analyzed to confirm the validity of the matrix asphalt model. Molecular simulation software was used to develop a microscopic matrix asphalt self-healing model at the nanoscale. Cracking width of asphalt microcracks was represented by setting different vacuum layer thicknesses as the asphalt self-healing model. Density and diffusion coefficient of the self-healing model were obtained by running the molecular software to understand the entire process of asphalt healing. The self-healing mechanism of the matrix asphalt was analyzed. Results showed that the entire self-healing process of asphalt could be clearly divided into four stages, namely, external environment energy endowment, model end healing, asphalt microcrack healing, and self-healing model self-diffusion stages. Molecules of each component in the asphalt self-healing process diffuse and move mutually

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under constant temperature conditions. The diffusion coefficient of saturated components and polar aromatic was higher than that of asphaltenes and aromatic components.

Keywords: asphalt self-healing, different temperatures, four-component movement, matrix asphalt, molecular dynamics, self-healing mechanism.

Introduction

Asphalt properties alter with changes in the temperature of the environment because asphalt is a temperature-sensitive material (Wang & Al-Qadi, 2013; Dan et al., 2019). Asphalt materials tend to “flow” at high temperatures and may return to their initial state (strength and stiffness) road performance, i.e., asphalt self-healing behavior under certain environmental conditions. Coupling of load-temperature-water causes fatigue microcracks in asphalt pavement. The majority of cracks in roads originate from microcracks in asphalt materials. The self-healing behavior can effectively repair microcrack structure of asphalt road surface. Road cracks start from the initial sprouting of microcracks in the asphalt material and gradually expand to cracking. The surface material fatigue fractures gradually form macrocracks after cracking (Si et al., 2002). Crack damage further deepens and results in loose pavement surfaces, potholes, and other forms of damage. Analyzing the self-healing behavior of asphalt is necessary to slow down the damage process of road surface.

Bazin & Saunier (1967) pioneered experiments on asphalt concrete materials to confirm their self-healing properties for fatigue damage. Consequently, numerous experiments were subsequently conducted by other researchers. The link between self-healing properties of asphalt and road structure, temperature, material type, and fatigue loading was analyzed and demonstrated. Fiber reinforcement (Zhang & Hu, 2001), addition of modifier materials (Xu et al., 2010), and improvement of road surface structure (Cui et al, 2008) are often used worldwide to improve the performance of asphalt materials and enhance elasticity and tensile capacity. Xu (2002) analyzed the effect of SBS modification and self-healing of matrix asphalt from the perspective of fatigue damage healing using DSC and bending fatigue tests. The results confirmed that the SBS modifier exerted a promotional effect on asphalt healing and demonstrated a healing trend consistent with that of the matrix asphalt. Hongzhou Zhu (Zhu et al., 2020) analyzed the temperature on self-healing properties of asphalt. Microwave heating of the asphalt mixture was performed to determine the surface temperature, and the tensile strength ratio from the experiment was used as the healing index. The

asphalt mixture material demonstrated enhanced healing recovery at the maximum surface temperature of 80°C. These methods mitigate and inhibit the development of microcracks in the analyzed asphalt from macroscopic aspects. Zhou Xinxing (Zhou et al., 2019) analyzed the healing performance of silicone and polyurethane mixed modifier (ASP) on asphalt. Through a large number of experiments, it shows that ASP modifier can enhance the self-healing ability of asphalt when the temperature increases. (Behnia & Reis, 2019) analyzed the fracture healing performance of asphalt concrete by using acoustic emission instrument and disc compression tensile test. The results show that the healing performance of asphalt pavement is improved by more than 13% after 12 hours of cooling. Some experts and scholars even analyze the effect of asphalt regenerant on asphalt self-healing performance recovery. Ben An Shu (Shu et al., 2019) added regeneration agent to the aged asphalt to improve the original “micro flow” performance of the asphalt and the self-healing performance of the aged asphalt. (Shirzad & Hassan, 2019) analyzes its influence on asphalt self-healing performance from the aspects of asphalt blending, healing time, healing temperature and fatigue damage. Through the healing of internal cracks, it is concluded that the influence of temperature and healing time on asphalt self-healing performance is far greater than that of fatigue damage. Yuan Shuai Dong (Dong et al., 2019) tested temperature, damage degree, asphalt type and other factors, and obtained that the improvement of concrete mix proportion could effectively improve the asphalt healing performance. Mansour Fakhri (Fahri & Bahmai, 2020) uses scrap metal as an additive to adjust the healing performance of asphalt. The heat conduction of steel slag is better than that of steel fiber. Grossegger’s research on self-healing activation energy of asphalt is consistent with the effect of thermal expansion on asphalt, and it is found that its thermal expansion improves the self-healing performance of asphalt (Grossegger & Garcia, 2019). In-depth analysis of the self-healing phenomenon of asphalt from a microscopic point of view, such as molecular structure and component composition of asphalt, is difficult to perform using traditional experimental arguments.

The analysis of internal forces of the asphalt molecular system is difficult to obtain from experiments. However, simulations are easily analyzed with molecular simulation software. Molecular dynamics (MD) in software has become an effective method for simulating atomic and molecular levels. MD has been gradually applied to the analysis of structural properties of asphalt materials in recent years. The internal structure and properties of materials are related to their analysis. Scholars have used MD simulations to analyze oxygenation aging (Xu & Wang, 2017; Qu et al., 2018), modification mechanism (Wang et al., 2018;

Long et al., 2020), and interfacial adhesion mechanism (Liu et al., 2020; Xu & Wang, 2016) of asphalt mixtures. Cong Yufeng (Cong et al., 2005; Guo, 2016) used molecular simulation to analyze the phase solubility of linear and star-type SBS modifiers in asphalt. Guo analyzed adhesion of mineral oxides to asphalt and showed that Fe_2O_3 demonstrated the maximum adhesion work and optimal adsorption effect in asphalt. Based on previous experience, this paper uses molecular simulation software to construct a self-sealing asphalt model; firstly, to establish the representative molecules of each component of asphalt and, secondly, to optimize the structure and energy of each molecule. A representative asphalt molecular system is built through software. The asphalt molecular system is constructed as an asphalt self-healing model. The self-healing model is used to analyze the whole process mechanism of asphalt self-healing and reveal the asphalt healing properties of four components and different temperatures.

1. Matrix asphalt model construction

The complex chemical molecular structure of asphalt can be considered a structural body formed by complex molecules of hydrocarbons and nonhydrocarbons. Asphalt molecules contain O, N, S, H, and C elements among others. The element content (Xu Meng, 2019) is about: H: 10.22%, O: 0.95%, N: 0.79%, S: 3.80%, C: 80–88%. Scholars (Corbett, 1969) have experimentally classified asphalt molecules into three (Zhang & Greenfield, 2007), four (Hansen et al., 2013.), and six (Zhang & Greenfield, 2008) components due to their complexity based on molecular chemical properties and solubility in specific solvents (Corbett, 1969). Zhang et al. (2007) simulated a three-component asphalt molecular model with $\text{C}_{22}\text{H}_{46}$ to represent saturated fraction (Storm et al., 1994; Bunker & Li, 1981; Groenzin & Mullins, 2000; Li & Greenfield, 2014.) and asphaltene molecules of 1,7-dimethylnaphthalene on the basis of intensive research on microscopic molecules. Li & Greenfield (2014) proposed a four-component twelve-molecule asphalt structure and developed the AAA-1 asphalt model consisting of twelve molecules. Rheological properties (Xu, Wang, & Sun, 2017), diffusion behavior (Xu & Wang, 2018; Sun & Wang, 2019; Xu & Wang, 2016), and adhesion properties of the 12-molecule asphalt model were investigated (Xu & Wang, 2016; Sun, Ren, & Fried, 1998). Asphalt properties can be appropriately represented with the gradual improvement of the 12-molecule structure.

As shown in Figure 1, 12 molecules were used to build the asphalt model using Materials Studio software and molecular proportions were in accordance with the AAA-1 asphalt model. Compass II force field,

which is the first force field that unifies the analysis of organic and inorganic molecular systems for processing, was used for model analysis to explain material properties, such as alkanes, metals, and metal oxides (Sun et al., 2016; Painter, 1993), accurately. The run function can be efficiently adjusted to obtain highly accurate analytical values when dealing with multiple systems. An increasingly accurate asphalt model is obtained with the application of this force field for analysis. The model is set up in a cubic periodic frame and divided into OX, OY, and OZ directions in the Cartesian spatial coordinate system. OA, OB, and OC denote the side lengths of OX, OY, and OZ directions in the asphalt molecular model, respectively (Figure 2). N, V, T, and P represent the constant number of molecules, volume, temperature, and pressure of the model, respectively. The pressure value was set to 0.101 MPa (simulating asphalt at atmospheric pressure). The asphalt model temperature was set to 333.15 K (simulating the mixing of asphalt materials at 170 °C). The single molecule is geometrically optimized in five temperature cycles from 300 K to 500 K and then annealed. The optimized molecule is analyzed under the NVT system, Compass II force field, and atom-based van der Waals analysis to obtain the stable state of the molecule. Finally, the asphalt molecular model was constructed.

The asphalt model building process is presented as follows (Figure 3):
(1) Use amorphous cell module to build the asphalt model, with the

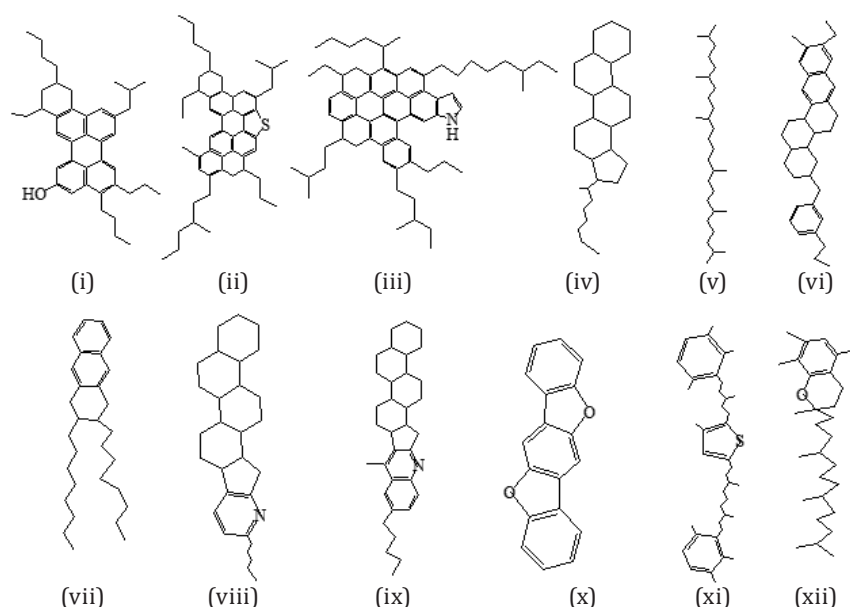


Figure 1. Matrix asphalt 4 groups 12 molecules

initial density set to 1 g/cm³; (2) Use the geometry optimization task in forcite module to obtain the asphalt model in the energy minimum state; (3) Run the annealing mode at a temperature range of 300–500 K for five cycles to stabilize the structure; (4) Run the kinetic optimization for 100 ps (1 ps = 10⁻¹² s) in the NVT system to ensure that molecules of components can move randomly; (5) Continue to run the kinetic optimization for 50 ps in the NPT system to compress the volume of the model; (6) Place the model in the NVT system to simulate the kinetic run for 20 ps and ensure that the molecular structure of the asphalt model can be stabilized. The obtained structure is in the steady state after these steps. Hence, the asphalt model can appropriately represent real asphalt material.

Table 1. Molecular compositions of virgin asphalt

Virgin asphalt composition	Molecule	Order number	Numbers	Mass ratio	Solubility ratio in experiments	
Asphaltene	Phenol	i	3	5.42	17.77	16.20
	Thiophene	ii	3	6.72		
	Pyrrole	iii	2	5.63		
Saturate	Hopane	iv	4	5.05	10.40	10.60
	Squalane	v	4	5.35		
Aromatic	PHPN	vi	11	16.19	32.93	31.80
	DOCHN	vii	13	16.74		
Polar aromatic	Quinolinohopane	viii	4	5.32	38.90	37.30
	Phridinohopane	ix	4	5.95		
	Benzobisbenzothiophene	x	15	13.80		
	Thio-isorenieratane	xi	4	7.26		
	Trimethylbenzene-oxane	xii	5	6.57		

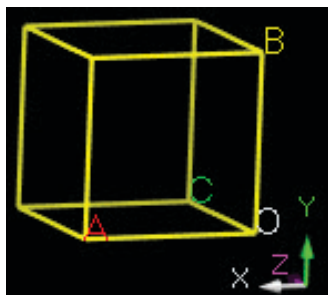


Figure 2. Model frame

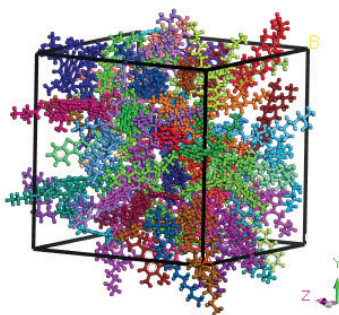


Figure 3. Matrix asphalt model

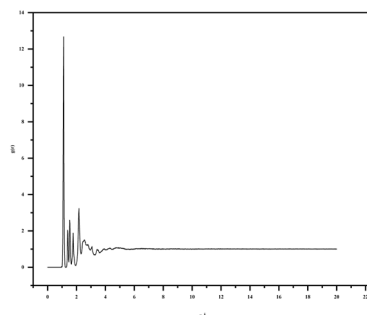


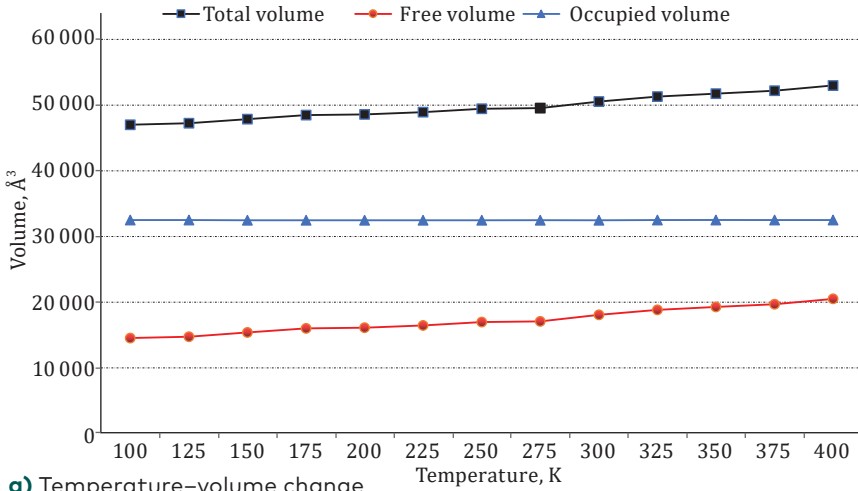
Figure 4. Average orientation shift diagram of matrix asphalt

2. Representative analysis of the virgin model

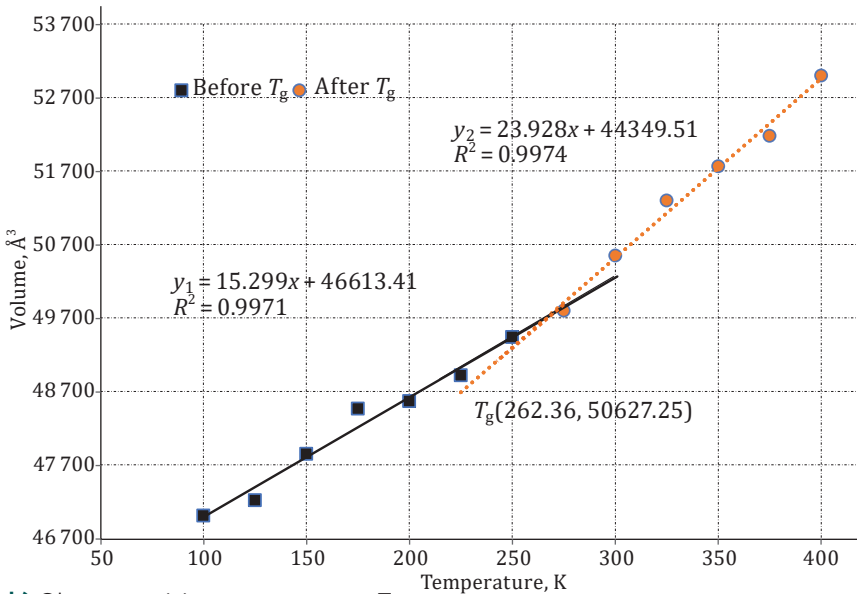
Parameters of density, solubility, and mean square displacement (Table 2) were used in this study to confirm the realism of the asphalt model. A density value of 0.98 g/cm^3 obtains an error value within 5% compared with the experimental interval value of $1.02\text{--}1.04 \text{ g/cm}^3$. This finding meets the requirements of asphalt simulation. The solubility parameter (δ), an indicator of the degree of mutual compatibility of the two materials, is the degree of stability between molecules of each component of asphalt materials and their functional groups. High similarity in molecular polarities indicates high stability when mixed with each other. The solubility value can be obtained by calculating the arithmetic square root of the cohesive energy density (CED) index. The calculated cohesion energy value is 370.95 J/cm^3 ; hence, a solubility value of $19.26 (\text{J/cm}^3)^{0.5}$ is consistent with the experimental value range.

The radial distribution function parameter indicates the particle distribution within the molecular model of the matrix asphalt. The peak at $r = 1 \text{ \AA}$ in Figure 4 indicates an orderly and concentrated distribution of atoms in the asphalt model in the spherical decent space at $r = 1 \text{ \AA}$. Asphalt atoms are distributed in an orderly manner in the space from $1 \text{ \AA}$ to $5 \text{ \AA}$ but irregularly distributed beyond the $5 \text{ \AA}$ space, just as light component molecules of asphalt molecules surround asphaltene molecules in the spatial system. The interaction between component molecules forms a spatial skeleton. The interaction force is strong and atoms in the asphalt are distributed in an orderly manner when the spatial distance between component molecules is small but weaken and become randomly distributed beyond a certain distance. The mean square displacement curve of the asphalt molecular model is consistent with that of real asphalt.

The matrix asphalt model was subjected to kinetic operations under NPT synthesis at various temperatures (Figure 5) and analytical operations were performed at 200 ps. The obtained asphalt models were subjected to Connolly and Solvent model volume and surface area analysis. Free-volume and solid-volume values were obtained. The free volume represents the volume space of the matrix asphalt with temperature. The solid volume is the molecular occupied volume of the matrix asphalt. Glass transition temperature, T_g , of the matrix asphalt model is the characteristic temperature at which the asphalt changes from viscoelastic to brittle for temperature variation. T_g to $T_g + 100\,000 \text{ K}$ is the viscoelastic behavior of the asphalt rheology. Fitting the volume temperature function obtained T_g of 262.36 K , which is close to the temperature value of 261.73 K for the glass transition temperature of the matrix asphalt (Xu & Wang, 2016) measured by the SHRP program



a) Temperature–volume change



b) Glass transition temperature, T_g

Figure 5. (a) Temperature–volume change, (b) Glass transition temperature, T_g

Table 2. Validation of asphalt model parameters

Structure parameter	Density, g/cm^3	Solubility, $(\text{J/cm}^3)^{0.5}$
Simulation results	0.98	19.26
Experimental results	1.02–1.04	13.30–22.50

and within a certain error range that meets the requirements. In summary, the parameter analysis confirms that the asphalt molecular model can represent the real asphalt molecule.

3. Self-healing modeling

The setting vacuum layer was used as the microcrack after establishing the basic molecular model. The healing model is an asphalt molecular model–microcrack (vacuum layer)–asphalt molecular model. Microcrack widths were set to 10, 20, 30, 50, 80, and 100 Å (1 Å = 0.1 nm). After the healing model was constructed by the layer building module. The pressure was a standard atmosphere of 0.0001 GPa, and the algorithm was optimized for 1 500 000 steps with a time step of 0.1 fs and 5000 steps for each structure. The healing process of asphalt molecules was simulated using the kinetics of 150 ps in the forcite module under the NPT synthesis.

The maximum temperature of asphalt pavements in practice is close to 70 °C (Du et al., 2018; Peng et al., 2019), and exploring higher temperatures loses its practical significance. The viscoelastic temperature range of asphalt is T_g K to $T_g + 100$ 100 K. Excessively high temperatures may lead to asphalt aging and reduction of healing properties of asphalt. Furthermore, the healing of asphalt at temperatures from 30 °C to 70 °C was analyzed. Temperatures were set to 303.15 K (30 °C), 313.15 K (40 °C), 323.15 K (50 °C), 333.15 K (60 °C), and 343.15 K (70 °C) in the analysis of asphalt self-healing.

The matrix-asphalt 10 Å microcrack model illustrated in Figure 6 demonstrates OA = 38 Å, OB = 38 Å, and OC = 120 Å (C-fig.: OA, OB, and OC are prism lengths of the model space body in OX, OY, and OZ directions in the Cartesian coordinate system, respectively) in its initial model system. The initial density of the matrix-asphalt 10 Å healing model was 0.6150 g/cm³, and the healing model reached a density of 0.9870 g/cm³ after healing and kinetic optimization. The change of the model between the initial and the healing densities was consistent with the actual healing situation.

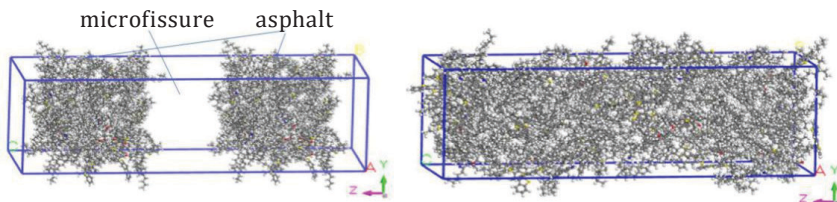


Figure 6. Initial and healed model of 10 Å microcracks in the matrix asphalt

4. Analysis of the asphalt self-healing process

The healing model was subjected to 200 ps kinetic data analysis to examine the asphalt self-healing process. The matrix asphalt healing process was divided into four healing time periods, namely, asphalt healing model kinetic preparation, asphalt self-healing model end healing, asphalt self-healing model microcrack healing, and asphalt self-healing model microcrack self-diffusion (equilibrium) stages, by combining curves in Figs. 7, 8, and 9.

5. Healing process of the asphalt self-healing model

5.1. Kinetic energy preparation phase of the asphalt self-healing model (energy given to the asphalt road pavement by the external environment)

Asphalt molecules in the initial model of asphalt self-healing are in a period of turbulence from 0 ps to 0.796 ps. The molecular simulation software endows the asphalt molecules with energy. The initial temperature of the software (the initial temperature value is set for the demand value of model molecules calculated by the relevant algorithm in the software) is set to a high-temperature condition of nearly 420 K and the temperature decreases sharply in the temperature–time curve

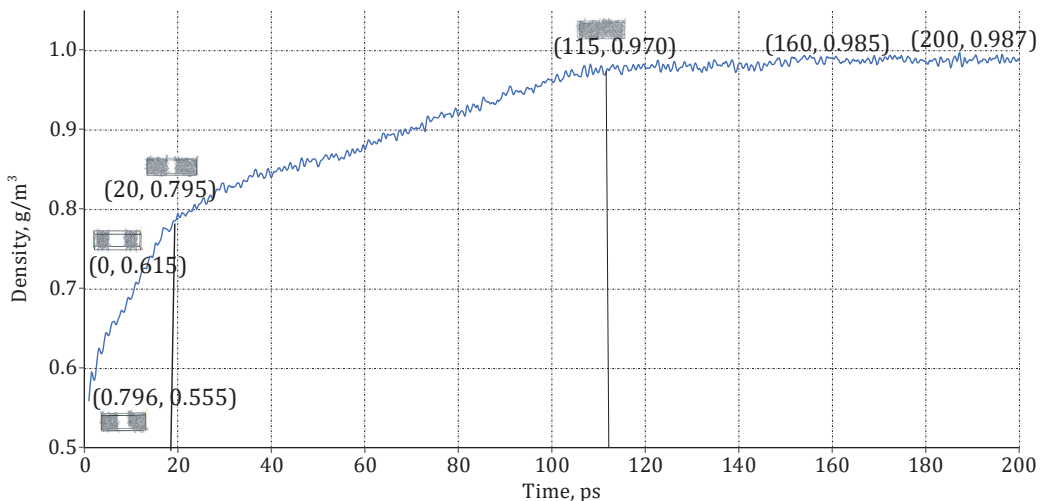


Figure 7. Density-time curve of the 10 Å microcrack healing process of the matrix asphalt

during this running time period. The high-temperature energy from the software to asphalt molecules is converted into kinetic energy at 0.7960 ps. The kinetic energy curve (Figure 8) increases first and then decreases similar to the energy–time curve. Potential and non-bonding energies both demonstrate decreasing trends. Figure 7 shows that the density decreases from 0 ps to 0.7960 ps and then increases with a “v”-shaped density curve. Asphalt molecules convert thermal energy into kinetic energy in the initial kinetic simulation of the healing model. The transformation of the kinetic energy into molecular motion causes a sharp decrease in the model density.

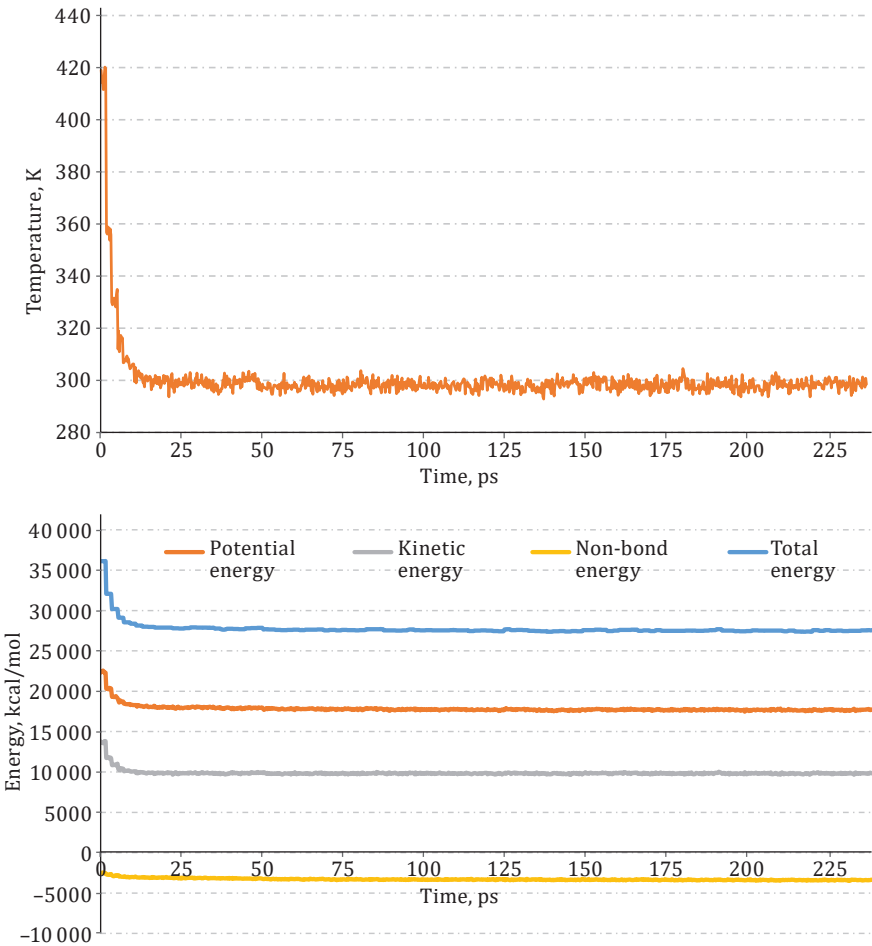


Figure 8. Temperature and energy–time curve of the 10 Å microcrack healing process of the matrix asphalt

5.2. Asphalt self-healing model end healing phase

The sharp increase in the density of the healing model between 0.7960 and 20 ps (Figure 7) indicates the rapid movement of molecules. The density is enhanced by filling the space through the movement of molecules. The molecular motion needs to overcome intermolecular interaction forces. Figure 9 illustrates that the first density plot is the 0 ps healing model with zero density at both ends, thereby indicating the absence of asphalt molecules at the ends. The healing model runs for 20 ps with a density value of 0.6000 g/cm^3 at both ends in the second figure. Molecular motion fills the ends of the healing model to ensure that both ends are fully equipped with molecules. The small density width of the middle microcrack indicates the movement of the asphalt molecules toward the microcrack. The movement to both ends and the vacuum layer space demonstrates density values. Figure 7 shows that the density value reaches 0.7950 g/cm^3 at 20 ps. The molecular movement trend is nearly proportional to the running time under the NPT system synthesis. The system temperature for the energy of the healing model is in dynamic equilibrium during this time period. The healing model maintains the kinetic properties of the initial kinetic energy.

5.3. Microcrack healing stage of the asphalt self-healing model

The model density profile changes slowly compared with the previous one from 20 ps to 115 ps (Figure 7). Molecules move mainly toward the intermediate microcrack space. The density value of the healing model increases from 0.7950 g/cm^3 to 0.9700 g/cm^3 . The duration of this running kinetics is mainly the structural recovery of the self-healing model system. The molecular motion consumes a portion of the kinetic energy in the previous time. The healing model is driven by the molecular motion of the asphalt, the model volume gradually compresses, and the density tends to increase. The length of the model in OX, OY, and OZ directions gradually decreases due to the compression of the model volume. The width of the healing model gradually decreases in the healing process, intermolecular forces gradually increase, the tendency of molecular motion in the healing model is slowed down, and asphalt molecules move steadily until the healing model reaches the stable state.

Figure 9 shows that the potential, kinetic, and nonbonding energies of the model system are in dynamic equilibrium. This finding indicates that the motion of asphalt molecules is stable during this time period.

The molecular motion in the model constantly demonstrates satisfactory kinematic properties driven by the initial kinetic energy. Figure 9 illustrates the density plots of the asphalt healing model in the OZ direction at 20, 40, 60, 80, and 100 ps. Increasing density values at the ends indicates that molecules move towards the ends. Hence, many molecules located at the ends and increased density values of middle microcracks enlarge with reduced width indicate that molecules move toward the middle. As shown in Figure 9, the density value is greater than 0 and the intermediate microcrack is occupied by molecules at 80 ps. The density reaches 0.6000 g/cm^3 at the microcrack location at 100 ps. Thereby indicating that asphalt molecules repair the microcrack. At 20–115 ps, the microcrack space is occupied by asphalt molecules from the initial tendency of molecular movement at 20–115 ps, thus implying that the asphalt self-healing model is undergoing structural recovery at that time.

5.4. Self-diffusion (equilibrium) phase of microcracks in the asphalt self-healing model.

The healing density profile is in dynamic equilibrium from 115 ps to 200 ps (Figure 7). The overall density of the asphalt healing model reaches from 0.9700 to 0.9870 g/cm^3 . At 200 ps, it reaches 0.9870 g/cm^3 , respectively. The system demonstrates an improved molecule distribution at that time mainly for the recovery of properties of the asphalt healing model. The density profile demonstrates decreased fluctuations and stabilizes at a certain density value, and the intermolecular structure and properties of the asphalt system recover to the initial state.

Figure 9 shows the enhanced structural repair at the end with density values at the two end regions of the asphalt healing model dynamically balanced at 0.9600 g/cm^3 values in the 120 ps, 140 ps and 160 ps plots. The density at the middle microcrack fluctuates dynamically at 0.9700 g/cm^3 at 160 ps. The dynamically balanced asphalt density profile indicates the complete structural recovery of the healing model. The asphalt performance based on the recovery of the asphalt microstructure demonstrates that the asphalt performance can be recovered. The asphalt self-healing model has been restored to its initial state at 115–200 ps.

The development of microcracks disrupts the molecular level within the asphalt molecular system and subsequently affects the performance of the asphalt on the macroscopic scale. Density curves of the asphalt healing model and the relative density curves in the OZ direction for each time course illustrate the healing of the matrix asphalt throughout the self-healing process. The healing process of asphalt microcracks is divided into recovery of microcrack width (structural recovery of asphalt molecules) and recovery of initial properties of asphalt molecules. The asphalt is restored to its initial state in the self-healing process from 0 ps to 200 ps. The structure and properties of the damaged asphalt are restored as before.

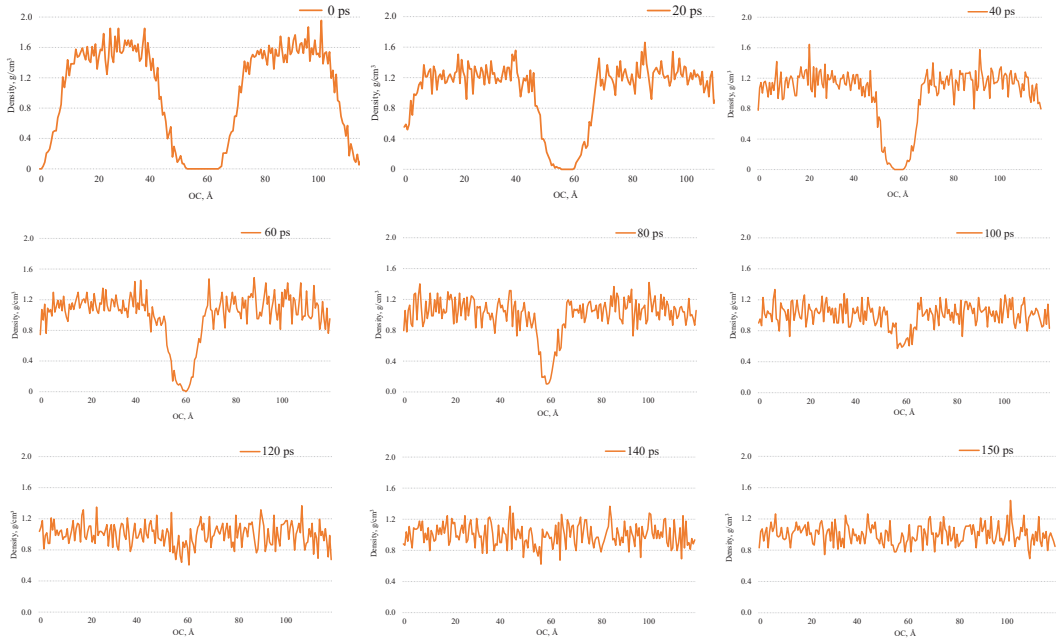


Figure 9. Density of OC (Oz direction) in each position of the healing model

6. Diffusion coefficient

Einstein proposed the theory that the average of the sum of squares of distances travelled by particles at random is proportional to time. The derived formula for the diffusion coefficient is expressed as follows:

$$\langle r^2 \rangle = 6Dt + C, \quad (1)$$

$$MSD_{(\Delta t)} = \langle [r(t - \Delta t) - r(t)]^2 \rangle, \quad (2)$$

$$D = \frac{1}{6t} \frac{dMSD}{d\Delta t}, \quad (3)$$

where $\langle r^2 \rangle$ is the mean displacement; D is the diffusion coefficient, $\times 10^{-8}$ (m²/s); C is a constant; and MSD is the mean square displacement of the model system (Å²) that represents the squared distance between the position of a random particle in the asphalt molecule at moment t and the initial position of the particle.

6.1. Analysis of the self-healing movement of the matrix asphalt at constant temperature

MSD slopes of 12 molecules and 4 components shown in Figure 10 are used to calculate diffusion coefficients from 20 ps to 70 ps. Diffusion coefficients of 4 components and 12 molecules were analyzed at the same temperature to explain their motion properties. The healing behavior of asphalt is explained in terms of diffusion motion. A large diffusion coefficient indicates high motility. A short time required for the asphalt to heal itself indicates its fast healing. Diffusion coefficients of asphaltenes and saturated, aromatic, and polar aromatic fractions are 0.09×10^{-8} m²/s, 0.12×10^{-8} m²/s, 0.10×10^{-8} m²/s and 0.13×10^{-8} m²/s, respectively. The diffusion coefficients of polar aromatic and asphaltene are low. The diffusion coefficients of aromatic and saturated fractions are close. It shows that the movement performance of polar aromatic and asphaltene is poor in the process of asphalt healing. The molecular structure of asphaltene is complex. The molecular weight is large. Besides carbon and hydrogen, there are oxygen, sulfur and nitrogen. The individual energy of the molecule will increase. The required activation energy barrier is high. The asphalt model needs more energy at the beginning of healing. Asphaltene is considered to play a skeleton role in asphalt molecules. The components in asphalt interact with each other and bind each other, limit the movement of asphaltene and polar aromatic. Among the representative molecules of asphaltene, the diffusion coefficient of thiophene is 0.07×10^{-8} m²/s. The diffusion coefficient is lower than the other 11 molecules.

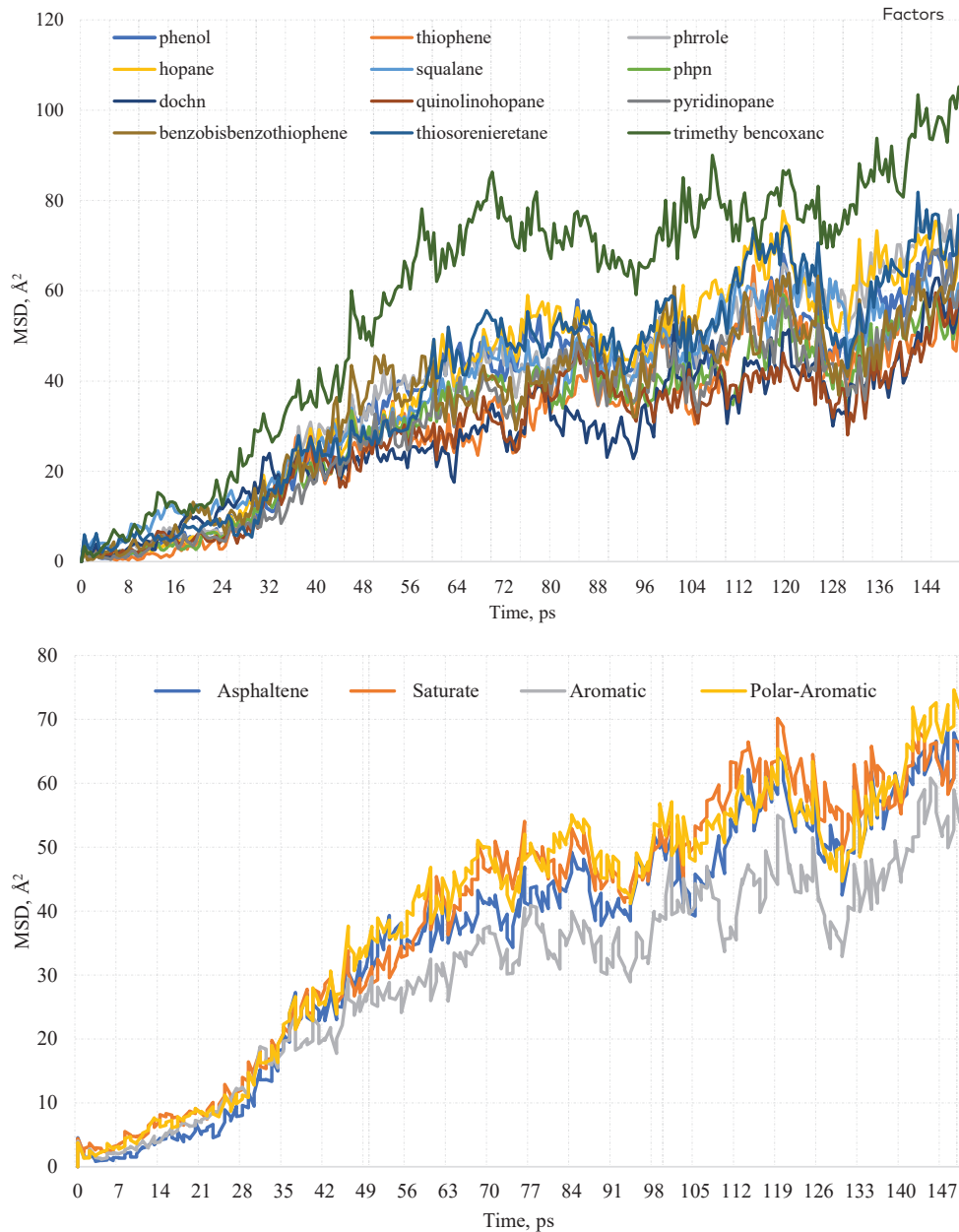


Figure 10. Matrix asphalt of the 80 Å healing model with a 12-molecule 4-component MSD

The saturated fraction and aromatic fraction of asphalt molecules have good mobility. The movement performance of asphaltene and polar aromatic is weaker than other components. The representative molecules of aromatics and saturates are mainly carbon and hydrogen. The representative molecules of asphaltene and rubber contain nitrogen, sulfur, oxygen and other elements attached to their molecular chains, which increase their energy barriers. The energy conversion time is longer than that of the other two components. The molecular chains of saturates and aromatics are long chain structure, which is beneficial to their movement in asphalt molecules. It can shuttle between molecules well and promote the process of asphalt self-healing.

6.2. Analysis of the self-healing movement of the matrix asphalt at different temperatures

The same component kinematic properties change with temperature (Figure 11). The structure of aromatic and saturated components is simple. Aromatic components have non-polar aromatic ring structure, which provides plasticity for asphaltene and polar aromatic components. Saturates are nonpolar chain hydrocarbon molecules with high hydrogen to carbon ratio and strong activity. Asphaltenes have large molecular structure. It has strong bond stretching energy that provides viscosity and colloidal properties for asphalt. The activity of asphaltene is the weakest. Asphaltene is surrounded by polar aromatic so as to endow molecular activity with ductility.

The diffusion coefficient of each component molecule in the matrix asphalt model increases with the increase of temperature. The four-component construction is used as an example to analyze healing properties of asphalt at different temperatures. Diffusion coefficients of all four components of asphalt molecules increase with increasing temperature. Diffusion coefficients increase for the same components at temperature gradients. The healing performance of the asphalt microcrack model improves. The diffusion coefficient of asphaltenes is the minimum, while that of polar aromatic is low at low temperatures. The gradual increase in the diffusion coefficient with increasing temperature indicates that molecular motion properties of polar aromatic are sensitive to temperature changes. With the increase of temperature, the diffusion coefficients of saturated and aromatic molecules increase gradually. It is higher than that of asphaltene and polar aromatic. It shows that the movement performance of saturated and aromatic components in asphalt molecules is easily affected by temperature. The diffusion coefficient of asphaltene does not change obviously with temperature. Asphaltene plays the role of skeleton and

cementation in asphalt system and become the support point of other components.

The representative molecular motion properties of each component in the asphalt healing model are expressed as diffusion coefficients to analyze healing properties of the asphalt model at different temperatures. The correlation between the diffusion coefficient and temperature T can be analyzed using the empirical formula of the Arrhenius model to explain the relationship between chemical reaction rate and temperature as follows:

$$D = A \exp \frac{-E_a}{RT}, \quad (4)$$

where A is the prefactor that reflects the self-healing ability of asphalt at high-temperature conditions or long periods of time (Yang et al., 2010), E_a is the initial energy required for molecular movement during asphalt healing (Tang et al., 2020), and R is the universal gas constant $8.314 \text{ J}/(\text{mol} \cdot \text{K})$. The fitted regression function of the diffusion coefficient versus temperature was analyzed for different temperature conditions of asphalt and modified bitumen (Table 5). The correlation coefficient r^2 of the regression function is higher than 0.9, which indicates the high accuracy of the regression model.

Table 5. Parameters of the Arrhenius Model

Category	$A, 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$	$E_a, \text{ kJ} \cdot \text{mol}^{-1}$	r^2
Matrix asphalt	8.67	31.10	0.9887

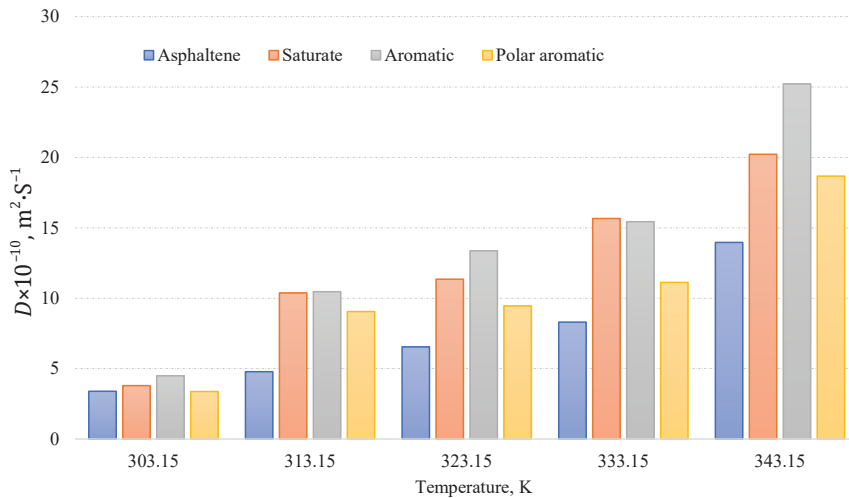


Figure 11. Diffusion coefficient of the matrix asphalt under different temperatures

By fitting calculation: $r^2 = 0.98811 > 0.9000$ and $A = 8.67 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$. It shows that the asphalt self-healing diffusion coefficient has a good linear correlation with the temperature index. The A value is the ability of asphalt molecules to diffuse and recover from the healing movement. This value indicates that only in high temperature conditions or long energy storage time is required (in order) to make the asphalt self-healing movement. The activation energy required for the initial movement of pitch molecules is $31.10 \text{ kJ} \cdot \text{mol}^{-1}$. It is smaller, revealing that the energy required for the initial self-healing movement of asphalt is smaller. Just like the first stage of asphalt self-healing: at high temperatures, the asphalt can quickly have heat. The heat energy is converted into kinetic energy, which promotes the movement of asphalt molecules. The mobility of asphalt molecules is enhanced, and the self-healing performance of asphalt is improved.

The activation energy required for the self-healing movement of the matrix asphalt is high at low temperatures. The required initial movement energy decreases as the temperature increases. However, the gradual increase of parameter A in asphalt self-healing indicates that the asphalt self-healing performance improves with the increase of temperature.

Conclusion

The following conclusions are derived from the present study:

- The length change in the OZ direction of the model space is evident during the self-healing process, while that in the OX and OY directions is the same. The length change in the three directions drives the volume change of the healing model. The movement of molecules drives the process of the asphalt self-healing model. Asphalt molecules first fill the space at the two ends of the healing model in the healing process and then move toward the middle microcrack part. The volume change of molecular entities of the asphalt healing model is small and mainly consisting of free-volume change. The width of microcracks gradually becomes narrow.
- Healing properties in the matrix asphalt are reflected in the diffusion coefficient. The mean square displacement analysis shows that asphaltenes, which are represented by three macromolecules, obtain the minimum diffusion coefficient. Its molecular structure in a large plane acts as the framework for asphalt and supports the system. Diffusion coefficients of saturated and aromatic fractions are moderate. Colloids present

the largest diffusion coefficients due to the highest diffusion coefficient of the trimethylbenzene-oxane molecule among the five representative molecules. Asphalt healing is mainly the diffusion of light components distributed in the microcrack space to carry out the restoration of the asphalt structure.

- At the same temperature, the diffusion coefficients of saturates and aromatics are larger. The diffusion coefficient of asphaltene is small, mainly because asphaltene molecules play a role of skeleton. A variety of representative molecules of saturates and aromatics are the chain structure. The representative molecule of polar aromatic has nitrogen, sulfur and oxygen atoms. The energy barrier required for its motion is higher than that of saturated and aromatic molecules. Saturates and aromatics account for a large proportion of asphalt molecules. The self-healing performance of asphalt molecular system is mainly the movement performance of saturated fraction and aromatic fraction.
- With the increase of temperature, the diffusion coefficient of matrix asphalt healing model increases. The motor ability of the healing model was enhanced. The components and overall diffusion coefficient of the healing model were improved. With the increase of temperature, the energy barrier required for the healing of asphalt molecular system is reduced. The initial activation energy of asphalt is reduced, which can transfer the motion energy to asphalt molecules.

The self-healing process of asphalt is analyzed in this study from the microscopic perspective. The asphalt self-healing model is simulated using MD. The real experimental values may be inaccurate due to the limitation of running time and simulation scale of the software. However, inter and intramolecular interaction mechanisms of asphalt can help explain the asphalt self-healing process.

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Disclosure Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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