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Review

The Progress of the Interfacial Diffusion between Virgin and Aged Asphalt Based on Molecular Dynamics Simulation: A Review

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Abstract: The utilization rate of reclaimed asphalt pavement is significantly low in the sustainable design process of asphalt roads. Numerous researchers have extensively investigated the recycling and utilization of reclaimed asphalt pavements from various perspectives. Molecular dynamics simulations could elucidate the diffusion phenomenon occurring at the molecular scale between virgin and aged asphalt interfaces. This review provides a comprehensive summary of the simulation methods and applications of molecular dynamics simulation in the interface diffusion problem between virgin and aged asphalt. Diffusion theory and model testing methods are discussed. The review proposes the basic steps of molecular dynamics simulation and summarizes the molecular models with the corresponding parameter settings of virgin asphalt and aged asphalt. Moreover, the current influencing factors on the interfacial diffusion problem of virgin and aged asphalt are discussed. The paper explores the validation parameters including density, viscosity, radial distribution function (RDF), glass transition temperature, and solubility parameters based on the existing research. Molecular dynamics simulation could simulate interface diffusion at a micro-scale and clarify the diffusion depth and influence range of different asphalts. The purpose of the study of molecular dynamics is to solve interface issues and advance optimization of reclaimed materials.

Keywords: virgin and aged asphalt interface; molecular dynamics; diffusion theory; model parameters; influencing factors

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1. Introduction

Highway construction plays a crucial role in the process of national economic development, serving as a vital component and symbol of the rapid growth of public transportation [1]. Currently, asphalt pavement utilizes a combination of diverse materials and mineral aggregates to create a cohesive mixture. Specialized equipment is used to form distinct structural layers. Subsequently, appropriate construction machinery is employed to repeatedly roll and enhance the pavement's strength. Nevertheless, asphalt materials are inevitably subjected to aging problems due to the intricate physical conditions such as temperature, humidity, pressure, and ultraviolet radiation. Simultaneously, after enduring prolonged exposure to repeated vehicle loads, the pavement reaches the end of its service life. The original pavement structure becomes inadequate to meet usage requirements, resulting in the development of various pavement diseases. While sustainable road design could effectively solve the problems of reclaimed asphalt pavement generated during maintenance and repair, the utilization rate of reclaimed asphalt pavement remains not ideal [2].

Currently, the road system is in the maintenance and repair stage. One of the core issues of the utilization rate of reclaimed asphalt pavement (RAP) materials is the compatibility of interface diffusion between virgin and aged asphalt [3]. From a macro-scale

perspective, a number of scholars have studied and evaluated RAP materials using the three major indicators of asphalt, performance indicators such as dynamic modulus, and splitting strength [4]. Quantitative analysis of the contact interface and diffusion between virgin and aged asphalt at the micro-scale has become a new trend in research [5]. Many researchers have initiated investigations at the micro-scale, using various scientific techniques including nanometer zinc oxide as a tracer, atomic force microscopy (AFM) [6], gel permeation chromatography (GPC) [7], Fourier transform infrared spectrometry (FTIR) [8], and other analytical tools to assess the degree of contact diffusion between virgin and aged asphalt in reclaimed mixtures [9,10]. Molecular dynamics simulation has become an important tool for exploring new research and effectively simulating the composition of RAP materials at the micro-scale. The molecular behavior of virgin and aged asphalt could be simulated. To make the models more in line with the effective molecule components in reality, asphalt models containing different components could be established. In addition, it is possible to simulate the diffusion of the contact interface, ascertain the diffusion depth of virgin asphalt in the aged asphalt, and clarify the mutual influence range.

It should be pointed out that there are no chemical bond-breaking and binding processes in molecular dynamics simulation for the diffusion of virgin and aged asphalt interfaces. The models only have mechanical contact without any chemical reactions [11]. The structures and interactions between different molecules could be intuitively described from a micro-scale based on molecular dynamics simulation, and the physical properties could be quantitatively analyzed. The current molecular dynamics research covers the adhesion performance of asphalt and aggregates, compatibility of asphalt modifiers, aging and reclaiming behavior, asphalt self-healing ability, basic performance of asphalt, and the diffusion and migration depth of interface components between virgin and aged asphalt. The influence of rejuvenators on the interfacial diffusion characteristics is very important. In practice, the characteristics of the inter-diffusion system formed by rejuvenators and aged asphalt could influence the diffusion effects with virgin asphalt during the reclaiming process. The molecular structure of rejuvenators is a crucial factor in molecular dynamics simulation. The diffusion characteristics of the system would be affected by the sizes of rejuvenator molecules [12,13]. Finally, the content and temperature directly affect the diffusivity of the inter-diffusion system [14]. It could be seen that molecular dynamics provides a means for studying multi-phase composite materials. The internal composition, strength formation, performance variation, and structural molecular behavior characteristics were explored.

Current research primarily concentrates on the molecular level of the asphalt–aggregate interface and the modifiers. However, there has been a lack of discussion regarding the diffusion interface between virgin and aged asphalt using molecular dynamics models and associated testing methods.

The review route of the paper is shown in Figure 1. This paper mainly focuses on the molecular dynamics simulation and system of the virgin and aged asphalt mixed diffusion system based on the current research situations. Firstly, this paper integrates the interface diffusion theory of mixed virgin and aged asphalt, highlighting the strengths and limitations of the current theory. Secondly, a summary of the asphalt molecular structures and the applicability, advantages, and disadvantages of testing methods is provided. In addition, the paper provides an overview of the main virgin and aged asphalt models used in simulation and the practical applications of various models in interface contact processes. Firstly, for other researchers, this paper could provide theoretical evidence and validation parameters. Secondly, it could help to solve the problem of low utilization during the use process from the perspective of the interface of aged asphalt. Finally, it could provide future work recommendations to analyze and explore diffusion issues from multiple perspectives. The influence factors of the diffusion interface between virgin and aged asphalt are analyzed, and the current problems are considered. The molecular model and parameters could be considered to weigh the advantages for reference. This paper

aims to summarize the characteristics of asphalt diffusion behavior and the research routes are considered to clarify diffusion issues.

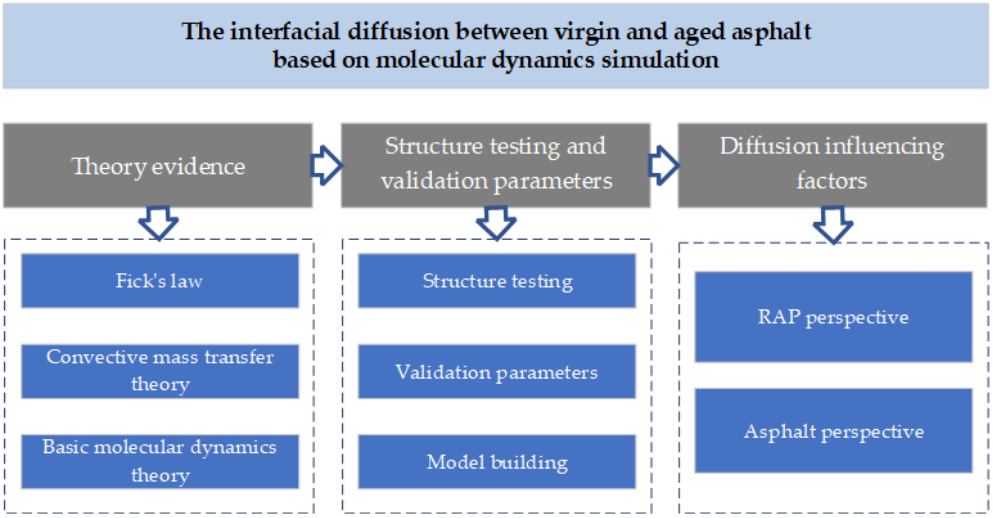

Figure 1. Review of main routes.

2. Theory Evidence

2.1. Asphalt Diffusion Theory

2.1.1. Fick's Law and Composite Theory

Fluids of different concentrations diffuse from the high concentration phase to the low concentration phase during interface contact and remain in equilibrium. Based on Fick's first law, t was introduced to describe the relationship between the concentration of a fluid at a certain point and time. Fick's second law [15] is shown in Equation (1):

$$\frac{\partial C(x)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \quad (1)$$

where C is the concentration of virgin asphalt, t is the diffusion time, D is the diffusivity, and x is the position of virgin asphalt in the aged asphalt.

The rate of concentration change was positively correlated with the concentration gradient second-order differential and diffusivity. The D was used to describe the difficulty of diffusion, which was related to environmental temperature, viscosity, and asphalt molecular size. In addition, for solving this partial differential Equation (1), it was necessary to define the boundary conditions of the diffusion system. With the initial conditions unchanged, the concentration of virgin asphalt was 1 in the upper half (x from L to 2L) and 0 in the lower half (x from 0 to L), and the system would not completely diffuse (x from 0 to 2L), as shown in Figure 2.

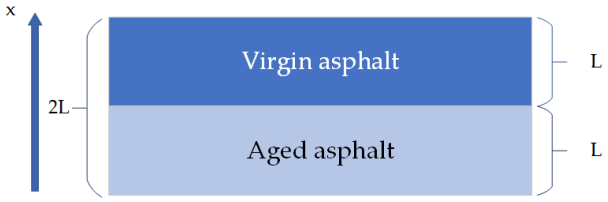

Figure 2. The boundary conditions of the diffusion system. (L was the boundary size of each part).

He Y. [16] established a mathematical model based on Fick's second law to study the rheological properties of rejuvenators. Karlsson R. [17] proposed a one-dimensional simplified model. The model assumed that the layer of virgin asphalt (rejuvenators) tends to diffuse towards the aged asphalt. Therefore, the virgin and aged asphalt diffusion

systems would form composite structural layers with different concentration gradients in the production and transportation process of reclaimed asphalt. The situation was satisfied with the composite theory and had a composite effect [4,18]. Related research proposed a viscosity equation for two-phase mixing, Since the complex shear modulus of asphalt is affected by the amount and viscosity of reclaimed asphalt, the viscosity equation was transformed to characterize the complex modulus of asphalt after mixing, as shown in Equations (2) and (3) [19,20]:

$$\eta_{mix} = \frac{\eta_A^a \eta_B}{\eta_B^a} \tag{2}$$

$$G_{mix} = \frac{G_A^a G_B}{G_B^a} \tag{3}$$

where η is the viscosity, G is the complex shear modulus, A and B are two types of mixtures, and a is the initial concentration of A and B.

Fick's law provided a theoretical basis for the diffusion problem of virgin and aged asphalt during the equilibrium process. However, the actual diffusion flux was not only related to a unique diffusivity but also to the probability function of the diffusivity [21]. In addition, the membranes on the surface of aged asphalt would hinder the diffusion of virgin asphalt, and aged asphalt could not be diffused completely in the actual process. And the diffusion of rejuvenators was also significantly different from the actual situation.

2.1.2. Convective Mass Transfer Theory

The meaning of convective mass transfer is the mass transferred between a fluid and a solid contact surface or two kinds of immiscible fluids during motion. There was a significant difference in mass concentration gradient for the diffusion process between virgin and aged asphalt. So, it was consistent with the convective mass transfer theory to some extent [22]. The mass transfer flux was related to the difference between the convective mass transfer coefficient and concentration, as shown in Equation (4):

$$N_A = k_c \cdot \Delta C_A \tag{4}$$

where N_A is the mass flux of convective mass transfer, k_c is the coefficient of convective mass transfer, and ΔC_A is the difference in the concentration of component A between two moving fluids.

The convective mass transfer coefficient k_c depended on the physical properties of the fluid, the geometric shape of the mass transfer contact interface, the flow state, and the cause of flow generation. So, the diffusion degree of virgin and aged asphalt (rejuvenators) was mainly influenced by three factors [22]: the kinematic viscosity of virgin asphalt (rejuvenators), the diffusion ability of virgin asphalt (rejuvenators), and the degree of mixing of the mixture. Yang Y. [23] mixed aged asphalt containing mineral powder with virgin asphalt and evaluated the reclaimed efficiency by detecting the content of transferred mineral powder. Tao X. [24] demonstrated the transfer mechanism of aged asphalt between virgin and aged aggregates based on convective mass transfer theory. The flow state of fluids could be divided into laminar and turbulent flow. Fluids typically would reach a turbulent state when at high speeds or obstructed. Asphalt was greatly affected by viscosity, so the laminar flow characteristics would be more in line with the situation. A stable laminar flow state could provide a relatively stable mass transfer process. However, due to the influence of factors such as viscosity, temperature, and flow conditions, there were challenges to simulate convective mass transfer processes. As a complex mixture, the convective state of asphalt could only be determined in one aspect using the Reynolds number, and just the two boundary conditions were represented in reality. The core issue of convective mass transfer was to determine the coefficient of convective mass transfer. Some typically simplified models proposed by researchers (such as the film model and penetration model) were still insufficient in representing the diffusion state of asphalt [25].

2.2. Basic Theory of Molecular Dynamics

Molecular dynamics simulation is not limited by detection techniques and could effectively supplement the shortcomings of macroscopic experiments. From a micro-scale perspective, the micro-scale behavior of macroscopic experiments was explored. Molecular dynamics simulation is mainly based on classical Newtonian mechanics. The details of the motion of micro-scale molecules were obtained by solving the differential equation of Newton's second law [26], as shown in Equation (5):

$$a_i = \frac{d^2 r_i}{dt^2} = \frac{F_i + f_i}{m_i} \tag{5}$$

where m_i is the mass of the i-th atom, r_i is the position vector of the i-th atom, F_i is the force exerted, and f_i is a known function of the positions and velocities of all atoms.

The finite difference method could be used to solve this equation. Many calculation methods have been proposed, such as the Verlet algorithm, velocity Verlet algorithm, leap-frog algorithm, Beeman algorithm, etc. Appropriate algorithms should be selected to improve the efficiency of simulation calculations while meeting the simulation accuracy. Among them, the leap-frog algorithm and velocity Verlet algorithm were widely used [27]. The leap-frog algorithm was modified and optimized based on the Verlet algorithm and is commonly used to determine the optimal molecular configuration and other issues.

The five types of ensemble molecular dynamics simulations include canonical ensemble (NVT ensemble), microcanonical ensemble (NVE ensemble), isothermal–isobaric ensemble (NPT ensemble), isentropic–isobaric ensemble (NPH ensemble), and generalized ensemble. In the isothermal–isobaric ensemble, the number of moles (N), pressure (P), and temperature (T conservation) should be close to laboratory conditions and measured well in the asphalt interface model [19]. Geometric optimization or energy minimization methods could be used to reach equilibrium in different simulation systems. Molecular dynamics visualization software mainly consists of the Material Studio series (2023 v7.0), J-OCTA (v9.1) cross-scale simulation software, and open access software package LAMMPS (v1.2).

The basic steps of molecular dynamics simulation for asphalt diffusion systems are shown in Figure 3. The main steps are model construction, parameter setting, validation, and result analysis. In the asphalt mixed system, the first step is to select a suitable asphalt model, which will be explained later. In the mixed system of asphalt, the interaction forces between various molecules determine the total energy of the entire molecules. Therefore, after selecting the main representative asphalt components, it would be necessary to use appropriate force fields to effectively simulate different molecular forces while ensuring simulation speed. The main force fields applied in asphalt mixture systems include optimized potentials for liquid simulations (OPLS), general AMBER force field (GAFF), consistent valence force field (CVFF), COMPASS, etc. Condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) could effectively simulate and predict the structure, vibration, and thermodynamic properties of various single molecules and condensed states. COMPASSII was further optimized to launch the force field based on Material Studio 7.0. And this force field was the most widely used in asphalt mixed systems. The initial model was obtained by using geometric optimization or energy minimization after selecting the force field. Model parameters were adjusted and validated for accuracy. Finally, the corresponding modules were used to analyze the rheological properties, thermodynamic properties, physical properties, and reaction characteristics.

In addition, modules such as Visualizer, Amorphous Cell, Mesocite, and Forcite are common computational analysis modules. And some studies have also involved Perl scripts in Material Studio software for processing data. Among them, Amorphous Cell with the Monte Carlo method to build material models was widely applied in asphalt, aggregate, modifier, and diffusion problems. The basic attributes and application scenarios of the main modules are shown in Table 1.

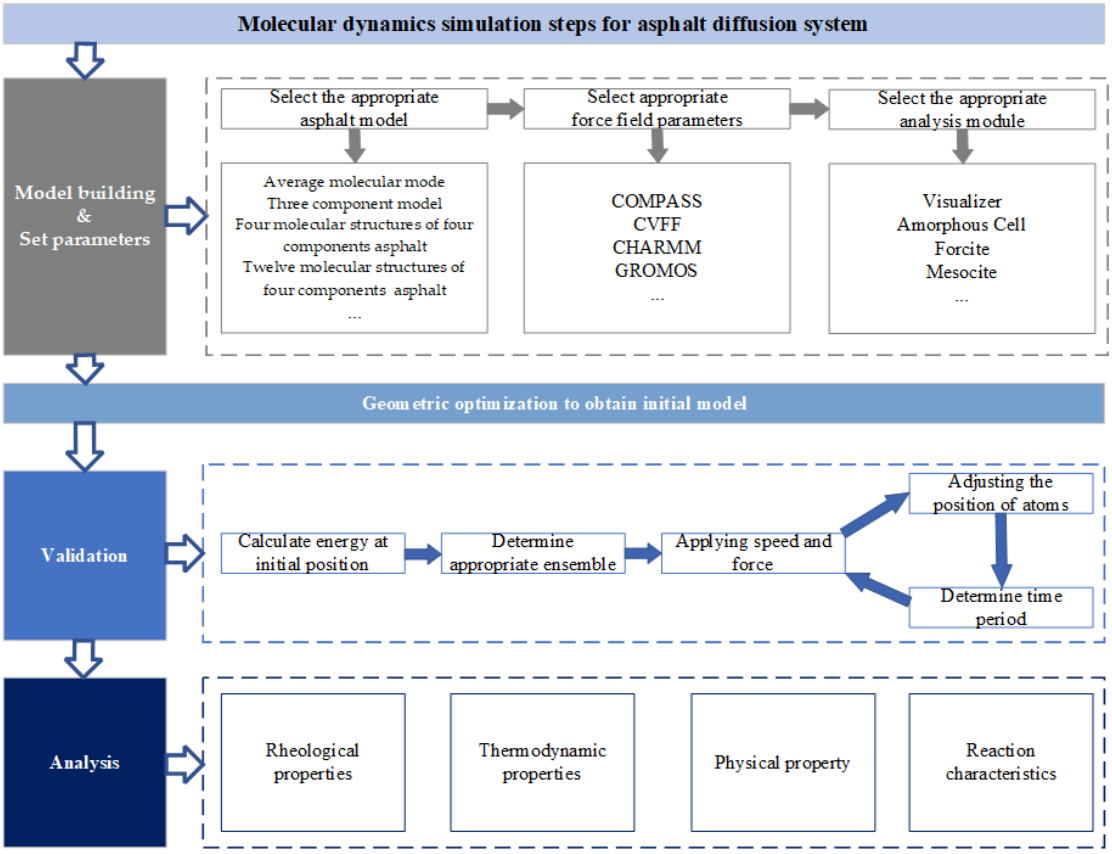

Figure 3. Basic steps for molecular dynamics simulation of asphalt diffusion systems.

Table 1. Main molecular dynamics modules.

Main Modules	Characteristics	Application
Visualizer	Graphical interface, a part of model building	It mainly builds and adjusts visualized 3D model
Amorphous Cell	Build an amorphous cell model by Monte Carlo method	It mainly constructs polymer blend systems with different components, ratios, solutions, and interface models
Forcite	Fast energy calculation of systems, geometric optimization and energy minimization, analyze different ensembles	It was applied in organic materials, inorganic small molecules, high-polymer materials, commonly used in asphaltene and modifiers
Mesocite	Two methods: coarse-grained and dissipative particle molecular dynamics, simulating at the mesoscopic level	It was applied in polymer dilution and dissolution, surface adsorption, surface activity, and composite materials

3. Structure Testing and Validation Parameters

It is crucial to choose the appropriate asphalt molecule to establish a molecular dynamics model. A large number of scholars used the average molecular formula of asphalt to construct a basic molecular model according to the actual mass ratio, and the model was adjusted to meet the actual test results. Due to the difficulty of identifying and quantifying molecular structure, there is still great controversy regarding asphaltenes [28,29]. Therefore, the assembly method is used to model the molecular structure of asphalt.

3.1. Main Methods for Determining Molecular Structure

3.1.1. Alumina Chromatographic Column Method

This method divides asphalt into four components and uses n-heptane to precipitate asphaltene. The de-asphaltene fraction is separated into four components using an alumina chromatographic column.

The alumina chromatographic column method could separate asphalt effectively, determine the content of each component, and meet the needs of molecular dynamics simulation. The chromatographic column surface could interact with polar functional groups due to the hydrophilicity to achieve the separation of asphalt components. The main process of separating asphalt is shown in Figure 4.

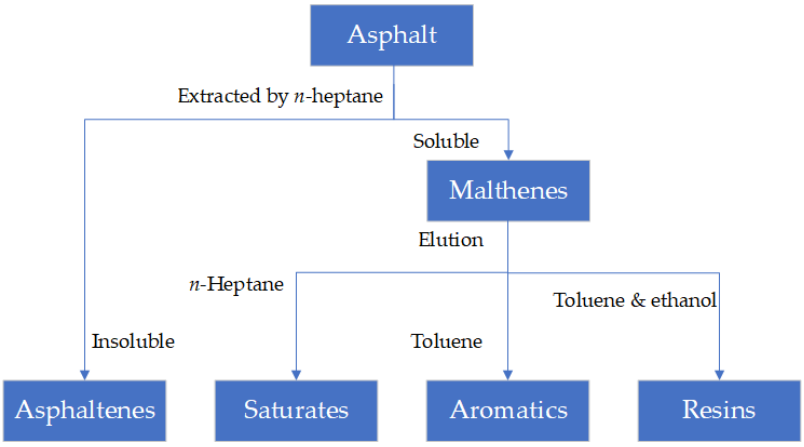

Figure 4. The main process of separating asphalt [30].

3.1.2. Thin-Layer Chromatography with Flame Ionization Detection (TCL-FID)

Thin-layer chromatography with flame ionization detection is a new method developed based on the thin-layer chromatography column method. A thin quartz rod instead of a silica gel plate is used for thin-layer chromatography. The surface is coated with adsorbents such as alumina and silica. The sample should be unfolded and separated on the chromatographic rod. Afterwards, the chromatographic rod passes through the hydrogen flame and the device detects the ion current generated by the hydrogen flame. Finally, the molecular content can be determined by measuring the current intensity. Note that selections of expansion solution and solution mixing ratio could have a significant impact on the test results. Because of the differences in polarity of different components, the expansion solution could cause significant changes in the content of some components [31–33]. Therefore, an expansion solution with moderate polarity should be selected for testing.

Compared with the alumina chromatographic column method, this method could be fast and efficient, with less pollution, fewer reagents used, and high sensitivity. However, there is no unified standard for large-scale promotion currently, and the application analysis in practical engineering would be also difficult. The comparison between the two methods is shown in Table 2.

Table 2. Comparison of two testing methods.

Test Method	Principles	Result Source	Features
Alumina chromatographic column method [32]	The chromatographic column serves as a stationary phase, achieving separation based on the adsorption capacity of different polar components	The ratio of the actual mass of each component to the total mass of the test sample	• Wide application and accurate measurement • Slow detection, complex process, and artificial factors

Table 2. *Cont.*

Test Method	Principles	Result Source	Features
TCL-FID [34]	Extended separation of different solvents combined with hydrogen flame ionization detection	The ratio of peak area to the total peak area of each component in the graph	• Easy operation, fast detection, reliability, and low pollution • Rarely available standards, difficulty in actual analysis

3.2. Establishment and Validation of a Virgin and Aged Asphalt Interface Model

It would be particularly important to choose the appropriate molecular structure of asphalt when studying the interface between virgin and aged asphalt. The selection criteria are mainly based on the following points:

- Representative molecular mixed phases could approach the characteristics of real mixed phases;
- Each component of virgin and aged asphalt should comply with structural validation tests;
- The simulation calculation accuracy of assembly models should be improved.

3.2.1. Molecular Structure of Virgin Asphalt

In 1993, Jennings P.W. [35] proposed eight main average molecular structures of asphalt by nuclear magnetic resonance methods on the basis of the SHRP program (SHRP-A-335) and conducted further research and demonstration [36]; structures are shown in Figure 5. The molecular structure could characterize the overall chemical properties within a certain range and be beneficial for integrating with real asphalt on a physical level. But the position distribution of macromolecules and the interaction forces between asphalt molecules were not considered. In addition, there would be a lack of diversity in the chemical polarity of the internal structure. The model differed greatly from the complexity of real asphalt models. Therefore, the structure cannot be used for molecular dynamics research yet.

After a period of research, a large number of scholars proposed many molecular structure models based on previous models, such as the Storm model [37], Murgich model [38,39], Artok model [40], Groenzin model [41], Takanohashi model [42], and Mullins model optimized from the early Yen model [43,44]. In 2007, in order to approach the true structure of asphalt molecules more closely for dynamic simulation, Zhang L.Q. and M.L. Greenfield [45] selected two recommended asphaltene structures based on previous research, as shown in Figure 6. The three-component asphalt model consisting of asphaltene, saturated asphalt, and naphthenic aromatic molecules was constructed. The mass ratio was approximately 20:60:20 and the molecular number was approximately 5, 30, 45 for each group. Afterwards, molecular dynamics simulations were conducted using the OPLS-AA force field. Additionally, the density and thermodynamic properties were analyzed and predicted. This model could achieve molecular dynamics simulation for specific structural analysis and prediction [46]. But the model lacked polar components in the three-component system, so there would be significant differences in simulated viscosity and density compared to actual asphalt systems. In addition, the selected asphalt molecules come from different sources. The difference would make the molecular simulation lack validation reliability. In subsequent research, the four-component SARA of asphalt was used as a major classification, proposing four molecular structures of four-component asphalt [47] and six molecular structures of four-component asphalt [48]. The most widely used twelve molecular structures of four-components asphalt are from the Derek model [49,50]. Although increasing the computational complexity of simulation research, the four-component structure could better characterize the molecular structure of asphalt and be more in line with real asphalt systems than the three-component system.

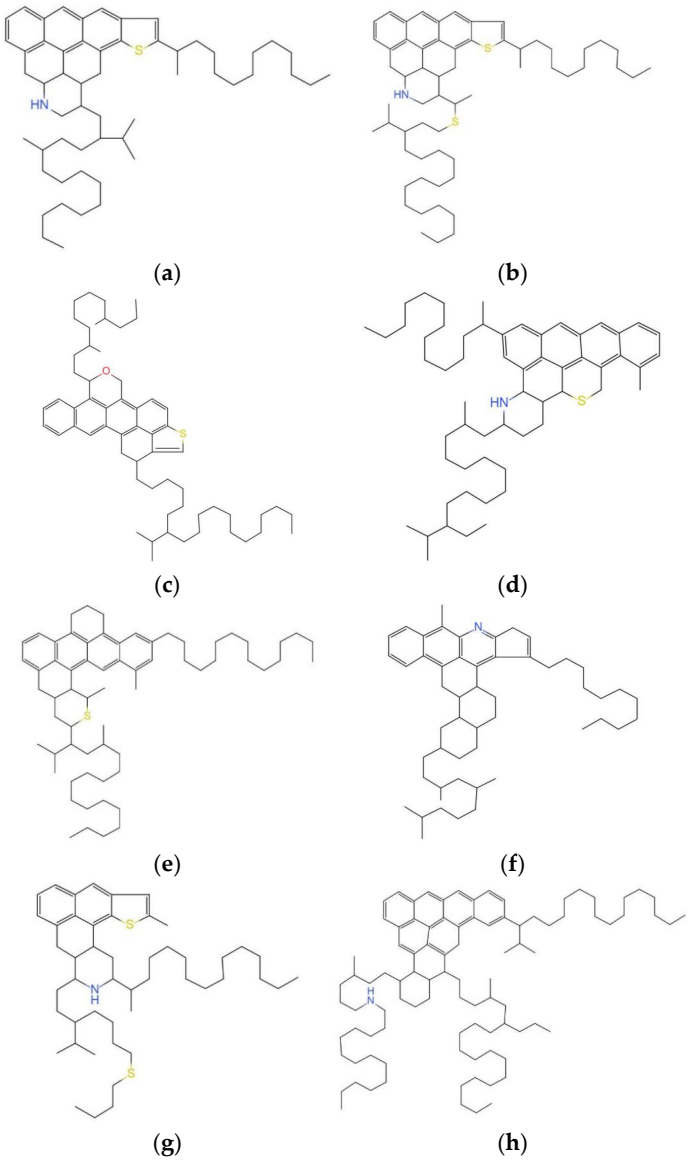

Figure 5. Main structures of asphalt average molecular model: (**a**) AAA-1; (**b**) AAAK-1; (**c**) AAAF-1; (**d**) AAB-1; (**e**) AAC-1; (**f**) AAG-1; (**g**) AAD-1; (**h**) AAM-1.

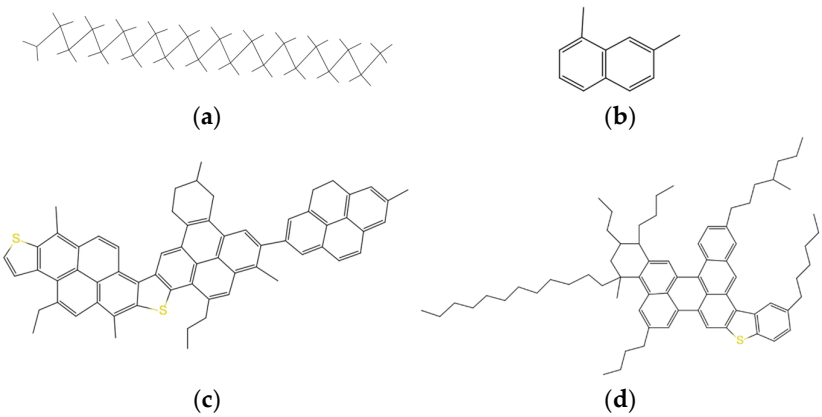

Figure 6. Three-component model molecular structure: (**a**) Saturate; (**b**) Resin; (**c**) Asphaltene I; (**d**) Asphaltene II.

The molecular structure model of asphalt not only should consider the presence and content of different molecules but also the natural geometric shape of the molecules. Unreasonable and unnatural geometric shapes would have a negative impact on the simulation effect. Li D. [49,51] used quantum density functional theory and classical force field calculations to demonstrate that the previously proposed model was feasible. But there would be still asphaltene structures in high-energy unstable states. The team analyzed and proposed the molecular structure of AAA-1 grade asphalt in the SHRP program, as shown in Figure 7. And the molecular formulas and molecular weights are shown in Table 3. Although the model had a higher molecular weight, the simulated density was closer to that of real asphalt.

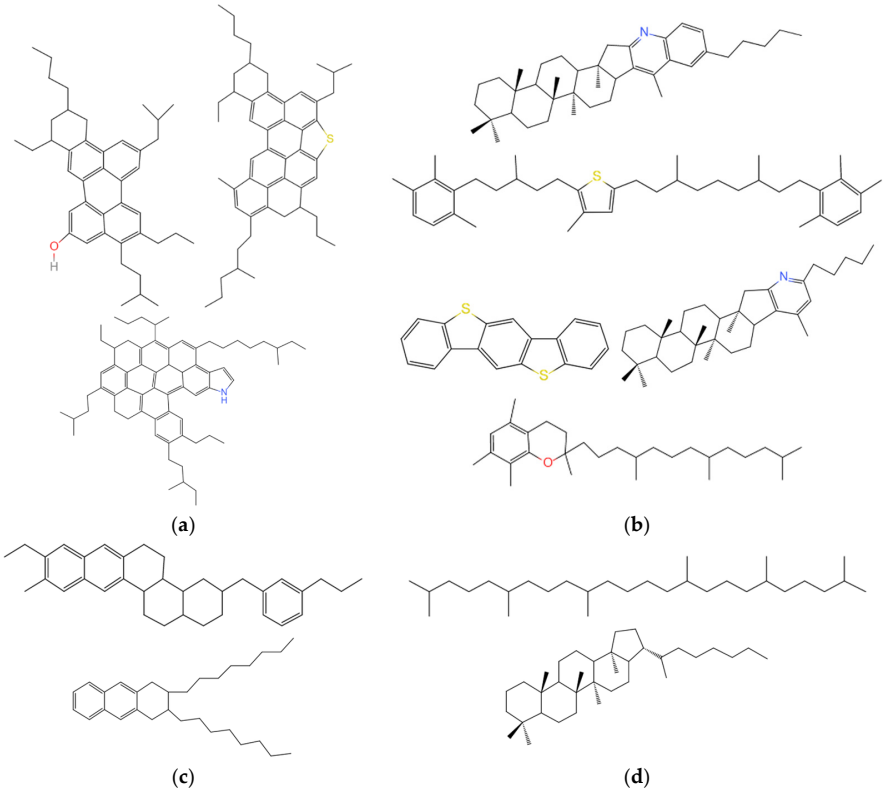

Figure 7. Twelve molecular structures of four-component asphalt: (**a**) Asphaltenes; (**b**) Polar Aromatics; (**c**) Naphthene Aromatics; (**d**) Saturates.

Table 3. Various molecular formulas and related information [49].

Molecular Component	Molecular Formula	Atomicity	Molecular Weight
Asphaltene	$C_{42}H_{54}O$	97	575.0
	$C_{66}H_{81}N$	148	888.5
	$C_{54}H_{62}S$	114	707.2
Polar Aromatics	$C_{40}H_{59}N$	100	554.0
	$C_{40}H_{60}S$	101	573.1
	$C_{18}H_{10}S_2$	30	290.4
	$C_{36}H_{57}N$	94	573.9
	$C_{29}H_{50}O$	80	414.8
Naphthene Aromatics	$C_{35}H_{44}$	79	464.8
	$C_{30}H_{46}$	76	406.8
Saturates	$C_{30}H_{62}$	92	422.9
	$C_{35}H_{62}$	97	483.0

3.2.2. Molecular Structure of Aged Asphalt

During the diffusion process of virgin and aged asphalt, the aged asphalt should play an important role in being activated. The rejuvenator would activate the aged asphalt to achieve efficient diffusion. The aging process of asphalt is still in a black box state, and the aging mechanism is believed to be mainly oxidation aging. Tarefder R. [52] attempted to use molecular dynamics to simulate and compare the internal chemical and thermodynamic properties of asphalt after oxidative aging. The team compared and analyzed the performance changes after using different levels of oxygen atoms. However, the range of added oxygen atoms was relatively small. The overall molecular structure of asphalt could not be better characterized and reflect the oxidation process. Studies have shown that certain types of carbon and sulfides in asphalt are highly susceptible to oxidation [52,53]. The asphalt comes into contact with oxygen, so the atoms in the active functional group would be replaced by oxygen atoms, as shown in Figure 8. The formation of carbonyl compounds in the structure altered the physical and chemical properties of molecules [54,55].

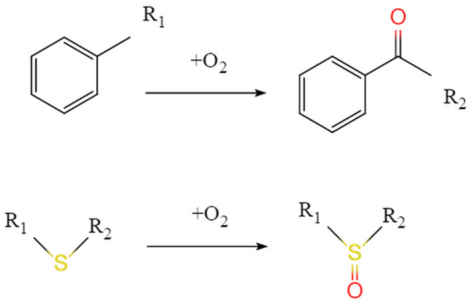

Figure 8. Carbonyl compounds: ketone group, sulfoxide group.

As highly sensitive functional groups in the molecular structure, benzyl carbon and sulfide would be replaced by oxygen atoms to form new oxides. Relevant studies pointed out that ketones and sulfoxides should be identified in the main functional groups of asphalt molecules after oxidation [56]. The molecular structure model of aged asphalt is represented by introducing ketone and sulfoxide groups into SARA classifications. The main molecular structure of aged asphalt is shown in Figure 9. The relative content of functional groups could be obtained by quantitatively analyzing the index of carbonyl (ICO) and the index of sulfoxide (ISO) of molecules with different aging degrees by Fourier transform infrared spectroscopy (FTIR) [48,57], as shown in Equations (6) and (7):

$$\mathrm{ICO} = \frac{\mathrm{A}(1700)}{\mathrm{A}(1460) + \mathrm{A}(1375)} \tag{6}$$

$$\mathrm{ISO} = \frac{\mathrm{A}(1030)}{\mathrm{A}(1460) + \mathrm{A}(1375)} \tag{7}$$

where A() is the absorption peak area near the corresponding wavelength of the functional group measured in infrared spectroscopy.

The results indicated that the content of functional groups varies in different degrees of aged asphalt, and ICO of RTFOT was close to zero. ICO of long-term aging would increase with aging time. Moreover, the saturated fraction had fewer sensory energy groups and was less prone to oxidation.

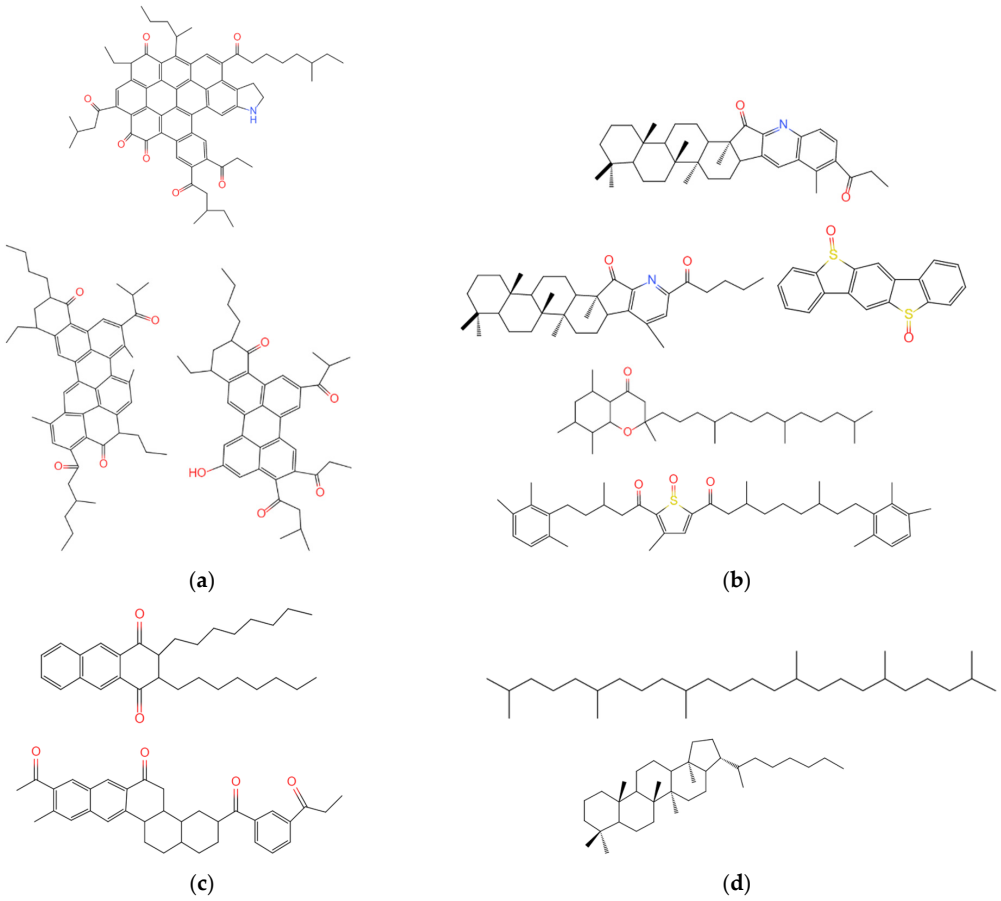

Figure 9. Main molecular structure of aged asphalt: (**a**) Aged asphaltene; (**b**) Aged polar aromatics; (**c**) Aged naphthene aromatic; (**d**) Aged saturate.

In addition to changing the corresponding molecular structure, it would also be necessary to adjust the molecular number of each component in the structure. It should be pointed out that as the aging degree of asphalt gradually increases, the lightweight components would transform into heavy components, and the content of asphaltene and resin would also gradually increase. When reconfiguring the molecular numbers of each component, simulation should be close to test results [58]. It should also be noted that in the virgin and aged asphalt interface system, the size of different asphalt models would affect the output results of the final calculation model. And the total atomic size between the two models should not differ too much to avoid size effects causing distortion of the results.

The aging of asphalt is not a single oxidative aging. There is currently a lack of research on other aging methods based on molecular dynamics. Hu C. [59] proposed a periodic soaking aging method for asphalt by preparing nitric acid rain, mixed acid rain, and sulfuric acid rain. FTIR was used to quantitatively analyze the functional group changes in asphalt, and molecular dynamics models were used to discuss the effect of acid rain on asphalt aging. Cui Y. [60] selected asphalt molecular combinations with different aging methods and used molecular dynamics to simulate the diffusion system between rejuvenator and aged asphalt. The results indicated that the diffusion degree of the rejuvenator would decrease with simulation time, and the diffusivity of composite ultraviolet-aged asphalt would be lower than that of composite water-aged asphalt. The team pointed out that materials with saturated and aromatic components could be added during the preparation process of rejuvenators to enhance the effectiveness.

In the issue of diffusion at the interface between virgin and aged asphalt, a suitable asphalt system could efficiently simulate the system and diffusion process. However, the molecular types in the structural models used in current research are still less than those

in real asphalt. And there should be significant differences in the molecular structure of asphalt from different sources. In the aged asphalt model, a large number of studies only considered the oxidation aging process and simulated aged asphalt through functional group substitution and molecular content changes. But the actual aging process is not singular, and different aging methods may lead to other reactions. Linking with actual asphalt systems remains a challenge whether in terms of the molecular structure of virgin asphalt or aged asphalt. In the simulation system of virgin and aged asphalt, it would be necessary to construct asphalt molecular structure systems from different sources and study the aging mechanism in the molecular structure of virgin and aged asphalt.

3.3. Molecular Structure Validation Methods

Molecular dynamics models are some of the components of studying interface diffusion problems. It is very important to validate the accuracy of the established asphalt molecular model, ensuring that the material composition, elemental composition, component content, spatial location, and functional group chemical properties of the model are within the real range. There are many indicator parameters for validating molecular simulations. The current main validation parameters are density, viscosity, radial distribution function, glass transition temperature, and solubility parameters based on the characteristics of the model.

3.3.1. Density

Density is the most commonly used and intuitive validation parameter for researchers, which can be directly obtained in molecular dynamics simulations [61]. The physical properties and chemical components of the SARA are not the same. The density of the saturated component is about 0.9 g/cm^3, that of the aromatic component is about 1.0 g/cm^3, that of the resin is about 1.07 g/cm^3, and that of the asphaltene is about 1.15 g/cm^3. And as a chemical continuous system, the density of asphalt is still studied based on the statistical average of each component [62].

The difference in tests and simulations between the twelve Derek molecular structure models at different temperatures was about 0.06 g/cm^3, and the results were closer to the actual value than the early asphalt model [49]. Liu F. [63] used the Forcite module for geometric optimization and selected the NVT ensemble for simulation, obtaining a density of 0.970 g/cm^3 for aged asphalt. The results were close to those of the real matrix asphalt. Gao F. [19] conducted molecular dynamics simulations on virgin and aged asphalt, and the density of the mixed system was approximately 1.00033 g/cm^3. The results were close to the density of asphalt. Zheng C. [64] pointed out that individual asphaltene and resin molecules may form inseparable aggregates, which could be considered as individual molecules and affect the various physical constants of actual asphalt testing. The simulated density would inevitably differ from the actual asphalt density. The main reason is that the actual asphalt contains some impurities, and the simulated asphalt model still cannot represent the molecular structure of the actual asphalt.

In addition, the density is also related to the computability of the equipment. And the component mixed model would be limited by the computing equipment, making it difficult to simulate the continuity of asphalt. Through software iteration, GPU acceleration could be used to improve the calculation accuracy and expand the structural model.

3.3.2. Viscosity

Viscosity reflects the macro-scale molecular weight of asphalt structures and is also the main road performance evaluation index of asphalt mixtures. There are many methods for calculating viscosity in molecular dynamics simulations. The Stokes–Einstein (SE) method used in early studies is only applicable to low temperatures. The calculation methods used mainly include the Williams–Landel–Ferry equation based on glass transition temperature, the Rouse model based on diffusivity, and the rend method suitable for high-viscosity fluids, as shown in Equations (8)–(11).

SE method [50,65,66]:

$$\eta = \frac{k_B T}{6\pi D R} \tag{8}$$

where k_B is the Boltzmann number, T is the temperature, D is the diffusivity, and R is the molecular radius.

WLF equation [67]:

$$\log \alpha_T = \log \frac{\eta_T}{\eta_r} = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \tag{9}$$

where α_T is the displacement coefficient, η_T and η_r are the viscosity at T and T_r, T_r is the reference temperature, C_1 and C_2 are empirical parameters.

Rouse model [68]:

$$\eta = \frac{\rho R T R_g^2}{6MD} \tag{10}$$

where ρ is the system density, M is the molecular weight, R_g^2 is the mean square radius of gyration, R is the general gas number, and D is the diffusivity.

Reverse non-equilibrium molecular dynamics (rNEMD) [69]:

$$j_z(p_x) = \frac{-\eta \partial v_x}{\partial z} = \frac{P_x}{2tA} \tag{11}$$

where $j_z(p_x)$ is the Z-direction momentum flux, $\frac{\partial v_x}{\partial z}$ is the shear rate, P_x is the momentum, t is the simulation time. $A = \mathrm{L}_x \times \mathrm{L}_y$, where L_x is the X-direction length of the simulated box and L_y is the Y-direction length of the simulated box.

3.3.3. Radial Distribution Function (RDF)

The radial distribution function generally refers to the probability of other particles being distributed in a system compared to a certain particle when the coordinates of a particle are determined. The RDF could analyze the interaction force between each molecule and could be used to characterize the degree of disorder of the entire system. The parameters are directly exported from the simulation results [70], as shown in Equation (12):

$$g(r) = \frac{d_N}{\rho 4\pi r^2 dr} \tag{12}$$

where N is the number of particles, ρ is the system density, and r is the distance from the central particle.

When r decreases, the value of the equation would increase, leading to a maximum. Molecules would aggregate at this position and exhibit an ordered state at close range. The molecular interactions are usually divided into hydrogen bonds (r = 2.6~3.1 Å) and van der Waals forces (r = 3.1~5.0 Å). It is believed that van der Waals forces should be the main intermolecular forces [71]. Yang J. [72] validated that the van der Waals force of the established model is within the range and pointed out that the radial distribution function of the asphalt molecular model tended to flatten and approach 1 after reaching 5 Å. The radial distribution function of atoms in the asphalt model is shown in Figure 10.

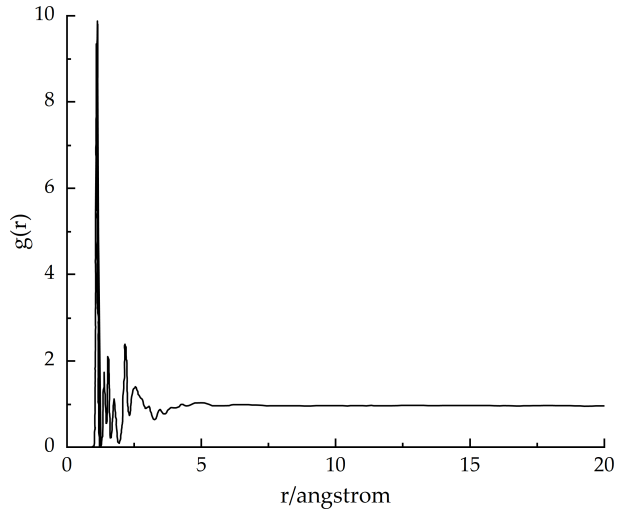

Figure 10. The radial distribution function of atoms in the asphalt model [72].

3.3.4. Glass Transition Temperature

The glass transition temperature is the transition temperature of a material from a high elastic state to a glass state and is a necessary characteristic of amorphous polymers. The free volume theory is used to explain the glass transition behavior of asphalt. The definition of the glass phenomenon area is shown in Figure 11 [73]. Qiu Y. [74] validated the reliability of the glass transition temperature of the asphalt molecular model by differential scanning calorimetry (DSC). Tabatabaee [75] transformed the physical change model into an isothermal time model and confirmed that the glass transition temperature of asphalt is between 30 and 50 °C. Tang W. [76] carried out tests on virgin asphalt and modified asphalt. The results showed that the glass transition temperatures were 227.85 K and 268.28 K, respectively.

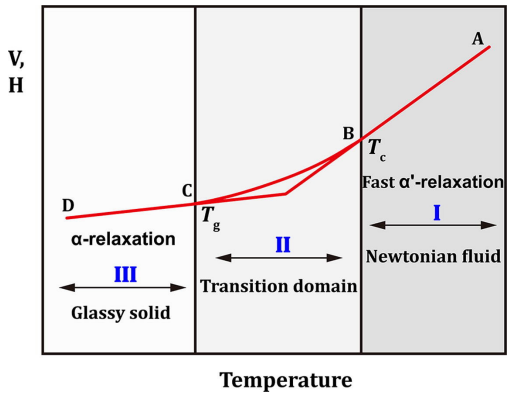

Figure 11. Definition of glass phenomenon area [73].

3.3.5. Solubility Parameter

The solubility parameter is another important molecular force validation parameter in asphalt systems. The compatibility of components is reflected within the structure. The Hansen solubility parameter [77] is shown in Equation (13):

$$\delta = \sqrt{CED} = \sqrt{\frac{E_{coh}}{V}} = \sqrt{\delta_{vdw}^2 + \delta_{ele}^2} \quad (13)$$

where CED is the cohesive energy density of a material and refers to the energy used to eliminate intermolecular forces per unit volume of the system. E_{coh} refers to the cohesive

energy, V represents the structural volume, δ_{vdw} and δ_{ele} represent the contribution of van der Waals forces and classical interactions, respectively.

Zhu J. [78,79] used molecular dynamics to validate the solubility parameters of anti-stripping agents and found that anti-stripping agents with a solubility parameter difference of less than 2 $(J \cdot cm^{-3})^{1/2}$ had good compatibility with asphalt. The Hansen solubility parameters of asphaltene, aromatics, and saturated fractions were simulated by Zhou X. [68] in a range from 13.3 to 22.5.

Many parameters could be used to validate the asphalt molecular model in the virgin and aged asphalt diffusion system. The density and solubility parameters are the most commonly used by researchers. However, there are differences in the test results for different validation parameters. And excessive parameter fluctuations cannot fully validate the authenticity of the model. Therefore, multiple parameters and indicators should be selected to comprehensively validate the rationality.

3.4. Module and Parameter Selection

After validating the structure, it is necessary to consider some parameters such as force field, module algorithm, ensemble selection, etc. The modeling and parameter selection of asphalt molecular structure by different scholars are shown in Table 4.

Table 4. Modeling and parameter selection of asphalt molecules.

Author	Asphalt Type	Molecular Structure	Platform	Force Field	Module Selection	Ensemble Selection
Li Derek (2013) [49]	Virgin	SARA-12 [1]	Windows: LAMMPS Linux: Spartan	OPLS-AA	Monte Carlo	——
Cao L. (2021) [80]	Virgin and modified	SARA-12	Windows: Material Studio	COMPASS	Visualizer Amorphous Cell	NPT NVT
Ruixin Z. (2020) [81]	Aged	SARA-12	Windows: Material Studio	COMPASSII	Forcite	NVT NPT
Zhao D. (2020) [82]	Virgin	SARA-12	Windows: Material Studio	PCFF Dreiding COMPASSII	Visualizer Amorphous Cell	NVT NPT NVE
Xu M. (2015) [63]	Virgin and aged	SARA-12	Windows: LAMMPS	CVFF	Monte Carlo	NVT NPT
Cui Y. (2020) [60]	Aged	SARA-12	Windows: Material Studio	COMPASSII	Visualizer Amorphous Cell	NVT NPT
Qiu Y. (2020) [74]	Virgin	SARA-4 [2]	Windows: Material Studio	COMPASS	Visualizer Amorphous Cell Forcite	NVT NPT
Xu M. (2016) [83]	Virgin and aged	SARA-12	Windows: LAMMPS	COMPASS	Monte Carlo	——
Wang H. (2015) [84]	Virgin	SARA-12	Windows: Plimpton1995	CVFF	Monte Carlo	NVT
Guo Meng (2017) [85]	Virgin	SARA-12	Windows: Material Studio	COMPASS	Visualizer Amorphous Cell	NVT
Bahasin (2011) [86]	Virgin	Average	Windows: Material Studio	COMPASS	Visualizer Amorphous Cell	——
Xu G. (2016) [87]	Virgin	SARA-4	Windows: Material Studio	COMPASSII	Visualizer Amorphous Cell	NVT NPT

Table 4. *Cont.*

Author	Asphalt Type	Molecular Structure	Platform	Force Field	Module Selection	Ensemble Selection
Sun W. (2020) [88]	Virgin	SARA-4	Windows: Material Studio	COMPASSII	Visualizer Amorphous Cell	NVT NPT
Sun D. (2018) [89]	Virgin	Average	Windows: Material Studio	Universal COMPASSII	Visualizer Amorphous Cell	NPT
Ding Y. (2018) [90]	Virgin and modified	SAR-8 [3]	Windows: LAMMPS	——	NEMD method	NVT

[1] SARA-12 refers to twelve molecular structures of four-component asphalt. [2] SARA-4 refers to four molecular structures of four-component asphalt. [3] SAR-8 refers to eight molecular structures of three-component asphalt.

Different research perspectives require different molecular dynamics models and related parameters. In addition, current research is mainly based on the Windows platform. Material Studio and open access installation package LAMMPS are the most commonly used. In terms of force field selection, the COMPASS series is mainly used. Amorphous Cell, NVT, and NPT are more suitable selections.

4. Diffusion Influencing Factors

4.1. RAP Perspective

Some researchers analyzed the influencing factors of interfacial diffusion between virgin and aged asphalt. The micro-scale material properties, mixing time, mixing temperature, simulation parameters, and ultimately evaluating the degree of diffusion were considered. Different RAP contents also had an impact on the diffusion effect. After the contact and diffusion of virgin and aged asphalt, the complex shear modulus changed. Therefore, based on the partial diffusion theory, an index was proposed for the degree of blending (DOB) of the interface between virgin and aged asphalt [91,92], as shown in Equation (14):

$$DOB = \frac{G{\cdot}coarse - G{\cdot}design}{G{\cdot}fine - G{\cdot}design} \quad (14)$$

where *G·coarse* and *G·fine* are the complex shear moduli of blended reclaimed asphalt coated on the surface of the aggregate above and below the boundary sieve pore size after mixing, respectively. *G·design* refers to the complex shear modulus of the virgin asphalt and recycled agent wrapped on the surface of the new aggregate obtained by the specific surface area method when RAP fully conforms to the black stone theory.

DOB could characterize the degree of mixing between virgin and aged asphalt. Gustavo M. [93] proposed a new method to characterize the degree of activity (*DOA*) of asphalt mixtures, based on the ITS method shown in Equation (15):

$$DOA(\%) = 100 \times \frac{ITS_{RA}(X^{\circ}\mathrm{C})}{\max ITS_{RA}} \quad (15)$$

where *RA* (*X* °C) refers to the ITS results of the reclaimed material at a specific temperature "*X*". The results indicated that there was a very good correlation when using two different reclaimed mixtures.

The DOB between virgin and aged asphalt could be improved by increasing the mixing temperature and duration. If the mixing temperature were increased by 15 °C, the DOB would increase by about 7%. However, with the aging phenomenon, the saturated and aromatic components in the aged asphalt could not fully perform their adhesion. The increase in asphalt content would result in spatial deviation between aggregates. It would lead to a decrease in micro-scale adhesion ability and ultimately a deterioration in the high-temperature performance of asphalt mixtures [64]. It should be pointed out that the more severe the aging of asphalt, the worse the moisture stability of reclaimed asphalt

mixtures. Aged asphalt with low adhesion actually would promote the diffusion effect of virgin and aged asphalt and improve the degree of resistance to moisture damage to a certain extent.

Many scholars studied the content and size of RAP. Arianna S. [94] proposed an accurate quantitative indicator for estimating the "re-activated" binders in RAP by studying the main characteristics of different RAPs. The results indicated that the content of re-activated binder was directly proportional to its film thickness (RTF) for hot reclaimed materials. It was believed that the RTF was constant and the calculation was based on the concept of re-activated film thickness. The effective volume of re-activated binder could be determined through RAP grading, and there would be a phenomenon of RAP agglomeration for small particle aggregates. Cialdini E. [95] used an electron microscope to observe asphalt samples and validated CT scanning simulation results. The results showed that the diffusion of virgin and aged asphalt depended on their relative positions. And it should be also pointed out that the interface problem between virgin and aged asphalt could not be visually observed, and the degree of diffusion at stress concentration was relatively low. Yu S. [96] used an intermittent graded mixing method to determine the mixing effect of different RAP contents based on partial fusion theory. The performance of the mixed system was not highly sensitive to the content when the RAP content was 20%. The mixed ratio needs to comprehensively reflect the source of RAP, aggregate gradation, and mixing time to ensure the performance of the mixture.

4.2. Asphalt Perspective

In addition to RAP characteristics, the characteristics of asphalt and rejuvenators at the micro-scale should have a significant impact on the interface. Chen L. [97] tested the rheological properties of the interface between virgin and aged asphalt based on a dynamic shear test (DSR) and simulated the reclaiming mechanism by molecular dynamics. The results indicated that the grade of virgin asphalt would have a significant impact on the degree of diffusion. The diffusion rate significantly increased as the gradation increased. Under different conditions of asphalt grade and heating temperature, the diffusion rate would show different functional changes. When the heating temperature is 130 °C and the heating time is 60 min, the DOB of 90# asphalt increases by about 10% compared to 70# asphalt. Xiao Y. [98] conducted molecular simulations based on Material Studio software and used DSR to evaluate the reclaimed effect of rejuvenators on aged asphalt. The results indicated that the degree of aging would have a significant impact on the reclaimed effect of rejuvenators. And in long-term aged asphalt, the rejuvenators could better diffuse and promote the recovery of the reclaimed asphalt. Ding Y. [99] used molecular dynamics to simulate the diffusion between virgin and aged asphalt and used GPC to validate the results. The results showed that adding rejuvenators in aged asphalt could effectively improve the diffusion system. There is a good logarithmic relationship between DSR and the fusion rate of simulation. The key to the diffusion rate of the whole system was the diffusion degree of macro-scale molecules and it was pointed out that the diffusion effect of temperature on asphaltene was higher than that of resin and aromatics. The coefficient of variation differs by about 10%. In addition, Newcomb [100] pointed out that the molecular weight of different components was one of the key factors affecting the diffusion rate of asphalt molecules. The most obvious self-diffusivity was found in saturated components, followed by aromatic components, resins, and asphaltenes. The selection of ensembles is another key factor affecting the final simulation results, and different ensembles are suitable for constructing different simulation environments. During the process of simulating the interface diffusion between virgin and aged asphalt using NVT ensemble, voids appear in the crystal cells, leading to an increase in the final self-diffusivity. Gao F. [19] pointed out that it would be possible to combine actual situations and used NPT ensemble for simulation. The results showed that under the NPT ensemble, virgin and aged asphalt could quickly come into contact, resulting in a rapid increase in density.

In summary, molecular dynamics could effectively simulate the diffusion system between virgin and aged asphalt interfaces and accurately and efficiently present the evolution of the entire system over time. Molecular dynamics simulations still have certain limitations, as the reliability is crucial. Therefore, it is necessary to further optimize the model, improve computational efficiency, and reduce the negative effects caused by software simulation in order to establish a macro and micro cross-scale study of molecular dynamics at the interface between virgin and aged asphalt.

5. Conclusions and Perspective

- The paper summarizes the main theories of interface diffusion and the basic characteristics and application scenarios of each module in software, proposing the basic steps of molecular dynamics simulation. Two methods for measurement of the molecular structure of asphalt are summarized and compared. The alumina chromatographic column method is widely used and could be suitable for most measurement situations. The TCL-FID method needs to be promoted and used according to unified standards.
- The structures of virgin and aged asphalt molecules are summarized. The twelve molecular structures of four-component models have improved the accuracy of simulation, and the simulation parameters are close to those of real asphalt. Under the control of calculation speed, the model could effectively represent the molecular structure of real asphalt. Multi-parameter and multi-indicator validation could reduce the negative impact caused by different parameter fluctuations. The COMPASS series of force fields could effectively simulate the complex structures of various molecules and predict thermodynamic performance, being suitable for interface problems. The AC module and NPT ensemble and NVT are selected based on actual problems.
- This paper analyzes the current influencing factors affecting mixed diffusion systems. From a RAP perspective, DOB is related to the mixing temperature. DOB increases by approximately 7% every 15 °C. When the RAP content is 20%, the effect of the content on partial mixed systems is not significant. From the perspective of asphalt, different types of asphalt have a crucial impact on the degree of diffusion. When the heating temperature is 130 °C and the heating time is 60 min, the DOB of 90# asphalt increases by about 10% compared to 70# asphalt. In addition, there is a good logarithmic relationship between DSR and the fusion rate of simulation. The diffusion effect of temperature on asphaltene is higher than that of resin and aromatics. The coefficient of variation differs by about 10%.
- In current research, molecular dynamics simulations have limitations on the time scale. Asphalt pavement can involve long-term problems. It is not possible to directly simulate the long-term aging effect. Finally, some studies have used more types of molecular models in aggregate interfaces. However, various types mean the expansion of the entire model, which influences computational efficiency and spatial structure authenticity. So, in the modeling of virgin and aged asphalt, the molecular structure components of asphalt should be expanded, and a complete, unified, and realistic asphalt molecular model dataset should be formed from different sources and aging methods. The optimization of parameters such as the interaction potential function and initial conditions should be taken into account. Sensitivity analysis and validation of parameters should be taken seriously. The simulation of adding different additives such as modifiers and rejuvenators to the system should be considered. Additionally, it is recommended to combine macro-scale tests and molecular levels to clarify the mechanisms of low temperature and salt damage.

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Abbreviations

AC	Amorphous Cell
AFM	Atomic Force Microscope
CED	Cohesive Energy Density
CHARMM	Chemistry at HARvard Macromolecular Mechanics
COMPASS	Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies
CT	Computed Tomography
CVFF	Consistent Valence Force Field
DOA	Degree of Activity
DOB	Degree of Blending
DSC	Differential Scanning Calorimetry
DSR	Dynamics Shear Rheometry
FTIR	Fourier Transform Infrared Spectrometry
GAFF	Generation Amber Force Field
GPC	Gel Permeation Chromatography
GPU	Graphic Process Unit
GROMOS	Groningen Molecular Simulation
ICO	Index of Carbonyl
ISO	Index of Sulfoxide
J-OCTA	J-Open Computational Tool for Advanced Material Technology
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
NVT, NVE, NPT, NPH	N: the Number of Moles; V: Volume; P: Pressure; T: Temperature; E: Energy; H: Enthalpy
OPLS	Optimized Potentials for Liquid Simulations
PCFF	Polymer Consistent Family of Force Field
RAP	Reclaimed Asphalt Pavement
RDF	Radial Distribution Function
rNEMD	Reverse Non-Equilibrium Molecular Dynamics
RTF	RAP Film Thickness
RTFOT	Rolling Thin Film Oven Test
SARA	Saturates, Asphaltene, Resin, and Aromatics
SE method	Stokes–Einstein method
TCL-FID	Thin-layer Chromatography with Flame Ionization Detection
WLF	Williams–Landel–Ferry

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