Research on the Mechanism of Surfactant Warm Mix Asphalt Additive-Based on Molecular Dynamics Simulation

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Abstract: Warm mix asphalt (WMA) technology can bring certain environmental and technical benefits through reducing the temperature of production, paving, and compaction of mixture asphalt. Recent studies have shown that some WMA additives are able to reduce the temperature by increasing the lubricating properties of asphalt binder-based on the tribological theory, this paper studied the mechanism of adsorbing and lubricating film of base asphalt and WMA on the surface of stone by molecular dynamics (MD) simulation method, and the effect of surfactant WMA additive on the lubrication performance of the shear friction system of “stone–asphalt–stone”. The model of base asphalt lubricating film, including saturates, aromatics, resin and asphaltene, as well as the model of warm mix asphalt lubricating film containing imidazoline-type surfactant WMA (IMDL WMA) additive molecule, were established. The shear friction system of “stone–asphalt–stone” of base asphalt and warm mix asphalt was built on the basis of an asphalt lubrication film model and representative calcite model. The results show that the addition of IMDL WMA additive can effectively improve the lubricity of asphalt, reduce the shear stress of asphalt lubricating film, and increase the stability of asphalt film. The temperature in the WMA lubricating film rises, while the adsorption energy on the stone surface decreases with the increase of shear rate, indicating that the higher the shear rate is, the more unfavorable it is for the WMA lubricating film to wrap on the stone surface. In addition, the shear stress of the WMA lubricating film decreased with increasing temperature, while the shear stress of the base asphalt lubricating film increased first and then decreased, demonstrating that the compactability of the asphalt mixture did not improve linearly with the increase of temperature.

Keywords: warm mix asphalt; additive; molecular dynamics simulation; lubrication; mechanism

1. Introduction

Warm mix asphalt (WMA) refers to a form of asphalt mixture with mixing and compaction temperatures 20–55 °C lower than typical hot mix asphalt (HMA) [1–3]. The goal of WMA is to produce mixtures with substantially the same road performance and construction workability as HMA under significantly reduced production temperatures [4–8]. Due to the decrease of production temperature, WMA technology boasts many environmental benefits such as reducing fuel and energy consumption, cutting down harmful gas emissions and preventing construction personnel from toxic asphalt smoke [4,5,9–12], which has been developed rapidly in the past decades. The decrease of temperature also has
many technological benefits such as delaying aging of asphalt cement, extending transport distance, improving compaction effect during cold weather, reducing pavement cooling time for faster opening to traffic, and using higher blends of recycled asphalt pavement material (RAP) in the mixture [13–15]. It also brings potential economic benefits for the reduction of energy consumption, and less wear of asphalt plant equipment and extension of service life of asphalt pavement.

At present, WMA technology can be divided into three categories [16,17]: foaming asphalt, wax (or organic) additives and chemical additives. However, thus far, the mechanism by which WMA technology makes the mixture easy to mix and compacted at low temperatures is not fully understood [18]. It was found that the reduction in binder viscosity caused by WMA additives was insufficient to explain the decrease in the production and compaction temperature of the final mixture in the field [2,19,20]. Conversely, in some cases, the addition of WMA additives strengthens the viscosity of the binder [18]. In addition, in some studies on the workability of WMA and HMA mixtures, it has been found that the compactability of the mixtures does not linearly improve with the increase of temperature, but becomes worse above a certain temperature [21,22], which makes it clear that viscosity reduction is not the only mechanism responsible for the performance of WMA at low temperatures. Recent studies have shown that improving the lubricity of asphalt binder and reducing the dynamic friction between stones may be a further mechanism of WMA [1,21–23]. The frictional behavior or relative motion of the binder as a lubricating film between two stones may play an important role in the mixing and compaction of WMA. Therefore, it is important to study the lubricating effect of WMA additives to further reveal the workability of warm asphalt mixes at low temperatures.

Dynamic friction is a physical phenomenon caused by the contact and relative movement of two or more objects, which leads to energy consumption and wear. Lubricants are widely used in many fields to reduce dynamic friction, and the performance of lubricants is usually characterized by appropriate tribological tests [21]. Tribology is the study of the interaction between surfaces in relative motion. The friction of a material placed between two solid surfaces in relative motion is usually described by a Stribeck curve [24]. As shown in Figure 1, Stribeck curve can be divided into four lubricative regions [21,24,25]:

- In the mixed state (B), the lubricating oil forms fluid dynamic pressure as the velocity increases, which reduces direct contact between the two surfaces, thereby easing friction.
- In the elastohydrodynamic state (C), friction is minimized when the surfaces are no longer in contact.
- In the hydrodynamic region (D), friction depends primarily on the viscous resistance of the lubricant at high sliding speeds. Specifically, the friction of the whole system rises again as the internal friction of the lubricant increases.

Tribology has a wide range of engineering applications in materials science, but it is an emerging discipline in asphalt technology [1,21–23]. Ingrsia et al. characterized the properties of asphalt binders with chemical WMA and wax WMA additives-based on the concept of tribology. They found that asphalt binders containing WMA additives had lower friction [1]. Gallego et al. introduced the lubrication test method for determining the influence of surfactant additives on the lubricity of asphalt binder. The study shows that the use of surfactant additives in asphalt binders can reduce the friction coefficient [23]. Canestrari et al. reviewed the latest progress of tribological tests used in the study of asphalt binder, as well as beneficial suggestions for improving these test methods [21]. Bairgi et al. studied the effect of foaming on the friction and rheological properties of foam asphalt. The results show that the foaming process changes the frictional resistance of foamed asphalt binder, especially in the state of elastohydrodynamic and fluid lubrication, the foaming process reduces the friction coefficient. Compared with rheological properties, the friction properties of foam WMA are more related to the improvement of working performance [22].
rheological properties, the friction properties of foam WMA are more related to the internal microstructure of the binder than the macroscopic properties of the asphalt binder. Additionally, the WMA additives can potentially reduce asphalt mixture production and compaction energy consumption by improving the lubricating effect of the asphalt binder [1,23]. Therefore, the tribological test has been introduced to characterize the lubrication properties of asphalt binder recently. The friction test of asphalt binders is mainly carried out by a tribological device mounted on a dynamic shear rheometer (DSR) with a specific geometry. However, studies have shown that attention should be paid to the geometric shape of the friction device, the selection of the matrix, the wear condition, and the determination of test procedures and conditions when studying the performance of lubricants through friction experiments [21]. Meanwhile, Puchalski found that the friction value of asphalt is low at high temperatures (such as those used for mixing and compacting asphalt mixture), and the chemical WMA additive can form a boundary lubricating film to protect aggregate particles from direct contact with solids, thus reducing the friction between particles [26].

At the same time, previous studies have shown that the surfactant WMA additive has little influence on the viscosity of asphalt binder within the recommended dosage range [19]. It can be reasonably speculated that the lubrication form of WMA additive between stones belongs to boundary lubrication with low temperature and high load, that is, adsorption lubrication. It is mainly completed by the physical or chemical adsorption film formed by the WMA additive adsorbed on the surface of the stone. In addition, macroscopic lubrication problems can still be studied by friction experiment, which requires a precise experimental condition [21]. While in view of the boundary lubrication of asphalt binder at high temperature, the traditional macroscopic lubrication concept, theory and related experimental methods are difficult to reveal the lubrication mechanism accurately and deeply, as the adsorption lubrication film of binder will have a special size effect different from the macroscopic lubrication film. With the development of computer technology, molecular dynamics (MD) simulation has become a powerful and feasible method for material design and performance prediction, as well as a hot spot in the fields of materials, solutions, surfaces, biochemistry and drugs. MD simulation is an important method to study the interface behavior and micro-lubrication because of its mature theory,
high computational efficiency and incomparable advantages in experiments. Luo et al. studied the adsorption lubrication mechanism and failure mechanism of low-sulfur diesel components on iron surface by means of molecular simulation, and investigated the influence mechanism of anti-wear additives on lubrication performance [27]. Chen et al. studied the adsorption lubrication performance of six esters/N-tetradecane on iron surface by molecular simulation method. The results reflected that the lubrication performance of low-sulfur diesel oil could be improved through increasing ester volume fraction and changing ester components [28]. Chen et al. carried out a quantitative study of the friction coefficient and mechanism of MoS$_2$ nanoparticles on the basis of molecular dynamics (MD) simulation [29]. Under the conditions of hydrodynamic and boundary lubrication, Godlevskii et al. considered the possibility of determining the characteristics of the lubricating layer by computational MD, and provided an example of solving the adsorption, supramolecular self-organization and rheological parameters of the model lubricant in the lubricating layer [30]. However, there is no research report on the application of molecular simulation in the asphalt–stone lubrication friction.

The purpose of this paper is to study the interface lubrication characteristics between asphalt and stone surface by molecular dynamics (MD) simulation, as well as build lubricating films containing asphalt and WMA (asphalt + WMA additive) in accordance with four fractions including saturates, aromatics, resin and asphaltene, as well as imidazoline type surfactant WMA additive. Then the shear lubrication simulation model of “stone–asphalt–stone” is constructed-based on asphalt lubrication film and typical calcite mineral-matrix. The molecular model is verified by literature reports or laboratory results, and the action mechanism of warm mix asphalt is studied by investigating shear rate, shear stress, WMA additive distribution and adsorption energy.

Asphalt is a complex chemical mixture composed of a variety of hydrocarbons and heteroatoms such as sulfur, oxygen and nitrogen [31–33]. Therefore, the specific chemical composition of asphalt cannot be accurately identified and quantified by the currently available analytical and experimental instruments [34]. Nevertheless, modern separation technology can divide asphalt into different components-based on the similarity of the components in polarity and molecular characteristics. According to the four-component classification method proposed by the American Society for Testing and Materials (ASTM) D4124-09, asphalt can be divided into saturates, aromatics, resin and asphaltene, commonly known as four SARA components [31,34]. This paper studied the lubrication and friction behavior between asphalt and aggregate consistent with the four-component asphalt model proposed by Guo et al. [35].

Although surfactant WMA additives have been used for more than a decade, the composition and structure of WMA additives have been rarely reported. Taking palmitic acid and organic polyamines as raw materials, Zhao et al. synthesized a new imidazoline type surfactant WMA (IDML WMA) additive. The research results showed that IMDL WMA additive had good warm mixing effect [19]. Therefore, IMDL WMA additive molecular model was adopted as WMA additive in the molecular simulation model of WMA lubricating film in this paper.

The molecular models of natural rocks have different structural characteristics due to different rock-forming minerals and diagenetic conditions. In road engineering, stone is usually divided into acid stone and alkaline stone. In China, alkaline stone is often used to prepare asphalt mixture in practical projects because of the better adhesion between alkaline stone and asphalt. The main mineral composition of alkaline stone is calcite (chemical formula is CaCO$_3$). The mineral surface model in this paper is a calcite crystal retrieved from the Cambridge Structural Database (CSD). After the mineral is selected, the mineral crystals need to be dissociated to expose the natural surface containing in the original crystal form and the broken surface caused by the machining process. The stone used in asphalt mixture is mainly processed natural stone. When the external force is applied, the stone minerals break along the surface with weak interlayer bonding strength. Studies have indicated that the exposed surface is closely related to layer spacing, bonding
properties, surface electrical properties and surface free energy \[34,36\]. With the increase of layer spacing, the mineral surface is more easily exposed in nature as the binding strength between layers and surface free energy gradually decreases. As part of the trigonal system, calcite’s surface structure and growth mechanism have been extensively studied, including low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), X-ray diffraction (XRD) and atomic force microscopy (AFM) \[34\]. Studies show that the calcite surface \[1\] is the most exposed dissociation surface for the layer spacing is the largest in the exposed surface, the bonding strength between layers is the weakest. It was also confirmed by relevant molecular simulations and surface energy calculations on the calcite surface \[37\]. Therefore, this paper takes calcite crystal (104) as the friction surface to study the lubrication friction of asphalt.

2. Calculation Method of MD Simulation

2.1. Calculation Parameters

In this paper, two “stone–asphalt–stone” molecular lubrication friction models are constructed. The difference between the two models is that the asphalt lubrication film of the intermediate layer is the base asphalt model and the WMA (base asphalt + WMA additive) model, respectively. The four-component model (including saturates, aromatics, resin and asphaltene) proposed by Guo et al. was adopted for the asphalt model \[35\] (Figure 2a), and IMDL WMA additive proposed by Zhao et al. was used for WMA additive \[19\] (Figure 2b). The stone cell, the friction surface, the size of friction surface system and the thickness of the model is calcite, calcite (104), 2.4287 nm × 2.4750 nm × 1.6738 nm and 6 layers respectively (Figure 2c). All calculations are carried out in the forcite module of the Material Studio 8.0 software package. The selected force field is Compass II derived from ab initio method of quantum mechanics. In the geometric optimization of a single molecule, except that Atom-based algorithm is used to calculate the interaction of Van der Waals force and Coulomb force, Ewald algorithm and Atom-based algorithm is adopted to calculate the Coulomb force and Van der Waals force respectively. The geometric optimization of the asphalt four-component molecule and the WMA additive molecule are conducted by Geometry Optimization of Forcite, and the optimized molecular configuration is shown in Figure 2. Andersen and Berendsen methods were used to control the temperature and pressure during the MD simulation, and the count step was set to 1.0 fs.

Figure 2. The optimized models: (a) asphalt SARA four fractions; (b) imidazoline surfactants WMA additives; (c) calcite (104) surface.
2.2. Details of MD Simulation

2.2.1. Construction of Asphalt Lubricating Film Cell

Before constructing the shear model, it is indispensable to establish the asphalt lubricating film model and determine the density of the asphalt lubrication film. Two asphalt lubricating films were used in shear simulation calculation to compare the difference of lubricating properties between WMA and base asphalt, and analyze the influence of WMA additive on the lubricating properties: One is the base asphalt lubricating film without WMA additive, the ratio of the number of molecules is saturates: aromatics: resin: asphaltene = 5:7:3:1; the other is WMA lubrication film containing IMDL WMA additive, the ratio of the number of molecules is saturates: aromatics: resin: asphaltene: WMA additive = 5:7:3:1:3. The Amorphous cells of asphalt lubrication film were constructed with Amorphous Cell modules and the green cells were geometrically optimized. Then the cells were pre-balanced at 200 ps by isobaric–isothermal ensemble (NPT) at set temperature, and the dynamic pre-equilibrium was carried out at 300 ps after annealing. In order to check the equilibrium state of the above molecular model, Figure 3 shows the change of energy (including potential energy, kinetic energy, non-bond energy and total energy) of WMA lubricating film system with simulation time during NPT simulation. During the NPT simulation of 298 K, all types of energy were stable when the simulation time exceeded 20 ps. The density of asphalt cell at the corresponding temperature is 1.018 g/cm³, which is nearly consistent with the asphalt density data measured in the laboratory (1.02 ± 0.02 g/cm³), indicating that the calculation parameters of molecular simulation are reasonable and effective.

![Energy change](image)

Figure 3. Energy of warm mix asphalt lubricating film model during NPT equilibrium at simulation temperature of 298 K.

2.2.2. Construction of Calcite Cell

Calcite is selected to establish the mineral matrix model. The chemical formula of this mineral is CaCO₃. In the chemical composition, CaO and CO₂ accounts for 56.03% and 43.97% respectively. As a typical alkaline stone, it is the most popular stone type in China. The calcite model was imported from the Material Studio 8.0 software package and cut
with the surface module. The cutting surface was calcite (104), and the size of calcite was expanded to keep consistent with the size of asphalt cell.

2.2.3. Construction of Shear Simulation Model of “Stone–Asphalt–Stone”

After optimizing the asphalt cell, the amorphous cell of asphalt and WMA is constructed by Amorphous cell module as the nano friction layer of stone. The shear friction system model of “stone–asphalt–stone” is constructed by the build layer tool. The model is divided into three layers, in which the middle layer is asphalt lubrication mold, the upper and lower layers are the surface layer of calcite crystal cells, and a 2.0 nm vacuum layer is set on the upper calcite surface to avoid the interaction between friction surfaces due to periodic structure. The “stone–asphalt–stone” shear friction system model is shown in Figure 4.

![Figure 4](image)

Figure 4. The structure model of the shear flow of asphalt confined between calcite (104) surfaces (a) calcite; (b) calcite (104) surface; (c) asphalt surface; (d) “calcite–asphalt–calcite” composite interfacial model.

2.2.4. Simulation Process of Shear Molecular

After the construction of the molecular simulation model of shear friction, the canonical ensemble (NVT) was adopted to calculate the molecular dynamics of the shear friction system at 100 ps at a set temperature, such that the shear friction system can fully relax. Then, the Confined Shear method of Forcite module was used to simulate the lubrication of asphalt film between stone surfaces. In the shear simulation process, the atoms on the surface of the stone cell can only move in a simple harmonic manner at their equilibrium position except moving along the x-axis as a whole, and the shape and temperature of the whole stone cell surface remain basically unchanged. Temperature scan and shear rate scan were carried out in the simulation process. The simulated shear temperature range was 100 to 170 °C temperature interval. The shear rates were 1, 2, 3, 5, 10, 20, 40, 60, 80 and 100 m/s respectively, and the corresponding shear simulation time was set as 2000, 1000, 666, 400, 200, 100, 50, 33, 25 and 20 ps to ensure the consistency of the relative displacement between the upper and lower stone surfaces after the completion of the simulation. Taking the shear rate of the WMA lubrication film at 20 m/s as an example, the situation of the “stone–asphalt–stone” shear friction model at different times is shown in Figure 5.
3. Results and Discussion

3.1. Effect of Shear Rate

The factors influencing the compaction process of asphalt mixture mainly include: compaction work, system temperature, asphalt dosage, etc. Meanwhile, the tribological experiments of asphalt were introduced to further explore the mechanism of WMA additive in recent years. In the tribological experiments of asphalt, the shear rate, temperature and the amount of asphalt were the main factors affecting the experimental results. Therefore, the design idea of asphalt tribological test was used for reference in the shear molecular simulation study of asphalt lubricating film, and the lubrication of asphalt lubricating film on stone in the “stone–asphalt–stone” shear friction system was investigated under different shear rates.

After the completion of the confined shear molecular dynamics simulation of the friction system, the simulation parameters such as the shear stress of the asphalt lubricating film, the temperature distribution and the rate distribution inside the lubricating film can be obtained, and the response process of the asphalt lubricating film under the shear friction on the stone surface and the mechanism of WMA additive can be analyzed based on the above-mentioned parameters.

3.1.1. Variation Rule of Shear Stress

Shear stress is the resultant force that the molecules of the contact surface at the interface of the asphalt lubrication film are subjected to by the internal molecules along the shear direction (refers to the $x$-axis in this paper) in unit area when the asphalt lubrication film shear motion along the stone surface. It is divided into upper and lower surface shear stress. Shear stress is an important index to evaluate the lubrication effect of asphalt lubrication film on friction between stones. Figure 6 shows the change of the shear stress on the upper and lower surfaces of the WMA lubrication film along the $x$-axis with time, where the shear rate is 20 m/s and the shear temperature is 120 °C.
Figure 6. Changes of stress of warm mix asphalt lubricating film with simulation time at shear rate of 20 m/s.

As can be seen from Figure 6, the lubricating film bears a heavy load with over 2 GPa shear stress when the thickness of asphalt lubricating film reaches nanometer level. The strength of the shear stress on the upper and lower surfaces of the asphalt lubrication film is basically equal while the direction is opposite, that is, the shear stress on the two surfaces is basically balanced. However, the shear stress on the upper and lower surfaces of the WMA lubrication film fluctuates with the time, and there is no obvious rule. It is found that the shear stress tends to a fixed value after noise reduction. Therefore, it is significant to take the average value when investigating the changes of shear stress at different shear rates. Base asphalt lubricating film at 170 °C and WMA lubricating film at 120 °C were selected for analysis in accordance with the mixing temperature of above-mentioned asphalt. The average shear stress on the upper and lower surfaces of the two asphalt lubricating films along the x-axis with the change of shear rate is shown in Figure 7.

Figure 7. Effect of shear rate on the stress of the (a) base asphalt lubricating film at simulation temperature of 443 K; (b) warm mix asphalt lubricating film at simulation temperature of 393 K.
As shown in Figure 7, the shear stresses on the upper and lower surfaces of the base asphalt lubricating film and the WMA lubricating film are basically equal in magnitude and opposite in direction at all shear rates, that is, the shear stresses shall maintain balance. In addition, the shear stress of lubricant film of base asphalt and WMA shows different variation trends with the increase of shear rate. In the friction system of base asphalt lubricating film (Figure 7a), the shear stress decreases and then increases with the increase of shear rate. The adsorption of asphalt lubricating film on the stone surface needs to go through a process because of large molecules of asphalt lubricating film. At the beginning of shear, base asphalt molecules adsorb on the stone surface and form a lubricating film with the increase of shear speed. The friction and shear stress reduced as the contact between stone surfaces gradually decreases. When the shear rate reaches 5 m/s, the surface of the stone is completely covered by the asphalt lubrication film and the lubrication film is in the most stable state with minimum friction force and shear stress. When the shear rate is greater than 5 m/s in the working area, the shear stress on the lubrication film and the friction on the stone surface begin to rise with the continuous increase of the shear rate, resulting in lubrication failure for the asphalt lubrication film may not be functioned. However, compared with the friction system of base asphalt, the friction system of WMA lubrication film (Figure 7b) shows different variation trends, that is, the shear stress rises with the increase of shear rate. The growth rate of shear stress is inconsistent over different shear rate ranges. When the shear rate is less than 10 m/s, the shear stress of WMA lubricating film is greatly affected by the shear rate with fast increase trend, while in the range of 10–40 m/s, the shear stress of WMA lubrication film is less affected by the shear rate and changes slowly. However, when the shear rate is higher than 40 m/s, the shear stress rises linearly with the increase of the shear rate. This reflects that the lubrication film of WMA is subjected to a certain shear friction stress during shearing, which rises rapidly with the increase of shear rate. When the shear rate is 10–40 m/s, the lubrication film of WMA and the shear stress are relatively stable under the action of WMA additives. When the shear rate is higher than 40 m/s, the friction stress of the warm mixed asphalt lubricating film on the stone surface begins to increase, while the lubrication effect of the warm mixed asphalt lubricating film on the stone is weakened, resulting the effect of WMA additives fail to work.

In the entire range of shear rate examined, the shear stress of the base asphalt lubricating film is always greater than that of the WMA lubricating film at the same shear rate, even though the former is at a relatively high temperature (the higher the temperature, the smaller the viscosity and viscous resistance). This indicates that the addition of WMA additive reduces the friction stress of the lubricating film of the binder, thus revealing the mechanism of warm mixing action of WMA additive at the molecular level. At the same time, the addition of WMA additive creates a stable working area for the lubricating film of the binder, in which the shear stress hardly rises with the increase of shear rate, corresponding to the working area where WMA additive plays a warm mixing role.

3.1.2. Influence of Shear Rate on Temperature Distribution in Asphalt Lubricating Film

In the process of lubrication and friction between asphalt binder lubricating film and stone surface, the lubricating film will be subjected to the shear action of stone surface and the interaction between molecules in the binder, which will inevitably generate heat and lead to the increase of asphalt lubricating film temperature. The temperature of each position of the lubricating film is different as the temperature transfer will be affected by the heat transfer rate of asphalt lubricating film. In this paper, the influence of shear rate on the temperature distribution of warm mixed asphalt lubricating film along the film thickness direction (z-axis) was investigated, as shown in Figure 8.
As can be seen from Figure 8, the temperature distribution in asphalt lubricating film during the shear simulation presents a complex variation rule with the increase of shear rate. When the shear rate is less than 5 m/s, the internal temperature of the lubricating film hardly changes without obvious regularity because of the small amount of friction force and the heat generated in the friction process. When the shear rate is between 10 m/s and 40 m/s, the temperature of the lubricating film increases as enough heat generated by the friction process. However, the heat generated by friction cannot be transmitted out in time because the thermal conductivity of asphalt lubricating film is poor. Therefore, the temperature of the lubricating film tends to gradually rise from the adsorption interface to the interior, and the temperature reaches the maximum at the central position of the film. According to the study in Section 3.1.1, the stable working area of WMA lubricating film is 10–40 m/s, where the lubricating film plays a stable lubrication role. At the same time, the fluidity of the whole lubricating film is enhanced due to the increase of temperature, which contributes to the mutual movement of stones in the process of mixing and compaction. When the shear rate is higher than 40 m/s, a large amount of heat is generated in the friction process, which leads to a sharp rise in the temperature of the lubricating film. The temperature of the lubricating film in the whole thickness range reaches equilibrium quickly, and the temperature of the lubricating film near the center is close. It is also found that in the whole shear rate range, the temperature in the asphalt lubrication film rises with the increase of the shear rate.

In the process of mixing and compaction of asphalt mixture, the asphalt film can act as a lubricant between the stones when the asphalt has fluidity through heating. It is found in the simulation that process the shear stress on the lubricating film rises with the increase of shear rate, that is, the temperature in the asphalt lubricating film rises as the friction force on the stone surface and the heat generated by friction increases. The viscosity of asphalt lubrication film fell sharply when the temperature inside the asphalt lubrication film is too high. At this point, the stone between asphalt lubrication film is in a state of dilution, the lubrication effect on stones is weakened or invalid as the internal pressure is reduced, and the stones are easier to rub, which is not conducive to asphalt mixing and compaction. This is the fundamental reason that the compactibility of the mixture failures to improve linearly with the increase of temperature, while it becomes worse above a certain temperature, as mentioned in related studies [21,22]. It is further shown that reducing the viscosity of asphalt is not the only mechanism for WMA workability at low temperature.
3.2. Effect of System Temperature on Shear Stress

The boundary lubrication is directly related to the equilibrium of adsorption and desorption of the lubricating film on the adsorption surface. Langmuir adsorption theory believes that temperature is the main factor affecting adsorption, and the higher the temperature is, the higher the adsorption rate of lubricating film molecules on the adsorption surface will be. Meanwhile, higher temperature will break the dynamic equilibrium process of adsorption and desorption as adsorption is an exothermic process, resulting in the increase of adsorption capacity. Therefore, the effect of system temperature (373, 383, 393, 403, 413, 423, 433, 443 K) on the shear friction of WMA lubricating film and base asphalt lubricating film was further studied at the shear rate of 20 m/s in this paper. The average shear stress of the upper and lower surfaces of WMA lubrication film and base asphalt lubrication film along the x-axis at different temperatures is shown in Figure 9.

![Graph showing the effect of system temperature on shear stress](image)

Figure 9. Effects of temperature on the stress of the film.

According to the results in Figure 9, the shear stress on the upper and lower surfaces of the WMA and the base asphalt lubricating film is equal within the temperature range of 373–443 K. The shear stress of the WMA film is less than that of the base asphalt film at the same temperature, and the difference between above-mentioned stress is widening with the increase of temperature, which further indicates that the addition of WMA additive reduces the shear stress of the lubricating film. In addition, the shear stress of lubricating film of WMA and base asphalt shows different trends with temperature change. With the increase of temperature, the shear stress of the lubricating film of WMA shows a decreasing trend, while the shear stress of the lubricating film of base asphalt shows a trend of first increasing and then decreasing with maximum shear stress at 413 K. This shows that the compactibility of the mixture does not improve linearly with the increase of temperature, but becomes worse above a certain temperature, which is consistent with the previous research results [21,22]. The change of shear stress is not apparent in the entire temperature range, indicating that in a certain temperature range, the system temperature is not the main factor affecting the lubrication effect of WMA film on stone.

3.3. Effects of WMA Additives

Many existing studies have shown that adding surfactant WMA additives to asphalt can improve the lubricity of asphalt lubricating film and form boundary lubricating film to reduce the friction between particles through protecting aggregate particles from the direct...
contact of solids [26]. However, the reason why surfactant WMA additives can promote the lubricity of asphalt has not been concluded, and there is a lack of theoretical research in this field.

3.3.1. Effect of WMA Additive on Shear Stress of Friction System

In this paper, the effect of imidazoline type surfactant WMA (IMDL WMA) additive on asphalt lubricity was investigated by molecular dynamics simulation, and the warm mixing mechanism of surfactant WMA additive was studied theoretically. Figure 10 shows the shear stress on the upper and lower surfaces of WMA and base asphalt lubricating film at different shear rates at 120 °C.

![Figure 10](image)

Figure 10. Effects of the IMDL WMA additive on the stress of the film.

As shown in Figure 10, due to the addition of IMDL WMA additive, the shear stress of WMA lubricating film is significantly lower than that of base asphalt lubricating film at the same shear rate. Therefore, the addition of IMDL WMA additive can improve the lubricity of asphalt binder, reduce the friction between asphalt and stone, and promote the mixture to be better mixing and compaction, which theoretically explains the mechanism of surfactant WMA additive. It can be seen that the shear force of the WMA lubricating film changes little when the shear rate is in the range of 10–40 m/s, which is basically not affected by the shear rate. Therefore, this area is the stable working area of the WMA lubricating film. The stable working area of the base asphalt lubrication film is in the shear rate range of 5–10 m/s, which is less than that of the WMA. Therefore, it can be concluded that the stability of the boundary lubrication film of asphalt binder improved by the addition of IMDL WMA additive, such that it can provide stable lubrication under a larger and wider load range, it is easier to meet the mixing and compaction conditions of asphalt mixture in actual production.

3.3.2. Density Distribution of IMDL WMA Additive Molecules between Frictional Surfaces

According to boundary lubrication theory, the strength of the adsorbed lubricating film is far better than that of the flow since the boundary adsorption film loses its mobility by adsorbing on the surface of the lubricating substrate, it can be kept on the friction surface more stably. Therefore, the reason why the adsorption film can maintain stable and reliable lubrication under high shear is inseparable from its adsorption on the substrate surface.

The IMDL WMA additive enjoys high polarity due to its imidazoline group, which belongs to the basic group. Compared with asphalt, it is easier to form a lubrication film on the stone surface to effectively prevent the direct contact between the friction surface. The density distribution of IMDL WMA additive molecules in the WMA lubricating film along the z-axis between the friction surfaces of the stone is shown in Figure 11.
As can be seen from Figure 11, compared with the initial configuration, IMDL WMA additive molecules moves toward the friction interface after the friction system is fully relaxed and reaches equilibrium. Accordingly, WMA additive molecules preferentially adsorb the stone surface to form a lubricating film, which separates the stone from the asphalt friction surface and provides an interface with low shear resistance. This phenomenon further explains the reason why the lubricating effect of WMA lubricating film is better than that of base asphalt lubricating film at the same temperature and shear rate from a micro level.

Figure 12 shows the effect of adding IMDL WMA additive on the number of molecular density distribution of asphalt components. As shown in Figure 12, compared with the base asphalt, the number density distribution of asphalt molecules on the friction surface in the WMA decreased significantly after the addition of IMDL WMA additive. This is because the IMDL WMA additive would preferentially move to the friction surface and replace the asphalt molecules on the friction surface. Therefore, the distribution of WMA additive molecules in asphalt lubricating film was indirectly verified.
3.3.3. Adsorption Energy of Asphalt Lubrication Film on Friction Surface

The adsorption property of asphalt lubrication film on stone surface has an important impact on its lubrication effect. These properties unique to asphalt lubrication film under nanometer lubrication condition are determined by the interaction of asphalt lubrication film and stone friction surface in physical and chemical nature, which is mainly reflected by adsorption energy.

Adsorption energy is the energy required to divide the “stone–asphalt–stone” shear friction system into two independent systems. The bonding strength of the asphalt and stone surface is quantified by calculating the adsorption energy of the asphalt and stone surface, to reflect the lubrication effect of the asphalt lubrication film between the friction surfaces. The bond energy is constant in COMPASS force field. The change of total energy of asphalt and stone system and the “stone asphalt–stone” shear friction system are caused by the non-bond energy (van der Waals force and static electricity), that is to say, the adsorption energy of “stone–asphalt–stone” shear friction system can be determined by the non-bond energy. The adsorption energy of the “stone–asphalt–stone” shear friction system is calculated by Equation (1).

\[ E_{\text{binding}} = (E_{\text{asphalt}} + E_{\text{aggregate}}) - E_{\text{total}} \]  
(1)

where \( E_{\text{binding}} \) is the adsorption energy between asphalt and stone, kcal/mol; \( E_{\text{asphalt}} \) is the energy of asphalt lubrication film without stone, kcal/mol; \( E_{\text{aggregate}} \) is the energy of stone surface without asphalt lubricating film, kcal/mol; \( E_{\text{total}} \) is the total energy of the “stone–asphalt–stone” friction system in the simulated output results, kcal/mol.

Adsorption energy is the result of energy dissipation in the process of thermodynamic equilibrium of bitumen–stone interface. According to Equation (1), the greater the difference between \( E_{\text{asphalt}} + E_{\text{aggregate}} \) and \( E_{\text{total}} \), the greater the adsorption energy of asphalt lubrication film on the stone surface. The adsorption energy of the WMA lubrication film on the stone surface in the shear simulation process calculated in accordance with Equation (1) is shown in Figure 13.

![Figure 13](image_url)  
**Figure 13.** Binding energies (\( E_{\text{binding}} \)) of warm mix asphalt lubricating film between calcite (104) surfaces.
As shown in Figure 13, when the shear rate is lower than 5 m/s, the adsorption energy of the warm mixed asphalt lubrication film on the stone surface decreases rapidly. When the shear rate is higher than 5 m/s, the reduction rate of adsorption energy slows down, while when the shear rate reaches 80 m/s, the adsorption energy gradually tends to be stable. In general, the adsorption energy of the WMA lubricating film on the stone surface decreases with the increase of the shear rate, which indicates that the higher the shear rate is, the more unfavorable it is for the WMA lubricating film to be wrapped on the stone surface, or even to rupture, such that the lubrication effect of the WMA lubricating film on the friction surface is weakened.

4. Conclusions

This paper studied the mechanism of adsorption and lubrication between the base asphalt and WMA lubrication film on the stone surface, and the effects of shear rate, system temperature and WMA additive on the adsorption and lubrication performance based on the tribological theory and molecular dynamics simulation method. The results show that:

1. In the friction system of warm mix asphalt and base asphalt, the shear stress changes differently with the increase of shear rate. The WMA lubricating film remains stable when the shear rate is in the range of 10–40 m/s, which means the shear stress of the warm mixed asphalt lubricating film is less affected by the shear rate and changes slowly. However, when the shear rate is higher than 40 m/s, the shear stress rises linearly with the increase of the shear rate. In the friction system of base asphalt lubricating film, the shear stress decreases first and then increases with the increment of shear rate. When the shear rate reaches 5 m/s, the lubricating film is in the most stable state with minimum friction force and shear stress.

2. The increment of shear rate leads to the increase of temperature in the lubricating film of WMA. When the shear rate is less than 5 m/s, the internal temperature of the lubricating film hardly changes without obvious regularity because of the small amount of friction force and the heat generated in the friction process. When the shear rate is in the range of 10–40 m/s, the temperature of the lubricating film increases gradually from the adsorption interface to the interior and reaches the maximum at the center of the film. When the shear rate is higher than 40 m/s, the temperature of the lubricating film rises sharply as a large amount of heat is generated during the friction process.

3. With the increase of temperature, the shear stress of the lubricating film of WMA shows a decreasing trend, while the shear stress of the lubricating film of base asphalt shows a trend of first increasing and then decreasing with maximum shear stress at 413 K, which indicates that the compactability of the mixture does not improve linearly with the increase of temperature. In addition, system temperature exerts little impact on shear stress, which is not the main factor affecting the adsorption lubrication of WMA.

4. The addition of IMDL WMA additive can effectively improve the lubricity of asphalt and stability of asphalt film by reducing the shear stress of asphalt lubricating film. After the friction system is balanced, the IMDL WMA additive molecules are mainly distributed at the friction interface and preferentially adsorbed on the stone surface to form a lubricating film. Besides, the adsorption energy of the WMA lubricating film on the stone surface decreases with the increase of the shear rate, which indicates that the higher the shear rate is, the more unfavorable it is for the WMA lubricating film to be wrapped on the stone surface, or even to rupture, such that the lubrication effect of the WMA lubricating film on the friction surface is weakened.

The above research results are of great significance in guiding the selection and development of WMA additives, as well as the determination of mixing and compaction temperatures of mixture, showing a broad application prospect. In the future research the authors will further explore the effects of different structures of WMA additives and
different compositions of stones on the lubricating friction performance in combination with experiments.

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**Abbreviations**

| Abbreviation | Description |
|--------------|-------------|
| WMA          | warm mix asphalt |
| MD           | molecular dynamics |
| IMDL WMA     | imidazoline type surfactant WMA |
| HMA          | hot mix asphalt |
| RAP          | recycled asphalt pavement |
| DSR          | dynamic shear rheometer |
| ASTM         | American Society for Testing and Materials |
| CSD          | Cambridge Structural Database |
| LEED         | low energy electron diffraction |
| XPS          | X-ray photoelectron spectroscopy |
| SEM          | scanning electron microscopy |
| XRD          | X-ray diffraction |
| AFM          | atomic force microscopy |
| NPT          | isobaric-isothermal ensemble |
| NVT          | canonical ensemble |

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