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Molecular Dynamics Simulation and Experimental Analysis of the Effect of Ultrasonic Disposal on the Compatibility of NanoAsphalt

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Abstract: Based on LAMMPS molecular dynamics simulation of nano-silica(nano-SiO$_2$) and asphalt molecular motion trajectory in the ultrasonic environment, the nano-SiO$_2$ modified asphalt mixed model was proposed, and then the ultrasonic vibration process was simulated by the periodic displacement method. The solubility parameter and viscosity of the mixed model were simulated and calculated to reveal the compatibility changes of the modified asphalt from a microscopic perspective. Different temperatures and ultrasonic frequencies were achieved by changing the temperature parameter and the period parameter of the simple harmonic motion equation. Besides, to characterize the effect of ultrasonic vibration on the promotion of nano-SiO$_2$-asphalt compatibility, the prepared nano-SiO$_2$ modified asphalt was subjected to viscosity testing through viscosity change. The results show that the simulation could accurately predict the experimental phenomena, and the molecular simulation can be used as an effective method to study the properties of asphalt materials. The compatibility of nano-SiO$_2$ and asphalt is positively correlated with ultrasonic temperature and ultrasonic frequency to some extent. The compatibility effect is best at 130°C, 40 KHz. When the ultrasound frequency exceeds a certain value, the effect of promoting compatibility is not obvious.

Keywords: nano-SiO$_2$ modified asphalt; ultrasonic cavitation; molecular dynamics; compatibility

1. Introduction

In recent years, nanotechnology has gradually been penetrating into the field of materials engineering. Nanomaterials modified road asphalt is one of the important research directions. It is a technology that introduces nanomaterials into asphalt materials by various methods to improve various properties of asphalt with nano-effects, such as high temperature stability, fatigue resistance, friction properties (anti-slip performance), antiaging performance, water stability, etc. [1–4]. The key of asphalt modification effect lies in the compatibility between nano-modifier and asphalt [5,6]. Compatibility is defined thermodynamically as the ability of two or more substances to form homogeneous systems in any proportion. For nano-modified asphalt, this means that “the nano-modifier reacts with the matrix asphalt as fine particles or is uniformly and stably dispersed in the matrix asphalt without delamination, coalescence or segregation” [7].

Only if the compatibility is improved can the nanoparticles and the matrix asphalt combine well and improve the material properties. On the contrary, if the compatibility is not good, not only will the material properties not be improved, but the material properties will also be deteriorated. Therefore, an in-depth study of the compatibility issues between nanomaterials and asphalt is of great significance for the application of nano-modified asphalt. According to studies [8,9], the compatibility depends not only on the amount of modifier content and the nature of the matrix asphalt, but also on the compatibility promotion measures. For nano-modified asphalt, the incorporation of surfactants to improve the interfacial properties of nanomaterials and asphalt is a typical chemical promotion measure for compatibility, and the use of a high-speed shearing machine to
make nanomaterials more uniformly dispersed is a common physical promotion measure for compatibility [10,11]. Ultrasonic wave acting on liquid media will produce mechanical effect, cavitation effect, thermal effect, and chemical effect [12], which can promote the dispersion compatibility and even chemical reactions of different substances in liquid media and has been widely used in the field of materials engineering. The combination of high-speed shear and ultrasonic blending to prepare nano-modified asphalt has been reported, but so far it is regarded as a means of preparation, without in-depth study of its impact on compatibility [13–20].

By constructing molecular models, molecular simulation techniques can study the molecular dynamics properties under different force fields and different temperature and time conditions, thus explaining the interaction between asphalt molecules and modifier molecules from a microscopic perspective, and gradually playing an important role in the field of modified asphalt compatibility research. Zhu et al. [21] studied the compatibility of various anti-stripping agents with asphalt by molecular dynamics simulation, and Su et al. [22] found that the compatibility and mechanical properties of SBS with asphalt were better at 140 °C by molecular dynamics simulation. In addition, molecular dynamics simulation has been widely used in several fields, such as biochemistry, mechanical engineering, etc. Pavel et al. [23] studied the structural parameters of RH6G molecules in melamine barbiturate supramolecular system by molecular simulation and experiments. Zhou et al. [24] used molecular dynamics and quantum chemistry to calculate the interaction energy between haspin and tubercidin. Zhai et al. [25] studied the polishing process of silicon carbide under ultrasonic condition by molecular dynamics simulation.

In this paper, we used molecular dynamics simulation to reveal the microscopic compatibility mechanism and chose nano-SiO$_2$ as a representative nanomaterial. The four-component (AS, R, Ar, S) model of asphalt, matrix asphalt model, amorphous nano-SiO$_2$ molecular model, and nano-SiO$_2$ modified asphalt mixed model were proposed based on Materials Studio software, and then the models were exported to LAMMPS software for molecular dynamics simulation under different ultrasonic vibration conditions. LAMMPS is an open source software with a wide range of applications, such as aggregation and self-assembly behavior of nanoparticles on water surfaces [26], thermal/mechanical properties of atomic systems near pores [27], shear deformation behavior of single-crystal metal Ni [28], etc. However, since LAMMPS does not have a graphical interface, it needs to be used in conjunction with visualization software such as Materials Studio. Since ultrasonic vibrations cannot be implemented in Materials Studio software, LAMMPS software was used to implement ultrasonic vibrations propagating periodically by applying periodic displacements to the nano-hybrid model based on the ultrasonic cavitation principle. Periodic boundary conditions were applied in the y and z directions, and open boundary conditions were used in the x direction to realize boundary sinusoidal oscillations to simulate the periodic variation of the ultrasonic cavitation structure, and the temperature parameters and period parameters were changed to realize the variation of ultrasonic temperature and frequency. By calculating the solubility parameters and viscosity, the dynamic changes of the internal molecular structure of SiO$_2$ nanoparticles and matrix asphalt when they are miscible are demonstrated microscopically, and the influence of two factors, ultrasonic frequency and ultrasonic temperature, on the compatibility is analyzed. Further, the viscosity entity test was conducted to verify the effect of ultrasound on the compatibility of the nanoparticles and asphalt and to determine the optimal ultrasonic treatment conditions based on the existing experimental conditions.

2. Simulation Models and Methods
2.1. Asphalt Molecular Model Construction
2.1.1. Asphalt Four-Component Model

In terms of asphalt average molecular models, Jennings developed eight models for standardized asphalt samples in the SHRP (Strategic Highway Research Program) study based on the results of NMR spectroscopy, namely AAA-1, AAB-1, AAC-1, AAD-1,
AAF-1, AAG-1, AAK-1, and AAM-1 [29]. These models provide a convenient way to approximate the structure of asphalt molecules, but the study does not consider the effect of fractionation and ignores some internal structures of the asphalt itself, which needs further improvement. With the continuous development of molecular simulation technology, a more accurate asphalt model has been established, and gradually developed from the asphalt average molecular model to the asphalt multi-component model-three-component and four-component models. The composition of several classical asphalt systems is shown in Table 1.

Table 1. Molecular composition of typical bitumen systems.

<table>
<thead>
<tr>
<th>Author</th>
<th>Time</th>
<th>Asphalt System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jennings [29]</td>
<td>1993</td>
<td>AAA-1, AAB-1, AAC-1, AAD-1, AAF-1, AAG-1, AAK-1, AAM-1</td>
</tr>
<tr>
<td>Zhang [30]</td>
<td>2007</td>
<td>Asphaltene: C_{64}H_{52}S_2 Saturation: C_{22}H_{46} Resin: 1,7-dimethylnaphthalene</td>
</tr>
<tr>
<td>Zhang [30]</td>
<td>2007</td>
<td>Asphaltene: C_{72}H_{90}S Saturation: C_{22}H_{46} Resin: 1,7-dimethylnaphthalene</td>
</tr>
<tr>
<td>Li [31]</td>
<td>2014</td>
<td>Asphaltene A: C_{42}H_{54}O Asphaltene B: C_{46}H_{61}N Asphaltene C: C_{31}H_{62}S Saturation A: C_{30}H_{62} Saturation B: C_{35}H_{62} Aromatics A: C_{33}H_{44} Aromatics B: C_{30}H_{46} Resin A: C_{40}H_{90}N Resin B: C_{40}H_{90}N Resin C: C_{18}H_{10}S_2 Resin D: C_{36}H_{57}N Resin E: C_{20}H_{50}O</td>
</tr>
<tr>
<td>Zhu [21]</td>
<td>2016</td>
<td>Asphaltene: C_{53}H_{57}NOS Saturation: C_{22}H_{46} Aromatics: 1,7-dimethylnaphthalene Resin: C_{100}H_{106}</td>
</tr>
<tr>
<td>Bo [32]</td>
<td>2020</td>
<td>Asphaltene: C_{63}H_{76}S_2N_2 Saturation: C_{22}H_{46} Aromatics: 1,7-dimethylnaphthalene Resin: C_{100}H_{106}</td>
</tr>
</tbody>
</table>

The average molecular structure method is less expensive to calculate and takes less time to simulate the same time scale, but it cannot show the diversity of asphalt molecules and especially cannot describe the four-component interactions of asphalt, while the three- or four-component assembly method can compensate this deficiency well and takes less time compared to the twelve-component method, and the accuracy gap is not very obvious. The study on the compatibility of anti-stripping agents [33] and rubber powder [34] with asphalt based on the molecular dynamics showed that the simulation results were in good agreement with the experimental results using a four-component average molecular structure model of asphalt. Therefore, in this paper, the four-component analysis method of Zhu [21] was used to construct the asphalt model. The unit of thick-ringed aromatic hydrocarbons connected with cycloalkanes and alkyl side chains and containing heteroatoms [35] was used as the representative molecular model of asphaltenes (see Figure 1a). The layered structure molecule composed of polycyclic aromatic hydrocarbons and alicyclic hydrocarbons with different lengths of side chains and corresponding groups [36] was used as the representative molecular model of resin (see Figure 1b). The docosane (C_{22}H_{46}) [37] with the highest content of alkanes in asphalt was used as the representative molecular model of saturates (see Figure 1c), and 1,7-dimethylnaphthalene [33,34], which is closer to the molecular structure of saturated and aromatic fractions of actual road asphalt as a
representative molecular model of aromatic fraction (see Figure 1d). This four-component model has also been applied and verified for rationality by scholars such as Yanjun Qiu [38].

![Representative molecular model of asphalt](image)

**Figure 1.** Four-component molecular model of asphalt (C atoms in gray, H atoms in white, N atom in blue, O atom in red, S atom in yellow) (a) Asphaltene; (b) Resin; (c) Saturation; (d) Aromatics.

In summary, the four-component molecular model of asphalt was established, as shown in Figure 1.

2.1.2. Asphalt Four-Component Content

In this study, 90# road petroleum matrix asphalt was used and the separation of the four components of asphalt was performed according to the American standard ASTM D4142 [39]. The asphaltene was precipitated from the specimen with n-heptane, filtered, and the soluble fraction entrapped in the precipitate was removed by reflux of n-heptane, and then the precipitate was dissolved by reflux of toluene to obtain asphaltene. The deasphalted fraction was adsorbed on an alumina column and washed out with n-heptane, toluene, and toluene–ethanol unfolding in turn, corresponding to the saturated fraction, aromatic fraction, and gum. The results are shown in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As</th>
<th>S</th>
<th>Ar</th>
<th>R</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix asphalt</td>
<td>10.1</td>
<td>23.7</td>
<td>53.7</td>
<td>12.5</td>
<td>100.0</td>
</tr>
</tbody>
</table>

In Materials Studio software, using Amorphous Cell module, according to the ratio of four components shown in Table 2, combined with the relative molecular mass of each component selected in this paper, the ratio of the number of molecules in asphalt can be calculated as As:Ar:S:R = 3:72:16:2, and put into a cubic box with the size of 30.8 Å × 30.8 Å × 30.8 Å to obtain a model of asphalt macromolecule consisting of 3567 atoms. At this time, the initial molecular configuration is often not a stable structure. In order to obtain a more realistic molecular geometric configuration, the geometric
optimization method is usually used in molecular dynamics. In other words, when the intermolecular force is the smallest, the molecular geometric configuration is adjusted to make the molecular bond length and bond angle close to the “natural” state, and then the optimal arrangement of atomic positions is obtained [40]. In the Forcite module, Geometry Optimization task is selected, and the steepest descent method and conjugate gradient method are adopted, respectively. The maximum number of iterations is set as 500 steps and 5000 steps. After geometrical optimization of the initial configuration of the asphalt simulation system, five cycles of annealing treatment from 300 K to 500 K of the system temperature are completed. The system temperature is then slowly reduced by the annealing treatment to reach the equilibrium state of the structure at each temperature. This cyclic annealing process eliminates residual stresses and brings the asphalt molecular structure to the energy ground state, as shown in Figure 2. The purpose is to reduce the energy of the system, so that the system is in a stable state with low potential energy; the second is to eliminate the unreasonable structure of the blending system, so that the model structure is more reasonable. The entire simulation was performed using the COMPASS II force field as the molecular force field, which was obtained by modifying the COMPASS force field, which has a better coverage for organic and inorganic materials, so it is widely used to describe the force field of asphalt mixture system [41,42].

![Asphalt molecular model](image)

**Figure 2.** Asphalt molecular model.

2.1.3. Asphalt Molecular Model Validation

To ensure that the simulated structure is representative, the accuracy of the constructed asphalt molecular model needs to be verified, and the density of asphalt at 298 K is selected for comparison with the performance index of the actual asphalt material. As shown in Figure 3, the density of the asphalt model system decreases and then increases with time during the dynamic optimization process. The presence of internal stress in the asphalt system makes the volume suddenly increase during NPT, releasing the internal stress, which leads to a sudden decrease in density. In the NPT simulation process, box size is changed by the influence of normal temperature and pressure, the volume of the system has a clear tendency to shrink, the intermolecular space is reduced, the density therefore becomes larger, and with the growth of relaxation time, the system tends to steady state. The final density is stabilized in the range of 0.96~0.98 g/cm³, which is close to the real density, and the difference with the actual density of asphalt material at 298 K was controlled within 5%. According to Figure 3, it can be judged that the established asphalt molecular model can represent the real asphalt molecular structure.
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![Figure 3. Density variation curve of asphalt molecular model.](image)

The atomic radial distribution function $g(r)$ within and between the molecules of the asphalt molecular model was analyzed using the Forcite module in Materials Studio ($r$ is the distance from the central molecule), and the results are shown in Figure 4. As can be seen from Figure 4, the curve of the atomic radial distribution function within the molecule of the asphalt molecular model flattens and tends to 0 after the peak; the curve of the atomic radial distribution function between the molecules gradually rises and reaches its maximum value, then the curve flattens and tends to 1. Asphalt is a typical amorphous material. The atoms are arranged in an orderly state in the macromolecules, with short-range order and long-range disorder, and the intermolecular force is mainly van der Waals force [43]. According to Figure 4, it can be considered that the established asphalt molecular model can represent the real asphalt molecular structure.

![Figure 4. Radial distribution function (RDF) for distances of intra-molecular and inter-molecular atoms in asphalt molecular models.](image)
2.2. Amorphous Nanosilica Construction

Molecular models of SiO$_2$ in the crystalline or amorphous state can be imported from the Materials Studio materials library, or modeled based on SiO$_2$ cell parameters. For better integration with the experiment, amorphous nano-SiO$_2$ consistent with the test material was selected for introduction. When building a silica cell on this basis, both shape and radius can be set, choosing a spherical shape consistent with the test material. Taking a model with a radius of 5.5 Å as an example, the configuration is shown in Figure 5 below.

![Figure 5. The amorphous nano-SiO$_2$ model (O atoms in red, Si atoms in orange).](image)

2.3. Nano-Asphalt Blend Model

A blend system of nano-SiO$_2$ and asphalt was established in the Amorphous Cell module. The nano-modifier admixture in the nano-modified asphalt is usually controlled between 1% and 5%. In order to be consistent with the prepared nano-modified asphalt, the SiO$_2$ content is set at 5% for the asphalt-SiO$_2$ blending ratio in this paper. The model is first simulated with a step size of 1.0 fs and a total time of 200 ps. The total number of atoms, volume, and temperature of the control system are kept constant during the simulation, which is called NVT system synthesis. Under the NVT system, the volume size of the system does not change, but the asphalt nano-SiO$_2$ mixed system aggregates into clusters during the process, and the total energy of the system decreases and gradually stabilizes, as shown in Figure 6. The isothermal isobaric system, NPT, was then compressed for 150 ps at a pressure of 1 atm (the atomic number N, pressure P, and temperature T of the system were kept constant, and the total momentum was zero), so that the system is further stabilized to further analyze the data and obtain the model of a blending system, as shown in Figure 7.

![Figure 6. Energy change of relaxation process of mixed system.](image)
3. Molecular Dynamics Simulation of Ultrasonic Field

3.1. Ultrasonic Dispersion Principle

Ultrasonic vibration is the use of ultrasound to effectively disperse nano-SiO$_2$ particles in the matrix asphalt, while the ultrasonic dispersion is mainly caused by the mechanical, thermal and chemical effects of ultrasonic cavitation resulting in the separation, intensification of movement, and dispersion of suspended particles in liquid. When sound waves propagate in a liquid, they produce pressure undulations in space and appear in a negative pressure state below the static pressure. When the liquid is in a negative pressure state, the molecules are subject to a smaller pressure or tension between the action. At this time, the original structural defects (cavitation nuclei) inside the liquid will gradually grow and form cavities visible to the naked eye, a phenomenon known as acoustic cavitation [44]. The degree of dispersion and particle size of the suspended particles have an important influence on the processing, preparation, and molding of the material [45]. At present, the dispersing effect of ultrasound has been widely used in biological, chemical, and pharmaceutical fields [46,47]. The indirect type is used in the experimental part of this paper.

In the process of ultrasonic treatment of liquid, the shock wave generated by the collapse of cavitation bubbles is the cause of particle dispersion in the liquid. When the energy generated by ultrasonic cavitation acts on the particle clusters is suspended in the liquid, separation can occur through erosion or fracture, and the dispersion effect of ultrasound on tiny particles is divided into two processes: erosion and fracture. Erosion refers to the separation of particles from the surface of parent aggregates from the parent to form independent individuals. Fracture refers to the aggregates that have been separated from the parent and continue to break into fragments of different sizes due to cracks or surface defects under the action of ultrasound, as shown in Figure 8. Ultrasonic dispersion of these two states occurs simultaneously or independently, depending on the state of the particles, the size of the energy, the liquid environment, and other factors. In addition, the local vortex and turbulence generated by the cavitation effect will intensify the movement of the particles and enhance the mixing effect on the particles, which can make the particles more uniformly dispersed in the liquid.
3.2. Realization and Parameter Setting of Ultrasonic Vibration in Molecular Simulation

Ultrasonic vibration cannot be realized in Materials Studio software. Hisashi Okumura [48] investigated the damage of amyloid fibrils by ultrasonic cavitation using the MD. In the modeling process, they implemented ultrasonic boundary conditions by applying a sinusoidally varying periodic pressure. The setting method of this boundary condition is reasonable because the effect of ultrasonic wave is essentially that there is an alternating period of positive and negative pressure in the propagation process of medium. It is well known that the frequency of ultrasonic waves is generally high (greater than 20 kHz), so the pressure that varies according to a sinusoidal waveform is very similar to the pressure that varies according to a positive or negative square wave. Therefore, based on the principle of ultrasonic cavitation, LAMMPS software is used to simulate the propagation of ultrasonic vibration periodically by applying the periodic displacement to the nano-mixing model. Periodic boundary conditions are applied in the y and z directions. Open boundary conditions are applied in the x direction to achieve boundary sinusoidal oscillations and simulate the periodic variation of the ultrasonic cavitation structure.

The ultrasonic disposition simulation part is done in LAMMPS, and the ultrasonic vibration action is performed on the imported nano-asphalt mixed model with COMPASS force field, NVE system synthesis, and the time step is set to 1.0 fs with a total vibration time of 5 ns. The frequency variation of ultrasonic waves is achieved by changing the vibration period. In this paper, the periods are set to 50 ps, 25 ps, and 20 ps, the corresponding ultrasonic frequencies are 20 GHz, 40 GHz, and 50 GHz, and the amplitudes are set to 1 Å (a = 1 Å). The choice of high-frequency ultrasound can both simulate the overfrequency technology of some large equipment and explore the effect of high-frequency ultrasound conditions on the compatibility of the two, but can also improve the efficiency of the calculation.

4. Simulation Results and Analysis

4.1. Effect of Ultrasonic Field on Solubility Parameters

The cohesive energy density (CED) and solubility parameter δ are usually chosen to reflect the compatibility between asphalt and modifier when analyzing the compatibility using MD simulation [49]. The smaller the difference in solubility parameter δ between the two materials, the easier they are to mix with each other. According to the theory of mixing heat of polymer blends, the cohesion energy density is the energy required to eliminate all intermolecular forces of 1 mol of material, which is a physical quantity characterizing the
strength of intermolecular forces of material, and the square root of the cohesion energy density is the solubility parameter $\delta$. The relationship between them is shown below.

$$\delta = \sqrt{\frac{E_{coh}}{V}}$$  \hspace{1cm} (1)

$E_{coh}$ is the cohesion energy (J); $V$ is the real molecular volume (cm$^3$);

Molecular dynamics simulations were performed for the nano-SiO$_2$-asphalt blend system under NVT regular system synthesis. 298 K, 363 K, 383 K, 403 K, and 423 K were used for the simulated temperatures, 20 GHz, 40 GHz, and 50 GHz were used for the ultrasonic frequencies, and medium accuracy was chosen for the calculation. The time step is set to 1.0 fs and the total simulation time is 5 ns. The software’s built-in analysis directly analyzes the molecular trajectory data to obtain the solubility parameters of the blended system at different temperatures. The ultrasonic disposal simulation part is done in LAMMPS, where the imported nano-asphalt mixing model is simulated by NPT and NVT. The ultrasonic vibration part time step is set to 1.0 fs, and the total running time is 5 ns and the PCFF force field is used to calculate the solubility parameters by calculating the LJ (Lennard-Jones) potential energy magnitude of the mixing system at different disposal frequencies and temperatures to obtain the cohesion energy density. The formula is shown in (2):

$$\delta = \sqrt{\frac{E_{LJ}}{V}}$$  \hspace{1cm} (2)

$E_{LJ}$ is the cohesion energy (J); $V$ is the real molecular volume (cm$^3$).

Figure 9 shows the solubility parameters of the nano-asphalt mixture system at five different temperatures for four different disposal conditions. The solubility parameters of the nano-asphalt mixture system in all four disposition states decreased with increasing temperature. This is due to the increase in the kinetic energy of polymer molecules, the enhanced thermal motion of molecules, and the increase in macroscopic volume when the temperature increases, resulting in a gradual decrease in the density of intramolecular aggregation energy. After ultrasonic treatment, the solubility parameters of the nano-asphalt mixture system at all temperatures decreased, and the decrease in solubility parameters was the largest at the ultrasonic frequency of 20 GHz and temperature of 403 K. This indicates that ultrasound has the effect of promoting the miscibility of nano-SiO$_2$ and asphalt. However, the frequency should not be too large, and when the ultrasonic frequency is too large, its effect on the compatibility of nanoparticles with asphalt is not obvious.

Figure 9. Solubility parameters of nano-silica modified asphalt at four different frequencies and temperatures.
4.2. Effect of Ultrasound Field on Viscosity

In addition to solubility parameters, some researchers have shown that the solution viscosity properties of the blends can be used to judge the compatibility [50]. The viscosity of the matrix asphalt increases with the addition of the nano-modifier, and after dissolution by adsorption, the entanglement points of its molecular chains in the system space increase, forming a localized mesh structure and even finally a continuous phase of filaments or webs in the asphalt, and the presence of these webs creates an obstacle to the free movement of the asphalt molecules, thus greatly increasing the viscosity of the system [51]. The introduction of the ultrasonic field not only makes the molecules subject to the action of field but also makes them have a certain energy, which accelerates the vibration frequency of the molecules and also reduces the viscosity of the liquid. Mohapatra [52] et al. studied the effect of ultrasonic cavitation on asphaltene content, rheological properties, and metal content under different ultrasonic frequencies and power input conditions. It was found that under the condition of ultrasonic frequency of 574 KHz and 50% output power, the asphaltene content was lower and the strong attractive interaction between asphaltene particles was reduced, which led to the reduction of asphalt viscosity and improved the transport performance of asphalt.

Molecular dynamics simulations were also performed for the nano-SiO$_2$ asphalt blend system under NVT regular system synthesis. 298 K, 363 K, 383 K, 403 K, and 423 K were used for the simulated temperatures and 20 GHz, 40 GHz, and 50 GHz for the ultrasonic frequencies. The time step is set to 1.0 fs and the total simulation time is 5 ns. Select the frame with the lowest energy after dynamics optimization and use the “Shear” command to obtain the viscosity value. While the ultrasonic disposal simulation part was done in LAMMPS, NPT and NVT simulations were performed on the imported nano-asphalt blend model with PCFF force field, using the same parameter settings and the viscosity of the asphalt mixed system was calculated by the Green–Kubo method [53], which is an accurate and effective method to calculate the viscosity of the asphalt system. The formula is as follows:

$$\eta = \frac{V}{K_B T} \int_0^{\infty} \langle P_{xy}(t)P_{xy}(0) \rangle dt$$  \hspace{1cm} (3)$$

where $V$ is the volume, $T$ is the temperature, $K_B$ is the Boltzmann constant. In the formula, the equation is averaged with pointed brackets, the average of the total time of the simulation calculation is taken, and $\langle P_{xy}(t)P_{xy}(0) \rangle$ is the pressure autocorrelation function. Since this autocorrelation function decays to zero at long time scales, the integration converges to yield the viscosity value.

The core factor affecting the viscosity of the liquid lies in the intermolecular forces of the liquid—the smaller the intermolecular forces, the lower the viscosity. The intermolecular force directly affects the compatibility, specifically the better the compatibility, the higher the intermolecular force. As can be seen from Figure 10, due to the cavitation and mechanical vibration of ultrasonic waves, the ultrasonic waves at three different frequencies play a role in viscosity reduction at the beginning of the introduction of the ultrasound field action. When the temperature exceeds 110°C, the viscosity increases, and the increase in viscosity is not significant. It can be seen intuitively that when the temperature is 403 K and the ultrasonic frequency is 20 GHz, the viscosity change is the largest and the ultrasonic treatment effect is the best. However, when the ultrasonic frequency is too high, the effect of nanoparticles to promote compatibility with asphalt is not obvious, which is consistent with the best treatment conditions obtained by solubility parameters. The simulation tests illustrate that the promotion of compatibility is not obvious when the ultrasonic frequency is too high.
The relation curve of viscosity increases rate of modified asphalt with temperature and frequency under ultrasonic.

5. Experiment
5.1. Test Materials and Instruments

The test was conducted using 90# road petroleum matrix asphalt. The nano-SiO$_2$ model is amorphous spherical SiO$_2$ particles, which is consistent with the simulation parameters setting. The ultrasonic generator is a self-made instrument, the test apparatus is shown in Figure 11, the ultrasonic power is 120 W, the controllable time is 0–60 min, the controllable temperature is 20–160 °C, the ultrasonic frequency is changed by replacing the vibrator, which is set to 28 KHz, 40 KHz, and 52 KHz, the sound field intensity value at 40 KHz is measured by the sound intensity meter, and the sound field intensity distribution is plotted by Origin as shown in Figure 12. The asphalt rotary viscosity test instrument uses the DV-II + PRO viscometer, which is a relative method of measuring viscosity, through several groups of different shapes of rotor, adapted to the determination of different viscosity ranges of fluid.

Figure 10. The relation curve of viscosity increases rate of modified asphalt with temperature and frequency under ultrasonic.

Figure 11. Self-made ultrasonic generator. (a) Top view (b) Main view.
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Figure 11. Self-made ultrasonic generator. (a) Top view (b) Main view.

Figure 12. Sound field intensity distribution at 40KHz frequency. (a) Top view (b) Main view.

5.2. Viscosity Test and Result Analysis

The 5% nano-SiO$_2$ modified asphalt prepared by high-speed shear was subjected to ultrasonic disposal, and the ultrasonic frequency 28 KHz, 40 KHz, 52 KHz, and ultrasonic temperature 363 K, 383 K, 403 K, 423 K were changed to record the viscosity change of the ultrasonic treatment process, and the relationship curve of the rate of viscosity change of the modified asphalt with temperature and frequency under the action of ultrasonic was obtained. The test results are shown in Figure 13. In the temperature range of 363 to 383 K, the viscosity of nanoasphalt shows a significant decrease with the increase of temperature. This is because as the temperature increases, the internal structure of asphalt is changed by ultrasonic cavitation, which breaks the long molecular chains of asphalt and changes from large molecules to small molecules. Under the mechanical action of ultrasonic, it intensifies the relative motion between smaller molecules and inert larger molecules in asphalt, thus increasing the intermolecular friction, and the C-C bond will be broken, breaking the large molecular clusters. In summary, ultrasound plays a role in reducing viscosity. When the temperature exceeds 383 K, the viscosity of nano-asphalt increases, and the viscosity increase rate increases first with the increase of temperature and then slowly decreases, indicating that the agglomeration between nanoparticles is improved at this time because of the dispersion effect of ultrasound, and the interaction between nanoparticles and asphalt is enhanced, that is, ultrasound plays a facilitating role in the miscibility of nanoparticles and asphalt. However, to avoid overheating ultrasonic disposal (because when the temperature is too high, with the further action of ultrasonic thermal mechanical energy, the chances of particle collision also increase), nanoparticles will reoccur agglomeration phenomenon, so the ultrasonic disposal temperature should not be too high. Comparing the change of viscosity–temperature curve under three different ultrasonic frequencies in Figure 13, the viscosity increase rate was the largest when the ultrasonic frequency was 40 KHz and the temperature was 403 K, which was the best ultrasonic treatment condition. The viscosity increase rate is about 46%. When the ultrasonic treatment frequency was 52 KHz, the promotion of compatibility effect was reduced instead.
The above experimental results show that ultrasound can indeed promote the miscibility of nanoparticles with asphalt. This is consistent with the results of the MD simulation, which proves the accuracy of the simulation conclusions. However, due to the limitation of ultrasound frequency in the experiment, the high frequency ultrasound simulated by simulation could not be reached, so the optimal ultrasound conditions could not be determined by simulation, but it can be obtained by combining the experimental and simulation results that the ultrasound frequency should not be too large. When the ultrasound frequency exceeds a certain range, the effect of ultrasound on promoting the miscibility of nanoparticles and asphalt is not obvious. This is because when the ultrasound frequency is too high, the ultrasonic cavitation effect decreases with the increase of frequency. The cavitation effect affects the ultrasonic dispersion, so the promotion of the overall compatibility of nanoasphalt is not obvious. This is because when the ultrasound frequency is too high, the ultrasonic cavitation effect decreases with the increase of frequency. The cavitation effect affects the ultrasonic dispersion, so the promotion of the overall compatibility of nanoasphalt is instead weakened, and a relatively low ultrasound frequency should be selected.

5.3. Temperature Dependence Analysis

The optimal sonication conditions, determined from high temperature viscosity tests, were used to sonicate nanoasphalt and analyzed for temperature dependence. The influence law of ultrasound on the rheological properties of nanoasphalt was further investigated while determining the change in viscosity. The temperature-dependent study was carried out in the temperature scan mode of dynamic shear rheology test, the test temperatures were selected as 46 °C, 52 °C, 58 °C, 64 °C, 70 °C, and 76 °C, and the frequencies were set to 10 rad/s. Parameters such as complex modulus $G^*$ and phase angle $\delta$ are obtained at the same frequency and at different temperatures to evaluate the high temperature rheological properties of asphalt materials.

After ultrasonic treatment, the high temperature viscosity of nano-SiO$_2$ modified asphalt has changed, and it is thought that its internal structure will be changed as a result, and the change of structure will also cause the change of rheology and viscoelasticity of nano-modified asphalt. The complex modulus $G^*$ and phase angle $\delta$ of the two asphalts before and after ultrasonic disposal were measured by a dynamic shear rheometer at different temperatures from 46 to 76 °C varying at the same frequency, as shown in Figure 14.
5.4. Scanning Electron Microscope Analysis

Scanning electron microscopy (SEM) has high resolution and can provide a comprehensive observation of the microscopic morphology, composition, and structure of materials, and is now widely used in the field of microstructure analysis. In order to better observe the surface morphology and the distribution of SiO$_2$ in the matrix asphalt after ultrasonic treatment of nano-SiO$_2$ modified asphalt, two types of nanoasphalt before and after treatment under optimal ultrasonic conditions were scanned by SEM with electron microscopy, and the results are shown in Figure 15. We further plotted the particle size distribution of nanoparticles in the matrix asphalt before and after ultrasonic treatment.

Comparing the particle size distribution graphs, we found that the particle size distribution graphs were closer to the normal distribution after ultrasonic treatment, and the particle size decreased significantly, indicating that the nanoparticles were more uniformly dispersed in the matrix asphalt after ultrasonic treatment. Comparing the SEM images before and after ultrasonic treatment, it can be found that the nano-SiO$_2$ modified asphalt prepared by direct high-speed shear method (in the natural state without ultrasonic treatment) still had some nano-SiO$_2$ particles agglomerated together even after high-speed shear, in the form of larger diameter clusters. After ultrasonic treatment, some of the SiO$_2$ agglomerates were deconfined into small, indeterminate “raised” diameter particles, and the agglomeration phenomenon was significantly reduced and uniformly distributed in the matrix asphalt. The specific surface area of nanomaterials increased, which increased the adhesion area between nanomaterials and asphalt, enhanced adsorption, and increased the molecular interaction between the two. Thus, the bonding force and compatibility between nanoparticles and matrix asphalt are improved. The prerequisite for the modifier to play its full role is that it can be uniformly dispersed in the matrix asphalt. Therefore, the nanoasphalt after ultrasonic treatment not only improves the dispersion stability and compatibility, but also improves the modified asphalt properties.

Figure 14. Effect of temperature on complex shear modulus and phase angle of nanobitumen (46–76 °C). (a) complex modulus G$^*$; (b) phase angle δ.

It is obvious from Figure 14 that with the increase of temperature, the viscosity of nanoasphalt decreases, the fluidity increases, and the complex shear modulus becomes smaller. The nanoasphalt after ultrasonic treatment has an overall small complex shear modulus and an overall large phase angle. This is because in the temperature range of 46 °C–76 °C, the introduction of ultrasonic will make the viscosity of nanoasphalt decrease and make the viscosity test results more certain. At the same time, the high-temperature stability of the ultrasonically treatment nanoasphalt is also weakened.
observe the surface morphology and the distribution of SiO$_2$ in the matrix asphalt after ultrasonic treatment of nano-SiO$_2$ modified asphalt, two types of nanoasphalt before and after treatment under optimal ultrasonic conditions were scanned by SEM with electron microscopy, and the results are shown in Figure 15. We further plotted the particle size distribution of nanoparticles in the matrix asphalt before and after ultrasonic treatment.

Figure 15. Scanning electron micrograph before and after ultrasonic disposal 10,000×. (a) Scanning electron micrograph (10,000×) and particle size distribution before ultrasonic treatment. (b) Scanning electron micrograph (10,000×) and particle size distribution after ultrasonic treatment.

5.5. Infrared Spectroscopic Analysis

The interaction between SiO$_2$ particles and asphalt was analyzed by comparing the infrared spectra of nanoasphalt samples before and after ultrasonic treatment to investigate the changes in the molecular structure and internal functional groups of the two after ultrasonic treatment. The Fourier transform infrared (FTIR) spectrometer was used in the wavenumber range of 4000~450 cm$^{-1}$, and the number of scans was 32. Figure 16 shows the infrared spectra of SiO$_2$ nanomodified asphalt before and after the ultrasonic treatment.

As can be seen from Figure 16, the overall absorption spectra of the nano-SiO$_2$ modified asphalt before and after ultrasonic treatment are basically the same, indicating that the effect of ultrasound on the physical mixing between nanomaterials and asphalt is dominated. In the wavenumber range 4000~1300 cm$^{-1}$, the infrared absorption peaks are relatively sparse, mainly caused by the group stretching vibrations of C=C, -CH$_2$-, and C-H. Stronger absorption peaks appear in the infrared spectrum in the range 2800~3000 cm$^{-1}$, which are caused by the C-H vibrations of alkanes and cycloalkanes, with the strongest absorption being -CH$_2$-. The strong and broad absorption peaks at 1096 cm$^{-1}$ are due to the anti-symmetric stretching vibration of Si-O-Si, and the absorption peaks at 797 and 476 cm$^{-1}$ are due to the symmetric stretching vibration and bending vibration of Si-O bond. -O bond symmetric stretching vibration and bending vibration peaks. The peaks at 1454 cm$^{-1}$ and 1601 cm$^{-1}$ decreased after ultrasonic treatment compared with that without ultrasonic,
indicating that the number of aromatic rings decreased with the reaction. Additionally, the peak shape at 1454 cm\(^{-1}\) with ultrasonic treatment was narrower than that without ultrasonic, indicating that the CH\(_3\) ratio changed due to the better compatibility of the two. The enhanced absorption peak at 2800 cm\(^{-1}\) after ultrasonic treatment is mainly caused by the C=C stretching vibration as a double bond with higher bond energy, which is mainly shown macroscopically to improve the mechanical properties of the material. In the functional group region from 2000 to 1500 cm\(^{-1}\), the absorption peaks after ultrasonic treatment are weakened, which is due to the introduction of ultrasonic to change the molecular structure of SiO\(_2\) and asphalt, making the nano-SiO\(_2\) asphalt structure more stable. Therefore, there is both physical mixing and chemical reaction during ultrasonic treatment, and the two have good compatibility.

![Infrared spectra of nanopitch before and after ultrasonic treatment.](image)

**Figure 16.** Infrared spectra of nanopitch before and after ultrasonic treatment.

### 6. Conclusions and Outlook

This paper provides a comprehensive review of the compatibility between nano and asphalt materials using molecular simulations. Both experiments and simulations illustrate that ultrasonic frequency and temperature have a positive correlation effect on the compatibility of nanoparticles in asphalt with asphalt in a certain range. The conclusions are as follows:

1. Accurate molecular structures are the basis of MD simulations, and the choice of force field types and ensembles also plays an important role. Improvements in the molecular structure of asphalt have resulted in more accurate structures that are in great agreement with experimental data of real asphalt for certain properties.

2. The solubility parameters of nano-SiO\(_2\) modified asphalt under different ultrasonic disposal conditions were used as an evaluation index to evaluate the compatibility of nano-modified asphalt. The solubility parameter of the modified asphalt mixture system generally decreased after ultrasonic disposal, indicating that the compatibility between the two increased and the asphalt system is more stable. Ultrasonic treatment can promote the miscibility of nanoparticles in asphalt, however, the frequency of ultrasonic disposal should not be too high, otherwise the effect on promoting compatibility is not obvious.

3. The effect of ultrasound on the compatibility between nanoparticles and asphalt was analyzed using the viscosity increase rate. In agreement with the results of solubility analysis, a relatively small ultrasonic frequency should be selected when the ultrasonic frequency is high.

4. The lower ultrasonic frequency was selected for the viscosity solid test, and it was concluded that ultrasonic waves could promote the compatibility of nanoparticles with asphalt, but the compatibility promotion effect at the ultrasonic frequency of 52 KHz
decreased instead, indicating that the ultrasonic cavitation effect decreased instead with the increase of frequency when the ultrasonic frequency exceeded a certain range. It is consistent with the simulation results, which verifies the accuracy and reliability of the simulation results. It shows that molecular simulation is one of the effective means to analyze the compatibility of asphalt. The best ultrasonic disposal condition was determined by viscosity test as 40 KHz, 403 K.

(5) The nanoasphalt disposed under the optimal ultrasonic treatment conditions were subjected to temperature-dependent analysis, and it was found that the decrease in complex modulus and the increase in phase angle of the nanoasphalt modified with SiO₂ after ultrasonic treatment were due to the viscosity reduction by ultrasonic at this temperature band, which verified the conclusion of the previous viscosity test. The nanoparticles were also analyzed by SEM and IR spectroscopy before and after ultrasonic treatment, and it was found that the nanoparticles were more uniformly dispersed in the asphalt after ultrasonic treatment, and the interaction between them and the asphalt molecules was enhanced.

(6) Molecular dynamics simulations occur on the nanoscale of time, while ultrasonic disposal actually occurs on the macroscale of time. Here, the optimal disposal time cannot be fully obtained if the ultrasonic disposal process is simulated by molecular dynamics model; the four-component asphalt model and the limited number of molecules also cannot fully represent the complex asphalt material. However, molecular dynamics simulation provides a new solution for the prediction of asphalt properties. In the later stage, we can continuously solve these problems to make a closer prediction and further improve the model.

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