Movement behavior of residual oil droplets and CO₂: insights from molecular dynamics simulations

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Abstract

After primary and secondary recovery of tight reservoirs, it becomes increasingly challenging to recover the remaining oil. Therefore, improving the recovery of the remaining oil is of great importance. Herein, molecular dynamics simulation (MD) of residual oil droplet movement behavior under CO₂ displacement was conducted in a silica nanopores model. In this research, the movement behavior of CO₂ in contact with residual oil droplets under different temperatures was analyzed, and the distribution of molecules number of CO₂ and residual oil droplets was investigated. Then, the changes in pressure, kinetic energy, potential energy, van der Waals' force, Coulomb energy, long-range Coulomb potential, bond energy, and angular energy with time in the system after the contact between CO₂ and residual oil droplets were studied. At last, the $g(r)$ distribution of CO₂–CO₂, CO₂–oil molecules, and oil molecules–oil molecules at different temperatures was deliberated. According to the results, the diffusion of CO₂ can destroy residual oil droplets formed by the *n*-nonane and simultaneously peel off the *n*-nonane molecules that attach to SiO₂ and graphene nanosheets (GN). The cutoff radius r of the CO₂–CO₂ is approximately 0.255 nm and that of the C–CO₂ is 0.285 nm. The atomic force between CO₂ and CO₂ is relatively stronger. There is little effect caused by changing temperature on the radius where the maximum peak occurs in the radial distribution function (RDF)- $g(r)$ of CO₂–CO₂ and C–CO₂. The maximum peak of $g(r)$ distribution of the CO₂–CO₂ in the system declines first and then rises with increasing temperature, while that of $g(r)$ distribution of C–CO₂ changes in the opposite way. At different temperatures, after the peak of $g(r)$, its curve decreases with the increase in radius. The coordination number around C₉H₂₀ decreases, and the distribution of C₉H₂₀ becomes loose.

Keywords Tight reservoir · Silica nanopores · Residual oil droplets · Molecular dynamics simulation · Radial distribution function

Introduction

Tight oil, due to its vast reserves, has received great attention from the industry worldwide (Yan et al. 2017a; Zhao et al. 2017; Pu et al. 2020). However, the recovery rate of tight oil is far from satisfactory. To extract residual oil from reservoirs pores and fractures, many recovery attempts (Luo et al. 2021; Sun et al. 2021; Ji and Lee 2019; Du et al. 2021; Ahadi and Torabi 2018) were made using oil displacement agents including nanoparticles, surfactants, N₂, CH₄ and CO₂. The injection of conventional chemicals such as surfactants and polymers, the most commonly used agents in enhanced oil recovery (EOR) technology, has approached its limits due to high replacement costs and the unstable properties of these chemicals in extreme reservoir conditions (Abidin et al. 2012). On the other hand, the miscibility pressure of N₂ and

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crude oil is higher than that of CO₂ and crude oil, thus possibly causing gas channeling. In this regard, injecting CO₂ is considered one of the most promising EOR technology, as it can reduce greenhouse gas emissions through CO₂ sequestration (Jiang et al. 2019; Saira et al. 2020) and thus becomes an environmentally friendly displacement agent. In addition, injecting CO₂ into reservoirs can improve oil recovery through oil swelling, viscosity reduction, interfacial tension reduction, and other mechanisms (Bayat et al. 2015; Jadharwar and Sarma 2012; Cui et al. 2017). Also, injecting CO₂ into the mixed zone with oil increases the microscopic oil displacement efficiency and reduces the residual oil saturation in the swept zone (Amooie et al. 2017). Nonetheless, the research on the movement behavior of residual oil droplets in nano-pores after injection remains inadequate.

To investigate phase behaviors of crude oil at nano-scale, Alfi et al. (2017) designed and made three nano-chip models of different sizes (100, 50, and 10 nm) to study the nano-scale phase changes in hydrocarbon. They discovered that in the 10 nm model, the bubble point temperature of the liquid phase of hydrocarbon was higher than that of itself. The reason for this phenomenon is that the interaction between molecules and solid walls reaches an extreme value that hinders the phase changes in fluid within pores. Other than experiments, some numerical simulations were also conducted, including equation of state (EOS) and molecular simulation, to describe the hydrocarbon phase behaviors in tight reservoirs under nanopores. EOS model can be used to provide reliable descriptions of phase behaviors of complex mixtures and fluid in a large-scale system. Nevertheless, due to the unique thermodynamic properties of confined fluids, conventional EOS is not applicable for phase behaviors calculation in confined space (Zhang et al. 2017). Liu et al. (2017a) used the Peng-Robinson EOS model to explain phase behaviors of pure hydrocarbon C₈ and hydrocarbon mixtures C₁-GN in nanopores, yet the direct transfer of this method presents considerable errors. In comparison, molecular simulation can precisely portray the influence of interaction between liquid and pore wall to phase behaviors of confined fluid, thus revealing its internal mechanism (Liu and Zhang 2019).

Due to the constraints of experimental techniques, especially at nano-scale, the specific displacement process of CO₂ on residual oil droplets in nanopores remains unclear. The study of kinetic models has become the key to the study of some problems (Ghasemi et al. 2021; Seyed et al. 2017). Therefore, the current study aims to fully understand the process in which CO₂ displaces residual oil in nanopores by choosing MD simulation as the tool. This advanced simulation technology is capable of substituting part of experiments and fully demonstrating the dynamic evolution of components in a system. The popularity of this technique has proven its effectiveness as a tool to simulate current

molecular systems including carbon dioxide, octane value, water, silica, and graphene. Numerous simulations were conducted to investigate the interaction between CO₂ and oil compounds in nanopores through MD technology. Yu et al. (2020) studied the contact angle of water and brine as a function of temperature, pressure, salinity, ion type, and gas content by using MD simulation and compared the results with the literature data. Zhao et al. (2020) used molecular dynamics (MD) to simulate the multiphase flow of CO₂ and dodecane in nanopores at different flow rates and overestimated the mass fraction distribution along the flow direction using the Taylor dispersion model. Using the MD method, Luan et al. (2020) conducted a comprehensive simulation of the displacement process of trapped oil in water-bearing stagnant water pores driven by supercritical CO₂ molecules. Li et al. (2020a) simulated the miscible behavior of C₁₀H₂₂(C₇H₁₇N)/C₃H₈ system under high temperature and pressure in silicon pore model through MD simulation techniques. Chang et al. (2021) utilized MD techniques to simulate the oil droplets surrounded by nanofluid in reservoir throat and studied nano-mechanical properties of nano-particle systems with different wettability and local pressure distribution of nano-particle injected along nano-channel. By using the molecular dynamics simulation technique, Lian et al. (2021) studied the intermolecular interactions between crude oil compositions including saturated hydrocarbons, aromatic hydrocarbons, resins, asphaltenes, and amphoteric surfactants 3-(decyl dimethylhydrazone) propane-1-sulfonates (DDPS). From the research mentioned above, it is exemplified that the molecular dynamics simulation technique has been an effective tool to study flow and displacement at the nanoscale (Fang 2019; Fang et al. 2020). MD technology can manage to investigate the interaction between CO₂ and hydrocarbons in nanopores and analyze their properties change after contact.

Because of the complex interaction between CO₂ and crude oil in nanopores in tight reservoirs, residual oil droplets remain in the reservoir after the primary and secondary recovery. In this paper, the molecular dynamics simulation method was used to simulate the interaction between injected CO₂ and residual oil droplets formed in the reservoirs. Then, the movement behavior of CO₂ in contact with residual oil droplets at different temperatures was analyzed, and the molecular number distribution of CO₂ and residual oil droplets was studied. In addition, the changes in pressure, total energy, kinetic energy, potential energy, Van der Waals force energy, Coulomb energy, long-range Coulomb potential, bond energy, and angular energy with time in the system after CO₂ contact with residual oil droplets were investigated. At last, the $g(r)$ distribution of CO₂-CO₂, CO₂-oil molecules, and oil molecules-oil molecules at different temperatures were discussed.

Methods and models

In recent years, the research on the interaction relationship between gas and crude oil molecules in nanopores at different temperature and pressure conditions using the MD simulation method has drawn wide attention. In this paper, a SiO₂ nanopore model was established to simulate the movement behavior of CO₂ gas and C₉H₂₀ petroleum molecules in pores. There are various classical force fields available for selection, including three-site EPM2, SPC/E model, CLAYFF force field, COMPASS (Luan et al. 2020) force field, and OPLS-AA force field (Edgar et al. 2015). Herein, the force field for CO₂ was EPM2, CLAYFF force field was selected for quartz and nonane was modeled using the OPLS-AA force field. The OPLS-AA force field can be known from the full name of OPLS (Optimized predictive for liquid deposition) that this force field applies to the liquid system. OPLS contains two sets of force fields: OPLS-AA (total atomic force field) and OPLS-UA (joint atomic force field, regardless of hydrogen atoms). The common form of the potential function of this force field is as follows [Formula (1)–(6)]:

$$E = (r^N) = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{dihedrals}} + E_{\text{nonbonded}} \quad (1)$$

$$E_{\text{bonds}} = \sum_{\text{bonds}} K_r (r - r_0)^2 \quad (2)$$

$$E_{\text{angles}} = \sum_{\text{angles}} K_{\theta} (\theta - \theta_0)^2 \quad (3)$$

$$E_{\text{dihedrals}} = \sum_{\text{dihedrals}} \left(\frac{V_1}{2} [1 + \cos(\phi)] + \frac{V_2}{2} [1 - \cos(2\phi)] + \frac{V_3}{2} [1 + \cos(3\phi)] + \frac{V_4}{2} [1 - \cos(4\phi)] \right) \quad (4)$$

$$E_{\text{nonbonded}} = \sum_{i>j} f_{ij} \left(\frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} + \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} \right) \quad (5)$$

$$A_{ij} = \sqrt{A_{ii} A_{jj}} \quad \text{and} \quad C_{ij} = \sqrt{C_{ii} C_{jj}} \quad (6)$$

where E is the total energy; E_{bonds} , E_{angles} , $E_{\text{dihedrals}}$, $E_{\text{nonbonded}}$ denote the bonds energy, the angles energy, the dihedrals energy and the nonbonded energy; K_r is a prefactor; r , r_0 are the bond distance and the equilibrium bond distance; K_{θ} is a prefactor; θ , θ_0 are the value of the angle and the equilibrium value of the angle; V_1 , V_2 , V_3 , V_4 are prefactor; ϕ is a degree; f_{ij} represents the depth of the potential well; A_{ij} , C_{ij} represent the distance as which interaction energy of two particles is minimal; r_{ij} is the distance between particles i and j ; q_i , q_j

are the partial charges for particles i and j ; ϵ_0 is the dielectric constant.

The structures of gas molecules, crude oil, and rocks used in the simulation are shown in Fig. 1: (a) nonane (C₉H₂₀), (b) carbon dioxide (CO₂), (c) SiO₂ and its surface modified with hydrogen atoms (SiO₂-H), and (d) graphene nanosheets (GN). C₉H₂₀ molecule was selected as the oleic phase (Wang et al. 2019; Kamal et al. 2015; Buijse et al. 2013), while CO₂ molecule was selected as the gaseous phase.

The molecular dynamics (MD) model was established by combining the molecular structure in Fig. 1. As shown in Fig. 2, the initial miscible system was a rectangular box (25.50 × 100.00 × 162.18 Å³), consisting of oleic phase, gaseous phase, rock surface, and GN. A rock slit with a height of 6 nm was formed in the middle of the rock surface to explore the driving process and microscopic movement details of residual oil droplets caused by CO₂ in nanopores. The GN used in this study are a type of sheet structure, regardless of gravity and charge effect. They were fixed at both ends of the model to ensure the volume of the oleic and gaseous phases remain unchanged. To simulate real geological conditions, a complete hydroxylated silica surface was abstracted to represent the real reservoir pore surface (Koretsky et al. 1998; Li et al. 2020a; Luan et al. 2020; Zhang et al. 2020). In this simulation, SiO₂, SiO₂-H surfaces, and GN were fixed. The non-bonded potential energy was composed of long-range electrostatic interaction and short-range Van der Waals interaction. To ensure higher computational efficiency, the particle–particle particle-mesh (PPPM) solver is used for the calculation of the long-range electrostatic interaction, while for short-term van der Waals interaction the 6–12 Lennard–Jones potential is selected to describe the vdW term (Luan et al. 2020). The Nose–Hoover temperature controller is used to control the system temperature (Zhou et al. 2020).

In this model, the parallel Simulator (LAMMPS) free software package (Mehana et al. 2018; Zhao et al. 2020; Liu et al. 2017b; Yan et al. 2017b) was used and the simulation results were visualized and processed by VMD and Ovito. The structure of each molecule is first optimized, followed by the optimization of the potential energy of the initial configuration. The time step of the entire MD simulation is set to 1 fs. Then, The NVT relaxation of CO₂ and C₉H₂₀ was performed at 323.15, 343.15, 363.15, 383.15, and 403.15 K using the Nose–Hoover thermostat. And the pressure was controlled by the number of CO₂ molecules. The number of molecules in the reservoir was the number of molecules calculated from the gas density at the corresponding pressure and temperature. In this process, a wall was set in-between to isolate CO₂ and C₉H₂₀. After running for a certain duration, C₉H₂₀ started to form residual oil droplets on the SiO₂ surface. During the entire process, the graphene sheets were not involved in the reaction, and

Fig. 1 Molecular structures of **a** C_9H_{20} , **b** CO_2 , **c** SiO_2 -H, **d** GN

Fig. 2 The initial miscible system used in this simulation

MD calculation was performed using an NVT ensemble (constant particle number, volume, and temperature) with data collected within 365 ps.

The pressure during the system operation can be calculated by stress tensor, and the formation pressure can be obtained by the following equation (Fang et al. 2021):

$$P = -\frac{S_{xx} + S_{yy} + S_{zz}}{3V} \quad (7)$$

The stress tensor of an atom can be calculated according to the following equation, where a and b take on values x , y , z to generate the components of the tensor:

$$S_{ab} = -mv_a v_b - W_{ab} \quad (8)$$

The first term is the atomic kinetic energy, and the second term is the energy caused by intermolecular interaction. The specific calculation formula is as follows:

$$\begin{aligned} W_{ab} = & \frac{1}{2} \sum_{n=1}^{N_p} (r_{1a} F_{1b} + r_{2a} F_{2b}) + \frac{1}{2} \sum_{n=1}^{N_b} (r_{1a} F_{1b} + r_{2a} F_{2b}) \\ & + \frac{1}{3} \sum_{n=1}^{N_a} (r_{1a} F_{1b} + r_{2a} F_{2b} + r_{3a} F_{3b}) \\ & + \frac{1}{4} \sum_{n=1}^{N_d} (r_{1a} F_{1b} + r_{2a} F_{2b} + r_{3a} F_{3b} + r_{4a} F_{4b}) \\ & + \frac{1}{4} \sum_{n=1}^{N_i} (r_{1a} F_{1b} + r_{2a} F_{2b} + r_{3a} F_{3b} + r_{4a} F_{4b}) \\ & + Kspace(r_{ia}, F_{ib}) + \sum_{n=1}^{N_f} r_{ia} F_{ib} \end{aligned} \quad (9)$$

The meanings of each term in the above formula are paired energy (N_p), bond energy (N_b), angular energy (N_a), dihedral angular energy (N_d), non-bond energy (N_i), long-range Coulomb interaction (Kspace), and internal binding force (N_f), respectively. Among them, F_1 and F_2 are pairs of forces interacting on two atoms; r_1 and r_2 are the positions of the two atoms in the pairwise interaction.

The process of pressure changes under different temperatures (323.15, 343.15, 363.15, 383.15, 403.15K) can be calculated using the above method to reveal the movement behavior of CO₂ and residual oil droplets after contact.

Results and discussion

The microscopic movement process of CO₂ displacement residual oil droplets

N-nonane molecules were initially distributed in the right half of the quartz slit, while CO₂ molecules were in the left

half of the quartz slit. A wall is set in the middle to separate the n-nonane molecules from CO₂ (Fig. 3a). In the initial system configuration, the GN and SiO₂ were fixed during the simulation. GN functioned to cut off the external migration of CO₂ molecules and n-nonane into the quartz nano-fracture pores (details of the model initial configuration were briefly described in Sect. 2).

Figure 3b shows a snapshot of the system after the 165 ps relaxation balance, from which CO₂ can still be seen evenly distributed in the left half part, while the n-nonane molecules form a residual oil droplet in the lower part of the right. A small number of molecules were absorbed on the upper wall of the quartz slits and the GN on the right-hand side. The atomic number distribution of CO₂ and n-nonane along the horizontal axis (Z direction) of the calcite wall was calculated by using MD to simulate the atomic trajectory after equilibrium, as shown in Fig. 3b'. After equilibrium, a major peak appeared in the near-wall region of the z-molecular number distribution of the n-nonane phase, which indicates that the density of n-nonane is relatively high, and the wall surface of GN has a relatively strong adsorption capacity for n-nonane. In the equilibrium process of 365 ps, n-nonane is adsorbed on the quartz surface after initial relaxation equilibrium. As exemplified by the upper wall surface in Fig. 3b, it can be observed that the n-nonane molecules are absorbed on the quartz surface. As CO₂ molecules start to diffuse to the right side, they diffuse to the adsorbed n-nonane molecules. Then, n-nonane molecules slowly peel off from the quartz surface, forming a CO₂ adsorption layer on the quartz wall (Fig. 3b, c). This phenomenon indicates that CO₂ has a stronger adsorption capacity than n-nonane, and CO₂ can peel off the n-nonane molecules on the quartz surface.

Figure 3b', c' shows the distribution of CO₂ molecules and n-nonane molecules in the 0–16.18 nm slit in 365 ps. After initial equilibrium, CO₂ molecules were evenly distributed in the left half part, but a dense peak of CO₂ molecules occurred near the left graphene due to the adsorption effect of CO₂ molecules by GN. As the simulation progresses, the peak of CO₂ molecular density gradually decreases. The reason behind the phenomenon is that during the simulation process, CO₂ that diffuses into the n-nonane molecule increases the motion space volume of CO₂ and thus reduces the adsorption amount of CO₂ on GN. The maximum adsorption capacities at 165, 185, and 365 ps were 0.0123, 0.0108, and 0.0082/Å³, respectively. In addition, CO₂ was not evenly distributed at 185 and 365 ps. At the moment of 185 ps, with the increase in Z, the molecular number distribution of CO₂ gradually decreases mainly due to the difference in CO₂ concentration in the initial CO₂ diffusion stage. At 365 ps after equilibrium, the distribution of CO₂ molecular number in the right half with n-nonane molecules is larger than that in the left half, mainly because compared

Fig. 3 The microscopic movement process of CO_2 and C_9H_{20} in SiO_2 at a temperature of 363.15 K. **a** The molecular distribution of CO_2 and C_9H_{20} in the initial model; **b**, **b'** Distribution of CO_2 gas and residual oil droplets in pores after equilibrium simulation; **c**, **c'** Distri-

bution of CO_2 and residual oil droplets at the beginning of diffusion; **d**, **d'** Distribution of residual oil droplets on pore surface after CO_2 diffusion

to CO_2 molecule, the n-nonane molecule is classified as a macromolecule with adsorption effect on CO_2 , causing the CO_2 molecular number in the right half to be relatively larger.

After initial equilibrium, from the molecular number distribution map, the n-nonane molecule can be seen forming a residual oil droplet. After CO_2 diffusion, the oil droplets formed by n-nonane are gradually destroyed and eventually distributed in the right half part, which indicates that CO_2 diffusion can destroy the n-nonane residual oil droplets and thus distribute in the system. During the diffusion, n-nonane molecules also diffuse into CO_2 molecules. At 165 ps, the undiffused length to the left of the n-nonane molecule was 9.465 nm and decreased to 9.435 and 5.985 nm at 185 and 365 ps, respectively. In the actual oil-field recovery process, this phenomenon will facilitate the use of CO_2 to recover and thus improve the CO_2 -assisted ultimate recovery.

The effect of temperature on the microscopic movement process of CO_2 displacement residual oil droplets

Energy change characteristics at different temperatures

When the statistical mean of the systematic total energy, temperature, pressure, and other related physical properties become independent of time, it can be assumed that the system reaches equilibrium (Wang et al. 2015). In the CO_2 -crude oil system, the systematic total energy tends to stabilize within a simulation time of 365 ps, and the dynamic equilibrium is realized (Fig. 4b). During the simulation, the pressure, total energy, kinetic energy, potential energy, van der Waals force energy, Coulomb energy, long-range Coulomb potential, bond energy, and angular energy of the system exhibit identical change characteristics at different temperatures, while the initial and final values differ with increasing temperature.

Regardless of macroscopic and microscopic systems, temperature remains one of the key factors affecting the form of matter (Li et al. 2020b; Balogun et al. 2021; Pan et al. 2021). In this paper, the movement behavior of CO₂ and residual oil droplets in the nano-slit model was investigated at different temperatures. With increasing temperature, the pressure, total energy, kinetic energy, potential energy, van der Waals force energy, Coulomb energy, long-range Coulomb potential, bond energy, and angular energy of the system show different degrees of increase (Fig. 4). As shown in Fig. 4a, the initial pressure of the system varies greatly at different temperatures. At 170 ps, the pressure of the system dropped sharply due to the removal of the wall between CO₂ and C₉H₂₀, resulting in a large increase in the space available for CO₂ molecular activity. This phenomenon is also a result of the CO₂ diffusion process into nano-slit and n-nonane, in which CO₂ diffuses and dissolves into n-nonane, thereby reducing the system's overall pressure.

From Fig. 4b, the system can be observed reaching an equilibrium state at 300 ps. From Fig. 4c, it can be seen that the kinetic energy of the system remains constant as there is no external force or additional energy applied to the molecules in the system since the beginning of the simulation. Figure 4d shows the potential energy of the system. In the early stage of CO₂ diffusion, the system's potential energy increases greatly and gradually stabilizes in the later stage. During the diffusion of CO₂, the van der Waals force increases rapidly with the simulation, and then gradually flattens out (Fig. 4e). When CO₂ diffuses, both Coulomb energy and long-range Coulomb energy show different levels of decrease, while on the contrary angular energy and bond energy increases by varying extents (Fig. 4f–i).

Evidently, the diffusion of CO₂ can have different degrees of influence on the system pressure, total energy, potential energy, the van der Waals forces energy, Coulomb energy, long-range Coulomb potential, bond energy, and angular energy. With the increase in temperature, these influences are intensified by different levels. Therefore, recovery through proper use of CO₂ to peel off residual oil droplets can alter the overall system energy change.

Distribution of residual oil droplets at different temperatures

After equilibrium relaxation, n-nonane formed a crude oil droplet at different temperatures (323.15, 343.15, 363.15, 383.15, and 403.15 K) (Fig. 5b1–b5). After CO₂ starts to diffuse, CO₂ quickly fills the right half part where there is no n-nonane molecule. Then, the CO₂ diffuses into the n-nonane (Fig. 5d1–d5). The oil droplets at different temperatures are gradually destroyed, and eventually the residual

oil droplets and CO₂ coalesce. Correspondingly, Fig. 6a–e shows the distribution of CO₂ and C₉H₂₀ molecular number at 323.15, 343.15, 363.15, 383.15, and 403.15 K.

At 323.15 K, the movement behavior of CO₂ recovery on the residual oil droplets in the nano-slit is shown in Fig. 5a1–d1. The simulation results can be used to observe the diffusion of CO₂ into C₉H₂₀ and the movement behavior of C₉H₂₀ at 323.15 K. As shown in Fig. 6a, before equilibrium, CO₂ molecules and C₉H₂₀ molecules are distributed in the left and the right part, respectively. When the simulation reaches 165 ps, while CO₂ molecules remain evenly distributed in the left part, and C₉H₂₀ molecules form a residual oil droplet in the right part. When the time reaches 185 ps, the CO₂ rapidly diffused to the right, and the distribution of CO₂ molecules in nanopores declines along with the increase in z-axis distance. Meanwhile, in the right part, the residual oil droplets formed by C₉H₂₀ were gradually destroyed. With the increase in simulation time, CO₂ molecules diffused into C₉H₂₀ molecules due to the adsorption of C₉H₂₀ on CO₂ molecules. As a result, after simulation equilibrium, the number of CO₂ molecules in the regions with a large number of distributed C₉H₂₀ molecules was relatively high. Then, the residual oil droplets formed in the right part were completely destroyed, and the C₉H₂₀ molecules absorbed on the rock surface were peeled off. The distribution curve of C₉H₂₀ molecules in the region of 0–16.18 nm was relatively flat. With the progress of the simulation process, the molecular adsorption on the left and right sides of GN represented different states with a peak of CO₂ adsorption layer appearing near GN and declining with increasing time. At 165, 185, and 365 ps, the peak values of CO₂ adsorption near GN were 0.0110, 0.0098, and 0.0082/Å³, respectively.

At 343.15, 363.15, 383.15, and 403.15 K, the distribution patterns of CO₂ and C₉H₂₀ molecules are the same as those at 323.15 K (Figs. 5, 6), but the peak value of CO₂ adsorption by GN is different. At 165, 185 and 365 ps, the peak values of CO₂ adsorption near GN at different temperatures were: 0.0120, 0.0110, and 0.0095/Å³; 0.0120, 0.0108, and 0.0081/Å³; 0.0114, 0.0087, and 0.0079/Å³; 0.0112, 0.0088, and 0.0078/Å³, respectively (Fig. 6b–e).

At different temperatures, the final molecular number distribution of C₉H₂₀ molecules in the system varies. The higher the temperature, the farther the C₉H₂₀ molecule diffused to the left at 365 ps (Fig. 6f). At the temperature of 323.15, 343.15, 363.15, 383.15, and 403.15 K, the lengths of regions diffused for the first time are 7.89, 6.12, 5.75, 5.15, and 1.95 nm, respectively, which indicates that higher temperature brings stronger diffusion effect of CO₂ and C₉H₂₀ molecules. Thus, it can be seen that CO₂ has a strong dissolving ability to the residual oil droplets, which allows it to peel off residual oil droplets absorbed on the rock surface.

Fig. 4 Characteristics of change in pressure, total energy, kinetic energy, potential energy, Van der Waal force energy, Coulomb energy, long-range Coulomb potential, bond energy, and angular energy of CO₂ at 323.15, 343.15, 363.15, 383.15 and 403.15 K with time

In this regard, using CO₂ to extract crude oil can effectively remove the residual oil droplets in nano-pores from the rock wall surface, thus improving the oil recovery and the reservoir stimulation performance (Fig. 6).

Radial distribution function

The radial distribution function (RDF) is the most commonly used statistical method for describing molecular systematic structures. It can effectively demonstrate the distribution characteristics of some atom/molecule around one atom/molecule at a certain distance in the system. According

to the literature (Lian et al. 2021; Long et al. 2021; Zhao et al. 2021), the force between gas molecules and C atoms is relatively strong. On this basis, the distribution of CO₂ around CO₂ molecules (Fig. 7a) and C atom in C₉H₂₀ molecules (Fig. 7b) in nanopores at different temperatures were analyzed at a distance of 1.83 nm. The RDF curve between CO₂ and CO₂ and the curve between CO₂ and C atoms in different temperature systems are shown in Fig. 7.

Generally, RDF can be comprehended as the ratio of the density of a region with a radius of R and the average density of the system (Lee et al. 2020). The density of gas molecules around atom C is different from the average density of the

Fig. 5 The microscopic movement process of CO_2 and C_9H_{20} in SiO_2 . **a** The molecular distribution of CO_2 and C_9H_{20} in the initial model; **b** distribution of CO_2 gas and residual oil droplets in pores after equilibrium simulation; **c** distribution of CO_2 and residual oil droplets at the beginning of diffusion; **d** distribution of residual oil droplets on

pore surface after CO_2 diffusion. **a1, b1, c1, d1** at a temperature of 323.15 K; **a2, b2, c2, d2** at a temperature of 343.15 K; **a3, b3, c3, d3** at a temperature of 363.15 K; **a4, b4, c4, d4** at a temperature of 383.15 K; **a5, b5, c5, d5** at a temperature of 403.15 K

system. When the gas molecules are far enough away from the C atom, the region density is approximately equal to the system average density. The $g(r)$ reaching the maximum value means that at the corresponding distance R , the distribution of gas molecules reaches the highest level. At smaller distances, $g(r)=0$, indicating that at this distance, the repulsive force between the gas molecules and the C atoms is strong.

According to Fig. 8, at the stage where $g(r)=0$, the cut-off radius r of CO_2 – CO_2 is about 0.255 nm and C– CO_2 is about 0.285 nm, which evidently shows that the inter-atomic force between CO_2 is strong. When the attraction between gas molecules and C atoms is greater than the repulsive force, the number of gas molecules around C atoms gradually increases. Furthermore, the inter-atomic repulsive force between CO_2 atoms is small but with a large radius.

Fig. 6 Distribution of CO₂ and C₉H₂₀ molecules: **a** 323.15 K; **b** 343.15 K; **c** 363.15 K; **d** 383.15 K; **e** 403.15 K, comparison of C₉H₂₀ molecules distribution: **f** 323.15–403.15 K

Fig. 7 Radial distribution of **a** self-distribution of CO₂ molecules; **b** CO₂ distribution around C atoms in C₉H₂₀

When r is 0.425 nm, the maximum peak of CO₂–CO₂ occurs with a radius of 0.495 nm. With the increase in system temperature, the radius of the peak values of the $g(r)$ distributions of CO₂–CO₂ and C–CO₂ in the system remains

almost constant but with varying peak values. The study shows that temperature has little effect on the radius where the $g(r)$ distribution of CO₂–CO₂ (Fig. 8a) and C–CO₂ (Fig. 8b) reaches its peak. The maximum value of $g(r)$

Fig. 8 Peak values of $g(r)$ at different temperatures, **a** CO₂-CO₂; **b** C-CO₂

Fig. 9 The $g(r)$ distribution diagram of C-C at different temperature

distribution of CO₂-CO₂ in the system decreased at first and then increased with increasing temperature, while on the contrary that of C-CO₂ increased at first and then decreased.

For illustration, Fig. 9 depicts the radial distribution function $g(r)$ of C₉H₂₀-C₉H₂₀ at different temperatures, where r

is the calculated radius of the circle area. The results show that the $g(r)$ curve decreases with the increase in the radius after the peak value at different temperatures, indicating that the coordination number around each C₉H₂₀ molecule decreases and the distribution of C₉H₂₀ becomes loose. It

can be known from this phenomenon that when CO_2 molecules dissolve in C_9H_{20} , the volume of oil in the pores expands. Through analysis of Fig. 9a–e, with the increase in temperature, the CO_2 – C_9H_{20} analysis system takes a shorter time to reach equilibrium. In addition, within the same duration, C_9H_{20} molecules become looser, indicating that temperature has a certain influence on the volume expansion of C_9H_{20} when CO_2 is dissolved in C_9H_{20} .

Conclusions

- (1) CO_2 can destroy the residual oil droplets formed by n-nonane after diffusing into them and thereby distribute in the system. Meanwhile, n-nonane molecules also diffuse into CO_2 . It was found that at 165 ps, the undiffused length of the n-nonane molecule on the left was 9.465 nm and decreased to 9.435 and 5.985 nm at 185 and 365 ps, respectively.
- (2) The density of gas molecules around the C atom differs from the average density of the system. At the stage where $g(r)=0$, The cutoff radius r of CO_2 – CO_2 was about 0.255 nm and that of C– CO_2 was about 0.285 nm, which evidently showed that the inter-atomic force between CO_2 was relatively stronger. A maximum peak appeared at the $g(r)$ of CO_2 – CO_2 when r was 0.495 nm.
- (3) When temperature changes, temperature has little effect on the radius where the $g(r)$ distribution of CO_2 – CO_2 and C– CO_2 appears the maximum peak. The maximum value of $g(r)$ distribution of CO_2 – CO_2 in the system decreases at first and then increases with increasing temperature, while on the contrary that of C– CO_2 increases at first and then decreases.
- (4) When CO_2 molecules dissolve in C_9H_{20} , the volume of oil in the pores expands with the increase in temperature, the CO_2 – C_9H_{20} analysis system takes a shorter time to reach equilibrium. Within the same duration, C_9H_{20} molecules become looser, indicating that temperature has a certain influence on the volume expansion of C_9H_{20} when CO_2 is dissolved in C_9H_{20} .

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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