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RESEARCH PAPER

Molecular dynamics simulation of liquid alkane occurrence state in pores and slits of shale organic matter

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Abstract: Molecular dynamics simulation was used to study the occurrence state of liquid alkane in pores and slits of shale organic matter. On the basis of OPLS (Optimized Potentials for Liquid Simulation) force field, the alkane densities under different pressures and temperatures were calculated; the comparison with experimental results validated the effectiveness of this approach. With *n*-heptane as an example, the basic occurrence behaviors of alkanes in the pores and slits of organic matter were analyzed under formation conditions, and the effects of slit aperture, thermal maturity of organic matter, carbon chain length and isomers were also discussed. Results show that: (1) The density distribution of the alkanes across the pores and slits is not uniform, but presents a periodic fluctuation; (2) A "solid-like" alkane layer will form in the vicinity of the solid surface, and its density approximates to 1.9–2.7 times as large as that of the bulk-fluid; (3) Multiple adsorption layers are always shown for liquid alkanes and the thickness of each layer is 0.48 nm; the total number of adsorbed layers is influenced by the slit aperture and fluid composition. Finally, using this approach, the proportion of adsorbed-phase (18.2%) is determined for oil in an organic matter slit.

Key words: shale oil; organic matter; liquid hydrocarbon; occurrence state; alkane density; adsorption layer

Introduction

The pore space in shale mainly includes intraparticle pores within organic matter (OM), as well as intercrystalline pores, intergranular and intragranular pores related to inorganic matrix (IM)[1–5]. Among these different kinds of pores, organic pores are unique to and an important part of shale storage space. In comparison with other minerals, the interaction between organic matter and liquid hydrocarbons is stronger, so OM has a greater impact on the occurrence state of oil in shale[2,6]. In the present work, molecular dynamics (MD) simulation was employed to study the occurrence behaviors of liquid hydrocarbons in shale organic pores; the effects of pore size, thermal maturity, carbon chain length, and isomers on oil occurrence state were analyzed to provide a new idea and approach for the movability evaluation of shale oil. Because there is no obvious deviation between the static properties of liquid confined in slits and cylindrical pores of the same size[7], slit-shaped pores, instead of circular pores, were used to improve the simulation efficiency. This is also a common practice in current academia[8–9].

1. Force field model for the simulation of alkane occurrence state

Based on Newton's law of motion, molecular dynamics simulates the trajectories of atoms and molecules in multibody systems, from which the ensemble constituted by different states can be statistically analyzed to obtain the structures and properties. The reliability of MD depends on the choice of force field models. However, the force field applicable to different materials are different. For alkanes, the optimized potentials for liquid simulation (OPLS) is taken to describe the interatomic potentials[8,10]. Since the potential parameters in this force field are obtained from matching experimental data, OPLS is of high reliability. This force field includes two types (Fig. 1): all-atom model (OPLS-AA) and united-atom model (OPLS-UA). If OPLS-AA is used for MD simulations, the potential parameters of each atom are required; all the atoms

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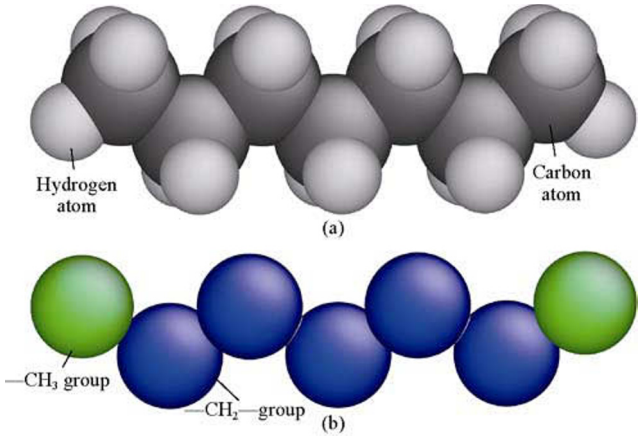

Fig. 1. All-atom (a) and united-atom (b) models for *n*-heptane.

are involved in the computation and move under the interactions of other atoms. However, in the OPLS-UA force field, both the —CH_3 and —CH_2— groups in alkane molecules are regarded as single particles and assigned potential parameters as one subunit; thus, the computation in the simulation would decrease significantly.

The density of *n*-heptane at various temperatures (70–100 °C) and pressures (18–30 MPa) were calculated using both OPLS-AA and OPLS-UA force fields. The computational results were compared with experimental values to pick out the model with better accuracy and higher efficiency. the model selected would be used to simulate liquid alkane occurrence state in shale organic pores and slits. To obtain the liquid alkane density using MD, the all-atom and united-atom models of *n*-heptane were constructed first (Fig. 1). Then the molecular structures were geometrically optimized using energy minimization method to get the steady configuration. After that, a number of optimized *n*-heptane molecules (150 was used here) were placed into a cubic simulation box; meanwhile, the system energy was monitored to prevent the atoms from overlapping or approaching each other. The periodic boundary condition was applied on all the directions of the simulation box. Following the minimization of the total energy, the system was relaxed for 1000 ps under NPT ensemble (constant number of atoms, isobaric, and isothermic conditions) at a time step of 1 fs. The first 500 ps was used to change the size of the simulation box to reach an equilibrium state, and the box sizes in the last 500 ps were collected for data analysis. The density of *n*-heptane at this pressure and temperature can be computed from the arithmetical average of the output values[8]. The simulation results and corresponding computational time under different conditions are summarized in Table 1, in which the experimental values were reported by National Institute of Standards and Technology's (NIST) Chemistry WebBook[11]. During the simulations, the same settings were used for both of the force fields: the cutoff distance of the van der Waals interactions was 1.2 nm, and the nonbonded potential parameters between different species were calculated using Lorentz-Berthelot combining rules. To further improve the computational efficiency, PPPM (particle–particle particle–mesh) algorithm was employed to compute the long-range electrostatic force in OPLS-AA; but for OPLS-UA model, because the —CH_3 and —CH_2— pseudo-atoms are neutral, there is no need to calculate the electrostatic force. All the MD simulations were performed on an 8-core workstation (CPU: i7-4770K) using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) distributed by U.S. Sandia National Laboratory[12].

Table 1 reveals that both the all-atom model and united-atom model can well simulate the property of liquid alkanes; the simulation result using all-atom model is much closer to the experimental value (with a relative error of only 0.169 4%), whereas the relative error of the united-atom model is a little larger (5.174 7% on average). But it can also be found that the computational time of OPLS-UA model is only 1/9 of that consumed by OPLS-AA model. Because the molecule number and time steps required for the study of alkane occurrence state are very large, OPLS-UA force field was used to simulate oil occurrence behavior in shale organic pores and slits. Nevertheless, the present method still applies to all-atom model.

2. Molecular dynamics simulation of alkane occurrence state

2.1. Model construction

The chemical composition of shale organic matter is ex-

Table 1. Comparison of the simulated *n*-heptane densities using different force fields with experimental values.

Temperature/ °C	Pressure/ MPa	Experimental results/(g·cm^{-3})	All-atom model results			United-atom model results		
			Density/ (g·cm^{-3})	Relative error/%	Simulation time/s	Density/ (g·cm^{-3})	Relative error/%	Simulation time/s
70	18	0.661 8	0.662 0	0.040 3	8 518.05	0.697 6	5.422 4	926.87
70	24	0.667 7	0.668 5	0.117 7	8 514.67	0.699 7	4.802 2	976.45
80	24	0.660 5	0.658 8	0.259 6	8 432.27	0.694 9	5.213 2	970.13
80	30	0.666 2	0.666 7	0.065 7	8 498.30	0.700 6	5.156 0	942.30
90	30	0.659 3	0.658 7	0.093 3	8 497.51	0.693 9	5.248 3	988.92
100	30	0.652 4	0.649 5	0.440 0	8 773.45	0.686 4	5.206 1	918.72
Average				0.169 4	8 539.04		5.174 7	953.90