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Original research paper

# Molecular simulation of shale gas adsorption in organic-matter nanopore☆

Tingshan Zhang [a,b,*], Yingjie He [a,b], Yang Yang [a,b], Kunyu Wu [a,c]

[a] State Key Lab of Oil & Gas Reservoir Geology and Exploitation Engineering, Southwest Petroleum University, Chengdu, 610500, China
[b] School of Resources and Environment, Southwest Petroleum University, Chengdu, 610500, China
[c] Institute of Exploration and Development, Qinghai Oil Field, CNPC, Dunhuang, 736202, China

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**Abstract**

Shale gas is a kind of unconventional oil-gas resource with tremendous potential. For thorough understanding of the methane adsorption and micromechanism in organic-matter nanopores of the shale and better acquaintances of the occurrence form, graphite slit-pores were set up as a representation of organic-matter nanopores by using Material Studio, and the grand canonical Monte Carlo method, molecular mechanics and molecular dynamics were used for the simulation of adsorption and diffusion behaviors in organic-matter pores on $CH_4$ and $CO_2$ at the shale gas common burial depth of 2−4 km in the Upper Yangtze Plate. The results indicated that the adsorptions of $CH_4$ and $CO_2$ were physical and the optimal storage depth was 2 km; The mixed adsorption data showed the rationality of exploit shale gas by injecting $CO_2$ to exchange $CH_4$, and the optimal burial depth was 4 km; The relative density of $CH_4$ and $CO_2$ along the normal direction of the pore inwall showed a trend of symmetric distribution and apparent adsorption stratifications appeared. As a whole, the self-diffusion coefficient of $CH_4$ and $CO_2$ increased with the increase of burial depth, and it's consistent with the reasons for such changes of adsorption amount and adsorption heat.


*Keywords:* Organic-matter pores; Adsorption; Diffusion; Carbon nanotube; Molecular simulation; Shale gas

## 1. Introduction

American “Shale Gas Revolution” has met with great success in recent years, having set off a wave of global exploration and development of shale gas [1−3]. Shale gas exists in organic rich mudstone in the form of free state and adsorbed state in most cases, with extensive development of organic nanopores in organic rich mudstone, being the important component of reservoir space for clay shale [4−7], organic porosity size is immediately associated with content of adsorbed gas [8]. Therefore, it is valuable to research adsorption effect of organic nanopores on shale gas and microcosmic mechanism thereof so as to further evaluate shale gas resource [9].

Although research of the influence of characteristic factors of shale including mineral composition and pore structure on adsorption and diffusion pattern of shale gas has been conducted for many years [10−14], the relevant researches of adsorption and diffusion mechanism of shale gas done by molecular simulation method under the condition of special hydrocarbon reservoir for shale gas are inadequate, although Liu et al. [15] adopted molecular dynamic method to simulate similarities and differences in adsorption and desorption of mixture prepared in the different proportions of $CH_4$ to $CO_2$ in

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* Corresponding author. State Key Lab of Oil & Gas Reservoir Geology and Exploitation Engineering, Southwest Petroleum University, Chengdu, 610500, China.

*E-mail address:* zts_3@126.com (T. Zhang).

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carbon nano tube, Cao et al. [16] made research on separation of $CH_4/CO_2$ in CNT different in tube diameter in terms of molecular dynamics, He et al. [17,18] also verified the feasibility to adopt CNT model to simulate dynamical characteristic of adsorption and diffusion of shale gas in organic nanopores of shale reservoir, but failed to analyze and interpret microscopic distribution as well as adsorption and diffusion mechanism of $CH_4$ and $CO_2$ in organic nanopores based on actual burial depth of shale in terms of geological condition and that the burial depth of organic nanopores is a touchstone to determine whether shale stratum block is available for commercial development [9,19].

Therefore, Grand Canonical Monte Carlo method, molecular mechanic method and molecular dynamic method to simulate adsorption effect of organic pores at the burial depth of shale gas [20] from 2 km to 4 km on $CH_4$ and $CO_2$ in Sichuan Basin and surrounding in Early Paleozoic Era (Qiongzhusi Formation, Wufeng Formation and Longmaxi Formation) under the condition that 0 km and 6 km are set as burial depth for reference, that surface temperature is 283 K, that pressure is 0.1 MPa, that geothermal gradient is 30 K/km and that pressure gradient is 15 MPa/km so as to calculate quantity and heat of adsorption in organic pore of shale reservoir at various burial depths and make a study of characteristic of microcosmic distribution, relative density, self diffusion coefficient of $CH_4$ and $CO_2$ in organic pore in shale reservoir and determine preferred burial depth of shale gas and optimal range of burial depth for shale gas available for exploitation $CO_2$ replacement technology so as to guide exploration and development of shale gas to a certain extent.

## 2. Simulation system

### 2.1. Model building and structural optimization

Adsorption effect of organic pore on shale gas is under the influence of many factors including pore shape, 0diameter, maturity of organic matter, category of organic matter and water saturation [21], however, the paper, based on basic research, builds CNT model to represent organic pore under the ideal condition for the first time so as to make a further report on relevant research of complex model (irregular shape, increase and decrease in functional group) to be built under multiple conditions mentioned above in future. CNT is an allotrope of carbon made up of hexagonal grid of carbon atom discovered in 1991, having widely been applied to researches on many fields as a result of its advantages including high specific surface area, corrosion resistance and high chemical stability [22−24].

In recent years, as a type of excellent adsorption material, it has been introduced to hydrocarbon field [17,18]. CNT is high in carbon content, having favorable adsorption effect on $CH_4$ as component of shale gas and being able to adjust tube diameter to nanometer scale, which tallies with the performance of organic nano pore in shale reservoir; in addition, the shale sample from shale gas associated with research area shows that organic nano pores are honeycombed in most cases (Fig. 1). The periodic model of CNT in simulation can be considered as parallel arrangement of the organic pores identical in size, being more consistent with characteristic of organic nanopores compared with graphite slit model; therefore, the paper adopts SWCNT to represent organic nanopore in simulation process. Structure parameter of atom arrangement mode in CNT is indicated as vector $(n,m)$, in case that $n = m$, it is armchair type; in case that $n > m = 0$, it is zigzag type; armchair type and zigzag type CNTs are different in conductivity, in case of serving as an external boundary to restrict internal fluid behavior, there is no difference between the two, the paper selects armchair type CNT for simulation. CNT diameter is as shown in formula (1):

$$d = \frac{a\sqrt{n^2 + m^2 + nm}}{\pi} \tag{1}$$

where a is lattice constant, a = 2.46 Å in CNT.

The paper takes molecular simulation software Material Studio (MS) as operation platform for entire simulation and calculation to build (19,19) armchair type SWCNT to represent organic pore by Single-Wall Nanotube command in Build Nanostructure of Visualizer module, with diameter d = 25.76 Å (the data is based on mean of pore diameters of 56 samples from 5 shale gas wells mentioned in the paper), tube length z = 73.79 Å, and area between SWCNT columnar structures to make up of pore space, and box with lattice parameters $a$ = 29.11 Å, $b$ = 29.11 Å, $c$ = 73.79 Å, $\alpha = 90°$, $\beta = 90°$ and$\gamma = 120°$used for simulation and directions X, Y and Z set to be periodic boundary condition so as to simulate macroscopic system by infinite repeat in space.

Given support and fixation by other part of rock, accordingly, SWCNT model is considered as rigid structure. In order to obtain stable SWCNT model, first, it is advisable to adopt smart of Forcite model in molecular dynamics to carry out configuration optimization of the initially built SWCNT model, with COMPASS force field [25,26] applicable to organic matter model, Ewald method for electrostatic interaction, Atom based method of summation for Van Edward force action, truncation radius of 13.5 Å, tooth width of 1 Å, buffer width of 0.5 Å, convergence precision of Ultra-fine. The stable configuration model for $CH_4$ and $CO_2$ are achieved by the same method (Fig. 2a and c).

### 2.2. Calculation method

Lennard-Jones (LGJ) potential energy model [27] is adopted to simulate interaction between fluid molecule and carbon atom of SWCNT as well as between fluid molecules mentioned in the paper, it is observed from formula (2) that Van Edward force existing between covalent bond molecules can be accurately described by simulation system by introduction of L-J potential function.

$$U(ij) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \tag{2}$$