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Full Length Article

Novel molecular simulation process design of adsorption in realistic shale kerogen spherical pores

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HIGHLIGHTS

- A workflow to model shale kerogen pore using realistic kerogen molecules.
- Visualization of non-uniform adsorbed gas density distribution in kerogen pores.
- Adsorption affinity in kerogen nano-pores decreases as pore size increases.
- Comparison of methane and carbon dioxide adsorption in kerogen pores.

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ABSTRACT

Adsorbed methane in shale organic nanopores is an important factor of the shale gas resource. The major component of shale organic matter, kerogen solids, consists of macro organic molecules and functions as the most important adsorbent. In this work, a novel molecular simulation workflow is proposed to generate organic pores on residue-type kerogen molecules and to simulate the gas adsorption in the pores. The molecular dynamics-based *cutter atom* pore generation method can construct pores with arbitrary shapes and sizes—approaching microscopy observations—2–50 nm shale matrix pores with reasonable physical significance. Grand canonical Monte Carlo simulations for CH_4 and CO_2 are performed on kerogen pores with various pore radii using two categories of molecular potentials. The ensemble averaging density distributions in the pores are calculated and analyzed, which concludes that the free gas state becomes distinguishable from the adsorbed state unless the pore radius exceeds 1 nm. Adsorbed layers at the kerogen pore surfaces are heterogeneous because of non-uniformly distributed adsorptive sites on the surfaces. Adsorption isotherms are simulated and thereafter fitted with the Langmuir equation comparing various molecular models and fluid types. The adsorption affinity indicated by the Langmuir pressure for the total adsorbed molecule number in all cases decreases as a function of increasing pore size.

1. Introduction

Shale gas has become an important part of global natural gas supply since the successful application of hydraulic fracturing and horizontal drilling techniques over the past decade. Understanding the methane storage mechanism in shale reservoirs is crucial to shale gas exploration and development. Typical shale reservoirs consist of fractures and matrices. The fractures, including both artificial hydraulic fractures and natural fractures, are central to the transportation of shale gas. The matrix provides abundant adsorption surfaces, which contributes to the total shale gas reserve. Taken together, the methane fluid in a shale reservoir mainly exists in two states: (1) as the free gas in fractures and pores and (2) as the adsorbed gas on fractures and pore surfaces. The adsorb state accounts for 20–85% [18] of the various shale gas accumulation mechanisms. In a typical shale gas production process, the free gas in fractures and large pores is first to permeate out, corresponding to a rapid production period of a typical length scale of under two years [28]. However, it is the adsorbed gas that dominates the later production process because of the slow desorption kinetics at the small pore surfaces, which limits diffusion from the matrix [35]. Therefore, understanding the adsorption in shale matrices provides insight in: (1) estimating total gas concentration in reservoir evaluation; (2) optimizing the production process design; and (3) developing new methods to enhance the desorption.

The shale matrix is a complicated porous medium, whose components can be classified into two categories: quartz minerals and

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organic matter. The insoluble organic matter in shale, according to Hunt's definition [19], is the origin of oil and gas and is termed *kerogen*. Although inorganic matter such as pyrite, illite and montmorillonite also contribute to the total surface area for shale gas adsorption, it is believed kerogen plays a more important role, because both the adsorbed and free gas contents are significantly influenced by the total organic carbon (TOC) [32,38,33]. The present work focuses on the adsorption in shale kerogen.

The conventional methods to investigate the adsorption behavior of shale gas are mainly found in experimental measurements of shale powder or cutting samples [13,38]. The final results these experiments provide are the isothermal adsorption curves of the sample at various temperatures. The experimental isotherms of shale samples are useful for reservoir evaluation and modeling, however, isothermal data only provide macroscopic information omitting adsorption details at the nanopore surface. Molecular scale computer simulation models, such as Molecular Dynamics (MD) and Monte Carlo simulation are attractive supplements to the macroscopic isothermal measured experiments, as such simulations can visualize the adsorption pattern in nanopores directly and provide additional details that is not possible to obtain by physical measurements alone.

Applications of molecular simulation in the field of adsorption researches is well known. Grand canonical Monte Carlo (GCMC) techniques were invented to improve the understanding of adsorption in microporous media [1,30]. Many investigations relating to gas adsorption and transport properties in shale or coal using molecular simulations are based on simplified solid components and geometries. Ambrose et al. presented a canonical ensemble (NVT)-MD simulation for Lennard-Jones (LJ) type methane in one dimensional carbon slit-pores to observe the fluid density distribution in the slits [3]. Mosher et al. reported GCMC simulations for LJ type methane in carbon slit-pores to calculate the adsorption isotherms [27] in the slits. Liu and Wilcox investigated CO_2 adsorption within the slit-pores of functionalized graphitic surfaces by GCMC simulations [22]. Boţan et al. developed artificial carbon-based spheres having nano and subnano porous structures with LJ potentials to investigate the nano-scale adsorption/diffusion coupled to mass transport [4]. All these works drew remarkable (but qualitative) conclusions on adsorption in carbon structures based on molecular simulations, however, crucially the models do not address the real life organic matter components found in shale or coal. It remains a challenge to model complex porous media such as coal and kerogen directly—the origins of which lie in the complexity of molecular components and structures.

Vandenbroucke reviewed the chemical and physical properties of kerogen and showed that all types of kerogen solids can be reconstructed at the molecular scale with elemental and functional-group analysis provided by pyrolysis, gas chromatograph, mass spectrometry, I.R. spectroscopy and ^{13}C NMR [31]. Combining organic matter molecular reconstruction and various molecular simulation techniques can improve findings on adsorption in shale organic matter. Zhang and LeBoeuf constructed molecules for Green River Shale kerogen and calculated the density and thermal expansion coefficient by MD [37]. Collell et al. provided new models for type II kerogen and analyzed the micropore structure for the solid [9]. Bousige et al. proposed a general kerogen molecule reconstruction method based on the carbon–carbon pair distribution function for all types of kerogen [5]. Together with these efforts on kerogen solid reconstruction, several works have taken the fluid phase into consideration. Collell et al. generated a single pore kerogen having radii from 4 to 7 Å using reconstructed kerogen molecules provided by Yiannourakou et al. and investigated competitive adsorption models in their subnano kerogen pores [34,7]. Falk et al. investigated the non-Darcy type alkanes transport in a kerogen nano-pore structure [11]. Zhang et al. simulated methane adsorption in the natural pores of the coal formed by large organic molecules [36]. Collel et al. studied the transport of a mixture of hydrocarbons through a kerogen membrane by non-equilibrium MD [8]. Compared with organic pores of simplified geometry and solid components, the reconstructed organic molecular-based pore can provide more reliable data of the fluids confined within. Such data, including adsorption isotherms and diffusion coefficients, is essential information for mesoscopic and marcoscopic descriptions of fluid transport in shale [6]. However, in realistic shale samples a large quantity of shale gas molecules preferentially reside in 2–50 nm kerogen pores rather than the natural kerogen subnano pores [23,10]. Revealing the shale gas adsorption and transport mechanism at the molecular scale requires methods to construct arbitrary radii kerogen pores in kerogen solids.

In the present work, We propose a new MD workflow to construct quasi-spherical kerogen pores having arbitrary radii, based on a specific type of realistic kerogen molecule together with its solid structure under typical reservoir conditions (80 °C, up to 20 MPa). This method well defines the pore radius allowing a group of adsorption isotherms to be generated as a function of radii. Additionally, the single component gas adsorption patterns in kerogen pores is presented by applying ensemble averaging on the three dimensional gas density distributions to characterize the adsorption in these nano-confined spaces. Thereafter the distributions are compared with those of regular spherical pores with LJ93 walls [24], which leads to a deeper understanding of the adsorption in kerogen pores with 1–10 nm diameters.

2. Construction of kerogen pores

2.1. Kerogen molecules and solids

Kerogen molecules typically consist of C, H, O, N and S. The molecular weight, elemental composition and molecular topology of kerogen molecules vary in their maturation and burial histories. The reconstruction for a group of kerogen molecules should be based on the experimental results of their molecular weight, elemental composition and functional group spectrum. The kerogen molecule model used in the present work has been reported by Vandenbroucke [31] and Collell et al. [7], which describes the coal-like kerogen sourced from liptinitic at the end of catagenesis. The element ratios are: H/C: ∼0.5, O/C: ∼0.02, S/C: ∼0.005, N/C: ∼0.005. This kerogen type has long maturation and poor methane generation potential, i.e. it is the residue of methane generation and represents a distinct form of shale gas storage, such as Barnett shale [39]. This kerogen model consists of 4–5 polyaromatic clusters bridged by short alkyl chains. The chain length is determined by the H/C ratio since the size of the polyaromatic cluster is composed of a set number of 4–6 benzene rings. Oxygen atoms appear randomly within the clusters or chains. Nitrogen and sulfur atoms exist in heterocycle form. Multiple kerogen molecules are randomly generated and relaxed using MD, with the total elemental ratios matching the target values.

The kerogen solid consists of multiple kerogen molecules. To investigate a typical kerogen solid material, we form a representative zone from previously constructed kerogen molecules, using the MD method with periodic boundaries. Molecules are set in a periodic block initially and then an isothermalisobaric ensemble (NPT) with a constant molecule number, *N*, pressure, *P* and temperature, *T* is simulated using LAMMPS software [29]. The DREIDING force field [26] is used to describe the intermolecular and intramolecular forces in kerogen molecules. The equilibrium kerogen solid yields a density of 1.2 g/cm^3. As pointed by Gasparik et al. [14], the structure and density of the kerogen solid constructed by