



Modeling the density profiles and adsorption of pure and mixture hydrocarbons in shales



Yixin Ma, Ahmad Jamili*

Mewbourne School of Petroleum Engineering, The University of Oklahoma, Norman, OK 73019, United States

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ABSTRACT

The production from shale resources in the US has shifted from the gas window to the condensate and oil windows recently due to the low natural gas price. Liquid-rich shales, such as Barnett, Woodford and Eagle Ford Shales, etc., are brought more attentions than ever before. Therefore, it is critical to understand the fluid phase behavior and their impacts on production in the condensate systems.

Fluid phase behavior in porous media is governed by not only fluid molecule–fluid molecule interactions but also fluid molecule–porous media wall interactions. In the shale formations, a large amount of hydrocarbons are stored within the organic matters where the pore sizes are in the order of nanometers. Inside these nanopores, the interactions between the fluid molecules and porous walls play such an important role that can change the fluid properties of the stored fluids. Our work focused on the predictions of fluid density distributions of both dry gas and liquid rich systems inside nanoporous media. Simplified Local-Density theory coupled with Modified Peng–Robinson Equation of State was used to predict the density profiles of pure and mixture hydrocarbons in confined pores. Adsorption isotherms were generated based on the density profiles calculated. The adsorption isotherms of pure methane and the methane/ethane binary mixture were calculated and compared to experimental data and molecular simulation results in the literature with excellent accuracy.

Our results showed that due to the fluid–wall interactions, the fluid density is not uniformly distributed across the pore width. In general, the fluid density is higher near the porous media wall than that in the center of the pore. It also showed the fluid density profiles are temperature, pressure, pore size and fluid composition dependent. In general, the adsorbed amount increased by increasing pressure and decreased by increasing temperature. The pore size range of interest is from 2 nm to 20 nm. In order to present the condensate system, a binary mixture of 80% methane and 20% n-butane was used. It was found that fluid composition for the fluid mixture was not uniformly distributed across the pore. Heavier component (n-butane) tended to accumulate near the wall while lighter component (methane) would like to stay in the center region of the pore. For the methane/ethane binary mixture, the composition of methane in confined space was found much smaller than the bulk methane composition. For example, the methane composition in confined silicalite is 7% when the bulk methane composition is 50% at 355 kPa and 300 K.

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Introduction

As more development and production activities are involved in shale plays in the North America, the thermodynamics of the fluids in shales draw attention in recent years. It is well known that in typical shale formations especially inside the organic content, the pore throat diameter tends to be in the order of nanometers whereas the molecule sizes vary from a minimum of 0.373 nm for methane to significantly larger values for higher carbon number

hydrocarbons. When the fluids are confined in these nanoscale pores, the molecular interactions are not only restricted to inter-fluid molecular interactions, but also the interactions between the fluid molecules and the pore wall, named fluid–wall interactions. The fluid–wall interactions describe the molecular interactions, such as attraction and repulsion forces between the fluid molecules and the solid molecules from the pore wall. The thermodynamics of the confined fluids become more complicated when the fluid–wall interactions are significant and not negligible. The strength of the fluid–wall interactions depends mainly on the distance between the fluid molecules and the pore wall. The closer the fluid molecules to the wall, the stronger the fluid–wall interactions. Therefore, when the pore size is small, the average distances

* Corresponding author.

E-mail address: ahmad.jamili@ou.edu (A. Jamili).

of the fluid molecules to the pore wall are small enough that the fluid-wall interactions become significant and at the same time the fluid–fluid interactions are weakened. The weakened fluid–fluid interactions shift the critical temperatures and pressures of the confined fluids. This has been observed from both simulation modeling and experimental studies reported in the literature (Thommes and Findenegg, 1994; Zarragoicochea and Kuz, 2002; Voronov et al., 2003; Zarragoicochea and Kuz, 2004; Singh et al., 2009; Zeigermann et al., 2009 and Singh and Singh, 2011). On the other hand, the fluid density is also affected by the fluid-wall interactions. In conventional reservoir formations, where the pore size is large, the fluids are practically uniformly distributed everywhere inside the pore and the fluid density remains constant across the pore under static conditions. However, in shale formations, the fluid density is not uniformly distributed across the pore width since the interactions from the pore wall attract more fluid molecules to the regions near the surface of the pore, forming an adsorbed phase. Known the properties of adsorbed and free fluids are the key to characterize the fluid behaviors in shales.

There have been numerous studies of the phase behavior in confined systems over a long time, especially in physical chemistry area (Sigmund et al., 1973; Udell, 1982; Kiselev et al., 2000; Rajendran et al., 2002; Neimark et al., 2003; Wu, 2006; Monsalvo and Shapiro, 2007; Travalloni et al., 2010a, 2010b). For example, Udell (1982) investigated thermodynamics of phase changes of single and multi-component in porous media. He pointed out that the transition from capillary condensation to thin film adsorption occurs when the liquid pressure becomes negative or when capillary pressure exceeds gas phase pressure. Kiselev et al. (2000) developed a crossover theory for critical and supercritical adsorption of pure CO₂ and SF₆ on silica and graphite systems, respectively. The model was optimized using experimental excess isotherm data to study the surface critical behavior. Travalloni et al. (2010a) developed a new version of the van der Waals Equation of State (EOS) including the square-well potential to study phase behavior of confined pure fluids and mixtures in porous media. Adsorption isotherms of pure fluids (methane, ethane, N₂, H₂, toluene, and 1-propanol) and their mixtures at low pressures (less than 6 MPa) were predicted and validated against experimental data. Although these studies focused more on non-hydrocarbon and/or close to atmospheric temperature and pressure conditions, they provide variety of thoughts and directions to help understand the phase behavior of hydrocarbons in shale formations.

Because of the boom of the unconventional plays, many publications discussing confined phase behavior in shale and coalbed methane have sprung up in the petroleum industry recently. Ambrose et al. (2012) performed molecular dynamic simulations to predict the density distribution of pure methane in nanometer slit graphite pores at 353 K and 21 MPa. Results showed multi-layer adsorption of methane occurred on the graphite walls with width ranging from 1.14 to 3.93 nm. In their later study, Didar and Akkutlu (2013), Monte Carlo simulations were performed to study the fluid behaviors of binary hydrocarbon mixtures (C1/C2 and C1/C3). They found that the fluid molecules of the heavier component preferred to stay in the adsorbed phase. Mosher et al. (2013) used grand canonical Monte Carlo (GCMC) simulations to investigate methane adsorption in micro- and mesoporous carbons. Results showed that methane adsorption loading was highly sensitive to pore size. The maximum methane excess adsorption at 298 K in 0.4-nm size pore was 12.5 times greater than that in the 9.0-nm size pore. These molecular simulation studies, although provide details of fluid behaviors in nanoscale pores, they are computationally intensive, which limits their applications in upscaling processes.

In this work, a numerical model built upon thermodynamic equilibrium relations, named Simplified Local Density (SLD) model

was used to capture the fluid behavior under confinement. The model was first developed by Rangarajan et al. (1995) to study the physical adsorption over large pressure area including the supercritical ranges. In their studies, Van der Waals EOS was used to couple with the SLD model to predict the fugacities and densities of the fluids. More developed EOS, such as generalized Peng–Robinson (PR) EOS and Elliott–Suresh–Donohue (ESD) EOS, were adopted to replace the Van der Waals EOS for better accuracy (Chen et al., 1997; Soule et al., 2001; Wu et al., 2005; Fitzgerald, 2005; Yang and Lira, 2006; Chen, 2007; Mohammad et al., 2009; Chareonsuppanimit et al., 2012). For example, Mohammad et al. (2009) extended the model to a generalized Peng–Robinson EOS and predicted CO₂ adsorption on coals. The two EOS parameters “a” and “b” were modified in the generalized Peng–Robinson EOS. The EOS parameter “a” was modified based on Chen et al. (1997) to consider the effects of interactions between fluid and wall on the internal pressure corrections. The other parameter “b” from Peng–Robinson EOS was generalized based on pure component adsorption data of different fluids on coals. The simulation results of their SLD model were in good match with the adsorption isotherm experimental measurements. In another study by Chareonsuppanimit et al. (2012), they tried both measurements and modeling on new Albany shale samples with N₂, CH₄ and CO₂. They found that the SLD model (coupled with generalized Peng–Robinson EOS) was able to predict the laboratory measurements, with average absolute percentage deviations of 4% and 9% for CH₄ and CO₂ adsorption isotherms, respectively. As we can see in these studies, the SLD model has been applied successfully to predict the adsorption isotherms. However, they did not provide details regarding fluid distributions across the pore, which is important to investigate fluid adsorption behavior, especially for multi component adsorption. In this paper, we focused on the predictions of the fluid density profiles and mixture composition distributions across the slit-shaped pores. From the fluid density profiles we found multi layer adsorption occurred near the pore walls. We also found that for multi component fluids, the heavier component tended to accumulate near to pore wall. This finding is in line with the results from molecular simulation studies published earlier (Didar and Akkutlu, 2013; Wang et al., 2015). By using the SLD model, it is possible to reduce the computational time of fluid confinement modeling significantly compare to molecular simulations, which is necessary for upscaling later on.

Simplified Local Density – Peng Robinson Equation of State Model

Single component model

The fluid density is highest near the pores wall and lowest in the center portion of the pores due to the fluid molecule–pore wall interactions exerted on the fluids inside the pores. This makes the fluid density a function of position with respect to the pore wall, $\rho(z)$, where z is the distance from the nearer solid wall of a slit shaped pore. The SLD-PR model was developed based on the chemical potential equality at any perpendicular position from the pore wall. The model has the following basic assumptions:

- At equilibrium, the chemical potentials at any point inside the pore are the same.
- At equilibrium, at any point where the fluid molecule–pore wall interactions are not negligible, the chemical potential of that point is equal to the summation of chemical potentials resulting from fluid molecule–fluid molecule and fluid molecule–pore wall interactions.
- The pore should have a perfect slit shape, which has uniform width.

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