



The effects of pore geometry on adsorption equilibrium in shale formations and coal-beds: Lattice density functional theory study



Ali Qajar^{*}, Hugh Daigle, Maša Prodanović

Center for Petroleum and Geosystems Engineering, University of Texas at Austin, Austin, TX 78712, United States

HIGHLIGHTS

- Lattice DFT model was extended to cylindrical and spherical geometries.
- Surface energy term of the model was modified.
- N₂ adsorption on different pore sizes and geometries was evaluated.
- The model was verified on synthetic porous media.
- Pore geometry for shale and coal samples was determined using the proposed model.

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ABSTRACT

Textural characterization is a critical step to assess and evaluate petrophysical properties of unconventional reservoirs, including shale-gas, coalbed and tight-gas systems. Gas adsorption, typically with N₂ at 77 K or CO₂ at 273 K, is the widely used method for such characterizations. To translate adsorption data into useful petrophysical quantities such as pore size, pore connectivity, and pore volume, one needs to exploit appropriate correlations to link molecular scale interactions and macro-scale phenomena. One important yet under-studied property of unconventional matrices is their true pore structure and its effects on fluid thermodynamics inside pore space. Herein, based on lattice density functional theory, we have developed a multilayer adsorption model with parameterized energy terms, to determine effects of pore shape and pore size (of shale and coal samples) on the thermodynamic state of reservoir fluid. The model is extended from its original slit pore geometry into cylindrical and spherical geometries to consider the effects of local pore curvature on adsorption energetics and uptakes mainly in mesopores (between 2 and 50 nm). In addition, the surface energy term is modified to consider the effect of the force field exerted by pore walls on both the adlayer and subsequent adsorbed layers. Modification of the energy term resulted in layer-by-layer, two-dimensional condensation followed by the final capillary condensation. The force field exerted by the pore walls together with local pore curvature shifted the condensation pressures toward lower relative pressures (P/P_0). By applying the model to N₂ porosimetry isotherms at 77 K for two reference samples, ordered mesoporous silica (SBA-15) and ordered mesoporous carbon (OMC), the model confirmed essentially cylindrical pore structure for both samples. The model was further applied to N₂ at 77 K porosimetry isotherms of Woodford shale and Cameo coal samples, and identified the pore structures of the samples as dominated by cylindrical and slit pore geometries, respectively.

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1. Introduction

The immense volume of natural gas stored in shale, tight gas and coal bed reservoirs promises them as long-term energy

resources. For instance, recent assessments have confirmed that, in the United States alone, 2400 Tcf of natural gas is stored in unconventional reservoirs [1]. Efficient extraction from these reservoirs requires knowledge about their pore structure, pore connectivity and coordination number, organic content, in situ composition, and maturity. Given the low porosity and low permeability of unconventional reservoirs, their productivity strongly depends on their pore size and pore connectivity. After all, the presence of small pores and throats increases the chance of pore blocking and trapping, all of which lead to low recovery [2–4].

^{*} Corresponding author at: Center for Petroleum and Geosystems Engineering, University of Texas at Austin, Austin, TX 78712, United States. Tel.: +1 814 441 9481.

E-mail addresses: ali.qajar@utexas.edu (A. Qajar), daigle@austin.utexas.edu (H. Daigle), masha@utexas.edu (M. Prodanović).

Quite a few experimental and simulation studies have been conducted to characterize pore structure and chemistry of unconventional reservoirs. This includes kerogen characterization via DRIFTS and NMR, textural characterization using gas adsorption, and development of pore network models to identify effects of pore connectivity on the shape of adsorption isotherms and adsorption–desorption hysteresis [5–11]. Unconventional gas reservoirs can be described as solid pore structures partially filled with organic matter, where the organic matter typically stores the majority of the gas, typically methane. The high organic/inorganic affinity ratio toward methane storage at elevated temperatures can be attributed to the supercritical state of methane and its selective adsorption onto the organic matter. However, when it comes to porosimetry, especially with N_2 at cryogenic temperatures, the condensable state of the adsorbate allows capillary condensation and pore-filling processes to cover all pore sizes ranging from ultra-micropores to macropores. In reservoir porous media, a relatively large portion of the total pore volume includes the void space between inorganic grains with pore sizes above 100 nm, and N_2 adsorption data approaching relative pressures of unity ($P/P_0 \rightarrow 1$) are required for accurate pore texture characterization. BJH, BET and density functional theory (DFT) based models have been widely used for such characterization [7–11]. Variable pore curvature, broad pore size distribution and non-uniform surface chemistry are some examples of non-ideal behaviors that contribute to pore-scale heterogeneities. Each of those models considers some of the contributing factors for such heterogeneities.

Due to the chemical and physical complexity of shale and coal formations, it would be ideal to employ a model that can easily fit experimental data, yet provide the critical information such as adsorption energetics, pore size and state of the adsorbed fluid [12–14]. The lattice DFT model represents a good framework for such analysis, since it defines adsorption at the pore scale as a layer-by-layer process in which molecules at each layer can interact with their neighboring layers, and the adlayer (the adsorbed layer adjacent to the pore wall) can additionally interact with the pore wall [15–17]. The model decouples lateral and surface adsorption energies, while it simultaneously identifies the density profile of the adsorbed layers in thermodynamic equilibrium at given temperatures and pressures. The model was originally developed for slit pore geometry, and did not consider the effects of surface energy on subsequent layers. More recent simulation studies showed that the Steele correlation for slit pores or Powl correlation for cylindrical pores provide more accurate predictions for the energetics of adsorption processes [18,19]. Herein, to consider the effects of pore curvature on adsorption equilibrium we extend the model to cylindrical and spherical pore structures. In addition, we propose a simple correlation to modify the surface energy term by extending its domain of interaction from the adlayer to subsequent layers.

2. Experimental

Four samples (shale, coal, synthetic carbon, and synthetic silica) were characterized in this study. All samples were classified as mesoporous because the majority of their pore volume comes from pores with sizes in the range of 2–50 nm. Still, the samples possessed notable micropore volume with pores below 2 nm size (As shown in Table 2, portion of micropore volume is ~7, 14, 30 and 20 vol% for shale, coal, synthetic carbon and synthetic silica samples, respectively). Natural samples included organic-rich Woodford shale (Upper Devonian, Oklahoma) and Cameo coal (Cretaceous, Colorado) with total organic carbon (TOC) of 17.2 wt% and 69.9 wt%, and vitrinite reflectance values of 0.58 and 0.56% R_o , respectively [20]. The synthetic samples included ordered

mesoporous carbon (OMC) derived from polymerization of phloroglucinol, and ordered mesoporous silica (SBA-15) with hexagonal pore structure [21,22]. The mean pore sizes of the synthetic carbon and silica samples were 9 and 8 nm, respectively.

Textural properties of the shale and coal samples were determined by standard N_2 adsorption at 77 K using a Micromeritics 3Flex Surface Characterization Analyzer instrument. Pore size distributions of the samples were determined by applying the BJH model to the adsorption branch of the N_2 uptake data. Micropore volumes of the samples were calculated from N_2 uptake at $P/P_0 = 0.14$, corresponding to pore-filling of pores 2 nm in diameter in the Horvath–Kawazoe (HK) model. Total pore volume was determined from N_2 adsorption uptake at $P/P_0 = 0.99$ [23]. Meso–macro pore volume was obtained by subtracting micropore volume from total pore volume.

3. Model development

3.1. Lattice DFT model

The lattice DFT model decouples surface interaction (the interaction energy between adsorbent and adsorbate) from lateral interaction (the interaction energy between adsorbate molecules). This allows us to consider inter-adsorbate interactions that will lead to two-dimensional and capillary condensation processes [16]. In one-dimensional adsorption, the model simulates the adsorption phenomenon as a layer-by-layer site-oriented process, in which any site can be filled with an adsorbed phase of a specific density, independent of the state of the other layers. Fig. 1a shows a schematic of the lattice of adsorption sites, where x_i shows the occupation density of the i th layer, x_b is the occupation density of a site in the bulk phase, E_0 is the surface interaction energy between the first adsorbed layer (adlayer) and the pore wall, and E_A is the lateral interaction energy between the adsorbate molecules. The occupation density is the probability of the site being filled, and can therefore only be a value between 0 and 1.

x_b corresponds to the gas phase pressure while E_A and E_0 are energy parameters. The equilibrium condition between the gas phase and the adsorbed phase requires the Gibbs free energies of the phases to be equal. To find x_i , for each adsorbed layer in slit pore geometry one can write the equilibrium equation as follows [16]:

$$RT \ln \frac{x_i(1-x_b)}{x_b(1-x_i)} - E_A(z_2x_2 + z_1x_1 - z_bx_b) - E_0 = 0 \quad (1a)$$

$$RT \ln \frac{x_i(1-x_b)}{x_b(1-x_i)} - E_A(z_2x_{i-1} + z_2x_{i+1} + z_1x_i - z_bx_b) = 0 \quad (1b)$$

$$RT \ln \frac{x_N(1-x_b)}{x_b(1-x_N)} - E_A(z_2x_{N-1} + z_1x_N - z_bx_b) - E_0 = 0 \quad (1c)$$

where z_b is the 3-dimensional coordination number in the bulk phase, z_1 is the 2-dimensional coordination number in each adsorbed layer, and $z_2 = (z_b - z_1)/2$ is the coordination with each of the adjacent layers. z_2 and z_1 are taken as 6 and 4, respectively. Since the first and the last adsorbed layers, i.e. 1 and N , are adjacent to the pore walls, they serve as the boundary conditions with additional surface energy term E_0 . In all equations, the first term represents changes of entropy while the other terms express enthalpic changes during adsorption. The Gibbs excess adsorption is expressed as the difference between the densities of the molecules in the adsorbed phase vs. that of the molecules in the gas phase, as follows:

$$\Gamma/C = \sum_i (x_i - x_b), \quad (2)$$

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