Adsorption of simple square-well fluids in slit nanopores: Modeling based on Generalized van der Waals partition function and Monte Carlo simulation

Lingli Kong, Hertanto Adidharma *

Department of Chemical Engineering, University of Wyoming, Laramie, WY 82071-3295, USA

HIGHLIGHTS

- Adsorption model based on Generalized van der Waals partition function is proposed.
- Closed-form expressions of the chemical potentials of confined fluid are obtained.
- Square-well fluid adsorption in slit square-well pores of any size is well predicted.
- Effects of bulk conditions and properties of adsorbate and pore are well captured.

ARTICLE INFO

ABSTRACT

A model based on the Generalized van der Waals partition function is derived to predict the adsorption of square-well fluid in slit pores of any size, the walls of which also have square-well potential. The space inside the pore is divided into several regions based on the extent of the attractive regions generated by the walls. Closed-form expressions of the chemical potentials of the confined fluid in different regions in the pore are obtained. The densities of fluid in different regions are calculated by equalizing the chemical potentials of fluid in those regions to that of the bulk phase. To examine the accuracy of the model, the Grand Canonical Monte Carlo (GCMC) simulation is also conducted. We find that the model well captures the effects of the bulk conditions and the properties of adsorbate and pore on the density of adsorbate in the pore. The model is also shown to be able to predict the adsorption of real gases in various activated carbons.

1. Introduction

Slit-like geometry is one of the most important pore shapes of adsorbents. Some activated carbons such as activated carbon fibers, which are important adsorbents, have been proven to have slit pores (Kaneko et al., 1992). In a recent study, it was also demonstrated that activated carbons having a wide pore size distribution (PSD) were very likely to have a mixture of pore geometries, and a PSD based on a mixed slit-triangular pore model was shown to better capture the adsorption isotherm and energy (Azevedo et al., 2010). Before such a mixed geometry pore model can be implemented, methods that can be used to describe the adsorption behavior in common pore geometries of different sizes have to be developed. Due to the importance of slit pores, as our

first attempt, in this work, we consider the adsorption of fluids in slit pores.

Molecular simulation is one of the most commonly used methods to predict the adsorbed amount of adsorbate in slit-like pores. A lot of works have been dedicated to the prediction of adsorption using computer simulation, in which some important simulation methods were developed. The most widely used simulation method for adsorption is the Grand Canonical Monte Carlo (GCMC) simulation (Wang and Karl Johnson, 1999; Kaneko et al., 1994). Kinetic Monte Carlo (kMC) and Meso-Canonical Ensembles (MCE) simulation methods have also been used to study argon adsorption in slit pores of open-end, closed-end, and closed pores (Phadungbut et al., 2015; Fan et al., 2014; Phadungbut et al., 2016).

In the molecular simulations of adsorption, several potential models, such as hard sphere/wall, Lennard-Jones, and square-well potentials, have been used to describe the adsorbate-adsorbate and adsorbate-adsorbent interactions. In this work,

* Corresponding author.
  E-mail address: adidharm@uwyo.edu (H. Adidharma).

those interactions are described using square-well potentials to make them consistent with the interaction potential used in the bulk phase; to describe the properties of the bulk phase, we use a version of Statistical Associating Fluid Theory (SAFT), i.e., SAFT2, which has been proven to describe square-well fluids very well.

In the adsorption simulation of square-well fluids in slit pores, researchers put more focus on the properties of confined fluid rather than the adsorbed amount. A calculation method, referred to as the virtual-parameter-variation method, was applied to an NVT simulation to obtain the spreading pressure and the phase equilibrium properties of square-well fluid confined in hard planar slits (Vörtler and Smith, 2000). An NVT simulation was also used to estimate the vapor-liquid coexistence and critical properties of square-well fluids when the dimensionality of the fluids was decreased from three to two by decreasing the hard wall separation distance, i.e., from bulk fluid to a planar monolayer of molecules (Vörtler, 2008). Another simulation method, i.e., the Grand Canonical Transition Matrix Monte Carlo (GC-TMMC) with fourth-order Binder cumulant and a simplified scaling law, was applied to estimate the critical point of the adsorbed square-well fluid on square-well walls (Singh and Singh, 2013). Gibbs Ensemble Monte Carlo (GEMC) simulation was also used to explore the properties of square-well fluid inside slit pores with symmetrical (two hard walls) and non-symmetrical (one hard wall, one square-well wall) wall potentials (Del Pino et al., 2003).

Molecular simulation offers us a convenient way of understanding the adsorption behavior of fluids or fluid properties in the pore. Yet performing simulations to collect data still takes time, especially when the adsorbent has a very wide PSD, and the results are usually limited to certain adsorbents and adsorbates. Theoretical models, on the other hand, can provide us with the prediction of the properties and behavior of various adsorbate-adsorbent systems in a relatively very short time. For adsorption in slit pores, Density Functional Theory (DFT) is one of the most important theories for developing adsorption models (Nguyen and Bhatia, 2004; Ravikovitch et al., 2001; Lastoskie et al., 1993). The theory is able to provide the detail of the local density within the pore. However, simpler theoretical or analytical models, in the expense of some information loss, could still be appealing. For square-well fluid adsorption in slit-like pores, the walls of which also have square-well potential, theoretical modeling poses different challenges because of the discontinuity of the potentials, which can make the wall-affected regions change considerably when pore width changes from only one layer of molecules to macropore size. A 1-D analytical model that could deal with the adsorption of square-well fluids confined to a 1-D pore was developed (Monson, 1990; Heuchel, 1997), but its extension to 3-D fluids is not obvious, if not impossible.

Another promising approach to describe adsorption is to use equations of state. The Statistical Associating Fluid Theory (SAFT) equations of state (EOS) for bulk square-well fluids have been developed and tested to various real fluids. To extend SAFT to describe the adsorption of square-well fluids on surfaces, 2D-SAFT has been developed (Martinez et al., 2007; Castro et al., 2010; Castro et al., 2012; Castro and Martínez, 2012). By assuming that the pair interaction between particles was different for the adsorbed and bulk phases, the quasi-2D approach was shown to be a valid approximation when the formation of well-defined layers was observed, i.e., when the attractive potential of the wall-fluid interaction is much higher than that of the fluid-fluid interaction. Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) coupled with Young–Laplace equation was also proposed to investigate and represent fluid-phase equilibria in nanopores (Tan and Piri, 2015). The approach, however, is not intended to describe the adsorption process prior to condensation. Travalloni et al. developed the extended van der Waals EOS for confined fluids in cylindrical pores based on the Generalized van der Waals Theory (Travalloni et al., 2010). By empirically defining the free volume, the coordination number, and the local distribution of the molecules inside the pore, their model seemed to work well and was shown to fit some experimental data. Schoen and Diestler developed a van der Waals-type EOS for LJ fluid based on the thermodynamic perturbation theory. However, the EOS was verified only for mesoscopic pores (Schoen and Diestler, 1998).

As indicated earlier, since the pore size may vary in a certain adsorbent, it is necessary to obtain a model that can predict the adsorbed amount of adsorbate in different sizes of nanopores, including micropores (less than 2 nm), mesopores (2–50 nm), and macropores (>50 nm). If we have the pore size distribution of the adsorbent, we can then predict the total adsorbed amount of adsorbate. For slit-like pores with square-well potential, the wall-affected regions will overlap when the pore is very narrow, which makes it difficult to obtain a single equation that works for all pore sizes.

In this work, we develop a model to describe the density, and thus the adsorbed amount, of confined square-well fluids in slit pores with square-well potential walls. Our approach is also based on the Generalized van der Waals Theory, but without introducing any empirical correlations. Not only can our model be applied to various square-well adsorbates and adsorbents, but it can also overcome the difficulty of adsorption prediction when the pore is so narrow that the wall-effected regions overlap. We also perform GCMC simulation, the results of which are used to verify the model. The model is then used to predict the adsorption of real gases in various activated carbons.

2. Simulation

In this work, we employ GCMC method to simulate the adsorption of spherical molecules in slit-like pores. The molecule-molecule interaction u_{mm} and the molecule-wall interaction u_{mw} are both modeled by square-well potentials. If the adsorbed molecule has a diameter of σ, the molecule-molecule interaction is:

$$u_{mm} = \begin{cases} +\infty & r_{mm} < \sigma \\ -\varepsilon & \sigma \leqslant r_{mm} < \lambda\sigma \\ 0 & r_{mm} \geqslant \lambda\sigma, \end{cases} \tag{1}$$

where r_{mm} is the center-to-center distance between two molecules, $\lambda\sigma$ is the range of the potential well, and ε represents the attractive potential of the molecule-molecule interactions. The molecule-wall interaction is given by:

$$u_{mw} = \begin{cases} +\infty & r_{mw} < \frac{1}{2}\sigma \\ -\varepsilon_p & \frac{1}{2}\sigma \leqslant r_{mw} < \frac{1}{2}\sigma + \delta_P \\ 0 & r_{mw} \geqslant \frac{1}{2}\sigma + \delta_P, \end{cases} \tag{2}$$

where r_{mw} is the distance between the center of a molecule and the surface of the wall, δ_p is the width of the region where the adsorbed molecule would be attracted to the pore wall, and ε_p represents the attractive potential of the molecule-pore wall interactions.

The GCMC simulation is performed in a box bounded in the z direction by the pore walls separated at a distance of W_p. The box lengths in the x and y directions (L_{xy}) are the same, the magnitude of which is adjusted such that the number of molecules at equilibrium is in the range of 100–200. Periodic boundary conditions and minimum image convention are employed in both x and y directions. The temperature T inside the pore is set equal to that of the bulk phase outside the pore. The simulation starts with a few molecules placed in the simulation box in a lattice configuration. In the GCMC scheme, there are two types of trial moves: (1) translation move of a randomly selected particle and (2) inser-