

Adsorption behaviors of supercritical Lennard-Jones fluid in slit-like pores

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ABSTRACT

Understanding the adsorption behaviors of supercritical fluid in confined space is pivotal for coupling the supercritical technology and the membrane separation technology. Based on grand canonical Monte Carlo simulations, the adsorption behaviors of a Lennard-Jones (LJ) fluid in slit-like pores at reduced temperatures over the critical temperature, $T_c = 1.312$, are investigated; and impacts of the wall-fluid interactions, the pore width, and the temperature are taken into account. It is found that even if under supercritical conditions, the LJ fluid can undergo a “vapor-liquid phase transition” in confined space, *i.e.*, the adsorption density undergoes a sudden increase with the bulk density. A greater wall-fluid attractive potential, a smaller pore width, and a lower temperature will bring about a stronger confinement effect. Besides, the adsorption pressure reaches a local minimum when the bulk density equals to a certain value, independent of the wall-fluid potential or pore width. The insights in this work have both practical and theoretical significances.

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1. Introduction

After Semenova et al.'s pioneering work on separating H_2O from ethanol by coupling the supercritical technology and the membrane separation process [1], such a coupling technology has attracted great attentions in chemical engineering [2–10]. However, it is still difficult to explain the process of how the supercritical fluid permeates through the porous membrane and to predict the behaviors of a confined supercritical fluid even if its bulk properties are completely known [11]. This is mainly due to the fact that thermodynamic and structural properties of a confined fluid are very different from, and often much richer than, those of its bulk counterpart.

It is difficult to investigate the properties of a confined fluid using experimental techniques; therefore, many theoretical and simulation studies have been carried out on this issue. Density functional theory is powerful when studying the thermodynamic properties of a confined fluid; by using this theory, simple fluids near a wall (*e.g.*, LJ fluid [12], Yukawa fluid [13], *etc.* [14]),

electrolyte in a charged cylinder pore [15], and Yukawa fluids in a slit-like pore [16–19] have been studied on their adsorption and structure properties. On the other hand, Gibbs ensemble Monte Carlo simulation is a widely used method in studying the phase behaviors of fluid. With this method, the vapor-liquid phase equilibria of several LJ binary mixtures confined in slit-like pores have been investigated [20,21]. Lastly, Grand canonical Monte Carlo (GCMC) simulation is noted for investigating the adsorption behaviors of fluid in confined space. For instances, the confined phase transition of water as well as water/ethanol mixture has been explored using GCMC simulation [22,23]; and via GCMC simulations, a LJ liquid in a slit-like pore [24–27] and a cylinder pore [24,25] have been studied on its adsorption properties. However, few researches has focused on the properties of supercritical fluid in confined space. As far as we know, only Do and Do [28] has studied the adsorption density of subcritical and supercritical LJ fluid in slit-like pores by GCMC simulation. There is still no investigations on other adsorption properties of supercritical fluid, like the adsorption pressure and adsorption enthalpy. This gives rise to a conspicuous drawback in our knowledge of supercritical fluid, and hence requires further study and efforts.

In this work, supercritical LJ fluid in slit-like pores were

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investigated by GCMC simulations on the aspects of adsorption densities, adsorption pressures and adsorption enthalpies. Their variation with the increase of bulk density were studied; meanwhile the impacts from the pore size, wall-fluid attractive potential, and temperature were taken into account. The adsorption density undergoes a sudden change at a certain bulk density; which implies that even under supercritical conditions, the LJ fluid can also undergo a vapor-liquid phase transition in the confined space.

2. Model and simulation details

The model of LJ fluid confined in a slit-like pore is illustrated in Fig. 1. The fluid-fluid intermolecular interaction is described using a Lennard-Jones (12–6) potential,

$$u(r) = \begin{cases} u^{LJ}(r), & r < r_{cut} \\ 0, & r \geq r_{cut} \end{cases} \quad (2.1)$$

$$u^{LJ}(r) = 4\epsilon_f \left[\left(\frac{\sigma_f}{r} \right)^{12} - \left(\frac{\sigma_f}{r} \right)^6 \right] \quad (2.2)$$

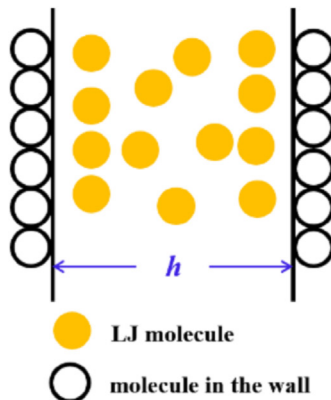
where r is the intermolecular distance, r_{cut} is the cut-off radius which is set to $5\sigma_f$, σ_f is the diameter of the fluid molecule, and ϵ_f is the energy parameter of the LJ fluid molecule.

The pore width is represented by h , and the area of the slit wall is set to $20\sigma_f \times 20\sigma_f$. Interaction between one wall and one fluid molecular is calculated using a Lennard-Jones (9–3) potential,

$$\phi(z) = \frac{2}{3} \pi \rho_w \sigma_{wf}^3 \epsilon_{wf} \left[\frac{2}{15} \left(\frac{\sigma_{wf}}{z} \right)^9 - \left(\frac{\sigma_{wf}}{z} \right)^3 \right] \quad (2.3)$$

where z is the perpendicular distance from a fluid molecule to the wall; ρ_w is the surface number density of molecules in the wall; ϵ_{wf} and σ_{wf} are the energy and size parameters for the wall-fluid interaction, which can be further obtained from the Lorentz-Berthelot mixing rules $\epsilon_{wf} = \sqrt{\epsilon_w \epsilon_f}$ and $\sigma_{wf} = 0.5(\sigma_w + \sigma_f)$. Subscripts w and f denote the wall and the fluid, respectively. Here, we suppose the molecules in the wall have the same size as the fluid molecule; and for concise, we define a quantity $\theta = \frac{2}{3} \pi \rho_w \sqrt{\epsilon_w \sigma_w^3}$ to describe the property of the wall. Therefore, Eq. (2.4) is rewritten to

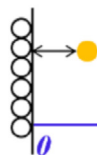
$$\phi(z) = \theta \sqrt{\epsilon_f} \left[\frac{2}{15} \left(\frac{\sigma_f}{z} \right)^9 - \left(\frac{\sigma_f}{z} \right)^3 \right] \quad (2.4)$$



Fluid-fluid interaction

$$u^{LJ}(r) = 4\epsilon_f \left[\left(\frac{\sigma_f}{r} \right)^{12} - \left(\frac{\sigma_f}{r} \right)^6 \right]$$

Wall-fluid interaction



$$\phi(z) = \frac{2}{3} \pi \rho_w \sigma_{wf}^3 \epsilon_{wf} \left[\frac{2}{15} \left(\frac{\sigma_{wf}}{z} \right)^9 - \left(\frac{\sigma_{wf}}{z} \right)^3 \right]$$

As one slit-like pore has two walls, the external potential for a fluid molecular confined in it should be:

$$V^{ext}(z) = \phi(z + 0.5\sigma_w) + \phi(h - z + \sigma_w) \quad (2.5)$$

GCMC simulations are implemented to study the adsorption behaviors of the supercritical LJ fluid in slit-like pores. Dimensionless quantities, $T^* = k_b T / \epsilon_f$, $\rho^* = \rho \sigma_f^3$, $h^* = h / \sigma_f$, $\mu^* = \mu / \epsilon_f$, $P^* = P \sigma_f^3 / \epsilon_f$, $q^* = q / \epsilon_f$, and $\theta^* = \frac{2}{3} \pi \rho_w \sqrt{\epsilon_w / \epsilon_f}$ are used for convenience, where k_b is the Boltzmann constant, and q is the adsorption enthalpy. The impacts from the wall-fluid potential, $\theta^* = 0.0, 5.0, 10.0, 15.0$, and 20.0 , the pore width, $h^* = 5.0$ and 10.0 , and the temperature $T^* = 1.5$ and 3.0 are investigated in detail. For a LJ fluid, the reduced critical temperature is $T_c^* = 1.312$.

Excess chemical potential is a necessary input parameter; however, it is not a directly measurable quantity. In this study, we try to link the properties of the LJ fluid confined in slit-like pores to a measurable quality of its bulk counterpart. Therefore, the excess chemical potential needed for the GCMC simulations is calculated based on the bulk density, using the modified Benedict-Webb-Rubin (MBWR) equation [29]. The obtained values for bulk LJ fluid under given temperatures and densities are given in Table 1, where the pressures of the bulk fluid were also calculated.

The pressure of the adsorbed fluid, P_{pore} , is calculated from the virial components paralleling to the wall in our GCMC simulations,

Table 1

The μ_{exc}^* and P_{bulk}^* of bulk LJ fluid under given temperatures and densities.

ρ_{bulk}^*	$T^* = 1.5$		$T^* = 3.0$	
	μ_{exc}^*	P_{bulk}^*	μ_{exc}^*	P_{bulk}^*
0.01	-0.0746525	0.01	-0.0132400	0.03
0.03	-0.2196246	0.04	-0.0346130	0.09
0.05	-0.3594689	0.07	-0.0486680	0.15
0.10	-0.6890141	0.12	-0.0543040	0.30
0.20	-1.2553000	0.18	0.0642477	0.62
0.30	-1.6762600	0.23	0.3967419	1.00
0.40	-1.9382000	0.29	1.0373850	1.53
0.50	-1.9830400	0.42	2.1364650	2.33
0.60	-1.6315000	0.77	3.9043980	3.61
0.70	-0.5995900	1.60	6.6009580	5.67
0.80	1.4320070	3.28	10.5298300	8.93
0.85	2.9419220	4.60	13.0714100	11.18
0.90	4.8678780	6.36	16.0738300	13.96
0.95	7.2852870	8.68	19.6030200	17.37
1.00	10.2516700	11.65	23.7259800	21.55

Fig. 1. Schematic diagram of LJ molecules adsorbed in a slit-like pore; and models for the fluid-fluid and wall-fluid interactions.

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