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Structure of liquid–vapor interface of square well fluid confined in a cylindrical pore

Yuri Reyes-Mercado*, Pedro Orea, Simón López-Ramírez, Yurko Duda

Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México D.F., Mexico

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ABSTRACT

By means of the canonical Monte Carlo simulations, the vapor–liquid (VL) equilibrium and structure of square well (SW) fluids confined in a single cylindrical pore with repulsive surface, have been studied. Coexistence curves of the confined VL interface are determined for a wide range of temperatures and pore diameters. It is demonstrated that the confinement not only reduces the VL coexistence region but also induces strong inhomogeneities of the VL interface: coexistence liquid densities are different at the pore center and at the wall surface. It may be considered as a preliminary step for an isolated droplet formation inside the pore, as well as a tentative reason of the two VL phase transitions of simple fluids adsorbed into disordered porous media.

1. Introduction

Behavior of confined simple fluids has been of great interest from both technological application [1–4] and fundamental science points of view [5–9]. Some examples of confining structures include micropores and nanopores in rocks, micelles, nanotubes, protein membrane channels, among many others. General trends of confinement effect have been investigated by means of statistical mechanics approaches which comprise integral equations [1,6,8–10] and density functional theories [1,11–13]. These approaches, as well as computer simulation techniques [1,3,9,14–18], have been successfully applied for the calculation of adsorption, structural properties and phase stability conditions of confined model fluids. To study a fluid confined in disordered porous media some pore models of simplified geometry like slits, cylinders, and spheres have been applied [3,6,9,15–17]. Besides, in many modern technological processes one needs to define the properties of nanoparticles (size, morphology, interaction between particles and with the substrate, etc.) confined into geometrically well-defined nanopores [4,19–21]. In such cases, the confined fluid behavior is crucially affected by the limited space and particle concentration at interfaces.

In the present work we consider a square well (SW) fluid confined into cylindrical pores of different diameters. The square well pair potential somehow reflects real molecular interactions and is more flexible to deal with than others such as the Mie potentials, for example. In some cases, such as colloid and cluster particles, the SW potential or its shrinking form, sticky hard spheres, are the usual models to work with [22]. Although, there have been a lot of studies devoted to the bulk structure and phase behavior of SW fluids [23–27], only few publications have reported the properties of confined SW fluids [28–32]. By applying canonical Monte Carlo (MC) simulation we attempt to establish correlations between structural and vapor–liquid (VL) interfacial properties of fluids confined into a cylindrical pore.

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* Corresponding author. Tel.: +52 55 9175 8269.
E-mail addresses: yurirm@lycos.com (Y. Reyes-Mercado), yduda@lycos.com (Y. Duda).

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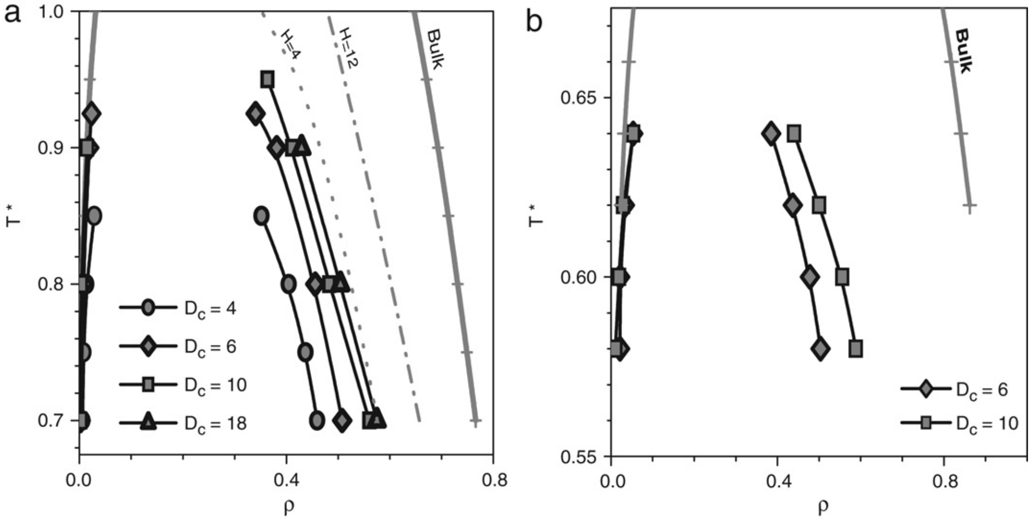

Fig. 1. (a) VL coexistence curve of the SW fluid ($\lambda = 1.5$) in the bulk [25], confined inside cylindrical pores of different diameters (symbols) and slit-like pores [38] of width $H = 4$ and $H = 12$ (grey lines); (b) VL coexistence diagram for the SW fluid with $\lambda = 1.25$ confined in cylinders of different diameters and the bulk system from Ref. [24]. The error bars, in the present and following figures, do not exceed the symbol size.

2. Potential Model and simulation details

The square well potential is given by

$$u_{ff}(r) = \begin{cases} \infty, & \text{if } r < \sigma, \\ -\epsilon, & \text{if } \sigma \le r < \lambda\sigma, \\ 0, & \text{if } r \ge \lambda\sigma, \end{cases} \tag{1}$$

where σ is the particle diameter, which is chosen to be the unity of length, $\sigma = 1$; λ is the range of the well and ϵ is the well depth. The reduced temperature is defined as $T^* = k_B T/\epsilon$ (k_B is the Boltzmann constant). The interaction ranges studied are $\lambda = 1.5$ and $\lambda = 1.25$. The fluid is immersed in a circular cylinder with radius R_C and infinite length. The pore walls are assumed to be impermeable for the fluid, thus fluid-wall potential is defined as

$$u_{wf}(R) = \begin{cases} \infty, & \text{if } R > R_C, \\ 0, & \text{if } R < R_C, \end{cases} \tag{2}$$

where R is the radial distance from the central axis of the cylinder.

The simulations of the SW fluid vapor–liquid coexistence were performed in a cylindrical pore with axial length $L_z = 40$. For the widest pore considered in this work $L_z = 30$ was chosen, in order to speed up calculation. Some simulation runs with different values of L_z were performed, but any finite size effects were not detected. The number of fluid particles in the simulation box, N, was in the range $200 \le N \le 2300$ depending on the pore volume, $V = \pi L_z (R_C + 0.5\sigma)^2$, and the reduced density was defined as $\rho = N\sigma^3/V$. The initial average number density was maintained between 0.20 and 0.25, depending on the temperature.

In the initial configuration for each temperature, particles were located at the middle of the cylinder surrounded by vacuum. Such setup allows us to obtain a liquid slab between two vapor regions, which provides two interfaces that are perpendicular to the central axis of the cylinder (see Fig. 1 of Ref. [27]). To model a pore of infinite length, periodic boundary conditions were imposed along the axial direction of the cylinder. Particles were moved using the Metropolis algorithm [33]. The acceptance of particle displacements was around 45% in all runs. The system was equilibrated during 2×10^6 steps. The averaged properties were calculated in 10^7 additional steps, divided in 30 blocks.

Coexistence vapor and liquid densities, ρ_V and ρ_L, respectively, and the interfacial width, δ, were obtained at the end of each simulation run by fitting the axial density profile, $\rho(z)$, to the following hyperbolic tangent function [7,18]

$$\rho(z) = \frac{1}{2}(\rho_L + \rho_V) - \frac{1}{2}(\rho_L - \rho_V)\tanh\left(\frac{2(z - z_0)}{\delta}\right), \tag{3}$$

where z_0 is the position of the Gibbs dividing surface. The density profiles are relocated such that $z_0 = 0$. The values of ρ_V and ρ_L are given in Table 1.