Phase behavior and fluid–solid surface tension of argon in slit pores and carbon nanotubes

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ABSTRACT

Phase behaviors of argon in several types of cylindrical and slit pores are examined by grand-canonical Monte Carlo simulations. Condensation processes in single- and multi-walled carbon nanotubes along with those in hard-wall tubes are compared. Effects of the pore size on pressure–tensor components, the fluid–wall surface tension, and the adsorption are also compared for the different fluid-pore interactions. The chemical potential at which the fluid begins to condense in the single-walled nanotube is greater than that in the multi-walled nanotube by an amount nearly equal to the difference in the potential-well depth of the fluid-pore interaction, and the adsorption isotherms overlap each other almost completely for narrow pores and partially for wider pores. Similar analyses are performed for slit pores of two different hydrocarbon models.

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1. Introduction

Structure and phase behavior of a fluid under extreme confinement are often much richer than those of the bulk fluid. The confined system is more complex in that its properties depend not only on the thermodynamic field variables such as the temperature and chemical potential but also on additional variables: e.g., the pore materials and geometry [1–4].

When the pore size is much larger than the size of particles, structures of the fluid and solid far from the pore walls are essentially identical to those of the bulk and a change in phase-equilibrium conditions is often described by a first-order term of the expansion of the thermodynamic variable with respect to the inverse of pore size. Examples are the Kelvin equation for the condensation pressure [2] and the Gibbs–Thomson equation for the melting-point depression [4]. But when the pore size is as small as several times the particle diameter, fluid properties including phase equilibrium conditions are qualitatively different from the bulk [5–8].

In the large-pore regime the pressure in the pore is well-defined as a scalar variable: call it P_{pore}. The pressure outside the pore is the equilibrium bulk pressure: call it P_{bulk}. When the fluid is in the same phase (liquid or gas) in and outside the pore, the corresponding pressures are the same: $P_{\text{pore}} = P_{\text{bulk}}$. When the fluid is in different phases, say α and β, in and outside the pore, $P_{\text{pore}} \neq P_{\text{bulk}}$ at given T and μ except at the bulk-phase equilibria. As special cases, when two phases coexist *in* the pore, e.g., at capillary condensation or freezing, the pressure difference $P_{\text{pore}} - P_{\text{bulk}}$ is given by Laplace's equation. The relation between P_{pore} and P_{bulk} remarked above remains the same for any size of pore in the large-pore regime, and the fluid–fluid and fluid–wall surface tensions are independent of the pore size. These are in fact necessary ingredients for the derivation of the Kelvin and Gibbs–Thomson equations. In the small-pore regime, on the other hand, the pressure is not a scalar but is a tensor. There is no bulk-like region in the confined fluid and so, in principle, the fluid phase in and outside the pore cannot be the same even if both are condensed phases. Therefore any component of the pressure tensor is different

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from P_{bulk} and the difference of any pressure–tensor component from P_{bulk} at two-phase equilibria is not given by Laplace's equation. The fluid–fluid and fluid–wall surface tensions are dependent on the pore size in this regime.

Another difference between large- and small-pore regimes is the effect of the fluid-pore interaction (e.g., hydrophobic or hydrophilic, strongly repulsive or attractive, etc): in the large pores the general pictures described above, including Kelvin and Gibbs–Thomson equations, hold for for any types of the fluid-pore interaction; however in the small-pore regime the phase behavior may be qualitatively different for different types of pore surface.

Here we examine effects of the pore size, pore geometry, and fluid-pore interaction on the phase behavior of a simple liquid. We perform grand-canonical Monte Carlo simulations of argon in single- and multi-walled carbon nanotubes and of argon in slit pores made of a solid hydrocarbon. We focus on the phase behaviors in the small-pore regime and compare isothermal adsorption/desorption for the non-attractive hard-wall and attractive soft-wall pores.

2. Models and simulation methods

2.1. System and potential function

Properties of a fluid confined in a pore of volume V at given temperature T and chemical potential μ are obtained by the grand-canonical ensemble Monte Carlo (GCMC) simulation [9,10]. We implement the GCMC simulations of the Lennard–Jones (LJ) fluid in the model slit pore and carbon nanotubes, and obtain the density, pressure–tensor components, and the fluid–solid surface tension as functions of μ, or bulk pressure P_{bulk}, T, and the pore size. The corresponding bulk properties are obtained by the GCMC simulation or a well-established equation of state for the LJ fluid [11].

The intermolecular interaction between fluid particles is taken to be the LJ potential function with a cut-off:

$$u(r) = \begin{cases} 4\varepsilon \left[\left(\dfrac{\sigma}{r} \right)^{12} - \left(\dfrac{\sigma}{r} \right)^{6} \right] & (r \leq 5\sigma) \\ 0 & (r > 5\sigma) \end{cases} \tag{1}$$

where ε and σ are the energy and size parameters for argon ($\varepsilon/k = 120$ K with k the Boltzmann constant; $\sigma = 3.4$ Å) and r the intermolecular distance. Periodic boundary conditions are imposed in one, two, and three directions, respectively, for the cylindrical-pore, slit-pore, and bulk systems. The reduced temperature $T^* = kT/\varepsilon$ is changed stepwise with an interval of 0.1. The reduced configurational chemical potential $\mu_c^*(\rho^*, T^*)$, defined by $\mu^*(\rho^*, T^*) - \mu_{id}^*(\rho^* = 1, T^*)$ the difference of the reduced chemical potential from that of the ideal gas of $\rho^* = 1$, is increased or decreased stepwise with an interval of 0.05 or 0.1. The mass of argon $m = 6.63 \times 10^{-26}$ kg is employed so that μ_c^* is converted to μ^*. At each thermodynamic state, 20×10^6 to 500×10^6 configurations are generated and 20×10^6 to 1.5×10^9 configurations are used for averaging. The thermodynamic conditions examined are listed in Table 1.

For both cylindrical and slit pore systems, hard-wall and soft-wall potentials are examined. As in the previous study [12] the hard-wall potential for the cylindrical pore is taken to be

$$\phi(r) = \begin{cases} \varepsilon_w & r \leq (D - \sigma)/2 = R - \sigma/2 \\ \infty & \text{otherwise} \end{cases} \tag{2}$$

where D is the diameter of the cylindrical pore and r the distance of a particle from the cylinder axis, and the corresponding potential for the slit pore is

$$\phi(z) = \begin{cases} \varepsilon_w & \text{if } |z| \leq (h - \sigma)/2 \\ \infty & \text{otherwise} \end{cases} \tag{3}$$

where h is the width of the slit pore and z the distance of a particle from the mirror plane of the slit pore. For these hard-wall systems, the strength of effective attractive interaction between the pore and a fluid particle is represented by the uniform potential field ε_w.

These hard-wall systems are compared with more realistic fluid-pore systems: argon adsorbed in carbon nanotubes and in slit pores of hydrocarbons. For the former systems, both single- and multi-walled nanotubes are examined. The potential ϕ for an interaction between a fluid molecule and the multi-walled carbon nanotube of n layers is given by integrating the argon–carbon LJ potential over a single carbon layer [13] and then summing the integrated potential over the n layers. The result is written as

$$\phi(r) = \pi^2 \rho_w \varepsilon_w \sigma_w^2 \sum_{i=1}^{n} \left\{ \frac{63}{32} \frac{1}{\left[\frac{R_i - r}{\sigma_w} \left(1 + \frac{r}{R_i} \right) \right]^{10}} F\left[-\frac{9}{2}, -\frac{9}{2}; 1; \left(\frac{r}{R_i} \right)^2 \right] \right.$$

$$\left. - 3 \frac{1}{\left[\frac{R_i - r}{\sigma_w} \left(1 + \frac{r}{R_i} \right) \right]^4} F\left[-\frac{3}{2}, -\frac{3}{2}; 1; \left(\frac{r}{R_i} \right)^2 \right] \right\} \tag{4}$$