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On the condensation/evaporation pressures and isosteric heats for argon adsorption in pores of different cross-sections

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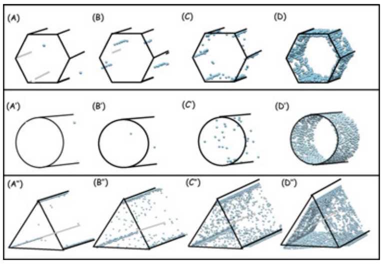
HIGHLIGHTS

- ▶ The shape of pore cross section does not affect the condensation and evaporation.
- ▶ The shape of pore cross section affects strongly adsorption at low loadings.
- ▶ Condensation does not occur on very weak surfaces.
- ▶ Condensation/Evaporation is governed dominantly by fluid–fluid interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

We investigate the effects of the pore cross-section, surface affinity and temperature on argon adsorption in different pore geometries. Three different pore cross sections were considered: cylindrical, hexagonal and triangular. We have placed particular emphasis on the condensation/evaporation (CE) pressures and the behavior of isosteric heat as a function of loading. It was found that CE is not affected by the shape of the pore cross section for a given surface area per unit volume and surface affinity. This is because the fluid–fluid interaction is the dominant factor in controlling condensation and evaporation steps. Although the pore cross section does not affect the CE behavior, strength of the adsorption potential can affect the pressures at which CE occurs. If the affinity towards the adsorbate is weak, the condensation pressure is higher because a higher pressure is required to build enough adsorbed layers before condensation can occur, and the evaporation pressure is also higher because it is easier to stretch the condensate as a result of weaker solid–fluid interactions. If the surface is sufficiently weak, the adsorbate only partially wets the surface, and this can result in unfilled pores, even when the pressure approaches the saturation vapor pressure. The study of CE behavior with temperature shows that the condensation pressure increases with temperature because a larger pressure is required to build up a sufficient number of layers before condensation can occur; similarly the evaporation pressure increases because it is easier to stretch the condensate at higher temperature. The reduction in the area of the hysteresis loop with temperature occurs because it easier to stretch the condensate than to build-up adsorbate layers; this is seen as a faster shift of the evaporation pressure towards the condensation step. The pore shape only affects the initial behavior of the isosteric heat versus loading with the order: triangular > hexagonal > cylinder, while the isosteric heat in the CE region is not affected by the shape because it is dominated purely by the fluid–fluid interactions.

1. Introduction

Confined fluids in pores of nano-dimensions exhibit different properties from the corresponding bulk fluids. The behavior of fluids under confinement is important in industrial applications such

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as catalysis, and adsorption also plays a major role in the characterization of porous solids.

In particular, carbonaceous materials are important porous solids because they are widely used as adsorbents for gas separation and purification in many industries. Among these materials, graphitized carbons such as carbon nanotubes have attracted a great deal of attention because their crystalline structures make them ideal solids for the study of the intrinsic interactions between adsorbate and adsorbent, and for investigating the effects of nanoconfinement on adsorption [1–6]. However despite their clearly defined crystalline structures, adsorption in the cylindrical spaces of carbon nanotubes is masked by the accompanying adsorption in the spaces between the tubes: interstices and grooves of the bundles of tubes.

Recently a new graphitized carbon material has been synthesized [7] with pore cross sections of hexagonal shape. TEM images obtained from this material show extended areas of hexagonal pores without small pores in the interstitial spaces. This makes the new material an excellent alternative to carbon nanotubes as a model solid for the study of condensation and evaporation. However, since the pore cross section of this material is hexagonal, a question is raised concerning the effects of pore shape on adsorption mechanism. Here we report computer simulations of argon adsorption in pores of different cross sectional shape: cylindrical, hexagonal and triangular.

Previous studies of the effects of pore shape on condensation and evaporation include a density functional investigation of adsorption in single pores with cylindrical, square and triangular cross sections by Malanoski and van Swol [8]; simulations of nitrogen adsorption in hexagonal and cylindrical pores of MCM-41 by Ustinov [9], and a simulation study of the effects of surface curvature and adsorption strength on 2D transitions of argon adsorbed in carbon nanotubes by Liu et al. [10]. Triangular pores have also been studied in earlier work [11–14] as a kernel for the characterization of activated carbon.

Our basis for comparison between pores of different shape is that they have the same surface area per unit volume. The energy surface heterogeneity increases in the order: cylinder < hexagon < triangle; amount of potential overlap between adjacent surfaces in the cross section increases in the order: cylinder < hexagon < triangle, and reflects the strong sites formed between the junctions of flat surfaces that make up the hexagonal and triangular pores, which can strongly affect adsorption at low loadings. However, since adsorbate tends to build more molecules into these regions, it is not clear whether this is important at higher loadings where condensation and evaporation occur. The investigation of this question is the main objective of this paper.

2. GCMC simulation method

We used Grand Canonical Monte Carlo simulation (GCMC) to calculate adsorption isotherms and isosteric heats of argon at 87.3 K on the different pores. Argon is simulated as a single Lennard Jones particle with parameters $\sigma_{ff} = 0.3405$ nm and $\varepsilon_{ff}/k = 119.8$ K [15]. The parameters used in our simulation are: (1) 50,000 cycles were run for the equilibration and sampling stages; each cycle consisting of 1000 attempts to move, delete and insert a particle with equal probability, (2) the box length and cut-off radius were set to 10 nm and 5 nm, respectively, and (3) the maximum displacement step length was initially set to half of the simulation box length in the axial direction, and adjusted during the equilibration stage to achieve an acceptance ratio between 20–25% [16].

In addition to pore shape we also studied the effects of the surface affinity. Four different models were used: a graphitic surface, a silica surface and two surfaces whose affinities are weaker than the silica and carbon surfaces, respectively. The parameters are given in Table 1 [17].

Table 1
Parameters for LJ potential.

	$\rho_s\varepsilon_{sf}/k_B(\mathrm{K/nm^2})$	$\sigma_{sf}(\mathrm{nm})$
Graphitized carbon	2212.4	0.340
Weak surface 1	1773.8	0.340
Silica surface	2620.0	0.300
Weak surface 2	1400.0	0.300

2.1. Cylindrical pore model

A homogeneous finite cylinder was used to model a single walled carbon nanotube. The interaction potential between the pore and an argon particle was calculated by Eq. (1) [18].

$$\phi_{sf} = 4\varepsilon_{sf}\rho_s R \sum_{n=3,6} a_n \sigma_{sf}^{2n} \int_0^{2\pi} I(\theta, r, z, n, R, L) d\theta \tag{1}$$

where the ρ_s is the surface density of solid atoms on the pore wall. The solid–fluid molecular parameters were calculated from the Lorentz–Berthelot rule:

$$\sigma_s = \frac{1}{2}(\sigma_s + \sigma_{ff})\varepsilon_{sf} = (\varepsilon_{ss}\varepsilon_{ff})^{0.5} \tag{2}$$

where σ_{ss} and ε_{ss} are the collision diameter and the well depth of the interaction energy of a pair of carbon atoms ($\sigma_{ss} = 0.34$ nm and $\varepsilon_{ss}/k_B = 28$ K).

The functions I_3 and I_6 of Eq. (1) are given by

$$I_6 = \frac{63}{128}\left(\frac{\sigma_{sf}}{R}\right)^{10}\left[1 - \left(\frac{r}{R}\right)^2\right]^{-10} F\left[-\frac{9}{2}; -\frac{9}{2}; 1; \left(\frac{r}{R}\right)^2\right] \tag{3}$$

$$I_3 = \frac{3}{4}\left(\frac{\sigma_{sf}}{R}\right)^{4}\left[1 - \left(\frac{r}{R}\right)^2\right]^{-4} F\left[-\frac{3}{2}; -\frac{3}{2}; 1; \left(\frac{r}{R}\right)^2\right] \tag{4}$$

where R is the pore radius, r is the radial distance from the pore center to the adsorbate, z is the axial distance from the middle of the pore to the adsorbate, and $a_n$is a constant ($a_3 = -1$ and $a_6 = 1$).

2.2. Hexagonal pore model

In previous work [19] we studied two models: a homogeneous (structure-less solid) model and a heterogeneous model that allowed for variation in the potential parameter at the hexagon junctions. The homogeneous model cannot account for experimental behaviour in the sub-monolayer region, but is satisfactory for the description of condensation and evaporation (CE) [7]. Since our aim here is to evaluate the effects of pore shape on the adsorption isotherm and isosteric heat in the CE region, we shall use the homogeneous model to reduce computation time. We also made a limited number of simulations using the heterogeneous model which were found to yield the same conclusions as the homogeneous model in the CE region. To model hexagonal pores of finite length (consistent with the cylindrical pores of Section 2.1) we decreased the solid–fluid potential close to the pore mouth as follows:

$$\phi_{f,s} = \begin{cases} \phi_{f,S(\text{infinite})} \times d^*/d_0 & (d^* \le d_0) \\ \phi_{f,S(\text{infinite})} & (d^* > d_0) \end{cases} \tag{5}$$

where $\phi_{f,S_{(\text{infinite})}}$ is the potential energy between a particle and an infinite homogeneous hexagonal pore [19], d^* is the distance between the adsorbate to the pore end, and d_0 is the length of pore mouth (Fig. 1). Each wall in the infinite homogeneous hexagonal pore is modelled by a Bojan–Steele (BS) surface. The interaction