Effects of temperature, pore dimensions and adsorbate on the transition from pore blocking to cavitation in an ink-bottle pore

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ABSTRACT

We have carried out comprehensive GCMC molecular simulations to study the effects of temperature (ranging from sub-critical to supercritical), cavity and neck dimensions, and adsorbate on the transition from pore blocking to cavitation in slit shaped ink-bottle pores. Varying these parameters affects, not only the position and the size of the hysteresis loop, but also its shape, which can change from H1, typical for pore blocking, to H1 or H2 combined with Type C (in the de Boer classification). The combined loops can either be fused loops or appear as two separate loops, one of which is of Type H1 and the other Type C. Another highlight of our simulation study is the double maxima in the adsorption isotherm at a super-critical temperature which results from the sigmoidal shape in the plot of bulk gas density versus pressure and the compression of the adsorbate in the confined space at high pressures.

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1. Introduction

Hysteresis associated with capillary condensation and evaporation in porous materials has been the subject of immense interest for over 100 years [1], especially the search for the controlling mechanisms of adsorption and desorption. Adsorption in mesopores gives rise to hysteresis when the temperature is less than the critical hysteresis temperature and pore size is greater than a critical value [2,3].

Materials such as activated carbon, porous glass and silica gel consist of interconnected networks of pores of various shape and size, and their experimental isotherms can exhibit single or double steps in the hysteresis loop [2,4–18]. When hysteresis shows two distinct steps, the first, at lower pressure, is associated with condensation and evaporation in the smaller pores and the second with the same processes in wider pores. If the adsorbate–adsorbent system is wetting, adsorption proceeds by molecular

layering, followed by condensation when both ends of a pore are exposed to the bulk surroundings, or by the advance of a meniscus from the closed end if one end of the pore is closed. Desorption, on the other hand, takes place by two processes which occur in conjunction: (1) the withdrawal of menisci from the pore mouth, and (2) the stretching of the condensed fluid in the interior region to a pressure where bubbles (cavities) appear in the adsorbate. When the first process dominates, the desorption mechanism is described as pore blocking, and as cavitation if stretching of the condensed fluid reaches the stability limit before the menisci have travelled to the pore interior. Both modes of evaporation can be illustrated by simulations using a simple ink-bottle pore model by tuning the neck size [19–23]. For a given adsorbate–adsorbent pair and temperature, the mechanism of desorption changes from pore-blocking to cavitation as the neck size decreases [20–24]. The cavitation pressure is a fluid property only when the cavity is large, typically greater than 7 nm for argon adsorption at 87 K, but is dependent on the cavity size for smaller cavities, because of the the overlap of adsorbent potential from closely spaced pore walls creates a stabilization effect [25,26]. The neck length can affect evaporation in an interesting way: Even when the neck size is

smaller than the value at which cavitation normally occurs, evaporation can switch to pore blocking when the neck is very short; the shorter the neck, the greater the desorption pressure. While the cavity size affects the cavitation pressure for small cavities and the neck dimensions (width and length) affect the governing mechanism for desorption, temperature can also affect the desorption mechanism, which changes from pore blocking to cavitation at high temperature, because stretching of the condensed fluid in the cavity, overrides the process of meniscus withdrawal. This has been observed both experimentally and theoretically [4,7,11]. The change of evaporation mechanism for a given adsorbent, can also switch from pore blocking to cavitation as the pressure is reduced, and this change depends strongly on the pore structure and temperature [11,18,27]. Finally, the adsorbate molecule can also affect the desorption mechanism; for example Reichenbach and co-worker [11] observed pore blocking for argon adsorption in porous glass at 77 K, but found cavitation to be the mechanism for nitrogen at the same temperature.

Despite numerous simulation studies, there is still no systematic investigation into the effects of pore dimensions, temperature and adsorbate on the switch in the mechanism of desorption, from pore blocking to cavitation, in ink-bottle pores. It is the objective of this paper to fill this gap.

2. Theory

2.1. Fluid–fluid potential model

Argon was modelled as a single Lennard Jones (LJ) site and the 2CLJ + 3q N₂ (two LJ sites and three partial charges) model was chosen for nitrogen [28]. Their molecular parameters are listed in Table 1.

2.2. Fluid–solid potential model

A graphitic ink-bottle pore, with planar walls, connected to a gas reservoir via a neck is shown in Fig. 1. We used the Bojan-Steele equation [29–31] to calculate the fluid–solid potential energy with a 0.34 nm spacing between the two adjacent graphite layers, which are finite in the y-direction and infinite in the x-direction. The box length in the x-direction is 5 nm and periodic boundary conditions are applied at boundaries in this direction.

2.3. Grand canonical Monte Carlo (GCMC)

The standard Metropolis algorithm [32] was applied with equal probabilities of move rotation, insertion, and deletion. The cut-off radius was set at half of the box length and 1.2×10^8 configurations were run for both equilibration and sampling.

The average absolute and excess volumetric densities are defined by:

$$\rho_{pore}^{ABS} = \frac{\langle N \rangle}{V_{acc}}; \quad \rho_{pore}^{EXC} = \frac{\langle N \rangle - \rho_b V_{acc}}{V_{acc}} \quad (1)$$

where ρ_b is the bulk molecular density, $\langle N \rangle$ is the ensemble average of the number of particles in the pore, and V_{acc} is the accessible pore volume [33].
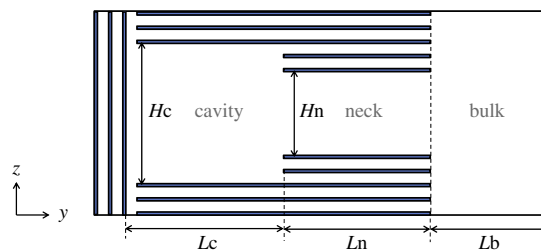

Fig. 1. Schematic diagrams of the ink-bottle pore with finite length in the y-direction and infinite length in the x-direction (perpendicular to the page). The length of bulk phase, Lb is fixed at 4 nm for all the systems studied.

The system was divided into meshes in the y- and z-directions to calculate the 2-dimensional (2D) density which is given by:

$$\rho(y,z) = \frac{\langle N_{(\Delta y, \Delta z)} \rangle}{L_x \Delta y \Delta z} \quad (2)$$

where N is the number of molecules in the mesh bounded by $(y-\Delta y/2, y + \Delta y/2)$ and $(z-\Delta z/2, z + \Delta z/2)$ and L_x is length in the x-direction. The mesh size was chosen to be $\Delta y = \Delta z = 0.1\sigma$.

3. Results and discussion

3.1. Ar adsorption at less than the critical hysteresis temperature

We first investigate argon adsorption in an ink-bottle pore whose cavity width is 3 nm and neck width is 2.3 nm. Note that in this small cavity and the force per unit area exerted by the cavitation pressure is less than the tensile strength of the bulk fluid because of the stabilization of the condensed fluid by the external field from the adsorbent. The lengths of the cavity and the neck were 10 nm. Fig. 2 shows the isotherms for temperatures from 60 K to 150 K. For ease of discussion, we define in Table 2 various terms that are used throughout the discussion.

3.1.1. Adsorption at 60 K

At this very low temperature, adsorption proceeds by molecular layering, followed by the formation of a meniscus at the bottom of the cavity because of the enhanced solid fluid interactions at the corners and the enhanced fluid–fluid interaction resulting from the shorter distances between neighbouring molecules at the curved interface (Fig. 3, top graph).

Once the meniscus is formed, the cavity behaves like a closed end pore while the neck behaves like an open end pore because of the gas-like fluid at its two ends. The meniscus then advances towards the junction as the pressure is increased (to Point A1) because at 60 K this process dominates the growth of molecular layers in the neck. When the meniscus has reached the junction (Point A2), the neck changes from an open end pore to a closed end pore (closed by the condensed fluid at the junction). Since the neck is smaller than the cavity, there is an advanced condensation in the neck (Point A3). The term "advanced" is because the condensation in the neck would occur at a higher pressure if its two ends were open to gas phase. The reason for this advanced condensation is because once the cavity is filled, any closed end pores whose sizes

Table 1
Molecular parameters for Ar and N₂.

Model	Site	x (nm)	y (nm)	z (nm)	σ (nm)	ε/k_B (K)	Charge (e)
Ar	Ar	0	0	0	0.3405	119.8	0
2CLJ + 3q N₂	N	0.055	0	0	0.331	36	−0.482
	N	−0.055	0	0	0.331	36	−0.482
	Centre	0	0	0	0	0	0.964