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A molecular simulation study of adsorption and desorption in closed end slit pores: Is there a hysteresis loop?

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HIGHLIGHTS

- Detailed simulation of gas in pores with one end closed.
- Hysteresis exists in closed end pores of nano-dimensions.
- Continuous structuring of the adsorbed phase is the principal reason for hysteresis.
- Kelvin equation with bulk liquid values is not applicable for closed end pores.

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ABSTRACT

This paper reports detailed simulations of adsorption and desorption of argon in closed end slit pores with the aim of investigating the existence of hysteresis. The classical thermodynamic approach implies that there should be no hysteresis in a closed end pore because it assumes that the condensed phase is identical to a uniform bulk liquid and that the interface between the gas-like region and the dense adsorbate region is the same when the pore fills as when it empties. Our simulations show that hysteresis is possible and we support this assertion with evidence from a critical analysis of the classical equation. Our extensive results show that hysteresis can occur in closed end pores because of the continuous structuring of the adsorbed phase induced by the combined effects of the solid–fluid interaction and the fluid–fluid interaction.

1. Introduction

Adsorption isotherms for gases in meso-porous adsorbents exhibit hysteresis at temperatures below a critical hysteresis temperature, T_{ch} (Everett and Haynes, 1973; Horikawa et al., 2011; Thommes, 2004) which depends on the parameters characterising the adsorbent pores (cross sectional shape and width, inter-connectivity, and the form of the adsorbent–adsorbate potential) and also on the adsorbate. The drive to improve our understanding of the microscopic origin of hysteresis has been greatly facilitated by the synthesis of ordered mesoporous solids and advances in computer simulation (Horikawa et al., 2011). Several attempts have been made to tailor adsorbent solids in order to study the dependence of hysteresis on pore structure, for example by synthesising pores with either open ends, or with one end closed, or pores with narrower openings to the surrounding gas (Bruschi et al., 2008, 2010; Wallacher et al., 2004). In particular, the possible existence of hysteresis in closed end pores has been a controversial topic that has important consequences for more complex materials where pore cross sections may vary from place to place. The classical Kelvin equation implies that there would be no hysteresis in a cylindrical closed end pore because it assumes that the condensed phase is identical to a uniform bulk liquid and that the interface separating the gas-like region and the dense adsorbate region is the same when the pore fills as when it empties. In slit pore geometry this interface would be cylindrical rather than hemispherical, but a similar classical argument would apply. The assumption that the adsorbate resembles the bulk fluid has never been verified experimentally, and it is shown in this paper that this is the principal reason for the failure of the classical equation in the analysis of adsorption in closed end pores. Our simulations show that there is a continuous re-structuring of the adsorbed phase as adsorption progresses which is controlled by the strength of the solid–fluid interaction.

Experimental studies have shown conflicting results: for example isotherms in aluminium and silicon adsorbents with closed end pores exhibit hysteresis loops (Bruschi et al., 2008; Coasne et al., 2002; Wallacher et al., 2004). However, these real materials may have irregularities on the surface that could be responsible for the

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hysteresis (Bruschi et al., 2008; Puibasset, 2009). In an experimental adsorption study of very wide closed end pores where effects due to the external adsorbent field are expected to be negligible, no hysteresis was found (Mistura et al., 2013).

Theoretical studies using DFT or lattice model calculations have tended to the view that hysteresis does not occur in closed end pores (Parry et al., 2007; Roth and Parry, 2011), or may be attributed to irregularities in the pore walls (Naumov et al., 2009). Similarly, computer simulation studies have not reached a conclusive agreement because of their limited exploration of the parameter space. Sarkisov and Monson used molecular dynamics (MD) and Grand Canonical Monte Carlo (GCMC) to study adsorption in slit pores with closed ends but did not find hysteresis in the models they examined (Sarkisov and Monson, 2001) a conclusion supported by Wallacher et al. and by Bruschi et al. (Bruschi et al., 2010; Puibasset, 2009). On the other hand, Ancilotto et al. (2011), in their simulation study of cylindrical pores with closed ends, did find hysteresis but attributed this to the formation of a thin film of adsorbate spanning across the pore mouth. Our recent Monte Carlo simulations (Fan et al., 2013; Nguyen et al., 2013) of adsorption, in closed-end cylindrical and slit pores, also reveal the existence of a hysteresis loop in these models, but without the need to invoke this explanation.

In this paper we explore the effects of various parameters on the existence and properties of the hysteresis loop in closed end pores. A number of simulations discussed here have been presented in our previous correspondence, and are supplemented by new results which together present a comprehensive picture of the factors affecting hysteresis in closed end pores.

2. Theory

2.1. Interaction energies and pore models

We used argon as a model adsorbate and its intermolecular potential energy of interaction was described by the 12-6 Lennard–Jones (LJ) equation, with a collision diameter $\sigma_{ff} = 0.3405$ nm and a reduced well-depth $\varepsilon_{ff}/k = 119.8$ K.

The model was a slit-like pore with finite walls in the y-direction and infinite walls in the x-direction; one end of the pore was closed and the open end was connected to a bulk gas reservoir to ensure mechanical equilibrium between the pore and the surroundings (Fig. 1). The pore walls including the closed end consisted of three homogeneous graphene layers with a constant surface density of 38.2 nm^{-2} and a spacing $\Delta = 0.3354$ nm. The solid–fluid potential energy was calculated from the Bojan–Steele equation (Bojan and Steele, 1988, 1993, 1998) with molecular parameters $\sigma_{ss} = 0.34$ nm and $\varepsilon_{ss}/k = 28$ K to represent a carbon atom. The cross collision diameter and well-depth of the solid–fluid interaction energy were calculated by the Lorentz–Berthelot mixing rule.

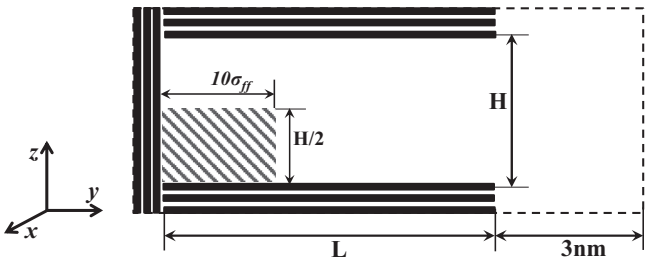

Fig. 1. Schematic of the closed-end slit-shaped pore. The pore width H is defined as the distance between the planes passing through the centres of carbon atoms in the outermost layer of one wall to the corresponding plane of the opposite wall. The x-direction is perpendicular to the page.

2.2. Monte Carlo simulation

We used GCMC simulation to obtain isotherms, with 200,000 cycles in both the equilibration and sampling stages. Each cycle consisted of 1000 displacement moves and exchanges with equal probability, giving a total of 2×10^8 configurations, which was found to be adequate to achieve convergence. A few simulations with much longer Markov chains yielded identical results. In the equilibration stage, the maximum displacement length was initially set as half of the largest dimension of the box and was adjusted at the end of each cycle to give an acceptance ratio for displacement of 20% (Mountain and Thirumalai, 1994). The dimension of the simulation box in the x-direction was set at 10 times the collision diameter of argon and the other two directions were determined by the pore size H and length L. The gas reservoir had a length along the pore axis of 3 nm, and the dimensions in the other two directions were the same as those of the pore. Periodic boundary conditions were applied at the boundaries in the x-direction, and the cut-off radius was 5 times the collision diameter (which is half the dimension in that direction). The equation of state of Johnson et al. (1993) was used to relate pressure to the chemical potential, which was the input in GCMC simulation.

2.3. Mesoscopic analysis

The local density distribution in the z-direction from one of the pore walls is calculated from

$$\rho(z) = \frac{\langle \Delta N(z) \rangle}{L_x L_y \Delta z} \tag{1}$$

where $\Delta N(z)$ is the number of molecules with centres in the bin bounded by $[z, z+\Delta z]$. For the 2D-density distribution, the system was divided into bins in the z- and y-directions and the bin density is defined as

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

where $\Delta N(z, y)$ is the number of particles in the bin bounded by $[z, z+\Delta z]$ and $[y, y+\Delta y]$. The bin size in both directions was chosen to be $\Delta z = \Delta y = 0.1\sigma_{ff}$. The local density was calculated at the end of each cycle, and the ensemble average obtained at the end of the sampling stage. The results of 2D-density profile were smoothed by averaging the density within a radius of $0.5\sigma_{ff}$.

We also calculated the radial density distribution for molecules in the corners of the pore in order to examine any structural changes in the adsorbate in the neighbourhood of the closed end.

$$\rho(r) = \frac{\langle \Delta N(r) \rangle}{(4/3)\pi[(r+\Delta r)^3 - r^3]} \tag{3}$$

where $\Delta N(r)$ is the number of particles in the radial bin bounded by $[r, r+\Delta r]$ and the denominator is its volume. The bin size was chosen as $\Delta r = 0.1\sigma_{ff}$. The selected corner region of the pore is shown in Fig. 1 as a shaded area.

3. Results and discussion

3.1. Open and closed end pore at 87.3 K

The comparison between isotherms for argon adsorption at 87 K in the open end and closed end slit pores constructed from homogeneous solid are presented in Fig. 2; their widths and lengths are 3 nm and 20 nm, respectively. Although both hysteresis loops are of Type H1 according to the IUPAC classification, there are distinct differences between the two isotherms listed