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Simulation study of hysteresis of argon adsorption in a conical pore and a constricted cylindrical pore

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ABSTRACT

We present a detailed simulation study of the hysteresis loop in conical pores and in cylindrical pores with periodic constrictions to understand how the non-uniformity of the pore diameter along the pore axis would affect the hysteresis loop. The shape and size of the loop in the conical pores (with and without closed ends) are modified by the cone angle because of the change in the curvature of the menisci at the pore ends. In periodically constricted cylindrical pores, the shape and size of the hysteresis loop are not significantly altered by the pore length or by the presence of a closed end because condensation and evaporation in this type of pore occur in the individual pore sections. Similar hysteresis loops have been found in experimental studies, suggesting that structures of the type modelled here occur in real materials.

1. Introduction

It is well known that adsorption–desorption isotherms, measured on mesoporous solids, can exhibit hysteresis below a critical temperature [1–3]. The shape and size of the hysteresis loop depend, not only on the pore structure and pore size, but also on the relative sizes of the different pore sections [4]. One of the earliest attempts to classify loop shapes and relate them to structure was made by de Boer [3] who based his arguments on the unmodified Kelvin–Cohan hypothesis that pore-filling was controlled by a cylindrical meniscus, formed by the growing adsorbate layers, and that emptying was controlled by spherical menisci. de Boer identified five types of hysteresis loops which he named A to E, shown in Fig. 1.

The later IUPAC classification replaced A, B and E by the notation H1, H4 and H2 and introduced a new type, H3, which was specifically identified with flaky materials [5,6]. In a recent review [6], Sing and Williams concluded that there was no immediate need to change the IUPAC classification of hysteresis loops. According to de Boer, a type A hysteresis loop would be obtained from a number of different basic structures including open-ended cylindrical pores, tubular pores with alternating wide and narrow sections, and various 'ink-bottle' shapes. The most commonly observed E (or H2) loop was related to assemblies of these pore shapes in which there was a distribution of widths in the wide and narrow sections. These arguments have since undergone substantial revision. The pore radius used in both the Cohan and the Kelvin equations must be modified to allow for adsorbate 'thickness', and the thickness term was shown by Derjaguin [7] and later by Broekhoff and de Boer [8], to be dependent on the strength of the adsorbent field. In a paper published in 2001, Coasne et al. [9] showed that experimental isotherms, measured on independently-characterised isolated mesopores, gave a type E (H2) hysteresis rather than the expected type A (H1) hysteresis loop.

An alternative explanation for the commonly observed the type E (H2) loop shape is based on network percolation theory and linked to the ink-bottle model. In this type of extension of the model, it is proposed that wider pore sections in a network will retain liquid, trapped by adsorbate in surrounding narrower pore sections, at relative pressures lower than the critical Kelvin pressure, until the narrower pore sections can be emptied through an open path to the external vapour phase. It may be noted that network models might be regarded as an elaboration of simpler models with alternating wide and narrow sections.

In this work, we have examined the size and shape of the hysteresis loop for adsorption and desorption, for two simple pore topologies: a conical pore (with either an open or a closed end) and a cylindrical pore with constrictions along the pore axis, by means of Monte Carlo simulation. We have shown that in the open-ended conical pore, the shape of the hysteresis loop depends on the radius at the two ends, because the curvature of the meniscus at each end depends on the pore angle. A hysteresis loop of type C in the de Boer (dB) classification was found for this pore model. In a conical pore, when the wider end is closed, the mechanism of desorption was found to be similar to that in an ink-bottle pore in which the evaporation follows a cavitation and pore blocking mechanism [4,10–13] since this pore is a special case of an

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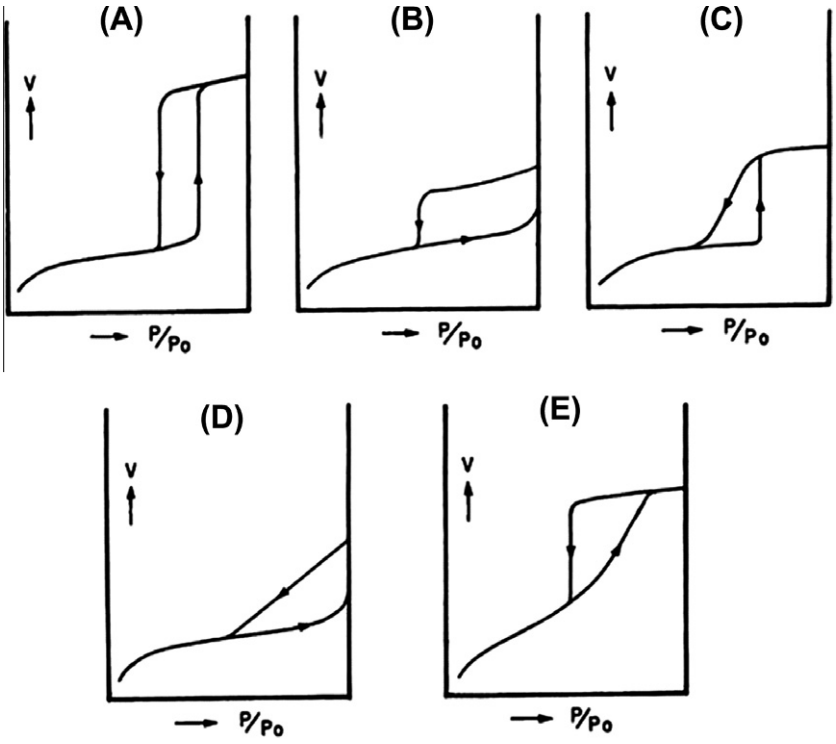

Fig. 1. Classification of hysteresis loop according to de Boer [3] (A).

ink-bottle pore in which neck size increases as desorption progresses.

We have also investigated the effects of constriction on the hysteresis loop for periodically constricted cylindrical pores. This investigation follows previous publications on the effect of surface defects on adsorption and desorption [14–22] and suggests an explanation for the negligible difference between condensation and evaporation pressures in pores with different lengths, and in pores with and without close ends [9,23,24], which is observed experimentally.

2. Interaction energies and pore models

We use the 12–6 Lennard–Jones (LJ) equation with the parameters $\sigma_{ff} = 0.3405$ nm and $\varepsilon_{ff}/k = 119.8$ K [25,26] to describe the intermolecular interaction energy of argon.

The interaction energy between an adsorbate and a single wall conical pore (Fig. 2) has been reported elsewhere [4]; here, we have used a three-layer graphitic conical pore. The pores with one closed end have a flat surface at the wider end, modelled by the Steele 10-4-3 potential [27]. The mean pore size of the pore with two open ends is defined as the pore diameter at the middle of the pore length:

$$\overline{D} = \frac{D_1 + D_2}{2}$$

To model the pores with periodical constrictions, we connected short cylindrical pores with a smaller pore radius to a long cylindrical pore in a periodic manner (Fig. 3). The unit cell of length L consists of one long section of larger radius and two very short sections with smaller radii at each end (see model 1 in Fig. 3). The interaction energy between an adsorbate and a finite cylindrical pore has been given in our previous work [28]. For pores with one closed end, we used the same pore models as shown in Fig. 3 with a graphite surface modelled by the Steele 10-4-3 potential [27] placed at one end of the pore. The wall of the large cylinder has three graphitic layers and the number of layers in the short cylinders depends on the size of the constrictions. The constrictions were given a length of 0.2 nm.

3. Monte Carlo simulation

To acquire the data in the GCMC simulation, we used 50,000 cycles in the equilibration stage and the same number for the sampling stage. Each cycle had 1000 displacement moves and exchanges which included insertion and deletion with equal

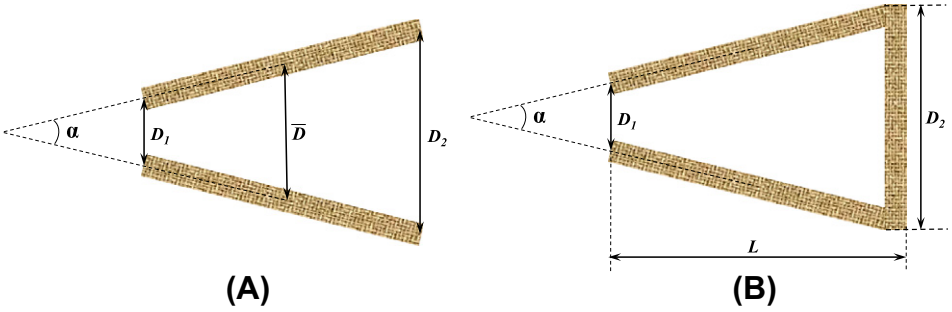

Fig. 2. Conical pore models with (A) two open ends and (B) one open end. D_1, D_2 and D are diameters of the narrow end, wide end and the mean pore size, respectively.