Adsorption in alumina pores open at one and at both ends†

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We have studied adsorption in regular, self-ordered alumina pores open at both ends or only at one end. The straight, non-connected pores have diameters ranging from 22 to 83 nm, with a relative dispersion below 1% in the pore size. Adsorption isotherms measured in open pores with a torsional microbalance show pronounced hysteresis loops characterized by nearly vertical and parallel adsorption and desorption branches. Blocking one end of the pores with glue has a strong influence on adsorption, as expected from classical macroscopic arguments. However, the experimental measurements show an unexpectedly rich phenomenology dependent on the pore size. For large pores ($D_p \geq 67$ nm), the isotherms for closed end pores present much narrower hysteresis loops whose adsorption and desorption boundaries envelop the desorption branches of the isotherms for the corresponding open pores of the same size. The loop for small closed end pores ($D_p = 22$ nm) is slightly wider than that for open pores while the adsorption branches coincide. For large pores, in contrast, the desorption branches of pores with the same $D_p$ overlap regardless of the pore opening. These observations are in agreement with our grand canonical Monte Carlo (GCMC) simulations for a cylindrical pore model with constrictions, suggesting that the alumina pores could be modeled using a constricted pore model whose adsorption isotherm depends on the ratio of the constriction size to the pore size ($D_c/D_p$).

Introduction

Advances in nanotechnology have allowed the fabrication of porous matrices formed from straight, unconnected pores with the characteristic size ranging from a few to a couple of hundred nanometers.1 Examples of such materials include porous silicon,2,3 silica SBA-154 and MCM-41,5 and porous alumina.6–8 Because of their regularity, these matrices have been exploited as templates for the realization of new functional materials.8–11

They have also been widely employed to study the behavior of fluids under confinement.12,13 On a planar open surface, an adsorbed fluid exhibits the coexistence between the adsorbate and the vapor-like phases, but the first-order boundary curve and the critical point are shifted when the fluid is confined in a pore. At a temperature $T$ below a critical temperature which depends on the pore size, vapor condenses at a pressure $P$ less than the saturation vapor pressure $P_v$. If the liquid completely wets the pore inner walls, the condensation pressure is related to the curvature $C$ of the meniscus formed in the pore using the macroscopic Kelvin equation:14

$$\ln \frac{P}{P_v} = -\frac{\gamma}{\eta_l k_B T} C$$

where $\gamma$ is the adsorbate surface tension and $\eta_l$ is the liquid argon number density both evaluated at $T$, and $k_B = 1.38 \times 10^{-23}$ erg K$^{-1}$ being the Boltzmann constant.

The order of the transition is determined by the confining geometry. In rectangular grooves, the capillary condensation is continuous if the liquid completely wets the cap, and first-order otherwise.15 In open cylindrical pores, Cohan16 originally proposed that the transition is first-order because of the different shape of the meniscus during adsorption (the adsorbate is added to the pore) and desorption (the adsorbate is removed from the pore). It follows that in a closed bottom cylindrical pore, a continuous transition is expected because the meniscus nucleates at the bottom corners and will be the same in both adsorption and desorption. Classical theories,17–20 mean field density functional theory,21–23 simulations of adsorption and desorption studied by mean field
Kawasaki dynamics of diffusive mass transfer into model pores and grand canonical lattice model Monte Carlo simulations have all given support to this macroscopic thermodynamic picture of adsorption in a single pore. In contrast to these theoretical predictions, experiments with mesoporous matrices, characterized by a trivial porous network topology, consisting of straight unconnected pores show that adsorption is always characterized by pronounced hysteresis loops irrespective of whether the pores are open at one or at both ends. Recent simulations on closed-end pores with diameters <10 nm have also shown that there is hysteresis when the adsorbate liquid completely wets the pore inner walls. The occurrence of hysteresis in these systems is attributed to solid-fluid interactions which are not accounted for in Cohan’s classical model. In adsorption there are two processes occurring simultaneously: the advance of the meniscus and the growth of the adsorbed layer at the coexistence boundary with the gas-layer; during desorption, the thickness of the adsorbate layer remains constant and the receding meniscus is the sole reason for the decrease in the adsorbed amount. However, no hysteresis is found experimentally in wide ($D_p \sim 200$ nm), very regular closed bottom pores formed by vertical and smooth walls made by advanced nanolithography, confirming that the classical Cohan model applies in this system.

Clearly the question of whether or not hysteresis can occur in closed end pores is not yet entirely resolved. Here, we compare the adsorption in open and closed end cylindrical pores of the same size over a wide range of pore sizes. According to Cohan’s model, for open cylindrical pores a liquid film covers the inner walls forming a cylindrical meniscus having a curvature $C_c = \frac{2}{D_p}$, where $D_p$ is the pore diameter. By contrast, in a pore that is closed at one end, the adsorbed film nucleates at the closed end to form a hemispherical meniscus with the curvature $C_h = \frac{4}{D_p}$. However, in both cases, evaporation from the filled pore proceeds through the same hemispherical meniscus. Thus, according to Cohan’s model, the adsorption branch for an open pore is located at a pressure $P_c$ given by

$$\ln \frac{P_c}{P_0} = -\frac{\gamma}{n_k T D_p} \frac{2}{D_p},$$

which is higher than that for a closed-bottom pore $P_h$ equal to

$$\ln \frac{P_h}{P_0} = -\frac{\gamma}{n_k T D_p} \frac{4}{D_p},$$

while the desorption branch corresponding to the open pore coincides with the adsorption branch of the closed end pore. This problem was originally addressed by studying the adsorption of nitrogen in porous silicon with pores open at one or at both ends. The two adsorption isotherms exhibit wide and asymmetric hysteresis loops with shapes resembling the type H2 loop in the IUPAC classification, typical of three-dimensional networks like Vycor. Furthermore, at a given pressure, the adsorbed amount before capillary condensation is smaller for the open pores than for the corresponding closed end pores and the condensation pressure is higher. In other words, in open pores the whole loop appears to be shifted to higher $P/P_0$ with respect to that found in closed end pores. The observed asymmetric loops have been reproduced by introducing strong morphological disorder in the pores although these simulations yield superimposable isotherms in contrast to the experiments. The occurrence of distinct hysteresis loops was explained as being a consequence of the distortion of the adsorbent caused by elastic strains during adsorption.

Thus, to further advance the study of the effect of the pore closure on adsorption, we have decided to repeat similar measurements using the porous alumina as an adsorbent. Porous anodized aluminum oxide (AAO) is characterized by a regular arrangement of the pores with a narrow pore size distribution (the dispersity of the pore diameter, defined as the standard deviation divided by the mean pore diameter, amounts to much less than 10% instead of 50% for porous Si) and uniform pore depth, as well as having solid pore walls without micropores. Adsorption isotherms for closed end porous AAO show steep, symmetric hysteresis loops corresponding to type H1 in the IUPAC classification (i.e., a hysteresis loop with parallel adsorption and desorption branches), which is generally associated with capillary condensation and evaporation in ordered mesoporous materials with cylindrical pores. In the following, we compare measurements for argon adsorption at 87 K on AAO membranes with open end pores of different nominal sizes with those obtained in the same matrices after the pores have been blocked on one side with glue. The experimental results are compared qualitatively with Monte Carlo simulation results in order to shed light on the microscopic mechanism of adsorption in these pores.

**Methods**

**Sample preparation**

The porous anodic aluminum oxide (AAO) samples employed in the present study were prepared by anodization of aluminum. In brief, as-received aluminum discs (2 cm in diameter, Goodfellow, 99.999%) were used in the anodization experiments. The aluminum discs were electrochemically polished in a vigorously stirred 1 : 4 mixture solution of 65% HClO4 and 99.5% ethanol (5 °C) in order to exclude any effects (e.g., localized field concentration) that could arise from the creation of surface roughness during the anodization. The finished aluminum disc was placed in an electrochemical cell with an O-ring (diameter = 1.5 cm), so that one side of the metal could be anodized. All anodization experiments in the present work were performed by using an electrochemical cell equipped with a cooling stage in thermal contact with the aluminum substrate in order to remove the reaction heat. Mirror finished aluminum discs were anodized either at 25 V in 0.3 M...
H$_2$SO$_4$ or at 40 V h in 0.3 M H$_2$C$_2$O$_4$ (1 °C) for the preparation of AAOs with different pore densities $n = 2.73 \times 10^{10}$ pores cm$^{-2}$ for H$_2$SO$_4$ anodization and $n = 1.05 \times 10^{10}$ pores cm$^{-2}$ for H$_2$C$_2$O$_4$ anodization. The anodized Al samples were then immersed in a mixed solution of 1.8 wt% CrO$_3$ and 6 wt% H$_3$PO$_4$ at 45 °C for 12 h to remove the oxide layer with a disordered pore structure. Next, the resulting Al substrates with highly ordered arrays of approximately hemispherical concavities were anodized under the same conditions as the first anodizations for the desired period of time (typically 6 to 12 h). Each concavity on the surface of the Al substrate serves as a pore initiation site during the second anodization process. According to our field emission scanning electron microscopy (FESEM, Hitachi S-4800) analysis, the average pore diameter ($D_p$) and the interpore distance ($D_{int}$) of as-prepared AAOs were determined to be $D_p = 22$ nm and $D_{int} = 60$ nm for H$_2$SO$_4$ anodization (referred to as H$_2$SO$_4$-AAO), and $D_p = 30$ nm and $D_{int} = 105$ nm for H$_2$C$_2$O$_4$ anodization (referred to as H$_2$C$_2$O$_4$-AAO). In the anodization of aluminum under the given set of electrochemical conditions, the thickness ($t_p$) of the resulting AAO (i.e., the length of nanopores) is linearly proportional to the total amount of charge involved in the electrochemical oxidation. Therefore, one may precisely control the thickness ($t_p$) of AAO by adjusting the anodization time. With our anodization conditions, the thicknesses of AAOs formed after six hours of anodic oxidation were found to be $t_p = 26.8$ and 35.8 μm for H$_2$C$_2$O$_4$ and H$_2$SO$_4$ anodizations, respectively.

The end of an as-prepared AAO sample was closed with a thin barrier layer of oxide that is in conformal contact with the underlying Al substrate. Open ended AAO membranes were prepared by selective removal of the underlying Al substrate using an aqueous etching solution at 1 C containing 3.4 g of CuCl$_2$·H$_2$O in 100 mL of 37 wt% HCl, followed by opening of the barrier layer with a 5 wt% H$_2$PO$_4$ solution (30 °C). In order to prevent undesired widening of AAO pores by the etchant solutions used for the removal of the Al substrate and the barrier layer, the central region of the back side of the anodized sample was selectively exposed to the etchant solutions, which could be achieved by placing the sample in an electrochemical cell with an O-ring (diameter = 1.0 cm). According to our SEM investigation, opening of the barrier layer took place after 20 min for H$_2$SO$_4$-AAOs and after 50 min for H$_2$C$_2$O$_4$-AAOs under the described processing conditions. In order to prepare AAO samples with larger pore diameters, wet-chemical etching of pore wall oxide was carried out by immersing through-channel H$_2$C$_2$O$_4$-AAO membranes in a 5 wt% H$_2$PO$_4$ solution (30 °C) for the desired period of time. According to our SEM image analysis, using the standard image processing software (i.e., Image J), the pore size difference between the largest and the smallest pore diameters turned out to be less than 1.5% for H$_2$C$_2$O$_4$-AAOs and 5% for H$_2$SO$_4$-AAOs. These differences in both types of AAO samples can be attributed to the detailed compositional nature of pore wall oxides. Throughout this paper, AAO samples with closed end are denoted as “Closed”, while AAO samples with pores open at both ends are denoted as “Open”. Fig. 1 shows the schematic cross-sections of the two pore geometries accompanied by SEM images of their morphology.

For this study, we prepared Open samples of nominal size $D_p = 83$ nm, $D_p = 67$ nm and $D_p = 22$ nm. Fig. 2 shows two characteristic SEM images of the top and bottom faces of the sample with $D_p = 83$ nm together with two histograms of the pore size distribution deduced from micrographs of the two ends, which present sharp, monomodal distributions (Fig. 2c and d). The dispersity of the pore diameter distribution for this sample amounts to about 1%, significantly less than the dispersity of 8% previously measured for AAO samples, and clearly represents a direct indication of the improvements achieved by the present nanofabrication processes. The results of similar analyses for the other samples can be found in ESL†). For the selective closure of the pore openings, we tried various strategies. At the end of long painstaking tests, the methodology adopted in this work consists of painting with a soft brush a thin layer of Loctite® Super Glue, a fast bonding, instant adhesive in a very humid environment for a very rapid cure. Then, the glue is covered with Stycast® 2850 FT (Emerson and Cuming), a two-component epoxy resin used in cryogenics because of its good thermal conductivity and low coefficient of thermal expansion. The use of the fast curing glue prevents the pores from getting filled by the liquid adhesive by capillarity. The epoxy is necessary to guarantee the mechanical integrity of the sample when it is cooled down to 85 K, otherwise the caps will crack because of the large thermal contraction of the glue. Fig. 3 shows some SEM images of the glue filling the end of the pores.
Adsorption measurements

We have measured adsorption isotherms with a torsional microbalance.47 Porous AAO samples, having a characteristic diameter of ≈2 cm and a thickness of ≈60 μm, are attached to the extremity of a tungsten rod driven to its torsional frequency by means of piezoelectric crystals. The sample is then outgassed in a vacuum at a temperature of 100 °C for a couple of days until the microbalance frequency stops rising. The sample cell is mounted in a custom made liquid nitrogen cryostat and cooling can be controlled by varying the pressure of the exchange gas with the cryogenic bath. For the samples painted with epoxy, cooling from room temperature was controlled to occur in about 12 hours to avoid thermal shocks. As the samples are exposed to increasing concentrations of argon vapor at \( T = 85 \text{ K} \), the resonance frequency decreases because of an increase in the total moment of inertia. From the vapor-density corrected frequency shifts it is then possible to derive the relative change of the oscillator moment of inertia, \( \Delta I / I_0 \), which is proportional to the mass of the adsorbed film.48

Grand canonical Monte Carlo simulation

We used the 12-6 Lennard–Jones (LJ) equation with the parameters \( \sigma_{ff} = 0.3405 \text{ nm} \) and \( \varepsilon_{ff} / k = 119.8 \text{ K} \)\(^{49,50} \) to model the intermolecular interaction energy of argon. The LJ parameters of oxygen atoms on the alumina surface are \( \sigma_{ss} = 2.7 \text{ Å} \) and \( \varepsilon_{ss} / k = 230 \text{ K} \).\(^{51} \) To model corrugation along the walls of an alumina pore, we used a cylindrical pore model with constrictions located periodically along the pore axial distance by connecting short cylindrical pores with smaller pore diameters to a long cylindrical pore in a periodical manner (see Fig. 4). The interaction energy between an adsorbate and a finite cylindrical pore has been given in our previous work.\(^{52} \) For pores with one closed end we used the same pore models and placed an alumina surface modelled by the Steele 10-4-3 potential\(^{53} \) at one end of the pore. The constrictions were given a length of \( L_c = 2\sigma_{ff} \).

To acquire the data in the grand canonical Monte Carlo (GCMC) simulation, we used 100 000 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 probability. This means that each simulation sampled \( 1 \times 10^8 \) configurations in the equilibration stage and a further \( 1 \times 10^8 \) configurations in the sampling stage. Furthermore, for the hysteresis region, we used 200 000 cycles, \( \text{i.e.} \) \( 2 \times 10^8 \) million configurations, for each stage to obtain reproducible adsorption and desorption boundaries of the hysteresis loop. These numbers are extremely large by normal MC standards, and our standard protocol also includes checking control charts to verify the convergence. In the equilibration stage, the maximum initial displacement length was half of the largest dimension of the simulation box and was adjusted at the end of every cycle to give an acceptance ratio of 20%. The cut-off radius was half of the largest dimension of the simulation box. Both ends of an open end pore were exposed to the surrounding gas to ensure that mechanical equilibrium is maintained between the pore and the surroundings. Because of the limitation of the computational capacity of our supercomputer, the simulation was not conducted for the experimental pore size but for a relatively large pore with \( D_p = 6 \text{ nm} \) and \( L_p = 20 \text{ nm} \). The adsorption for larger and longer

![Fig. 2](image-url) Representative top view (a) and bottom view (b) SEM images of the porous anodic aluminum oxide membrane with \( D_p = 83 \text{ nm} \). Scale bars are 200 nm. Histograms (c) and (d) indicate the corresponding pore size distributions.
pores is expected to be similar, with the hysteresis loop positions shifted to higher relative pressures \((P/P_0)\). To study the effect of constriction on the adsorption, we varied the constriction size \((D_c)\) while keeping the pore size \((D_p)\) and the constriction length \((L_c)\) constant. Specifically we considered the following pore models: A (no constriction, \(D_c = D_p\)), B, C and D with an increasing amount of corrugation \((D_c = 4.9\ nm, 2.8\ nm, \and 1.7\ nm,\ respectively)\).

The simulated adsorption isotherms are presented as the adsorbate density in the pore as a function of the relative pressure in the bulk phase. The vapour pressure of argon at 85 K used in the simulation was calculated from the equation obtained by Lotfi et al.\(^{54}\) as 64.3 kPa. The excess amount adsorbed is defined as the difference between the amount in the pore and the hypothetical amount of gas occupying the accessible volume at the same density as the bulk gas, and the adsorbate density is defined as the excess amount per unit accessible volume.\(^{55}\)

To obtain the mesoscopic density profile of the adsorbate in the pore, we divided the pore volume into two-dimensional bins in the radial and axial directions and ensemble-averaged the argon density in each bin during the sampling stage. The mesoscopic density profile is smoothed by coarse-grained averaging the local density distribution within the radius of half of the argon collision diameter in both radial and axial directions.

### Experimental results

The graph in Fig. 5 shows two typical adsorption isotherms for open pores having a size \(D_p = 83\ nm\) (continuous line) and for the same pores after one side has been blocked with glue...
(dashed line). These curves represent $\Delta l/l_0$ as a function of the relative pressure, $P/P_0$ of the surrounding vapor, where $P_0 = 65$ kPa is the bulk saturation pressure for liquid Ar at 85 K. They show negligible adsorption apart from a very steep and large step occurring close to saturation due to capillary filling of the pores, followed by a plateau indicating that the pores are full and a new rise very close to saturation caused by condensation of a thick liquid film on the two faces of the AAO disc. More interestingly, the plateau corresponding to the closed end pores is about 30% smaller than that of the open pores, indicating that the glue entered a fraction of the pore length due to capillary suction. To facilitate their comparison, the graph inset displays the data on a greatly enlarged scale close to saturation with the adsorption data normalized to the values of the plateaus observed after the capillary condensation. Both curves show pronounced hysteresis loops between the condensation and evaporation branches. This observation is consistent with previous results obtained for porous silicon,27,28,41 silicon29 and AAO30–32 and is likely to be a consequence of pore irregularities.28,40 The hysteresis loops have nearly parallel adsorption and desorption branches (type H1) suggesting that the pore roughness is not as significant as in disordered materials like porous silicon27,28,41 which exhibit asymmetrical hysteresis loops (H2 type).

Assuming pores of cylindrical shape, we have analyzed the position of the evaporation branches in Fig. 5 in terms of eqn (3), where the liquid Ar surface tension is $\gamma = 13.1$ erg cm$^{-2}$ and its number density $n_l = 2.1 \times 10^{22}$ atoms cc$^{-1}$, both evaluated at a temperature of 85 K, and we have assumed that liquid Ar completely wets the inner walls of the pore and the capping material.30 For the membrane, evaporation occurs in the interval $P/P_0 = 0.9715 \leq P/P_0 \leq 0.9737 = P_0/P_0$ with the midpoint at $P_{\text{mid-point}}/P_0 = 0.9732$. Here, $P_0/P_0$ [$(P_0/P_0^*)$] corresponds to a normalized adsorption of 15% (85%). This analysis yields $D_p = 78 \pm 3$ nm, where we assumed that $D_r = D_p \pm \sigma$, which is in substantial agreement with the value $D_p = 83 \pm 1$ nm derived from the real space images of the pores. Indeed considering the crudity of the thermodynamic model employed, this quantitative agreement is rather surprising. Since the desorption branch of the closed end pores is practically coincident with that of the open pores, the thermodynamic analysis yields essentially the same results, as expected.

However, the novel result here is that the hysteresis loop for the closed end pores is much narrower than that for the open pores and the adsorption and desorption boundaries of this loop envelop the desorption branch of the corresponding open end pores. Fig. 6 compares these results with the analogous ones measured in a different sample (II) with pores of the same nominal size. The fact that the loops are very similar is an indication of the good reproducibility of the fabrication methodology. The fact that the desorption branches coincide implies that the pores II have the same size as pores I, although the slight difference between the two adsorption branches suggests microscopic differences between the two samples. The results presented in Fig. 6 confirm the preliminary observation taken with distinct Open and Closed AAO samples having the same nominal size $D_p = 60$ nm (see Fig. 4 of ref. 30).

This behavior is shared by pores of smaller size. Fig. 6 also shows the hysteresis loops measured in Open and Closed samples with straight pores having $D_p = 67$ nm (i). It is evident that the hysteresis loop depends on the pore size. As $D_p$ increases, the condensation pressure moves closer to $P_0$, the loop gets narrower, and the two branches become more parallel and much steeper for both open and closed end pores. The shift of the loop to a higher relative pressure for larger pores is consistent with the Cohan’s model. The Closed samples present a much narrower hysteresis loop centered on the desorption branch of the corresponding Open samples. This is a partial confirmation of Cohan’s model based on the different shapes of the meniscus in adsorption and desorption. The recent observation32 of fully reversible adsorption in Closed samples made using a combination of advanced nanolithography and wet-etching that produce very regular pores with smooth walls suggests that the narrow but still observable hysteresis loops found on the Closed AAO samples are the result of their intrinsic morphological disorder. Hysteretic adsorption behavior has also been reported in numerical simulations on smaller pores with closed ends.35,37–39 According to these studies, the shift downward of the adsorption branch in closed end samples with respect to the corresponding open samples can be attributed to the stronger potential energy field due to overlap from adjacent adsorbent surfaces in the vicinity of the closed end.39 The difference between the two relative pressures can be roughly accounted for by the difference in the curvature between the hemispherical meniscus in closed bottom pores and the cylindrical one in open pores.34 At variance with these simulations,39 the hysteresis loops in Fig. 6 do not show branches more inclined for the Closed samples than the Open samples.

However, this behavior is in contrast to that found in straight pores with $D_p = 22$ nm. Fig. 7 shows the final part of
the isotherms measured in two different samples (1 and 2) before and after the pore capping. In both cases, adsorption is decreased by ∼20% after the pore is capped, suggesting that the glue filled a fraction of the pore length as already discussed. The inset shows the normalized hysteresis loops. In contrast to the isotherms for large pores ($D_p \geq 67$ nm), where the desorption branches of pores with the same $D_p$ practically overlap regardless of the pore openings, in these small pores the adsorption branches coincide, while the evaporation branches differ slightly. In particular, the loops for the closed pores are a little wider than those of the corresponding open pores. This behavior resembles that found on modulated alumina pores where the adsorption isotherms for Open and Closed matrices are almost identical.\(^{51}\) The explanation indicated by numerical simulations is that capillary condensation and evaporation in the modulated pores occur through the same filling and emptying mechanisms, which are driven by the smallest constrictions of the pores. By analogy, adsorption in straight pores with $D_p = 22$ nm can be explained assuming that the cross-section of the pores is not constant along their axes. Although this morphological feature is difficult to quantify, an SEM investigation of the pore cross-sections shows a variation in the pore diameter along its axis of about 1 nm, regardless of the value of $D_p$. Our study suggests that this geometrical irregularity is the determinant for the $D_p = 22$ nm pores but it becomes negligible for large pores ($D_p \geq 67$ nm), and this is substantiated by our computer simulation below.

**Simulation results**

The experiments have clearly shown that the irregularities in the width of the alumina pore walls have a predominant effect on the adsorption mechanism, leading to different features in the adsorption isotherms depending on the pore size. We have studied this corrugation effect using Monte Carlo simulations and the simple pore model described in Fig. 4. Assuming the degree of corrugation for the experimental alumina to be the same for all pore sizes, the relative size between the constriction and the pore ($D_c/D_p$) increases as the pore size ($D_p$) decreases. Since investigating large pores (greater than 20 nm) is impossible with our current supercomputer capacity, we chose a relatively large mesopore of diameter 6 nm and length 20 nm as a representative model. Instead of varying the pore size to study the corrugation effect, we kept the pore dimensions constant and varied the constriction size ($D_c$) accordingly. The corrugation or constriction effect, represented by the ratio $D_c/D_p$, increases as the constriction size $D_c$ increases. Detailed dimensions of these pores (from A to D) were mentioned previously.

Fig. 8 shows the adsorption isotherms of argon in pore A (uniform pore) and pore B (slightly corrugated pore) with two open ends and one closed end. There is only a slight shift between these isotherms which indicates that the adsorption mechanism in the pore B is negligibly affected by the constriction. This is demonstrated in the schematic adsorption mechanism illustrated in Fig. 9. The mechanism of adsorption of Open B is the same as that in a uniform cylindrical pore which has been reported elsewhere:\(^{37}\) molecular layering on the pore surface (point $A_1$) followed by a rapid capillary condensation to fill the pore (point $A_2$), while the desorption is governed by the receding menisci at two pore ends ($D_1$) followed by a sharp evaporation when the liquid bridge, formed between the menisci, becomes unstable (point $D_3$) and disappears leaving adsorbate layers on the pore wall (point $D_4$). In Closed pore B, the mechanism of adsorption is similar to that in a uniform closed end pore and is governed by the movement of the meniscus along the pore axis and the restructuring of the condensed phase in the pore, which is the underlying cause of the hysteresis. Details of the mechanism in a closed end cylindrical pore have been discussed previously.\(^{18}\) Thus, when the constriction effect is small ($D_c/D_p \sim 1$), the mechanism of adsorption in the constricted pore is similar to that in the

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**Fig. 7** (Color online). Final portions of Ar adsorption isotherms measured at 85 K in alumina straight pores of the same nominal size, 22 nm, open at both ends and with closed ends. Inset: hysteresis loops of the normalized hysteresis loops.

**Fig. 8** Adsorption isotherms of argon at 85 K in pores A and B with two open ends (filled symbols) and with one closed end (open symbols).
corresponding uniform pore. The closed end pore has a narrower hysteresis loop and the desorption branch of the open pore falls between the adsorption and desorption boundaries of the hysteresis loop of the closed end pore, which closely resembles the behavior found in the experiments with AAO pores $D_p \geq 67$ nm shown in Fig. 5 and 6. The reason for this is that evaporation occurs at a slightly higher pressure in the open pore because of the larger interface of the two menisci in this pore compared to only a single meniscus in the closed end pore.

In more corrugated pores (pores C and D), the isotherm behaves differently. Open and closed end pores of the same size yield almost identical isotherms as shown in Fig. 10. This is due to the fact that both condensation and evaporation are governed by the adsorption behavior in each section between two corrugations in the pore, and this means that the presence of a closed end is inconsequential. Once a phase transition occurs in one section within the pore, which normally starts at the middle of the open end pore or near the pore end in the closed end pore (Fig. 11a and b), this will act as an “ignition site” that induces the phase transition over the whole pore. This mechanism accounts for the sharp condensation/evaporation branches in the constricted closed end pore, as opposed to the more gradual transition in the uniform closed end pore (Fig. 9b). A comparison of pore C with pore D reveals that their adsorption branches are the same, but that their

Fig. 9 Adsorption isotherms and local density profiles of argon at 85 K in pore B with (a) two open ends and (b) one closed end.

Fig. 10 Adsorption isotherms of pores C and D with two open ends (filled symbols) and one closed end (open symbols).

Fig. 11 Adsorption isotherms and local density profiles of argon at 85 K in pore D with (a) two open ends and (b) one closed end.
desorption-branches show sharp jumps in density at different pressures. These phenomena, known as “cavitation” for pore D and “cavitation-like pore blocking” for pore C, have been commonly observed for ink-bottle and connected pores. In this particular pore model, the constrictions act like pore necks which control evaporation in the cavities.

Another interesting feature of the closed end corrugated pore is that there is a slight bend in the adsorption branch, consistently observed for both pores C and D (from point A2 to A3). This is due to the stronger solid-fluid interaction in the pore section near the closed end that is responsible for the condensation occurring at this location before the other pore sections. After this end section has been filled, the adsorbate layers in the other sections are still not thick enough to induce condensation and they continue to grow from point A2 to A3 until condensation occurs in the whole pore at point A4. This behavior was not observed experimentally because the pore sizes are greater in the experimental adsorbents and it is probable that strong sites exist in the middle of the pore that induce the initial condensation there, rather than that at the closed end.

Conclusions

We have fabricated porous alumina membranes characterized by straight, unconnected pores having a very narrow pore size distribution. With a torsional microbalance we have systematically studied the effect on adsorption of blocking one end of the pores. An unexpectedly rich phenomenology, dependent on the pore size, is found. For large pores \( D_p \geq 67 \text{ nm} \), the isotherms for closed end pores present much narrower hysteresis loops whose adsorption and desorption boundaries envelop the desorption branches of the isotherms of the corresponding open pores of the same size. By contrast, in the isotherms for smaller pores \( D_p = 22 \text{ nm} \), the loop of the closed end pores is slightly wider than that of open pores while the adsorption branches coincide. For the large pores, on the other hand, the desorption branches of pores with the same \( D_p \) overlap regardless of the pore openings. These observations are in agreement with our grand canonical Monte Carlo (GCMC) simulations for a cylindrical pore model with constrictions, which show that the adsorption isotherms depend on the ratio of the constriction size to the pore size \( (D_c/D_p) \). Overall, both experimental and simulation studies provide a clear demonstration of the effects that the corrugation of the pore walls has on adsorption, particularly in small pores. These results can be extended to other porous materials like porous silicon and silica SBA and MCM which share the same morphology: straight, non-connected pores having somewhat corrugated walls.

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