Comment on “Capillary Filling of Anodized Alumina Nanopore Arrays”

A recent Letter [1] presents a study of adsorption-desorption of perfluoromethylcyclohexane (PFMC) in an array of cylindrical pores in Al2O3. A hysteretic transition is observed. It is argued that its width (0.4 K) is 5 times smaller than the prediction by Cohan [2] (1.9 K) and that the data agree better with the Cole-Saam theory (CST) [3,4], which includes interactions with the pore walls. By carrying the comparison to its full extent, this Comment questions some conclusions of Ref. [1].

Adsorption is usually measured at constant temperature $T$ by increasing the pressure $P$ of a vapor from 0 to the saturated vapor pressure $P_{\text{sat}}(T)$. The CST calculates the liquid volume fraction $V$ as a function of $p = P/P_{\text{sat}}(T)$. Alvine et al. measure $V$ as a function of the temperature offset $\Delta T$ between the porous sample at $T_s$ and a liquid PFMC reservoir at $T_r$. They find that the volume fractions at the onset of filling ($V_c$) and the completion of emptying ($V_m$) compare well with the CST, but they explain that, in CST, “there is no prediction of the $\Delta T$ where the desorption transition initiates [$\Delta T_m$], and it is not possible to translate $V_c$ and $V_m$ into a hysteresis width.” We shall see that the CST does provide a relation between $V$ and $\Delta T$, which disagrees with the data. Before that, we criticize the calculation of adsorption made in Ref. [1] within a Derjaguin approximation to the CST: the film thickness $d$ before filling is assumed small compared to the pore radius $R$, leading to Eq. (7) of Ref. [1]. The solid curve in Fig. 3 of Ref. [1] gives the impression of describing well the filling, including the experimental filling temperature $\Delta T_{\text{exp}} = 1.9$ K. However, our calculation for $R = 11.8$ nm (used in Ref. [1]) produces a different curve, with $\Delta T_c = 2.7$ K and $d = 2.8$ nm at filling (instead of 3.3 nm [1]). To find $\Delta T_{\text{exp}}$ requires $R = 16$ nm, out of the range of electron microscopy measurements ($10.5 \pm 2.5$ nm) [1]. We now turn to the comparison with the full CST (assuming $d \ll R$).

In Ref. [1], $T_s$ sets the vapor pressure at $P_{\text{sat}}(T_r)$. As $T_s$ goes down to $T_r$, $P = P_{\text{sat}}(T_r)/P_{\text{sat}}(T_s)$ increases up to 1, and $V(p)$ can be converted into $V(\Delta T)$, using $\Delta T = -(N_{\text{mol}}k_B T_r^2/H_{\text{vap}})\ln p$, with $H_{\text{vap}} = 33.9$ kJ mol$^{-1}$ [1]. As $\Delta T/T_r$ is a few percent, we ignore the $T$ dependence of other parameters. If the pores all have the same $R = 11.8$ nm, the full CST predicts $\Delta T_c = 2.8$ K, $V_c = 0.43$, $\Delta T_m = 4.5$ K, and $V_m = 0.22$ (Fig. 1). The CST does not agree better with the data than the Cohan theory. To reproduce $\Delta T_{\text{exp}}$, one must change $R$ or the Hamaker constant $A$ for PFMC on Al2O3. $R = 16.2$ nm gives $\Delta T_c = 1.9$ K, $V_c = 0.38$, $V_m = 0.18$, but $\Delta T_m = 3.2$ K remains too high; anyhow, $R$ cannot be that large. Going back to $R = 11.8$ nm, $\Delta T_c$ depends weakly on $A$: one needs to divide $A$ by $10^4$ to find $\Delta T_{\text{exp}}$, but $V_c = 0.05$ and $V_m = 0.01$ are then too low and $\Delta T_m = 3.8$ K too high.

 Alvine et al. note also that “the desorption transition occurs at lower $\Delta T$ than either prediction” and “while some of the shift may be due to broadening of the transition by pore diameter polydispersity, this effect seems insufficient to fully account for the shift.” Following [4], where the CST was compared with helium data, we have tried a Gaussian distribution: the transitions broaden but remain centered on the same $\Delta T$ (Fig. 1).

The CST does not give a satisfactory account of the results, not only for desorption, as stated in Ref. [1], but also for adsorption. Complete wetting has been assumed. If wetting is only partial with a contact angle $\theta$, $\Delta T_m$ is lowered [2]. The hysteresis width is multiplied by $2\cos\theta - 1$; $\theta = 53^\circ$ would fit the experiment. It would be interesting to measure $\theta$. To improve the theoretical description, one may use simulations or density functional theory [5]. The existence of a hysteresis critical temperature $T_{\text{ch}}$, at which hysteresis vanishes [6], could also be relevant. From the ratio between the molecular diameter of PFMC and $R$, we estimate $T_{\text{ch}} \approx 430$ K, and $T_r/T_{\text{ch}} \approx 0.71$.

Frédéric Caupin
Laboratoire de Physique Statistique
ENS-CNRS-P6-P7
24 rue Lhomond, 75005 Paris, France

Received 19 January 2007; published 20 June 2007
DOI: 10.1103/PhysRevLett.98.259601
PACS numbers: 61.10.Eq, 05.70.−a, 68.08.Bc