

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 Al_2O_3 . 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 ΔT 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 ΔT where the desorption transition initiates [ΔT_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 ΔT , 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 $\Delta T_c^{\text{expt}} = 1.9$ 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 ΔT_c^{expt} requires $R = 16$ nm, out of the range of electron microscopy measurements (10.5 ± 2.5 nm) [1]. We now turn to the comparison with the full CST (without assuming $d \ll R$).

In Ref. [1], T_r 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 $\Delta T = -(N_A k_B T_r^2 / H_{\text{vap}}) \ln p$, 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 ΔT_c^{expt} , one must change R or the Hamaker constant A for PFMC on Al_2O_3 . $R = 16.2$ 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, ΔT_c depends weakly on A : one needs to divide A by 10^4 to find ΔT_c^{expt} , but $V_c = 0.05$ and $V_m = 0.01$ are then too low and $\Delta T_m = 3.8$ K too high.

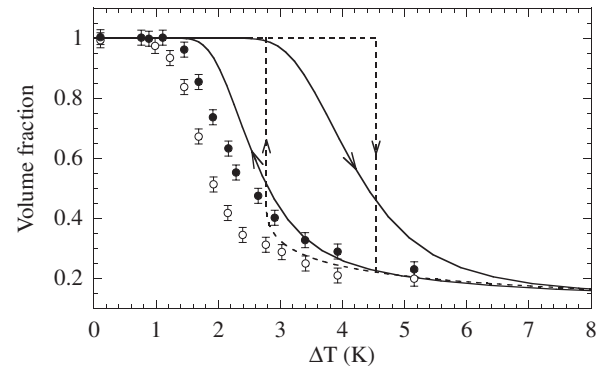


FIG. 1. Comparison of adsorption (\circ) and desorption (\bullet) data with the CST for a single pore radius $R = 11.8$ nm (dashed curves) and a Gaussian distribution of pore radii (average $R = 11.8$ nm, rms deviation 2.5 nm) (solid curves).

Alvine *et al.* also note that “the desorption transition occurs at lower ΔT 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 ΔT (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 θ , ΔT_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 θ . To improve the theoretical description, one may use simulations or density functional theory [5]. The existence of a hysteresis critical temperature T_{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 $T_r/T_{\text{ch}} \approx 0.71$.

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- [1] K. J. Alvine *et al.*, Phys. Rev. Lett. **97**, 175503 (2006).
- [2] L. H. Cohan, J. Am. Chem. Soc. **60**, 433 (1938).
- [3] M. W. Cole and W. F. Saam, Phys. Rev. Lett. **32**, 985 (1974).
- [4] W. F. Saam and M. W. Cole, Phys. Rev. B **11**, 1086 (1975).
- [5] L. D. Gelb *et al.*, Rep. Prog. Phys. **62**, 1573 (1999).
- [6] K. Morishige and M. Shikimi, J. Chem. Phys. **108**, 7821 (1998).