Letters to the Editor

Condition for an adsorption hysteresis loop to appear in narrow cylindrical pores

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Experimental studies of the adsorption isotherms in mesoporous materials with cylindrical channels having different diameters D have shown[1—4] that hysteresis loops are observed only for adsorbents with channel diameters $D^* \geq 4$ nm, although all the modern theoretical methods[5,6] (molecular dynamics, Monte Carlo method, the lattice gas model, the density functional theory) indicate that the hysteresis loops should exist at $D^* \geq 2$ nm.

Now we attempt to interpret this contradiction. The region of D sizes relates to small systems, in which, according to mathematical theory,[7] phase transitions are impossible. This is confirmed by precise results for $D = \lambda$ ($\lambda = 2^{1/6}\sigma$ is the monolayer size, σ is the size of the solid sphere of molecules in the Lennard-Jones potential).[7] An increase in the diameter to two or three cylindrical layers preserves the quasi-one-dimensional type of the system. This can be confirmed by direct precise calculations by the fragment method.[8] However, on further increase in D, the fluid should pass into the three-dimensional state in which phase transitions do occur. Therefore, there exists some critical size $D_1 = D/\lambda$ where the system still remains quasi-one-dimensional but at $D_2 = D_1 + 1$, the system loses the quasi-one-dimensional properties to acquire conditions for a phase transition at the critical temperature $T(D_2) > T$, resulting in a hysteresis loop exhibited by the isotherm at the temperature T.

Formally, the transition from one- to three-dimensional properties in cylindrical channels takes place at $D \to \infty$. Since phase transitions occur as well for intermediate two-dimensional systems, conditions for the loss of quasi-one-dimensional behavior should be formulated. This can be done using the properties of phase diagrams in porous solids.[9,10] An important feature of such diagrams is the presence of several domes, each corresponding to the successive filling of cylindrical layers. As the criterion for the possibility of phase transitions, one can propose the condition that the inner fraction of pore space, which is described by one common dome, should not be smaller than the fraction falling to the near-wall monolayers. If the near-wall fraction of the pore exceeds the central fraction, such pore would retain the quasi-one-dimensional properties, which preclude the phase transition.

This criterion can be easily expressed in the continual model as $R = [(D_1 - 2n_w)/D_1]^2 \geq 1/2$, where n_w is the number of near-wall monolayers (this coincides with the

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number of the corresponding domes in the full phase diagram). The n_w value can vary from 1 to 3 depending on the type of the adsorbate—wall potential. The value $n_w = 0$ corresponds formally to hydrophobic walls; the filling of narrow pores depends on the presence of impurities on them; however, this is not taken into account in the continual model. The proposed criterion allows one to estimate the region of sizes of cylindrical pores that retain the one-dimensional behavior. For these n_w values (1, 2, and 3), we get that the condition $R \approx 0.5$ is matched by pore diameters $D_1 = 8$, 14, and 20 λ.

The pore diameters found can be compared with the experimental data[1—4] for the adsorption of argon atoms and nitrogen molecules in mesoporous materials of the MSM-41 type. For both gases,[10] $n_w = 2$; therefore, with the size of molecules[11] $\sigma(Ar) = 0.3405$ nm and $\sigma(N_2) = 0.37$ nm, for a closely packed fluid structure with 12 closest neighbors, we obtain $D^* = 3.79$ and 4.12 nm, respectively. These values are in good agreement with published data according to which for the adsorption of argon, the hysteresis loop disappears[3] around $D \sim 3.6$—4.14 nm, while in the case of nitrogen adsorption, the onset of the hysteresis loop falls[4] to $D \sim 4.4$ nm.

Thus, the concept of quasi-one-dimensionality of the fluid located in narrow cylindrical pores reflects the size effects of the system and provides interpretation for the discrepancies between the theoretical and experimental estimates of D^*. The adjustment of experimental and theoretical D^* values opens up the way to the search for the pore size distribution function from the hysterersis loop data.

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