Quasi-2D Phase Transition of Methane Adsorbed in Cylindrical Silica Mesopores

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Recently, experimental small-angle neutron scattering (SANS) experiments identified a possible phase transition of methane adsorbed in MCM-41 and SBA-15, two cylindrical silica mesoporous adsorbents, indicated by a unexpected increased in the adsorbed fluid density at liquid-like conditions [1]. To better understand this observed phenomena, we used Monte Carlo and molecular dynamics simulations to examine the adsorption of methane in cylindrical silica mesopores of varying size and at varying temperatures and pressures. Our initial simulation results identified a roughly 10 % increase in the density of the liquidlike adsorbed phase for either an isotherm with increasing pressure or an isobar with decreasing temperature and that this densification is associated with a local maximum in the isosteric enthalpy of adsorption. Subsequent analysis of the simulated fluid, via computation of bond-orientational order parameters of specific annular layers of the adsorbed fluid, showed that the layers undergo an ordering transition from a disordered, amorphous state to one with two-dimensional hexagonal structure. Furthermore, this two-dimensional restructuring of the fluid occurs at the same thermodynamic state points as the aforementioned densification and local maximum in the isosteric enthalpy of adsorption. We thus conclude that the densification of the fluid is the result of structural reorganization, which is signaled by the maximum in the isosteric enthalpy. Owing to the qualitative similarity of the structural transitions in the simulated and experimental methane fluids, we propose this hexagonal reorganization as a plausible explanation of the densification observed in SANS measurements [2]. Lastly, we discuss why this structural transition has never been previously observed and how it may impact the transport properties of the adsorbed fluid.

References

[1] W-S. Chiang et al., Langmuir, 32:8849 (2016).[2] D.W. Siderius, W.P. Krekelberg, W-S. Chiang, V.K. Shen, and Y. Liu, Langmuir, 33:14252 (2017).