223f Density Functional Theory Model of Adsorption on Amorphous and Microporous Solids

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Recent progress in the theory of adsorption on porous solids, in general, and in the adsorption methods of pore structure characterization, in particular, has been related to a large extent to the application of the density functional theory (DFT) of inhomogeneous fluids. DFT has helped qualitatively describe and classify adsorption and capillary condensation in pores of different geometries. It has been shown that the non-local density functional theory (NLDFT) with suitably chosen parameters of fluid-fluid and fluid-solid interactions quantitatively predicts the positions of capillary condensation and desorption transitions of argon and nitrogen in cylindrical and spherical pores of ordered mesoporous molecular sieves, such as MCM-41, SBA-15, SBA-16 and others. At the same time, current implementations of NLDFT have a significant drawback: theoretical adsorption isotherms in the region of polymolecular adsorption exhibit multiple steps associated with layering transitions, which are not observed experimentally due to inherent energetic and geometrical heterogeneities of real surfaces. In this work, we present a novel non-local quenched solid density functional (NLQSDFT) model, which provides a realistic description of adsorption on amorphous surfaces without resorting to computationally expensive two- or three-dimensional DFT formulations. The main idea is to consider solid as a quenched component of the solid-fluid mixture rather than the source of the external potential. Introduction of the solid density distribution in NLQSDFT eliminates strong layering of the fluid near the walls that was a characteristic feature of NLDFT models with smooth pore walls. As a result, NLQSDFT predicts qualitatively correct isotherms in the multilayer adsorption region. Moreover, the effects of microporosity are naturally incorporated into the model. We present examples of calculated adsorption isotherms on amorphous and microporous solids, which are in qualitative agreement with experimental measurements on typical micro-mesoporous silicas, such as SBA-15, FDU-1 and others. The main advantage of the proposed approach is that NLQSDFT retains one-dimensional solid and fluid density distributions, and thus, provides computational efficiency and accuracy that are important for pore size distribution calculations from experimental data. NLQSDFT model offers a systematic approach to the account for the surface roughness/heterogeneity in pore structure characterization methods.