Simplified crossover droplet model for adsorption of critical and supercritical fluids in slit nano-pores

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Supercritical fluid (SCF) extraction technology is widely used in the pharmaceutical and food industries, in biotechnology, in nanoscale materials technology, and in microelectronics. Exploration of the possibilities offered by SCF extraction requires an accurate and detailed knowledge of the thermodynamic and interfacial properties of fluids in the volume and confined systems as well. However, so far nor a comprehensive "global" physical model for the excess adsorption of the supercritical fluids at solid-liquid interface in the volume and in nano-pores has been developed yet. In this work, we present a generalized crossover (GC) model for the excess adsorption of pure fluids at a flat solid-liquid interface, which reproduces scaling behavior of the excess adsorption in the critical region, and is reduced to the classical, van der Waals-type analytical model far away from the bulk critical point. In developing this model, we used the density-functional theory (DFT) approach for the order parameter profile calculations with a generalized corresponding states model for the local free-energy density [1]. The GC DFT model well represents the available experimental adsorption data for Kr/graphite, C_2H_4/graphite, C_3H_8/griphite, CO_2/silica, and SF_6/graphite systems in the entire density range and temperatures up to $1.7T_c$. In the critical region the GC DFT model is consistent with the predictions of the asymptotic renormalization-group (RG) crossover model for the critical adsorption in a semi-infinite system developed earlier [2]. For the excess adsorption on the critical isochore, both theories predict a scaling-law behavior, but fail to reproduce a "critical depletion" of the excess adsorption along the critical isochore of the SF_6/graphite system near T_c. We show that an anomalous decrease of adsorption observed in this system in the critical region can be explained by finite-size effect, and develop a simplified crossover droplet (SCD) model for the excess adsorption in a slit pore [3]. With the effective size of the pore of L=50 nm, the SCD model reproduces all available experimental data for SF_6/graphite, including the critical isochore data at $T \sim T_c$, within experimental accuracy and yields excellent quantitative description of all critical adsorption data obtained for this system and CO_2/silica gel system as well. Application of the SCD model to the excess adsorption of carbon N_2O on the silica gel is also discussed.

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