

## A simplified crossover droplet model for adsorption of pure fluids in slit pores

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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. The GC DFT model well represents the available experimental adsorption data for Kr/graphite, C<sub>2</sub>H<sub>4</sub>/graphite, C<sub>3</sub>H<sub>8</sub>/graphite, CO<sub>2</sub>/silica, and SF<sub>6</sub>/graphite systems in the entire density range  $0 < \rho \leq 3\rho_c$  and temperatures up to  $1.7T_c$ . In the critical region,  $0.5\rho_c < \rho \leq 1.5\rho_c$  and  $T \leq 1.15T_c$ , the GC DFT model is consistent with the predictions of the asymptotic renormalization-group crossover model for the critical adsorption in a semi-infinite system developed earlier. For the excess adsorption on the critical isochore, both theories predict a scaling-law behavior  $\Gamma \propto \tau^{-\nu+\beta}$ , but fail to reproduce a “critical depletion” of the excess adsorption along the critical isochore of the SF<sub>6</sub>/graphite system near  $T_c$ . We show that an anomalous decrease of adsorption observed in this system at  $\tau = T/T_c - 1 < 10^{-2}$  can be explained by finite-size effect, and develop a simplified crossover droplet (SCD) model for the excess adsorption in a slit pore. With the effective size of the pore of  $L=50$  nm, the SCD model reproduces all available experimental data for SF<sub>6</sub>/graphite, including the critical isochore data where  $\tau \rightarrow 0$ , within experimental accuracy. At  $L \gg \xi_b$  (where  $\xi_b$  is a bulk correlation length) the SCD model is transformed into the GC DFT model for semi-infinite systems. Application of the SCD model to the excess adsorption of carbon dioxide on the silica gel is also discussed.

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