# Simplified Crossover Droplet Model for Adsorption of Critical and Supercritical Fluids in Slit Nano-Pores

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#### ABSTRACT

In this work, we present a simplified crossover droplet (SCD) model for of pure fluids at a flat solid-liquid interface and in slit pores. The SCD contains size pore, L, as a parameter and at  $L \gg \xi_b$  (where  $\xi_b$  is a bulk correlation length) is transformed into the generalized crossover model for the excess adsorption in semi-infinite systems. With L=50 nm, the SCD model reproduces all available experimental data for  $SF_6$ /graphite, including the critical isochore data at  $\tau \rightarrow 0$ , within experimental accuracy. The SCD model also yields excellent description of critical adsorption data for CO<sub>2</sub>/silica gel system. Application of the SCD model to the description of experimental adsorption data for N<sub>2</sub>O/silicia gel system is also discussed.

#### **1 THEORETICAL BACKGROUND**

The surface excess adsorption of pure fluids on a planar interface surface is defined as

$$\Gamma_{\infty} = \int_{0}^{\infty} (\rho(z) - \rho_{b}) dz$$
 (1)

where  $\rho(z)$  is density of fluid at a distance z from the surface, and  $\rho_b = \rho(\infty)$  is the bulk density of the fluid. The density profile  $\rho(z)$ can be found from the optimization of the functional

$$\mathcal{F}[\rho(z)] = \int \left[\hat{A}(\rho) + c_0 \left(\nabla\rho\right)^2 + W_s(\rho)\right] dV \quad (2)$$

where  $\hat{A}(\rho) = \rho A(T, \rho)$  is a Helmholtz freeenergy density of the bulk fluid and  $W_s(\rho)$  is the surface contribution into the free energy density. Finally, the excess adsorption in a semi-infinite system is given by [1, 2]

$$\Gamma_{\infty} = \int_{\rho_{1}}^{\rho_{b}} \frac{\left(\rho - \rho_{b}\right)}{\left[\Delta \hat{A}(\rho)\right]^{1/2}} d\rho , \qquad (3)$$

where  $\Delta \hat{A}(\rho) = \hat{A}(\rho) - \hat{A}(\rho_b) - (\rho - \rho_b)\mu(T)$  is the excess part of the free-energy density, and  $\mu(T) = \mu(T, \rho_b)$  is the chemical potential of the bulk fluid. An equation of state for the surface order parameter,  $m_1 = \rho_1 / \rho_c - 1$ , which can be written in the form

$$4c_0 \Delta \hat{A}(\rho_1) = (2b_1 m_1 - h_1)^2 \rho_c^{-2}, \qquad (4)$$

provides a relationship between the surface ordering field  $h_1$  and surface density  $\rho_1$  at any fixed values of the temperature T and bulk density  $\rho_b$ . The temperature dependence appears in Eq. (4) through the excess free-energy density  $\Delta \hat{A}(\rho_1)$ , surface ordering field  $h_1$ , and parameters  $b_1$  and  $c_0$ . In Eq. (4) the parameter  $b_1 = b_{10}\sqrt{c_0k_BT}$ , while the surface field is represented by truncated Taylor expansion

$$h_1(\tau) / \sqrt{c_0 k_B T_c} = h_{10} + \sum_{i=1} h_{1i} \tau^i$$
, (5)

where  $b_{10}$ ,  $c_0$ , and  $h_{1i}$  are the system dependent coefficients.

#### **2 DROPLET MODEL**

In the crossover droplet model, a fluid near the critical point is considered as an "ideal gas" of homogeneous liquid droplets with the droplet radius equal to the correlation length of a bulk fluid at a temperature T and density  $\rho$ ,  $r = \xi_b(T, \rho)$ . According to this picture, Eq. (3) in the droplet model for the excess adsorption in a slit pore should be replaced by

$$\Gamma_{L} = \int_{\rho_{l}}^{\rho_{L/2}} \frac{\left(\rho - \rho_{L/2}\right)}{\left[\Delta \hat{A}(\rho)\right]^{l/2}} d\rho , \qquad (6)$$

where  $\rho_{L/2}$  is the density at the center of the pore at z = L/2. In the case, when the correlation length is much smaller than the distance between walls in the pore, or the same  $\xi_b \ll L/4$ , the density  $\rho_{L/2} = \rho_b(T, P)$ , equation (6) is transformed into Eq. (3), and a slit pore becomes physically equivalent to a semi-infinite system,

 $\Gamma_L \equiv \Gamma_\infty$ . In the opposite case, at  $\xi_b \ge L/4$ , the density  $\rho_{L/2}$  becomes very close to the surface density  $\rho_1$  ( $\rho_{L/2} \rightarrow \rho_1$ ), and, as a consequence,  $\Gamma_L \rightarrow 0$ . In the intermediate region, when the correlation length is still smaller than L ( $\xi_0 \ll \xi_b < L/4$ ), but the density at the center of the pore is not equal to the bulk density  $\rho_h$  $(\rho_1 > \rho_{L/2} > \rho_b)$ the excess adsorption exhibits a crossover between these two regimes,  $0 < \Gamma_L < \Gamma_\infty$ , with the maximum at  $\xi_h \cong L/4$ .

All thermodynamic properties for a bulk fluid in the simplified crossover droplet model are calculated with a generalized corresponding sates crossover model [3], while an explicit dependence of the density  $\rho_{L/2}$  on L and  $\xi_b$  is given by [2]

$$\rho_{L/2} = \rho_b - (\rho_b - \rho_1) \tanh\left(\frac{x^2}{1+x}\right), x = 4\xi_b / L \quad (7)$$

In Eq. (7) for the correlation length  $\xi_b$  we use the Ornstein-Zernike approximation

$$\xi_b = \sqrt{c_0 \overline{\chi}_T / \chi_0^+} , \qquad (8)$$

where  $\chi_0^+$  is the asymptotic amplitude in the power law  $\overline{\chi}_T \Big|_{\rho=\rho_c} = \chi_0^+ \tau^{-\gamma}$  (where  $\gamma=1.24$  is a universal critical exponent) for the isothermal  $\overline{\chi}_{T} = \rho T \left( \partial \rho / \partial P \right)_{T} P_{c} \rho_{c}^{-2} T_{c}^{-1}$ compressibility along the critical isochore  $\rho = \rho_c$  of a bulk fluid at  $\tau = T/T_c - 1 \rightarrow +0$ .

### **3 RESULTS AND DISCUSSION**

The first system, which we considered in this work, is adsorption of hexafluoride on graphitized carbon black measured by Thommes et al. [4]. The theory predicts monotonically increasing behavior of the excess adsorption in a semi-infinite system along the critical isochore at  $T \rightarrow T_c$ , which diverges as  $\Gamma \propto \tau^{-\nu+\beta} \propto \tau^{-0.6}$  at  $\tau \rightarrow 0$  [1]. However, the excess adsorption in this system increases only down to a reduced temperature of  $\tau \simeq 0.01$ , but then  $\Gamma$  decreases sharply on approaching  $T_c$ . The "critical depletion" observed in experiment [4] is treated in the SCD model, as a density profile deformation, which appears in a slit pore when the size of the pore becomes comparable with the correlation length of a bulk fluid. At fixed

temperature T, the condition  $\xi_h \cong L/4$  along the critical isochore  $\rho_b = \rho_c$  is achieved at in a slit pore with size  $L \cong 4\xi_0 \tau^{-\nu}$  (where  $\xi_0 = \sqrt{c_0/\chi_0^+}$ is an asymptotic critical amplitude and the critical exponent  $v=\gamma/2=0.62$ ), or in the pore with a fixed size L at the reduced temperatures  $\tau \cong (4\xi_0 / L)^{1/\nu}$ . Estimation of the characteristic size of the pore with equation  $L_{c}$ 

$$=4\xi_0\tau_1^{-\nu},\tag{9}$$

where  $\tau_1 = 0.01$  is the reduced reentrant temperature observed in the experiment [4] and  $\xi_0 = 0.15 - 0.2$  nm is a reasonable estimate for pure SF<sub>6</sub>. yields  $L_c = 50 - 70$  nm, that is close to the value  $L_c = 31 \, \text{nm}$  reported by Thommes and Findenegg [5]. Taking into account the uncertainty in determination of the parameters  $\tau_1$ ,  $\xi_0$ , and the characteristic size  $L_c$  itself, we contend that this prediction is very good. Comparison of the predictions of the SCD model with excess adsorption data obtained by Thommes et al. [4] is shown in Fig. 1.



Figure 1: Surface excess adsorption isochores [4] of SF<sub>6</sub> on graphitized carbon black as functions of temperature.

The surface constants  $b_{10}$  and  $h_{1i}$  in Eq. (4) for SF<sub>6</sub>/graphitized carbon system have been found from the optimization of the SCD model to experimental data with the fixed values of  $\xi_0$  and  $L_c$ . As one can see from Fig. 1, along the critical isochore the excess adsorption calculated with the SCD model passes a maximum and, in agreement with experimental data, goes to zero as  $T \to T_c$ . At densities  $\rho / \rho_c = 1.2$  and 1.3 the excess adsorption calculated with the SCD model increases only slightly as the saturated temperature  $T_s(\rho)$  is approached, while at subcritical densities, at  $\rho / \rho_c = 0.7$  and 0.8,  $\Gamma$  increases sharply as  $T \to T_s(\rho)$ .

Another confined system considered here, is adsorption of carbon dioxide on silica gel, which is an adsorbent with a broad pore size distribution ranging from micropores of 0.8 nm to 16 nm [6, 7]. The quantity measured in the experiment [6] was the excess adsorption  $n^{ex}$ defined as

$$n^{ex} = \frac{V_{tot}}{V_{tot}} \int_{V_{tot}} \left[ \rho\left(\vec{r}\right) - \rho_b \right] dV , \qquad (10)$$

where is specific pore volume  $v_{tot} = V_{tot}/m_{sorb}$ and  $m_{sorb}$  is the mass of the adsorbent particle with the pore volume  $V_{tot}$ . In order to apply the SCD model for calculation of this quantity, one needs to specify the geometry and size distribution of the pores. In this work, silica gel was described as a porous media with onedimensional slit pores of three different widths,  $L_1$  with volume fraction  $x_{1v}$ ,  $L_2$  with volume fraction  $x_{2v}$ , and  $L_3$  with the volume fraction  $x_{1} = 1 - x_{1} - x_{2}$  (11)

$$x_{3v} = 1 - x_{1v} - x_{2v} . \tag{11}$$

In this case, the excess adsorption  $n^{ex}$  can be written in the form

$$n^{ex} = \left[\sum_{i=1}^{3} \left(\frac{2\Gamma_i}{L_i} + \rho_{li}\right) x_{iv} - \rho_b\right] v_{tot}, \qquad (12)$$

where  $\Gamma_i$  is the surface excess adsorption in the pore of size  $L_i$  calculated with Eq. (6). For the specific pore volume  $v_{tot}$  and merging pore sizes  $L_1 = L_{min}$  and  $L_2 = L_{max}$  we adopted the values reported in Ref. [7], while the parameters  $x_{1\nu}$ ,  $x_{2\nu}$ , and  $L_{3,}$ , as well as the surface constants  $b_{10}, c_0, h_{10}, h_{11}$ , and  $h_{12}$  in Eq. (4), have been found from optimization of the SCD model to experimental data [6]. Comparison of the predictions of the SCD model with experimental data for CO<sub>2</sub>/silica gel is shown in Fig. 2. As one can see, in the entire density range  $0 < \rho \leq 2\rho_c$ and temperatures up to  $1.53T_c$  excellent agreement between experimental data and predicted values of the excess adsorption for CO<sub>2</sub>/silica gel [6] system is observed.

The last system considered in this work, is adsorption of N<sub>2</sub>O on silica gel. Similar to the CO<sub>2</sub>/silica gel system, the gel parameters  $x_{1\nu}$ ,  $x_{2\nu}$ ,  $L_3$ , and the surface constants  $b_{10}$ ,  $c_0$ , and  $h_{1i}$  (*i*=02) have been found from optimization of the SCD model to the excess adsorption experimental data obtained for this system by Di Giovanni *et al.* [6]. The results of our calculations in comparison with experimental data for  $N_2O$ /silica gel are shown in Fig. 3.



Figure 2: Excess adsorption isitherms [6] of  $CO_2$  on silica gel as functions of density.



Figure 3: Excess adsorption isotherms [6] of  $N_2O$  on silica gel as functions of density.

As one can see, at low densities  $(0 < \rho < 0.7 \rho_c)$  the SCD model yields very good representation of the excess adsorption data for N<sub>2</sub>O/silica gel system in the entire temperature range  $T_c < T < 1.5 T_c$ . However, at near-critical isotherms large systematic deviations between

experimental data and predicted values are observed at densities  $0.8\rho_c < \rho < 1.2\rho_c$ . The SCD model also fails to reproduce the excess adsorption data at high densities,  $\rho > 1.5\rho_c$ . As one can see, similar to CO<sub>2</sub>/silica gel, for liquid N<sub>2</sub>O at densities the SCD model predicts the values of the excess adsorption of about 0.8-1.1 mmol/g, while the experimental values for N<sub>2</sub>O/silica gel system at near-critical isotherms are almost two times higher,  $n^{ex} \approx 2 \text{ mmol/g}$ .

At present time we cannot say for sure what causes this discrepancy between experimental data and theoretical predictions for the excess adsorption in N<sub>2</sub>O/silica gel system at high densities. We can only assume that except the density profile deformation, some other physical effects, which have not been considered in the SCD model, should be taken into account. One of them can be appearance of the orientational order parameter near the wall, which in principle can increase the excess adsorption of liquid N<sub>2</sub>O on silica gel. In order to answer this question, additional theoretical and experimental studies are needed.

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