

## Critical Adsorption of a Pure Fluid on a Graphite Substrate

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The surface excess amount  $\Gamma$  of  $\text{SF}_6$  on graphitized carbon (measured by a new volumetric technique) rises sharply on approach to the critical point along an isochoric path from the one-phase region of the fluid. For a limited range of reduced temperatures ( $0.02 > t > 0.001$ )  $\Gamma$  varies as a power law in  $t$ . Our data yield an exponent  $x=0.5$ , whereas the Fisher-de Gennes scaling theory predicts  $x = \nu - \beta = 0.3$ . Close to criticality confined-geometry effects become important.

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Specovius and Findenegg<sup>1</sup> measured the adsorption of a dense gas above its critical temperature on a solid substrate and observed a pronounced increase of the surface excess amount on approaching the critical point. This phenomenon is similar to the *critical adsorption* of binary liquid mixtures near a critical solution point, caused by preferential adsorption of one of the components at a liquid-solid interface<sup>2,3</sup> or the liquid-vapor interface<sup>4,5</sup> of the mixture. Here we report preliminary measurements on the temperature dependence of the adsorption of a fluid on a patchwise homogeneous substrate along near-critical isochores, and we compare our data to the theory of Fisher and de Gennes.<sup>6</sup>

Theoretical models<sup>6,7</sup> attribute the critical-adsorption phenomenon to a short-ranged substrate-fluid interaction, causing a perturbation of the order parameter  $m$  over a distance  $z$  from the surface which is proportional to the correlation length of the bulk fluid. In our case,  $m$  represents the deviation of the density  $\rho_b$  from the critical density  $\rho_c$ . For  $\rho_b = \rho_c$  and reduced temperatures  $t = (T - T_c)/T_c$  close to criticality, when the correlation length  $\xi$  diverges as  $t^{-\nu}$ , the excess density profile  $m(z)$  is expected to vary as  $z^{-\beta/\nu}$  for  $a \ll z \ll \xi$ , and as  $\exp(-z/\xi)$  for  $z \gg \xi$ . Here,  $a$  is a molecular size, and  $\beta$  and  $\nu$  are critical exponents ( $\nu = 0.63$  and  $\beta/\nu = 0.5$  for a three-dimensional fluid). The integral surface excess amount per unit area then takes the asymptotic form (for  $m = 0$  and  $t \rightarrow 0$ )

$$\Gamma \equiv \int_0^\infty m(z) dz = \Gamma_0 |t|^{-x}, \quad (1)$$

with  $x = \nu - \beta$ . This power law for  $\Gamma$  follows directly from the scaling form for the density profile.<sup>6</sup> The same result is obtained by Widom<sup>8</sup> from a combination of thermodynamic and scaling arguments. The previous experiments,<sup>1-5</sup> although clearly demonstrating the existence of the critical-adsorption phenomenon, were not accurate enough to test the above prediction in a quantitative manner.

Whereas optical studies of critical adsorption<sup>2-5</sup> probe an effectively semi-infinite fluid bounded by an optically flat wall, direct measurements of the surface excess  $\Gamma$  require a large surface area and thus a solid

material in a disperse form. In this case the fluid is contained in between the solid particles and the density profile against one wall can be affected by the proximity of other walls. Such confined-geometry effects on the criticality of fluids between plates now represents a subject of considerable interest in itself.<sup>6,9</sup>

In this work, a graphitized carbon black (Graphon) with a specific surface area of about  $80 \text{ m}^2/\text{g}$  is used as the substrate. This material consists of particles of a mean diameter of  $\sim 35 \text{ nm}$ , the exposed surface of which is made up of patches of graphite basal plane. The particles are agglomerated to pellets of  $0.2\text{--}0.3 \text{ mm}$  diameter. The volume-filling ratio for the pellets is about  $0.5$ , and the overall volume fraction occupied by the solid is about  $0.25$ . A typical distance between surfaces of neighboring particles inside the pellets is then estimated to be  $10 \text{ nm}$ , with a wide distribution, from a few molecular diameters up to very large distances. A wall-to-wall distance of  $10 \text{ nm}$  corresponds to the correlation length of the supercritical fluid ( $\text{SF}_6$ ) at  $T - T_c \approx 0.4 \text{ K}$ . At temperatures closer to  $T_c$  we expect the adsorption behavior to be significantly affected by confined-geometry effects, but at greater temperature increments the behavior should be dominated by critical adsorption on a single wall.

The volumetric apparatus developed for this study<sup>10</sup> consists of an adsorption cell of variable volume containing the fluid and solid adsorbent, and a reference cell of fixed volume containing the fluid at the density of the experimental isochore. The pressure difference  $\Delta P$  between the two cells is monitored by a sensitive differential-pressure transducer. The volume of the adsorption cell can be varied by means of a piston-cylinder device and a metal bellows separating the experimental fluid from the hydraulic liquid. Volume changes of the adsorption cell can be measured accurately from the changes in the position of the piston. All parts of the apparatus containing the supercritical fluid are kept at a uniform temperature. The cells are loaded with the fluid at a reference temperature  $T_1$  (about  $15 \text{ K}$  above  $T_c$ ) and the pressure in the reference cell is measured accurately with use of a quartz-oscillator manometer. The density of the bulk fluid in

the adsorption cell is then adjusted to the density in the reference cell by zeroing of the pressure difference  $\Delta P$ , by operation of the piston-cylinder device. When the temperature is then lowered from  $T_1$  to  $T_2$ , adsorption increases and the volume of the adsorption cell has to be decreased from  $V_1$  to a new value  $V_2$ , to restore the zero-pressure difference  $\Delta P$  and thus the original bulk density  $\rho_b$ . The change in surface excess amount of the fluid between  $T_1$  and  $T_2$  at constant density  $\rho_b$  is then given by

$$\Gamma(T_2, \rho_b) - \Gamma(T_1, \rho_b) = \rho_b (V_1 - V_2) / A_s, \quad (2)$$

where  $A_s$  is the surface area of the substrate.

The density of the fluid in the reference cell ( $\rho_b$ ) was calculated from  $P$ - $\rho$ - $T$  data for the reference temperature ( $T_1$ ) and is estimated to have an error no greater than 1%.  $\Gamma(T_1, \rho_b)$  was measured by a gravimetric method. All  $\Gamma(T)$  data were taken on stepwise lowering of the temperature, with equilibration times from 6 to 30 h as  $T$  approached  $T_c$ . The mean error in the volume increments of the adsorption cell was 0.2% at  $T - T_c > 0.3$  K; closer to  $T_c$  the high compressibility and the resulting gravitational density gradient of the fluid in the system caused progressively increasing errors. Our sample of  $\text{SF}_6$  (purchased from Messer Griesheim, nominal purity  $> 99.9\%$ ) had a critical temperature  $T_c = 318.70 \pm 0.04$  K, in agreement with published values.<sup>11</sup> Details of the experiments will be published.<sup>10</sup>

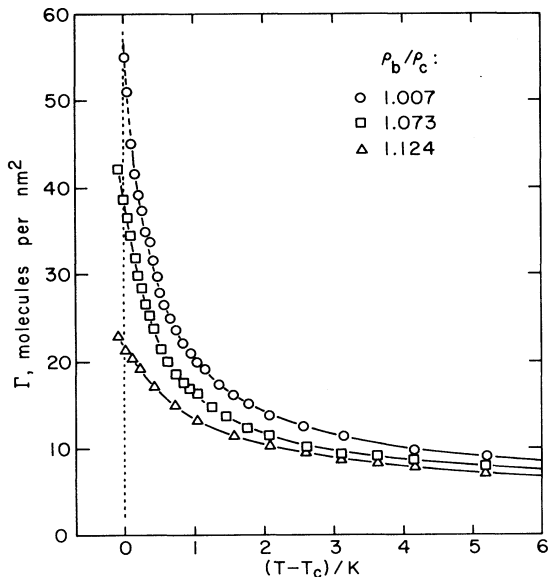


FIG. 1. Adsorption isochores of  $\text{SF}_6$  on Graphon for three reduced densities  $\rho_b/\rho_c$  of the bulk fluid above its critical temperature ( $T_c$ ). The surface excess number of molecules per unit area ( $\Gamma$ ) is plotted vs temperature ( $T - T_c$ ).

Figure 1 shows measurements of the surface excess amount  $\Gamma$  versus temperature along three isochores for reduced densities<sup>11</sup>  $\rho_b/\rho_c \geq 1$ . These results, as well as two further experimental isochores for  $\rho_b/\rho_c < 1$ , exhibit the expected sharp rise of  $\Gamma$  as  $T$  approaches the phase boundary. Figure 2 shows surface excess isotherms derived from these results. Note that the isotherms are not symmetrical about  $\rho_b/\rho_c = 1$ ; viz., for the same distance  $\rho_b - \rho_c$  from the critical density,  $\Gamma$  is higher at  $\rho_b < \rho_c$  than at  $\rho_b > \rho_c$ . This behavior at  $T > T_c$  reflects a much more pronounced asymmetry below  $T_c$ , where  $\Gamma$  becomes infinite on the phase boundary at  $\rho_b < \rho_c$ , but remains finite at  $\rho_b > \rho_c$ .<sup>13</sup>

We now analyze our near-critical isochores in terms of Eq. (2). Figure 3 shows a plot of  $\log \Gamma$  vs  $\log t$  for the isochore at  $\rho_b/\rho_c = 1.007$ . There is a linear region extending over more than one decade in  $t$  ( $0.020 > t > 0.001$ ). Linear regression of the data for this region yields an exponent  $x = 0.504 \pm 0.005$ . A similar analysis of the data for the isochore at  $\rho_b/\rho_c = 0.955$  yields  $x = 0.495 \pm 0.005$ . An error in the value of  $T_c$  of  $\pm 0.05$  K (a conservative estimate) would shift the resulting values of  $x$  by about  $\pm 0.025$ . We conclude, therefore, that the exponent has a value  $x = 0.50 \pm 0.03$ , significantly greater than the expected value,  $x = \nu - \beta = 0.31$ .

The prefactor  $\Gamma_0$  of Eq. (1) can be expressed by the surface excess number of molecules per unit area at  $T - T_c = 1$  K, viz.  $N^\sigma = (T_c)^x \Gamma_0$ . For our near-critical isochores we find  $N^\sigma = 20.5 \pm 0.3 \text{ nm}^{-2}$  ( $\rho_b/\rho_c = 1.007$ ) and  $N^\sigma = 21.4 \pm 0.3 \text{ nm}^{-2}$  ( $\rho_b/\rho_c = 0.955$ ). From these values we obtain an estimate for the ex-

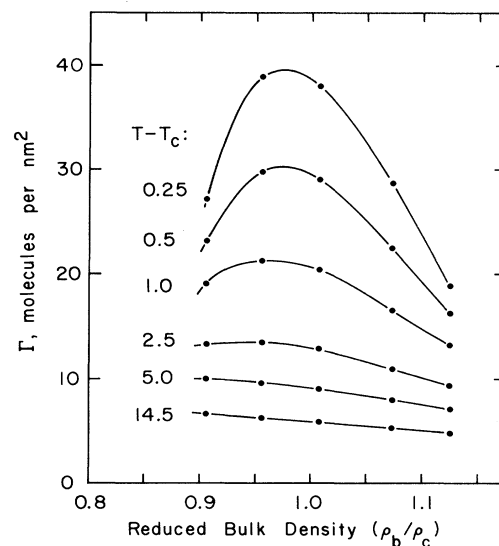


FIG. 2. Surface excess isotherms derived from the isochore data, showing a weak asymmetry of  $\Gamma$  about  $\rho_b/\rho_c = 1$ .

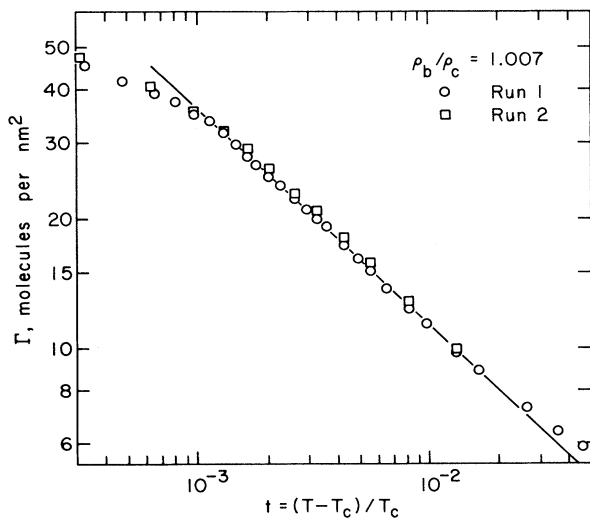


FIG. 3. Logarithmic plot of surface excess ( $\Gamma$ ) vs reduced temperature ( $t$ ) for a near-critical density of the bulk fluid. The solid line represents Eq. (2) with  $x = 0.505$ .

cess density  $m_0$  of the layer of fluid in direct contact with the wall. Assume the following form of the density profile<sup>3,5</sup>:  $m(z) = m_0$  for  $0 < z < a$ ;  $m(z) = bz^{-\beta/\nu}$  for  $a < z < \xi$ ; and  $m(z) = c \exp(-z/\xi)$  for  $z > \xi$  [i.e., we extrapolate the limiting power law for  $m(z)$  to the entire region between  $a$  and  $\xi$ , and the asymptotic exponential tail to the entire region beyond  $\xi$ ]. The parameters  $b$  and  $c$  are chosen such as to connect these three regions to a continuous profile. This model density profile then yields

$$\Gamma = am_0 \left[ \frac{2\nu - \beta}{\nu - \beta} \left( \frac{\xi}{a} \right)^{1 - \beta/\nu} - \frac{\beta}{\nu - \beta} \right]. \quad (3)$$

With Eq. (3) and  $\xi(T) = \xi_0 |t|^{-\nu}$  we can express  $\Gamma_0$  (or  $N^\sigma$ ) in terms of the parameters  $a$ ,  $m_0$ , and  $\xi_0$ . Using the above values of  $N^\sigma$  and a literature value<sup>12</sup> for the correlation length amplitude of SF<sub>6</sub> ( $\xi_0 = 0.2$  nm), and assuming  $a = 0.5$  nm, we obtain  $m_0 = 3.7$  nm<sup>-3</sup>. Thus, according to this estimate, the layer of fluid in contact with the substrate is compressed to a density more than twice as high as the critical density of the fluid ( $\rho_c = 3.05$  nm<sup>-3</sup> for SF<sub>6</sub>). This result supports the findings of an earlier study<sup>13</sup> of a wetting liquid-substrate interface, indicating that the perturbation of the order parameter of the fluid by the wall is indeed quite strong for the present type of system.

On the basis of Eq. (3) the apparent critical exponent for the nonasymptotic temperature regime becomes

$$x_{\text{app}} = (\nu - \beta)(1 + Ct^{\nu - \beta} + \dots), \quad (4)$$

with  $C = \frac{1}{3}(a/\xi_0)^{1/2} = 0.53$  for the present system. Thus for  $t = 10^{-2}$  the apparent exponent should be

about 10% higher than the asymptotic value. The much larger deviation of our experimental value from the scaling-law prediction indicates that the adsorption behavior is in fact not dominated by a  $z^{-\beta/\nu}$  dependence of the density profile. As in the temperature regime of our study the correlation length is not very large ( $\xi \approx 2$  to 12 nm), this  $z^{-\beta/\nu}$  dependence of the profile should extend over only a narrow range of distances ( $a \ll z \ll \xi$ ) and may be effectively replaced by the  $m(z) \sim \exp(-z/\xi)$  dependence of the tail region of the profile. In this case the integral surface excess should vary as  $\Gamma \sim \xi \sim t^{-\nu}$ , i.e., with an apparent exponent  $x_{\text{app}} = \nu$  instead of the asymptotic exponent  $x = \nu - \beta$ . It is possible that the rounding at  $t < 10^{-3}$  in Fig. 3 represents the onset of crossover behavior to the asymptotic regime. Alternatively, this behavior may be due to confined-geometry effects. As mentioned earlier, a second wall at a distance  $D$  from the adsorbing wall will cause a cutoff of  $m(z)$  at  $z = D/2$ , which will become important when  $\xi > D/2$ . A distribution of distances  $D$  will then cause  $\Gamma$  to level off as  $t \rightarrow 0$ ,<sup>14</sup> as is indeed observed in our experiments at  $t < 10^{-3}$ . To resolve these questions we are planning to study the critical adsorption of SF<sub>6</sub> on a form of exfoliated graphite with larger flat-wall dimensions and larger wall-to-wall distances than Graphon, and by approaching the critical point more closely than in the present work.

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<sup>14</sup>For a uniform distribution of wall-to-wall distances ( $0 < D < D_m$ ) the expression of Eq. (3) for  $\Gamma$  is modified only by a factor  $(1 - c\xi/D_m)$ , where  $c$  is a constant ( $0 < c < 1$ ).