Confinement Effects on the Critical Behavior of a Pure Fluid in Colloidal and Mesoporous Solids

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The effect of confined geometry on the adsorption behaviour of a near-critical fluid (SF_6) in contact with a colloidal graphite substrate and a mesoporous glass has been studied. We present results of experiments in microgravity and laboratory conditions and also of appropriate Monte-Carlo simulations. The surface excess concentration of the fluid was measured as a function of temperature along near-critical isochores using a volumetric technique. Whereas the surface excess of a fluid against a single planar surface is expected to increase in a monotonic way along the critical isochore it was found for the SF_6/colloidal graphite system that the surface excess reaches a maximum at $T - T_c$ ca. 0.5 K and then decreases sharply on further approaching the critical temperature T_c. This result was confirmed by repeating the measurements under microgravity conditions on the free-flying platform EURECA. The negative critical adsorption effect was also observed for near-critical isochores of SF_6 in a mesoporous controlled-pore glass. Grand canonical Monte-Carlo simulations for a fluid in a slit-pore suggest that the observed phenomenon is caused by depletion in the core region of the pore when the temperature approaches T_c. This depletion effect may be attributed to the peculiar situation of an equilibrium of a bulk fluid near its critical point with a pore fluid which is well away from its critical point. The critical state of the pore fluid is shifted to lower temperatures and coexists with a bulk fluid of a density much lower than the critical density [M. Thommes and G.H. Findenegg, *Langmuir* **10**, 4270 (1994)]. The experiments and Monte-Carlo simulations we report here focus on the inverse situation, i.e., the state of a non-critical pore fluid when the bulk fluid becomes critical and density fluctuations with lengths greater than the pore size are suppressed in the pore.