Density Profiles of Fluids near Surfaces: Surface Critical Behavior vs. Surface Phase Transitions

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Density profiles of fluids near solid surfaces were studied by extensive computer simulations of the liquid-vapor coexistence curves of water [1] and LJ fluids [2, 3] confined in various pores. The density profiles were used to study the spatial and temperature evolution of the local order parameter $\Delta\rho(z,\tau)$ (the difference between the local densities of the coexisting phases) and the local diameter $\rho_d(z,\tau)$ (the average of the local densities of the coexisting phases). In small pores, when the surface phase transition is suppressed, the surface critical behavior of $\Delta\rho(z,\tau)$ was found to be consistent with the universality class of the ordinary transition of Ising magnets: $\Delta\rho(z = 0,\tau) \sim \tau^{\beta 1}$, where $\beta_1 \sim 0.8$. The behavior of the diameter $\rho_d(z,\tau)$ is consistent with the laws of the normal transition in Ising magnets, and shows mainly regular temperature dependence, which continuously crosses over to the density profile at $T > T_c$, known as critical adsorption. The intrusion of the surface critical behavior into the bulk is governed by the bulk correlation length. The universality of the surface critical behavior of fluids, found in our studies, allows for the prediction of density profiles of fluids near various boundaries.

In larger pores, a wetting (drying) layer develops upon approaching the critical or wetting temperature [3]. This affects the density profile of the non-wetting phase. However, the density profile of the wetting phase should obey the universal laws of surface critical behavior up to the critical temperature.

[1] I. Brovchenko, A. Geiger, and A.Oleinikova, *J. Phys.: Cond. Matt.* **16**, S5345-S5370 (2004).
[2] I. Brovchenko, A. Geiger, and A. Oleinikova, *Eur. Phys. J. B* **44**, 345 (2005).
[3] A. Oleinikova, I. Brovchenko and A. Geiger, *J.Phys.: Condens. Matter* **17**, 7845 (2005).