Thermodynamic properties of fluids near solid surfaces

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Knowledge of the thermodynamic properties of fluids near surfaces is important for the correct analysis of various phenomena at fluid-solid interface. This requires, first of all, description of the fluid density distribution near a surface and of its temperature dependence. Distribution of a fluid density near a surface is determined by the competition of the effect of missing neighbors, which favors density depletion, and the attractive fluid-surface interaction, which favors density adsorption [1]. This competition gives a rise to a crossover from adsorption to depletion, when moving along the coexistence curve [2]. There is a line in the phase diagram of a fluid near some surface, along which the excess adsorption $\Gamma = 0$. For weakly-attractive surfaces, this line crosses the vapor branch of the coexistence curve. Upon strengthening a fluid-surface interaction, the crossing point moves to higher densities, meeting the critical point at some particular strength of a fluid-surface interaction (about -1.0 kcal/mol for water). Effect of the surface perturbations is determined by the bulk correlation length, which strongly depends on the proximity to the critical point. Therefore, a crossover from adsorption to depletion along some thermodynamic path (coexistence curve [2], supercritical isotherm [3]) is *non-monotonous* in general case. The temperature dependence of hydration water density in a liquid phase along the coexistence curve agrees with the theory of the surface critical behavior and is close to linear in a wide temperature range [1,4]. The thermal expansion coefficient α^h of hydration water near hydrophobic and moderately hydrophilic surfaces is notably larger than α of the bulk water. Near strongly hydrophilic surfaces, which give rise to the surfaces phase transitions, $\alpha^h > \alpha$ at low temperatures and $\alpha^h < \alpha$ at higher temperatures. Knowledge of the thermal expansivity of hydration water allowed the first evaluation of the intrinsic thermal expansion coefficient of a biomolecule in liquid water, which is found to be negative [5].

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