Using Molecular Simulation to Understand the Surface Phase Behavior of Fluids

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Fluids in the presence of one or more surfaces exhibit a rich variety of phase transitions that are absent in bulk fluids. Examples include wetting, prewetting, layering, and capillary condensation transitions. Even the simplest of systems display a broad range of phase behavior, with surface phase diagrams depending qualitatively upon the relative strengths and ranges of the fluid-fluid and fluid-substrate interactions. In this presentation, we describe our recent efforts aimed towards obtaining a better understanding of surface phase behavior through the use of molecular simulation. The first part of the presentation will be used to provide an overview of transition-matrix based Monte Carlo algorithms developed in our group that enable one to efficiently locate and characterize phase transitions. Results will then be presented that describe how the wetting behavior of a model substrate-fluid system evolves with temperature and the relative strength of the substrate-fluid interaction. Modeling results will be compared with experimental data and density functional theory calculations. Finally, we will describe a series of calculations that enable us to estimate the boundary tension along the prewetting saturation line. This quantity is related to the line tension associated with the formation of liquid droplets on a solid substrate. The magnitude of this tension has been the subject of debate recently, with experimental values spanning several orders of magnitude.