321b Monte Carlo Simulation of Molecular Adsorption

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Monte Carlo simulations involve the probabilistic sampling of a molecular system's configuration space. A key challenge in many applications is ergodicity, i.e. the proper sampling of ALL representative configurations of a system. This is especially true of adsorption systems where steric confinement and/or strong energetic attraction can bring about large energy barriers separating important regions of configuration space. Fortunately, recent advances in Monte Carlo methodology now allow for the simulation of thermodynamic properties of many important, but complex, molecular adsorption systems. We present here two examples from our recent research efforts. We first describe the application of a histogram re-weighting method to the problem of liquid-vapor phase equilibria of a fluid adsorbed in a templated porous matrix. We find, consistent with a replica Ornstein-Zernike integral equation approach within the optimized random phase approximation, Monte Carlo simulation to predict the presence of an enhanced phase envelop, and the possibility of multiple transitions, for simple fluids adsorbed in a matrix consisting of a quenched binary mixture with one component (the template) removed. We next describe the simultaneous application of multicanonical, jump walking, and configuration-bias methods to the problem of conformational transitions within a single protein molecule adsorbed to a solid substrate. We find the free energy profile of a lattice heteropolymer-model protein, with the internal energy serving as a “reaction coordinate”, to suggest the transition between folded (or nearly folded) and surface-denatured conformations to be highly dependant on the relative strength of surface-segment and segment-segment interactions. Finally, we speculate on future challenges involving the application of Monte Carlo methods to more complex adsorption phenomena of a biological nature.