28a Hydrophobic Hydration at Small and Large Lengthscales: Understanding, Manipulating and Predicting the Crossover

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Small and large hydrophobic solutes exhibit remarkably different hydration thermodynamics. Small solutes are accommodated in water with minor perturbations to water structure, and their hydration is captured accurately by theories that describe density fluctuations in pure water. In contrast, hydration of large solutes is accompanied by dewetting of their surfaces and requires a macroscopic thermodynamic description. A unified theoretical description of these lengthscale dependencies was presented recently by Lum, Chandler, and Weeks [J. Phys. Chem. 103, 4570-4577 (1999)]. Here we employ molecular simulations to study lengthscale dependent hydrophobic hydration under various thermodynamic conditions. We show that the hydration of small and large solutes displays disparate dependencies on thermodynamic variables, including pressure, temperature, and additive concentration. Understanding these dependencies allows manipulation of the small-to-large crossover lengthscale, which is nanoscopic under ambient conditions. Specifically, applying hydrostatic tension or adding ethanol decreases the crossover length to molecular sizes, making it accessible to atomistic simulations. With detailed temperature dependent studies, we further demonstrate that hydration thermodynamics changes gradually from entropic to enthalpic near the crossover. The nanoscopic lengthscale of the crossover and its sensitivity to thermodynamic variables imply that quantitative modeling of biomolecular self-assembly in aqueous solutions requires elements of both molecular and macroscopic hydration physics. We also show that the small-to-large crossover is directly related to the Egelstaff-Widom lengthscale, the product of surface tension and isothermal compressibility, which is another fundamental lengthscale in liquids.