

P011 Liquid-phase partition function from computer simulation
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Solvation thermodynamics plays a pivotal role in any aqueous phase binding event. Intensive, multistage computer simulation methods currently can determine binding free energies for small ligands but become impractical for larger systems. Nor do they give much insight into the free energy value, such as how much is contributed by water. For this reason, a method is sought to evaluate the solvent free energy directly from a single simulation. Here, liquid state partition functions are derived from computer simulations of pure water and pure argon to yield free energies that match experiment. In the spirit of cell theory, the water molecule is modelled by a six-dimensional anisotropic harmonic potential describing three translations and three rotations while the argon atom is modelled by a three-dimensional isotropic harmonic potential. The energy is measured directly from the simulation and the entropy is summed over each harmonic oscillator using either the quantum or classical form. Force constants of each oscillator are derived from the average magnitude of the force or torque along the respective degrees of freedom calculated in the simulation. Approximately two-thirds of water's entropy is found to come from translation and one-third from rotation. The agreement with experiment for both liquids studied so far validates the harmonic oscillator as a quantitative model for molecules in the liquid state.