

Obtaining Infinitely Dilute Partial Molar Properties from Computer Simulation

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We present three methods for obtaining infinitely dilute partial molar quantities (e.g., volume and enthalpy) from molecular dynamics simulations. Also compared are two approaches for obtaining fluctuating quantities (i.e., compressibility, heat capacity, and thermal expansion). The first uses fluctuations in the bulk properties of the system, while the second obtains the fluctuations from simulations over a range of temperatures and pressures. These methods both work by fitting the molar property of interest as a function of composition, taking partial derivatives to obtain the partial molar quantities, and then interpolating the infinitely dilute partial molar quantities. We show how these methods can be used to determine changes to peptide or protein thermodynamic properties upon undergoing a conformational change. A third approach, which requires only one simulation, is also introduced. This last method is based upon fluctuations in a local, grand-canonical region within a closed simulation system using the Fluctuation Theory of solutions.