

Nonphysical Sampling Distributions in Monte Carlo Free-Energy Estimation: Umbrella Sampling

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The free energy difference between a model system and some reference system can easily be written as an ensemble average, but the conventional Monte Carlo methods of obtaining such averages are inadequate for the free-energy case. That is because the Boltzmann-weighted sampling distribution ordinarily used is extremely inefficient for the purpose. This paper describes the use of arbitrary sampling distributions chosen to facilitate such estimates. The methods have been tested successfully on the Lennard-Jones system