

Liquid Water from First Principles: Validation of Different Sampling Approaches

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Abstract

A series of first principles molecular dynamics and Monte Carlo simulations were carried out for liquid water to assess the validity and reproducibility of different sampling approaches. These simulations include Car-Parrinello molecular dynamics simulations using the program CPMD with different values of the fictitious electron mass in the microcanonical and canonical ensembles, Born-Oppenheimer molecular dynamics using the programs CPMD and CP2K in the microcanonical ensemble, and Metropolis Monte Carlo using CP2K in the canonical ensemble. With the exception of one simulation for 128 water molecules, all other simulations were carried out for systems consisting of 64 molecules. It is found that the structural and thermodynamic properties of these simulations are in good agreement with each other as long as adiabatic sampling is maintained in the Car-Parrinello molecular dynamics simulations either by choosing a sufficiently small fictitious mass in the microcanonical ensemble or by Nosé-Hoover chain thermostats in the canonical ensemble. Using the Becke-Lee-Yang-Parr exchange and correlation energy functionals and norm-conserving Troullier-Martins or Goedecker-Teter-Hutter pseudopotentials, simulations at a fixed density of 1.0 g/cm^3 and a temperature close to 315 K yield an overstructured liquid with a height of the first peak in the oxygen–oxygen radial distribution function of about 3.0, an underestimated value of the classical constant-volume heat capacity of about $70 \text{ J K}^{-1} \text{ mol}^{-1}$, and an underestimated self-diffusion constant of about $0.06 \text{ \AA}^2/\text{ps}$.