

Isobaric-isothermal Monte Carlo simulations from first principles: Application to liquid water at ambient conditions

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Abstract

A series of first principles Monte Carlo simulations in the isobaric-isothermal ensemble were carried out for liquid water at ambient conditions ($T = 298$ K and $p = 1$ atm). The Becke-Lee-Yang-Parr (BLYP) exchange and correlation energy functionals and norm-conserving Goedecker-Teter-Hutter (GTH) pseudopotentials were employed with the CP2K simulation package to examine systems consisting of 64 water molecules. The fluctuations in the system volume encountered in simulations in the isobaric-isothermal ensemble requires a reconsideration of the suitability of the typical charge density cutoff and the regular grid generation method previously used for the computation of the electrostatic energy in first principles simulations in the microcanonical or canonical ensembles. In particular, it is noted that a much higher cutoff is needed and that the most computationally efficient method of creating grids can result in poor simulations. Analysis of the simulation trajectories using a very large charge density cutoff at 1200 Ry and four different grid generation methods point to a significantly underestimated liquid density of about 0.8 g cm^{-3} resulting in a somewhat understructured liquid (with a value of about 2.7 for the height of the first peak in the oxygen–oxygen radial distribution function) for BLYP-GTH water at ambient conditions. In addition, a simulation using a charge density cutoff at 280 Ry yields a higher density of 0.9 g cm^{-3} , showing the sensitivity of the simulation outcome to this parameter.

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