

# Toward a Monte Carlo program for simulating vapor–liquid phase equilibria from first principles

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## Abstract

Efficient Monte Carlo algorithms are combined with the **Quickstep** energy routines of CP2K to develop a program that allows for Monte Carlo simulations in the canonical, isobaric-isothermal, and Gibbs ensembles using a first principles description of the physical system. Configurational-bias Monte Carlo techniques and pre-biasing using an inexpensive approximate potential are employed to increase the sampling efficiency and to reduce the frequency of expensive *ab initio* energy evaluations. The new Monte Carlo program has been validated through extensive comparison with molecular dynamics simulations using the programs CPMD and CP2K. Preliminary results for the vapor–liquid coexistence properties ( $T = 473$  K) of water using the Becke-Lee-Yang-Parr exchange and correlation energy functionals, a triple-zeta valence basis set augmented with two sets of *d*-type or *p*-type polarization functions, and Goedecker-Teter-Hutter pseudopotentials are presented. The preliminary results indicate that this description of water leads to an underestimation of the saturated liquid density and heat of vaporization and, correspondingly, an overestimation of the saturated vapor pressure.

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