First principles Monte Carlo simulations of vapor–liquid equilibria: Density functionals, basis sets, and dispersion corrections[1] J. ILJA SIEPMANN, University of Minnesota, MATTHEW J. MCGRATH, Kyoto University, I-F. WILLIAM KUO, Lawrence Livermore National Laboratory, CHRISTOPHER J. MUNDY, Pacific Northwest National Laboratory — Gibbs ensemble Monte Carlo simulations are used to compute the vapor–liquid equilibria for water, methanol, and methane using Kohn-Sham density functional theory. Results for BLYP and PBE functionals, BLYP with Grimme D2 and D3 dispersion corrections, and various basis sets are compared. Although none of the combinations of functional, dispersive correction, and basis set is found to yield highly accurate predictions for liquid densities, vapor pressures, and heats of vaporization for all three compounds, the results for dispersion corrected BLYP with large basis set are promising.

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