

## Development of Polarizable Water Force Fields for Phase Equilibrium Calculations

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### Abstract

Recent simulation studies for four dipole-polarizable and for two fluctuating-charge water force fields have demonstrated that none of the force fields studied is capable of yielding a satisfactory description of the vapor-liquid coexistence curve from room temperature to the critical region. Here it is argued that the performance of these polarizable force field can be dramatically improved by introducing an additional coupling between the Lennard-Jones interaction parameters for a pair of oxygen sites and their partial charges (electronic configuration). Two different types of water models are presented which are based on either the three-site SPC or the four-site TIP4P water representations. Adiabatic nuclear and electronic sampling Monte Carlo (ANES-MC) simulations in the Gibbs, isobaric-isothermal, and canonical ensembles were carried out to calculate vapor-liquid coexistence curves, to determine the temperatures of maximum liquid density, and to evaluate dielectric constants along the coexistence line, respectively. The new SPC-pol-1 force field yields significantly better agreement with experiment for the saturated vapor and liquid densities, the heats of vaporization, and the liquid-phase dielectric constants than the fixed-charge SPC, SPC/E, TIP4P, and Errington/Panagiotopoulos (EP) force fields or than any other polarizable force field previously tested. However, the representation of the liquid water structure at ambient conditions is less satisfactory for the SPC-pol force fields. In contrast, the TIP4P-pol force fields produce much better low-temperature liquid structures and, in particular, a density maximum close to  $T = 277$  K, but their performance for the vapor-liquid equilibria in the near-critical region is less satisfactory. Finally, it is important to note that the SPC-pol-1 force field yields an average molecular dipole moment of 2.5 D for the liquid phase at ambient conditions, that is substantially smaller than the value of 2.7 D obtained for its minimum-energy hexamer cluster.