

Simulating Fluid Phase Equilibria of Water From First Principles

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Abstract

Efficient Monte Carlo algorithms and a mixed-basis set electronic structure program were used to compute from first principles the vapor–liquid coexistence curve of water. A water representation based on the Becke-Lee-Yang-Parr exchange and correlation functionals yields a saturated liquid density of 900 kg/m³ at 323 K, and normal boiling and critical temperatures of 350 and 550 K, respectively. An analysis of the structural and electronic properties of the saturated liquid phase shows an increase of the asymmetry of the local hydrogen-bonded structure despite the persistence of a four-fold coordination, and decreases of the molecular dipole moment and of the spread of the lowest unoccupied molecular orbital with increasing temperature.

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