

Influence of Bond Flexibility on the Thermophysical Properties of Water

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There are many alternative models for molecular simulation studies of water, which reflects the difficulty of accurately predicting all the diverse properties of water. The most widely used models are variants of either the four-site (TIP4P) or the three-site simple point charge (SPC, SPC/E) models. We observe that most attempts to optimize these fixed-point charge models for the prediction of thermophysical properties of water have maintained a rigid, fixed bond separation between the atoms, whereas the influence of intra-molecular vibrations has received relatively little attention. We performed Gibbs ensemble simulations on the vapor liquid equilibrium for two different flexible models SPC/Ft and SPC/Fw in comparison with the corresponding rigid SPC and SPC/E models, and found that the introduction of internal vibrations, and also their parameterization, has an observable effect on the prediction of the vapor pressures, saturation densities, heats of vaporization and the critical point. In addition, we have also studied the influence of the bond flexibility on the viscosities, diffusion coefficients and dielectric constants of water at elevated pressures and temperatures by MD simulations. Thus, we will present our simulation results on the different properties of water, which suggest that allowing bond flexibility yields a better reproduction of the realistic behavior of water by indirectly introducing polarizability effects. Thus, it is a promising alternative strategy for both improving the accuracy of phase equilibrium calculations, and providing models that allow for the accurate prediction of different properties at the same time.