

Fully Quantum Second Virial Coefficients of H₂O and D₂O from a High-Accuracy Flexible-Monomer Water Pair Potential

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Recently, we developed a path-integral method for calculating virial coefficients of flexible molecules, with full inclusion of quantum effects. In this work, we apply the method to calculate second virial coefficients from a recently developed state-of-the-art flexible-monomer pair potential for water. The potential has been fitted to high-quality *ab initio* calculations at about a quarter million grid points. Because the monomers are flexible rather than fixed at the H₂O geometry, the potential can provide a high-accuracy representation not only for H₂O but also for D₂O. These are the first calculations of the second virial coefficient for these molecules to analyze the influence of both flexibility and quantum effects. We present calculated second virial coefficients for both H₂O and D₂O between 200 K and 2000 K. Knowledge of uncertainty in the pair potential allows us to make reasonable estimates of the uncertainty in the second virial coefficient. For both H₂O and D₂O, our results are in reasonable agreement with the available experimental data, but extend to significantly higher and lower temperatures where current knowledge is lacking for these important fluids. The effect of flexibility on the second virial coefficient is found to be smaller than some previous estimates in the literature.