

Adiabatic Nuclear and Electronic Sampling Monte Carlo Simulations in the Gibbs Ensemble: Application to Polarizable Force Fields for Water

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Abstract

The adiabatic nuclear and electronic sampling Monte Carlo algorithm (ANES-MC) is extended to simulations in the Gibbs ensemble. While the maximum displacements used for translational, rotational, and volume trial moves can be adjusted to foster efficient sampling in the adiabatic limit, the transfer (swap) of particles always causes a major disturbance of the electronic structures of the two phases (supplying and receiving the particle). To re-equilibrate the electronic structures requires additional sampling of the electronic degrees of freedom. A simple, distance-dependent criterion for the preferential selection of the electronic degrees of freedom, for which a move is to be attempted, is shown to improve the efficiency of the particle swap move. The ANES-MC algorithm is applied to the polarizable SPC-FQ and TIP4P-FQ models proposed by Rick *et al.* [*J. Chem. Phys.*, **1994**, 101, 6141]. For both models simulations were carried out employing the standard constraint on the neutrality of individual molecules. In addition, for the SPC-FQ model the use of a constraint on the neutrality of an entire phase was investigated which allows for intermolecular charge transfer. Simulations in the Gibbs ensemble were performed to calculate the vapor-liquid coexistence curves from 323 to 523 K, while simulations in the grand canonical ensemble were carried out for the near-critical region. Dielectric constants at different state points were calculated from canonical ensemble simulations. Neither the SPC-FQ nor the TIP4P-FQ force fields give a satisfactory description of the vapor-liquid equilibria. In particular, the critical temperature is greatly underestimated by both models. While intermolecular charge transfer is found to have only a very small influence on the internal energy and the radial distribution functions at ambient conditions and along the coexistence curve, it increases the dielectric constant by approximately 30%.