

Simulating vapor–liquid nucleation of water: A combined histogram-reweighting and aggregation-volume-bias Monte Carlo investigation for fixed-charge and polarizable models

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Abstract

The method of histogram-reweighting was integrated with a recently developed approach using aggregation-volume-bias Monte Carlo and self-adaptive umbrella sampling to develop the AVUS-HR algorithm that allows for exceedingly efficient calculations of nucleation properties over a wide range of thermodynamic conditions. Simulations were carried out for water using both fixed-charge and polarizable force fields belonging to the TIP4P family (namely, TIP4P, TIP4P-FQ, TIP4P-pol2, and TIP4P-pol3) to investigate the nucleation of water over a temperature range from 200 to 300 K and the concentration of water clusters in the atmosphere at elevations up to 15 km. It was found that the nucleation free energy barriers and atmospheric concentrations are extremely sensitive to the force field, albeit all the models investigated in this study support the following general conclusions: (i) ice nucleation is not present under the thermodynamic conditions and cluster-size range investigated here, i.e. the critical nuclei possess liquid-like structures; and (ii) the atmospheric concentrations of water clusters under homogeneous conditions are very low with the mole fraction of hexamers being about 10^{-10} , a number probably too low to influence the solar radiation balance. Compared to the experimental data, the TIP4P-pol3 model yields the most accurate nucleation results, consistent with its excellent performance for the second virial coefficient and the minimum cluster energies.

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