Homogeneous Nucleation of Carbon Dioxide by Molecular Simulation

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Homogeneous nucleation of carbon dioxide is considered by molecular simulation of large systems, regarding both the pure fluid as well as mixtures with carrier fluids, such as air, which do not participate in the phase transition significantly. Canonical ensemble molecular dynamics simulation using the Yasuoka-Matsumoto method [1] is applied to nucleation in supersaturated vapors that contain more carbon dioxide than at saturation [2]. Furthermore, bubble formation in metastable liquids is simulated. Beside the nucleation process, the agreement of model predictions with experimental data is evaluated for vapor-liquid equilibrium properties, including the surface tension, of pure carbon dioxide as well as mixtures with practically relevant carrier fluids. Multi-criteria optimization is employed to assess the capacity of 2CLJQ models, which contain two Lennard-Jones sites and a point quadrupole, to reproduce both bulk and interfacial properties accurately. The set of all Pareto-optimal parameter combinations is computed, so that suitable molecular models can be tailored to the requirements of a particular application [3]. Simulation results for the carrier fluid influence on the nucleation rate are compared with the extension of the classical nucleation theory (CNT) by Wedekind et al. [4], which accounts for a pressure effect. It is confirmed that the presence of air as a carrier decreases the nucleation rate. However, this influence is significantly weaker than predicted by CNT. Furthermore, CNT predicts a temperature dependence of the nucleation rate in the spinodal limit, which is not found in the present molecular dynamics simulations.

References

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