

Vapor–Liquid and Vapor–Solid Phase Equilibria for United-Atom Benzene Models near their Triple Points: The importance of Quadrupolar Interactions

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Abstract

Gibbs ensemble Monte Carlo simulations were used to calculate the vapor–liquid and vapor–solid coexistence curves for benzene using two simple united-atom models. An extension of the Gibbs ensemble method that makes use of an elongated box containing a slab of the condensed phase with a vapor phase along one axis, was employed for the simulations of the vapor–solid equilibria and the vapor–liquid equilibria at very low reduced temperatures. Configurational-bias and aggregation-volume-bias Monte Carlo techniques were applied to improve the sampling of particle transfers between the two simulation boxes and between the vapor and condensed-phase regions of the elongated box. An isotropic united-atom representation with six Lennard-Jones sites at the positions of the carbon atoms was used for both force fields, but one model contained three additional out-of-plane partial charge sites to explicitly represent benzene’s quadrupolar interactions. Both models were fitted to reproduce the critical temperature and density of benzene and yield a fair representation of the vapor–liquid coexistence curve. In contrast, differences between the models are very large for the vapor–solid coexistence curve. In particular, the lack of explicit quadrupolar interactions for the 6-site model greatly reduces the energetic differences between liquid and solid phases, and this model yields a triple point temperature that is about a factor of two too low. In contrast, the 9-site model predicts a triple point of benzene at $T = 253 \pm 6$ K and $p = 2.3 \pm 0.8$ kPa in satisfactory agreement with the experimental data ($T = 278.7$ K and $p = 4.785$ kPa).

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