

Forcefield testing for molecular dynamics calculation of hydrocarbon phase diagrams

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Molecular dynamics simulations are performed to calculate vapor-liquid equilibrium of hydrocarbons and their mixtures. Three models are tested: TraPPE-UA united-atom forcefield [1], OPLS-AA [2, 3] and TraPPE-EH [4] all-atom forcefields.

The forcefields show good agreement with experimental vaporization curves of pure hydrocarbons. They also reproduce well the composition of liquid phase in binary mixtures as a function of pressure at isotherms, while some discrepancies from experimental data are observed in the saturated vapor compositions. The TraPPE forcefields show better agreement with experimental vapor-liquid equilibrium data than OPLS.

The effects of porosity on mixture phase diagram are qualitatively studied. The saturation curves in slit pores with Lennard-Jones walls are calculated. It is shown that nanopores may shift the co-existence curve. At certain wall-molecule interaction parameters, a significant widening of the pressure range of the retrograde condensation is found.

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