

Transferable Potentials for Phase Equilibria.

3. Explicit-Hydrogen Description of Normal Alkanes

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Abstract

Motivated by shortcomings of the available united-atom models for alkanes, a new explicit-hydrogen model for n-alkanes (TraPPE-EH, Transferable Potentials for Phase Equilibria–Explicit Hydrogen) is developed from fitting to one-component fluid phase properties. In addition to Lennard-Jones sites on carbon atoms, this model utilizes Lennard-Jones sites on the centers of carbon-hydrogen bonds. Configurational-bias Monte Carlo simulations in the Gibbs and canonical ensembles were carried out to calculate the one-component vapor-liquid phase equilibria for methane to n-dodecane, to determine the phase diagram of supercritical ethane and n-heptane mixtures, to obtain the Gibbs free energies of transfer for n-pentane and n-hexane between helium vapor and n-heptane liquid phases, and to study the high-pressure region of the equation of state for n-pentane and n-decane. The explicit-hydrogen representation with its more faithful description of the molecular shape of alkanes allows us to find a set of Lennard-Jones parameters that yields significantly better agreement with experiment for one- and multi-component phase equilibria than our united-atom alkane model, but the price is higher computational cost.