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Transferable Potentials for Phase Equilibria. 4. United-Atom Description of Linear and Branched Alkenes and Alkylbenzenes

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Abstract

The Transferable Potentials for Phase Equilibria-United Atom (TraPPE-UA) force field for hydrocarbons is extended to alkenes and alkylbenzenes by introducing the following pseudo-atoms: $CH_2(sp^2)$, $CH(sp^2)$, $C(sp^2)$, CH(aro), R–C(aro) for the link to aliphatic side chains, and C(aro) for the link of two benzene rings. In this united-atom force field, the nonbonded interactions of the hydrocarbon pseudo-atoms are solely governed by Lennard-Jones 12–6 potentials, and the Lennard-Jones well depth and size parameters for the new pseudo-atoms were determined by fitting to the single-component vapor-liquid phase equilibria of a few selected model compounds. Configurational-bias Monte Carlo simulations in the NVT version of the Gibbs ensemble were carried out to calculate the single-component vapor-liquid coexistence curves for ethene, propene, 1-butene, *trans*- and *cis*-2-butene, 2-methylpropene, 1,5-hexadiene, 1-octene, benzene, toluene, ethylbenzene, propylbenzene, isopropylbenzene, *o*-, *m*-, and *p*-xylene, and naphthalene. The phase diagrams for the binary mixtures of (supercritical) ethene/*n*-heptane and benzene/n-pentane were determined from simulations in the NpT Gibbs ensemble. Although the TraPPE-UA force field is rather simple and makes use of relatively few different pseudo-atoms, its performance, as judged by comparisons to other popular force fields and available experimental data, is very satisfactory.