

Beyond Lennard-Jones: Global Optimization of Force Fields for Organic Compounds

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Vapor pressure, critical properties, saturated liquid density, and compressed fluid density are used to characterize step potentials for n-alkanes and noble gases. Several potential models were tested to identify the most accurate. These include the Mie potential, the 14-12-8-6 potential, the exp-6, and the two-fluid Yukawa models. Data for the n-alkanes and noble gases include high temperature compressed fluid data that are sensitive to the softness of the potential, which turns out to be an important distinguishing factor. Optimization is facilitated by thermodynamic perturbation theory (TPT) combined with molecular dynamics of continuous potential models (CMD) using the LAMMPS simulator and Monte Carlo simulations (CMC) using GOMC and CASSANDRA. Reference fluid simulations can be performed for a range of potential parameters, with special attention to the repulsive characteristic (e.g. “m” in the m-6 Mie potential). Reference simulations are supplemented with limited simulations of the full potential with “draft” candidates for the optimal potential model, permitting the characterization of complete equations of state that permit variable values of the potential parameters. The methodology follows the publications of Ghobadi and Elliott (J. Chem. Phys., 141:094708, 141:024708, 140:234104). The potential parameters can then be optimized without further simulation. The optimized potentials are tested with full potential simulations. Vapor pressure deviations average near 5% for n-alkanes modeled with transferable united atom models, and 3% for noble gases. Saturated liquid density deviations average near 0.5% below a reduced temperature of 0.9. Compressed fluid densities deviations average near 0.3% for the better potential models. Critical temperatures are matched to within 1K. Critical pressures are matched to within 0.1MPa and critical densities are matched to within 0.01 g/cm³. These results establish a firm foundation for optimal force field development going forward to encompass branches, rings, alcohols, amines, etc.