

Improvement of a transferable force field for the prediction of self-diffusivity, viscosity, surface tension, and density of long-chained linear and branched alkanes and alcohols up to 573 K by molecular dynamics simulations

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Systems based on long-chained linear and branched alkanes and alcohols are of interest in many areas of process and energy engineering, such as the production of highly valued petroleum products. For an efficient process design, reliable information on the transport and equilibrium properties of such systems is required. An ongoing research project at AOT-TP aims to contribute to a fundamental understanding of the thermophysical properties of long-chained hydrocarbons and related alcohols as well as their corresponding mixtures with and without dissolved gases. A special focus is on viscosity and surface tension, as they govern heat, mass, and momentum transport in continuous phases and across phase boundaries. In addition to experiments providing an ensured database, molecular dynamics (MD) simulations are used to predict thermophysical properties. The accuracy of these predictions depends on how well the molecular interactions are described by the underlying force fields (FFs). Published FFs are typically transferable to a variety of molecules, but their performance in predicting both transport and equilibrium properties up to large temperatures can be limited. Extending a FF to be transferable also across temperature and pressure is imperative for predicting properties at process-relevant conditions, where experiments are expensive or technically challenging.

The objective of the present study is to further develop a transferable FF for the reliable prediction of transport and equilibrium properties of long-chained alkanes and alcohols at vapor-liquid equilibrium for temperatures between 298 and 573 K by MD simulations. As model systems, the linear alkanes *n*-dodecane, *n*-hexadecane, *n*-triacontane, and *n*-tetracontane, related branched isomers 2,2,4,4,6,8,8-heptamethylnonane (HMN) and squalane as well as the linear and branched alcohols 1-dodecanol, 1-hexadecanol, 1,12-dodecandiol, 2-butyl-1-octanol, and 2-hexyl-1-decanol were selected. We are therefore able to probe, over the complete temperature range, the effects of alkyl chain length, branching, and hydroxylation on the calculated results for the equilibrium properties self-diffusivity, surface tension, and density, as well as the transport property viscosity. For the representative testing set consisting of *n*-dodecane, *n*-octacosane, 1-dodecanol, and HMN, three well-established FFs are evaluated: the all-atom L-OPLS FF, which considers each atom explicitly, and the TraPPE and MARTINI FFs, which approximate the molecules in the form of pseudo united atoms and coarse-grained beads. The best-performing FF at ambient conditions is chosen for further optimization in order to accurately predict both the equilibrium and transport properties at higher temperatures. As reference, our own experimental data for viscosity and surface tension, determined with surface light scattering (SLS), and density, determined with a vibrating-tube densimeter, were employed.

Over the complete temperature range, the MARTINI FF gives on average the worst representation for the studied systems and properties among the three investigated FFs. The TraPPE FF shows the best prediction for the static properties surface tension and density, but significantly underestimates viscosity and overestimates the self-diffusivity. At temperatures around 298 K, the L-OPLS FF is the best representative for predicting all four properties of interest and is therefore chosen for further development. As temperature increases, the L-OPLS FF increasingly underestimates the density, leading to an underestimation of the viscosity and surface tension of the various test systems as well. It is therefore expected that a temperature-dependent correction to the prediction of densities will improve the prediction capability of the FF for the other properties as well. This correction is achieved by adjusting the Lennard-Jones parameters and partial charges of the atoms as a function of temperature, resulting in improved predictions for the transport and equilibrium properties over the complete temperature range. The optimized FF is then transferred to the seven remaining substances and predictions are compared to the experimental data.

