Supporting Information: Improvements and limitations of Mie λ-6 potential for prediction of saturated and compressed liquid viscosity

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SI.I. Input files

We provide example input files for simulating 2,2,4-trimethylhexane at 293 K with the Potoff force field in GROMACS (see attached .gro, .top, and .mdp files). Additionally, all files necessary to generate the results from this study can be found at www.github.com/ramess101/IFPSC_10.

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SI.II. MCMC from scoring function

Translating the scoring function into a Bayesian context is achieved by modeling the ϵ-σ CH and C uncertainties with a multivariate normal distribution, where the covariance matrix was obtained by assuming that the "generalized" CH and C parameter set should not be distinguishable (at the 95 % confidence level) from the "long" parameter set.

We apply the common assumption of transferability between UA sites, which implies that the parameter correlation between different UA sites, e.g., between $\sigma_{\mathrm{CH_3}}$ and σ_{CH}, is assumed to be negligible. In other words, we only account for the parameter correlation between ϵ_{ii}-σ_{ii} sets of the same UA site. The reason for this assumption is the reduced complexity of performing four independent two-dimensional MCMC runs compared to one eight-dimensional MCMC run.

SI.III. MCMC validation

This section provides a detailed example of how we obtain estimates for η and the corresponding uncertainty. The results depicted in Figures **??** through **??** are for propane with the Potoff model and $T^{\mathrm{sat}} = 166$ K. Figure **??** depicts a typical autocorrelation function ("enecorr.xvg" file) obtained by executing the GROMACS "energy –vis" command. By default, GROMACS partitions the complete simulation into twelve evenly sized time blocks. Therefore, the autocorrelation function in Figure **??** is the average of twelve different time origins.

GROMACS then performs a simple two-point trapezoidal integration of neighboring points to obtain the Green-Kubo integral. The Green-Kubo integral with respect to time is output in the "visco.xvg" file. Figure **??** presents the Green-Kubo integral from forty replicate simulations. Although a single replicate is often quite noisy at long times, the average of these replicates converges smoothly (see Figure **??**).

Figure **??** shows that the fluctuations, or standard deviation, increases with time but is adequately modeled with At^b. The line labeled "cut-off" in Figures **??** and **??** is the time at which $\sigma_\eta \approx 0.4 \times \eta^\infty$. Data beyond this time are excluded from the fit of the double-exponential function.

Bootstrap re-sampling provides an estimate of the uncertainty. Figure **??** shows that, typically, the bootstrapped distribution is quite normal. The lines labeled "bootstraps" in Figure **??** are the lower and upper 95 % confidence interval.