

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

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Abstract

Over the past decade, the Mie λ -6 (generalized Lennard-Jones) potential has grown in popularity due to its improved accuracy for predicting vapor-liquid coexistence compared to the traditional Lennard-Jones 12-6. This manuscript explores the hypothesis that greater accuracy in characterizing the coexistence properties may lead to greater accuracy for viscosity predictions. Four united atom force fields are considered in detail: the TraPPE-UA model of Siepmann and coworkers, the TAMie model of Gross and coworkers, the AUA4 model of Ungerer and coworkers, and the model of Potoff and coworkers. Equilibrium molecular dynamics simulations are analyzed using the Green-Kubo method for viscosity characterization. Simulations are performed for linear alkanes with two to twenty-two carbons and branched alkanes with four to nine carbons. Simulation conditions follow the saturated liquid from reduced temperatures of 0.5 to 0.85 and along the 293 K isotherm in the dense

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liquid region.

In general, the more accurate force fields for coexistence properties do indeed predict viscosity more accurately. For saturated liquids, both the Potoff and TAMie models provide roughly 10 % accuracy for linear alkanes, while deviations are closer to 20 to 50 % for TraPPE-UA. For branched alkanes, the behavior is more complicated but Potoff still provides roughly 15 to 20 % accuracy, while the TAMie force field results in deviations of 20 to 40 %, and TraPPE-UA has deviations of approximately 25 to 60 %. The deviations tend to increase with decreasing temperature, with the exception of the Potoff deviations for propane, which are nearly constant to the triple point temperature.

For compressed liquids, the Mie-based potential models perform better once again, but tend to overestimate the viscosity at very high densities. As these models also tend to overestimate the pressure at high densities, a fortuitous cancellation of errors leads to plots of viscosity with respect to pressure are accurate to within about 10 % up to 200 MPa. Experimental viscosity data tend to be sparse above 200 MPa, but accurate predictions are obtained for propane to 1000 MPa. Uncertainties increase substantially for simulations at high pressures and/or low reduced temperatures.

Keywords:

Thermophysical Properties, Molecular Simulation, Force fields, Molecular dynamics, Green-Kubo

1. Introduction

The design of efficient and reliable technical processes requires accurate estimates of thermophysical properties. Shear viscosity (η) is an important property for characterizing flow, e.g., sizing pumps, assessing flow assurance in fossil fuel recovery, and lubricating bearings in tribological applications. There are primarily three different means by which shear viscosity estimates are obtained: experimental measurement, semi-empirical prediction models, and molecular simulation (molecular dynamics, MD). Significant limitations exist for each of these methods.

For example, experimental measurements can be expensive, time-consuming, and challenging at extreme temperatures (T) and pressures (P). Experimental data tend to be distributed among several prototypes of linear, branched, ring, and polar molecules, with many gaps among a homologous series. Most experimental data are available below 200 MPa, while tribological applications may require estimates at pressures as high as 1000 MPa. Flow assurance applications are generally at pressures below 200 MPa, but at temperatures of 423 to 523 K. These ever expanding conditions of interest and economic constraints on new measurements foster increased research in predictive methods.

The National Institute of Standards and Technology (NIST) Reference Fluid Properties (REFPROP) provides “reference quality” viscosity correlations for experimentally well-studied compounds (around 100 species). Most compounds do not have sufficient *reliable* experimental data covering a wide range of temperatures, pressures, and densities (ρ) for developing “reference quality” correlations. These less-studied compounds require predictive methods that pool together data from several related molecular species.

Semi-empirical prediction models are typically not reliable over the industrially relevant ranges of $P\rho T$ [1]. For example, corresponding states methods are recommended for vapors, dense fluids, and high temperature liquids. These methods rely on the similarity of trends in the properties relative to a reference compound, e.g., methane and *n*-octane. Corresponding states methods are less reliable for more complex molecular structures, e.g., branched compounds. Typical compilations indicate that deviations from experiment may vary by 5 to 50 %, with little guidance about when to expect lower or higher accuracy.

For low temperature liquids, group contribution schemes are favored, but these tend to extrapolate poorly when applied to compounds or conditions outside the training set. More recent advances such as machine learning [2, 3] and entropy scaling [4] have shown great promise in prediction of historically challenging properties, such as viscosity, thermal conductivity, and surface tension. However, machine learning relies on large amounts of experimental data and often suffers from dubious extrapolation. While entropy scaling has a stronger theoretical basis, it requires a reliable reference viscosity and an adequate equation-

of-state, which may not be readily available for the compound of interest.

For these reasons, molecular simulation is an attractive means for estimating viscosity. However, there are two fundamental challenges impeding the use of molecular simulation as a mainstream chemical engineering tool for viscosity prediction. The first challenge is that obtaining reproducible results is more difficult for transport properties, such as viscosity, than for static properties. Recently, a “Best Practices Guide” was developed to address this challenge, namely, to improve reproducibility of viscosity estimates [5]. In this study, we apply these “Best Practices” and address some outstanding issues mentioned therein.

The second challenging aspect of obtaining accurate simulation estimates is that viscosity is extremely sensitive to the force field. In addition to the strong dependence on the non-bonded interactions, the bonded potential plays a much greater role for viscosity than for static properties. For example, varying the torsional potential has a significant impact on viscosity [6], while vapor-liquid coexistence is relatively unaffected [7]. Therefore, the ability to predict viscosities with molecular simulation requires both robust methods and adequate force fields.

We investigate the accuracy of united-atom (UA) Mie λ -6 force fields, a popular class designed for the engineering purpose of predicting thermophysical properties. Specifically, the force fields we compare are the Transferable Potential for Phase Equilibria (TraPPE-UA and TraPPE-UA2), Transferable Anisotropic Mie (TAMie), Potoff, and fourth generation anisotropic-united-atom (AUA4). The suitability of these force fields for quantitative viscosity prediction has been widely debated in the literature.

We investigate the accuracy of four force fields, namely, Transferable Potential for Phase Equilibria (TraPPE-UA and TraPPE-UA2), Transferable Anisotropic Mie (TAMie), Potoff, and fourth generation anisotropic-united-atom (AUA4). Each force field is a variation of the united-atom (UA) Mie λ -6 model, a popular class designed for the engineering purpose of predicting thermophysical properties. However, the suitability of these force fields for quantitative viscosity prediction, especially at high pressures, has been widely debated in the literature.

For example, depending on the compound structure and state conditions, some studies suggest that united-atom Lennard-Jones 12-6 models are inadequate for estimating viscosities and recommend the use of anisotropic-united-atom (AUA) or all-atom (AA) models for this purpose [8, 9, 10, 11]. Considering the significant increase in computational cost of AA simulations, two promising alternatives have been investigated, namely, Mie λ -6 and/or modified torsional potentials. The UA Mie λ -6 has been shown to accurately predict saturated liquid viscosity ($\eta_{\text{liq}}^{\text{sat}}$) without significant deprecation of other vapor-liquid saturation properties [12], i.e., saturated liquid density ($\rho_{\text{liq}}^{\text{sat}}$), saturated vapor density ($\rho_{\text{vap}}^{\text{sat}}$), and saturated vapor pressure ($P_{\text{vap}}^{\text{sat}}$). Alternatively, Reference 6 demonstrates significant improvement in viscosity prediction by modifying the torsional potential.

Reference 13 demonstrates that including viscosity data in the force field development can improve the identification of a unique set of transferable Mie λ -6 parameters, while simultaneously improving viscosity predictions. The force fields compared in this study were optimized solely with vapor-liquid coexistence data, i.e., dynamic properties, such as viscosity, were not included in their parameterization. Notwithstanding the potential benefits of including viscosity as a property of interest during force field development, we assess the accuracy of TraPPE-UA, TAMie, Potoff, and AUA4 for estimating viscosity as they currently stand, including their torsional potential models. While the Potoff and TAMie force fields have shown considerable promise in predicting static properties (in particular, $P_{\text{vap}}^{\text{sat}}$), their ability to predict dynamic properties has not been investigated previously.

The outline for the present work is the following. Section 2 explains the force fields, simulation methodology, and data analysis. Section 3 presents the simulation results for each force field, compound, and state point studied. Section 4 discusses some important observations and limitations. Section 5 recaps the primary conclusions from this work.

2. Methods

2.1. Force field

A united-atom (UA) or anisotropic-united-atom (AUA) representation is used for each compound studied, i.e., normal and branched alkanes are represented with CH₃, CH₂, CH,

and C sites. UA models assume that the UA interaction site is that of the carbon atom, while AUA models assume that the AUA interaction site is shifted away from the carbon atom and towards the hydrogen atom(s). Note that TraPPE and Potoff are UA force fields while TraPPE-2, AUA4, and TAMie are AUA force fields.

The results presented in this work are obtained using fixed bond-lengths. Each force field utilizes a 0.154 nm bond-length for bonds not involving a CH₃ site. The anisotropic-united-atom models (TAMie, AUA4, and TraPPE-2) use a slightly longer “effective” bond-length for CH₃ bonds (see Table 1). While the TAMie force field modifies only the terminal CH₃ sites, AUA4 displaces the interaction location of CH₂ and CH sites as well. For simplicity, we only utilize the AUA4 force field with compounds that are composed exclusively of CH₃ and C interaction sites, i.e., ethane and 2,2-dimethylpropane.

Table 1: Effective bond-lengths in units of nm for terminal (CH₃) UA or AUA interaction sites. Empty table entries for TraPPE-2 denote that the force field does not contain the corresponding interaction site type. Empty table entries in AUA4 arise because this force field uses a more complicated construction than the simple effective bond-length approach. Specifically, AUA4 requires CH₂ and CH interaction sites that are not along the C-C bond axis.

Bond	TraPPE, Potoff	TAMie	AUA4	TraPPE-2
CH ₃ -CH ₃	0.154	0.194	0.1967	0.230
CH ₃ -CH ₂	0.154	0.174	—	—
CH ₃ -CH	0.154	0.174	—	—
CH ₃ -C	0.154	0.174	0.1751	—

The same angle and dihedral potentials are used for each force field. Angular bending interactions are evaluated using a harmonic potential:

$$u^{\text{bend}} = \frac{k_{\theta}}{2} (\theta - \theta_0)^2 \quad (1)$$

where u^{bend} is the bending energy, θ is the instantaneous bond angle, θ_0 is the equilibrium bond angle (see Table 2), and k_{θ} is the harmonic force constant which is equal to 62500

K/rad² for all bonding angles. Dihedral torsional interactions are determined using a cosine series:

$$u^{\text{tors}} = c_0 + c_1[1 + \cos \phi] + c_2[1 - \cos 2\phi] + c_3[1 + \cos 3\phi] \quad (2)$$

where u^{tors} is the torsional energy, ϕ is the dihedral angle and c_i are the Fourier constants listed in Table 3.

Table 2: Equilibrium bond angles (θ_0). x and y are values between 0 and 3.

Bending sites	θ_0 (degrees)
CH _{<i>x</i>} -CH ₂ -CH _{<i>y</i>}	114.0
CH _{<i>x</i>} -CH-CH _{<i>y</i>}	112.0
CH _{<i>x</i>} -C-CH _{<i>y</i>}	109.5

Table 3: Fourier constants (c_i) in units of K. x and y are values between 0 and 3.

Torsion sites	c_0	c_1	c_2	c_3
CH _{<i>x</i>} -CH ₂ -CH ₂ -CH _{<i>y</i>}	0.0	355.03	-68.19	791.32
CH _{<i>x</i>} -CH ₂ -CH-CH _{<i>y</i>}	-251.06	428.73	-111.85	441.27
CH _{<i>x</i>} -CH ₂ -C-CH _{<i>y</i>}	0.0	0.0	0.0	461.29
CH _{<i>x</i>} -CH-CH-CH _{<i>y</i>}	-251.06	428.73	-111.85	441.27

Non-bonded interactions between sites located in two different molecules or separated by more than three bonds within the same molecule are calculated using a Mie λ -6 potential (of which the Lennard-Jones, LJ, 12-6 is a subclass) [14]:

$$u^{\text{vdw}}(\epsilon, \sigma, \lambda; r) = \left(\frac{\lambda}{\lambda - 6} \right) \left(\frac{\lambda}{6} \right)^{\frac{6}{\lambda - 6}} \epsilon \left[\left(\frac{\sigma}{r} \right)^\lambda - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3)$$

where u^{vdw} is the van der Waals interaction, σ is the distance (r) where $u^{\text{vdw}} = 0$, $-\epsilon$ is the energy of the potential at the minimum (i.e., $u^{\text{vdw}} = -\epsilon$ and $\frac{\partial u^{\text{vdw}}}{\partial r} = 0$ for $r = r_{\text{min}}$), and

λ is the repulsive exponent. The non-bonded Mie λ -6 force field parameters for TraPPE, TraPPE-2, Potoff, AUA4, and TAMie are provided in Table 4.

Table 4: Non-bonded (intermolecular) parameters for TraPPE [15, 16] (and TraPPE-2 [17]), Potoff [18, 19], AUA4 [20, 21], and TAMie [22, 23] force fields. The “short/long” Potoff CH and C parameters are included in parentheses. The ethane-specific parameters for TAMie are included in parentheses.

	TraPPE (TraPPE-2)			Potoff (S/L)		
United-atom	ϵ (K)	σ (nm)	n	ϵ (K)	σ (nm)	n
CH ₃	98 (134.5)	0.375 (0.352)	12	121.25	0.3783	16
CH ₂	46	0.395	12	61	0.399	16
CH	10	0.468	12	15 (15/14)	0.46 (0.47/0.47)	16
C	0.5	0.640	12	1.2 (1.45/1.2)	0.61 (0.61/0.62)	16
	AUA4			TAMie		
CH ₃	120.15	0.3607	12	136.318 (130.780)	0.36034 (0.36463)	14
CH ₂	86.29	0.3461	12	52.9133	0.40400	14
CH	50.98	0.3363	12	14.5392	0.43656	14
C	15.04	0.244	12	–	–	–

Note that TraPPE (TraPPE-2) and TAMie implement an ethane-specific set of CH₃ parameters. Also, Potoff reports a “generalized” and “short/long” (S/L) CH and C parameter set. The “short” and “long” parameters are implemented when the number of carbons in the backbone is ≤ 4 and > 4 , respectively. Due to their superior accuracy, we only provide results for the Potoff S/L parameter set.

Non-bonded parameters between two different site types (i.e., cross-interactions) are determined using Lorentz-Berthelot combining rules [24] for ϵ and σ , respectively, and an arithmetic mean for the repulsive exponent λ (as recommended in Reference 18):

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (4)$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (5)$$

$$\lambda_{ij} = \frac{\lambda_{ii} + \lambda_{jj}}{2} \quad (6)$$

where the ij subscript refers to cross-interactions and the subscripts ii and jj refer to same-site interactions.

2.2. Simulation set-up

Viscosity estimates can be obtained from both equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) simulations. The “Best Practices Guide” is currently limited to EMD methods and purports that NEMD might be necessary for high viscosities (greater than 0.02 Pa-s). One purpose of the present work is to demonstrate that, by applying these guidelines, EMD can also provide meaningful estimates for highly viscous systems.

Equilibrium molecular dynamics simulations are performed using GROMACS version 2018 with “mixed” (single and double) precision [25]. GROMACS was compiled using GNU 7.3.0, OpenMPI enabled, and GPU support disabled. Approximately three-fourths of the simulations were run using Linux 4.4.0-112-generic x86_64 on an Intel(R) Xeon(R) CPU E5-2699 v4 @ 2.20GHz machine while the remaining one-fourth were run using Linux 4.15.0-22-generic x86_64 on an Intel(R) Xeon(R) CPU E5-2450 0 @ 2.10GHz machine. Example GROMACS input files (.top, .gro. and .mdp) with corresponding shell and python scripts for preparing, running, and analyzing simulations are provided as Supporting Information.

Simulation specifications are provided in Tables 5 and 6. Note that each force field utilizes a 1.4 nm non-bonded cut-off distance, with the exception of Potoff which employs a 1.0 nm cut-off (as recommended in Reference 18). For most systems, 1 ns is a sufficient production time, while longer simulations are required for the more viscous systems, e.g., 2,2,4-trimethylpentane at elevated pressures.

When η is desired at a prescribed T and P , five simulation stages are required: energy minimization, NPT equilibration, NPT production, NVT equilibration, and NVT production. When η is desired at a prescribed T and ρ , the NPT stages are unnecessary and only

Table 5: General simulation specifications.

Time-step (fs)	2
Equilibration time (ns)	1
Production time (ns)	1, 2, 4, or 8
Cut-off length (nm)	1.4 (1.0 for Potoff)
Tail-corrections [26]	U and P
Constrained bonds	LINCS
LINCS-order	8
Number of molecules	400

Table 6: Integrator, thermostat and barostat specifications.

	NPT Equil.	NPT Prod.	NVT Equil.	NVT Prod.
Integrator	Velocity Verlet	Leap frog	Velocity Verlet	Velocity Verlet
Thermostat	Velocity rescale	Nosé-Hoover	Nosé-Hoover	Nosé-Hoover
Thermostat time-constant (ps)	1.0	1.0	1.0	1.0
Barostat	Berendsen	Parrinello-Rahman	N/A	N/A
Barostat time-constant (ps)	1.0	5.0	N/A	N/A
Barostat compressibility	4.5e-5	4.5e-5	N/A	N/A

three simulation stages are required: energy minimization, NVT equilibration, and NVT production. Note that, according to “Best Practices”, the final production stage simulations are always performed using the NVT ensemble.

As recommended by “Best Practices,” we utilize 30 to 60 independent replicates to improve the precision and to provide more rigorous estimates of uncertainty. To ensure independence between replicates, the entire series of simulation stages are repeated for each replicate.

Two different classes of viscosity are investigated in this study, namely, saturated liquid viscosity ($\eta_{\text{liq}}^{\text{sat}}$) and compressed liquid viscosities at a temperature of 293 K ($\eta_{\text{liq}}^{\text{comp}}$). Saturated liquid viscosities are estimated by performing NVT ensemble simulations at the saturation temperature (T^{sat}) and saturated liquid density ($\rho_{\text{liq}}^{\text{sat}}$). The simulation densities correspond to the REFPROP $\rho_{\text{liq}}^{\text{sat}}$, which is admittedly not necessarily the same as the force field $\rho_{\text{liq}}^{\text{sat}}$. This point is discussed in greater detail in Section 4.

Two different simulation protocols are implemented for estimating compressed liquid viscosities ($\eta_{\text{liq}}^{\text{comp}}$). Specifically, we perform simulations with each force field either at the same ρ or the same P . For the purpose of comparing trends between force fields and REFPROP, these two methods are essentially equivalent. From a practical standpoint, estimating η at a given P requires performing preliminary NPT ensemble simulations to determine the corresponding box size.

2.3. Data analysis

Following the “Best Practices” recommendation, we implement the Green-Kubo “time-decomposition” analysis to extract viscosity from EMD simulations. We refer the interested reader to References 5 and 27 for further details. In brief, the Green-Kubo integral is computed with respect to time according to

$$\eta(t) = \frac{V}{3k_{\text{B}}TN_{\text{reps}}} \sum_{n=1}^{N_{\text{reps}}} \sum_{\alpha \neq \beta} \int_0^t dt' \langle \tau_{\alpha\beta,n}(t') \tau_{\alpha\beta,n}(0) \rangle_{t_0} \quad (7)$$

where t is time, V is the volume, k_{B} is the Boltzmann constant, N_{reps} is the number of independent replicate simulations, $\langle \dots \rangle_{t_0}$ denotes an average over time origins (t_0), α and $\beta = x, y$, or z Cartesian coordinates, and $\tau_{\alpha\beta,n}$ is the α - β off-diagonal stress tensor element for the n^{th} replicate.

$\tau_{\alpha\beta,n}$ is recorded every 6 fs (3 time-steps) to adequately integrate the initial rapid decay of the autocorrelation function. To improve precision, Equation 7 averages several (between 30 and 60) independent replicate simulations, twelve different time-origins, and all three unique off-diagonal stress tensor components (hence the factor of 3 in the denominator of Equation 7).

The “true” viscosity is obtained by evaluating Equation 7 in the infinite-time-limit, i.e., as $t \rightarrow \infty$. However, the long-time tail of the Green-Kubo integral is often quite noisy and does not converge smoothly. For this purpose, we fit a double-exponential function to the “running integral”

$$\eta(t) = A\alpha\tau_1(1 - \exp(-t/\tau_1)) + A(1 - \alpha)\tau_2(1 - \exp(-t/\tau_2)) \quad (8)$$

where A, α, τ_1 , and τ_2 are fitting parameters and $\eta^\infty = A\alpha\tau_1 + A(1 - \alpha)\tau_2$ is the infinite-time-limit viscosity.

Since the Green-Kubo “running integral” suffers from extreme fluctuations at long times, Equation 8 is fit by minimizing a weighted sum-squared error objective function. Weights are equal to the inverse of the standard deviation (σ_η) of the replicate simulations. The time dependence of σ_η is modeled with At^b , where A and b are fitting parameters.

Following a heuristic proposed in Reference 27, data are excluded where $\sigma_\eta > 0.4 \times \eta^\infty$. Occasionally, this heuristic results in a cut-off that is too short, in particular for systems with slow dynamics, which lead to very poor fits. In such cases, it is necessary to modify the heuristic, e.g., exclude data where $\sigma_\eta > 0.8 \times \eta^\infty$. Erroneously large fluctuations also exist at very short times. Following “Best Practices,” only data for $t > 3$ ps are included in the fitting of Equation 8.

As recommended by “Best Practices”, uncertainties are obtained by bootstrap re-sampling. Specifically, the fitting process described previously is repeated hundreds of times using randomly selected subsets of replicate simulations. Furthermore, each repetition uses a randomly selected long-time cut-off between 0.35 and $0.45 \times \eta^{infy}$ to account for uncertainty in the $0.4 \times \eta^\infty$ heuristic. A 95 % confidence interval is obtained from the distribution of bootstrap estimates for η^∞ . An example of this process is provided as Supporting Information.

3. Results

Seven normal and seven branched alkanes of varying chain-length and degree of branching are simulated in this study. We only consider compounds with available REFPROP equations-of-state and viscosity correlations [28]. Specifically, we simulate ethane [29, 30],

propane [31, 32], *n*-butane [33, 34], *n*-octane [35, 36], *n*-dodecane [37, 38], *n*-hexadecane [39, 40], *n*-docosane [39, 41], 2-methylpropane [42, 43], 2-methylbutane [42, 41], 2-methylpentane [42, 41], 3-methylpentane [44, 41], 2,2-dimethylpropane [42, 41], 2,3-dimethylbutane [44, 41], and 2,2,4-trimethylpentane [45, 41].

Each compound was simulated using the TraPPE and Potoff S/L force fields. Potoff “short” parameters are employed for 2-methylpropane, 2-methylbutane, 2,2-dimethylpropane, and 2,3-dimethylbutane while Potoff “long” parameters are utilized for 2-methylpentane, 3-methylpentane, and 2,2,4-trimethylpentane. 2,2-dimethylpropane and 2,2,4-trimethylpentane were not simulated using the TAMie force field since we are not aware of any TAMie parameters for C sites. Only ethane and 2,2-dimethylpropane were simulated with AUA4.

Sections 3.1 and 3.2 present results for saturated liquid viscosities ($\eta_{\text{liq}}^{\text{sat}}$) and compressed liquid viscosities ($\eta_{\text{liq}}^{\text{comp}}$), respectively. In both sections, the *n*-alkane results are followed by the branched alkane results. Simulation results are compared with the REFPROP viscosity correlations and experimental data from the ThermoData Engine (TDE) database [46].

3.1. Saturated Liquid

3.1.1. Normal alkanes

Figure 1 compares the ethane results for saturated liquid viscosities obtained with the TraPPE, TraPPE-2, TAMie, Potoff, AUA4 and the Bayesian parameter sets for $\lambda = 13, 14, 15$, and 16. As the remainder of this section demonstrates, the over estimation of ethane $\eta_{\text{liq}}^{\text{sat}}$ is actually an anomaly for normal and branched alkanes. It is not uncommon for the smallest compounds in a homologous series, i.e., methane and ethane, to follow a different trend than the larger compounds. However, the relative magnitudes of the different force fields is consistent with other compounds, namely, TraPPE < TAMie < Potoff. This is expected since TraPPE utilizes a LJ 12-6, TAMie a Mie 14-6, and Potoff a Mie 16-6 potential. By comparing the results from TraPPE-UA2 with TraPPE-UA and the TAMie results with those of the Bayesian 14-6 potential, it appears that the anisotropic CH₃-CH₃ bond significantly reduces the viscosity of ethane.

Figure 2 compares the TraPPE, Potoff, and TAMie saturated liquid viscosities for propane,

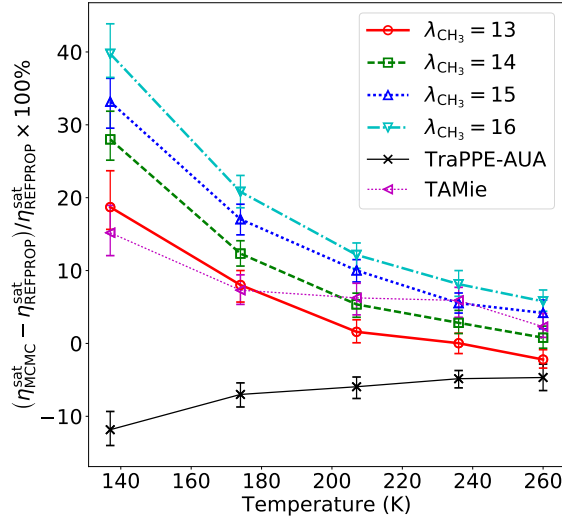


Figure 1: Saturated liquid viscosities for ethane. Colors/symbols denote different force fields.

n-butane, and *n*-octane. Similar to what has been demonstrated in previous studies, the TraPPE force field significantly under predicts $\eta_{\text{liq}}^{\text{sat}}$ (between 30 and 80 %) with the deviation increasing with decreasing temperature [12, 6]. By contrast, the Potoff and TAMie force fields agree with the REFPROP values for these compounds to within 10 %. While TAMie deviations increase near the triple point temperature of propane, Potoff deviations are nearly constant over the entire temperature range studied for each compound.

Figure 3 compares the TraPPE, Potoff, and TAMie saturated liquid viscosities for *n*-dodecane, *n*-hexadecane, and *n*-docosane. Although the TraPPE results for these compounds are similar to those observed in Figure 2 for smaller *n*-alkanes, TAMie and Potoff demonstrate a stronger temperature dependence for these larger *n*-alkanes. The cause of this trend is unclear but, since it is only observed for larger compounds, it is likely attributed to the torsional potential or the transferability of the CH₂ Mie λ -6 parameters.

3.1.2. Branched alkanes

Figures 4 and 5 compare the saturated liquid viscosities for each force field and branched alkane studied. Figures 4 and 5 present results for the compounds classified by Potoff

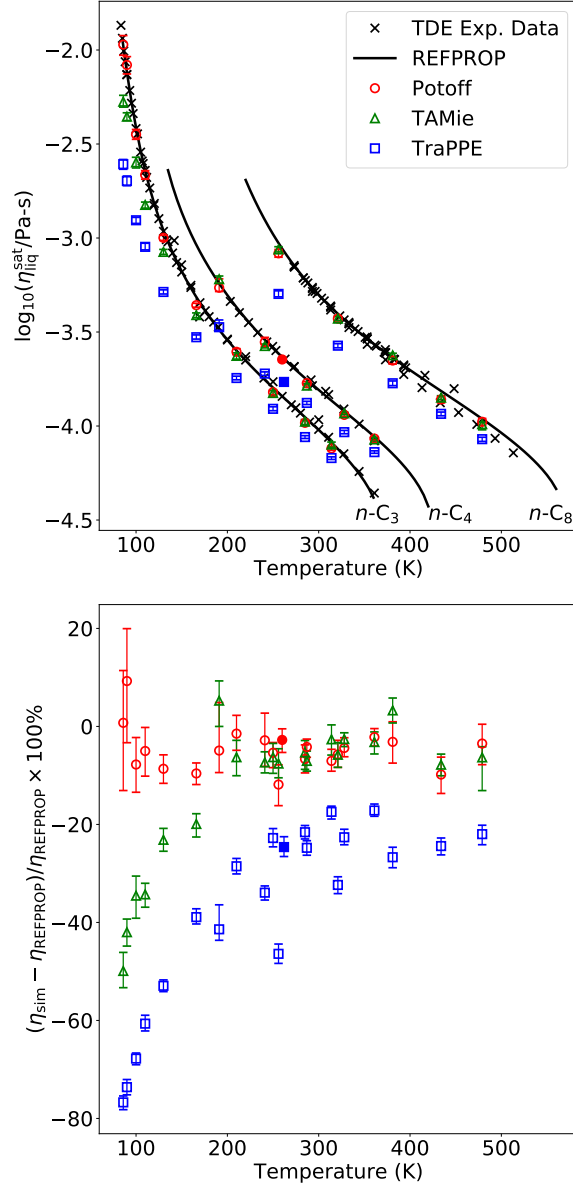


Figure 2: Saturated liquid viscosities for propane ($n\text{-C}_3$), n -butane ($n\text{-C}_4$), and n -octane ($n\text{-C}_8$). Top panel compares simulation results with REFPROP correlations and TDE data. Bottom panel computes the percent deviation between the simulation and REFPROP values. Colors/symbols denote different force fields. Error bars represent the 95 % confidence interval estimated with bootstrap re-sampling. Filled symbols correspond to simulations performed at the respective force field $\rho_{\text{liq}}^{\text{sat}}$ (see Section 4).

as “short” and “long”, respectively. Specifically, Figure 4 depicts 2-methylpropane, 2,2-

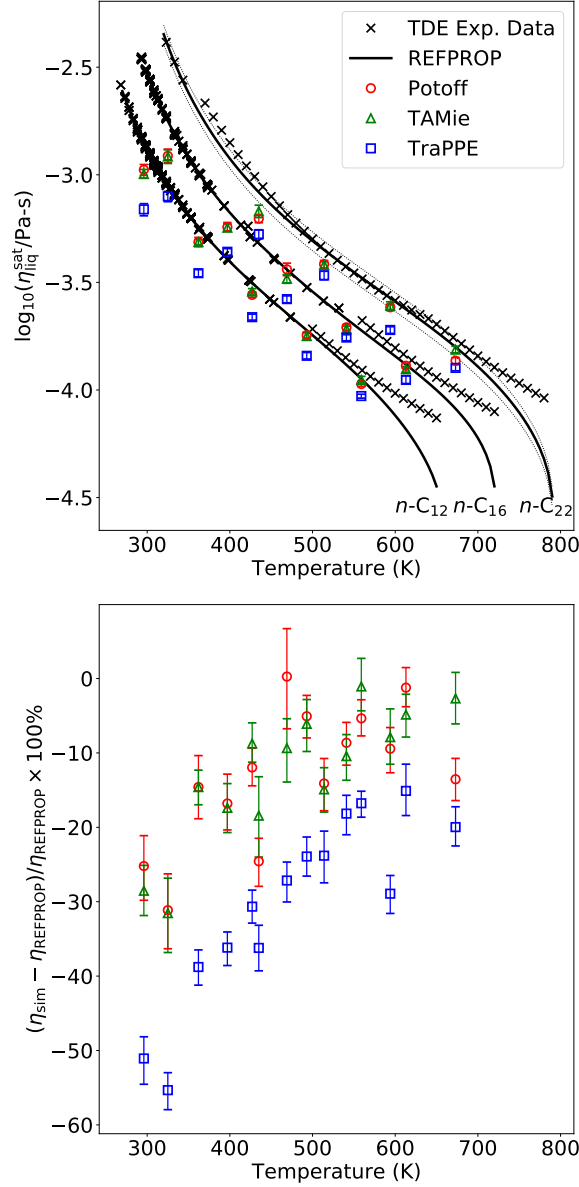


Figure 3: Saturated liquid viscosities for n -dodecane (n -C₁₂), n -hexadecane (n -C₁₆), and n -docosane (n -C₂₂). See caption of Figure 2 for detailed description.

dimethylpropane, 2-methylbutane, and 2,3-dimethylbutane, while Figure 5 contains 2-methylpentane, 3-methylpentane, and 2,2,4-trimethylpentane. Each compound was simulated using the TraPPE and Potoff force fields. However, only 2,2-dimethylpropane was simulated with AUA4 while 2,2-dimethylpropane and 2,2,4-trimethylpentane were not simulated using the

TAMie force field.

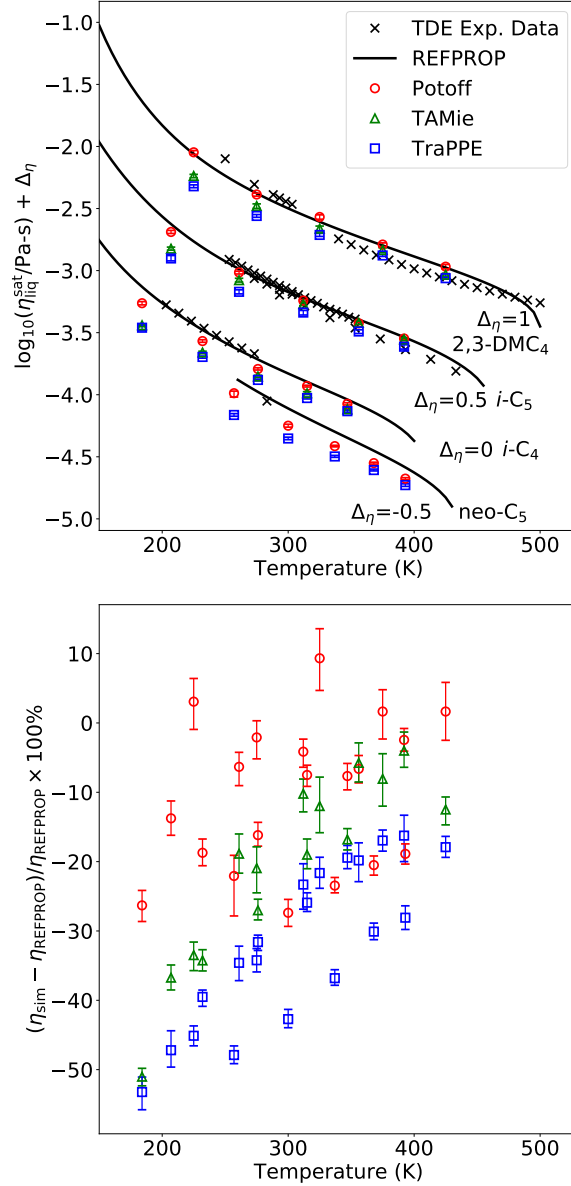


Figure 4: Saturated liquid viscosities for 2-methylpropane (*i*-C₄), 2,2-dimethylpropane (neo-C₅), 2-methylbutane (*i*-C₅), and 2,3-dimethylbutane (2,3-DMC₄). See caption of Figure 2 for detailed description. For clarity, values in top panel are shifted by $\Delta\eta$.

From Figures 4 and 5, we see that the Potoff S/L and TAMie force fields are not as accurate for these branched alkanes as for the normal alkanes. In particular, Potoff and

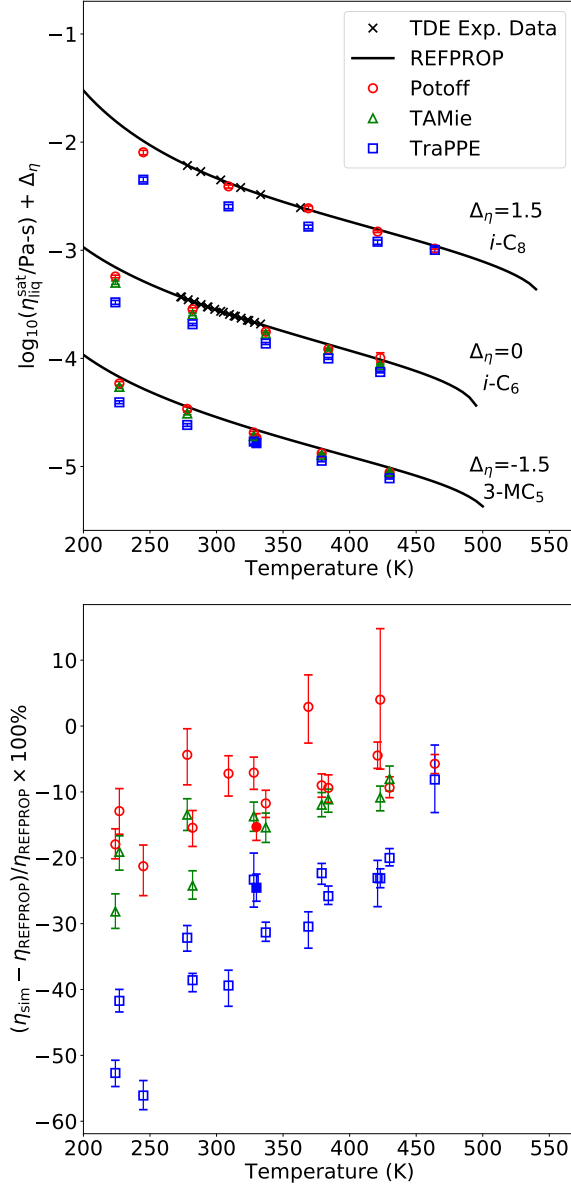


Figure 5: Saturated liquid viscosities for 2-methylpentane ($i\text{-C}_6$), 3-methylpentane (3-MC_5), and 2,2,4-trimethylpentane ($i\text{-C}_8$). See caption of Figure 2 for detailed description. For clarity, values in top panel are shifted by $\Delta\eta$.

TAMie demonstrate the same temperature dependence observed for other force fields, where the deviations are largest at lower temperatures. However, Potoff still provides considerable improvement compared to the LJ 12-6 based models, i.e., TraPPE and AUA4. Note that

the Potoff “short” and “long” parameters in Figures 4 and 5, respectively, provide similar accuracy.

The deviations for each force field are largest for 2-methylpropane and 2,2-dimethylpropane. Since these compounds are primarily composed of CH_3 UA sites, this poor performance is likely due to the assumption that the CH_3 non-bonded parameters are transferable from n -alkanes to branched alkanes. Improvement might be possible if the CH_3 parameters were different depending on the neighboring UA site type. However, it is important to note that the 2,2-dimethylpropane REFPROP viscosity correlation is not considered to be of “reference quality.”

3.2. Compressed liquid

Section 3.1 demonstrates that Mie λ -6 based force fields (Potoff and TAMie) are considerably more reliable for predicting saturated liquid viscosities than LJ 12-6 based force fields (TraPPE and AUA4). However, as the Mie λ -6 potential is too repulsive at short distances for $\lambda > 12$, the Potoff (16-6) and TAMie (14-6) force fields tend to over estimate pressure at high densities [47]. Since η also increases with larger values of λ , our *ansatz* is that Potoff and TAMie should over estimate η at high densities/pressures.

Surprisingly, Reference 12 shows that a (slightly modified) Mie 14-6 (for CH_3) and Mie 20-6 (for CH_2) potential can accurately predict the η - P dependence for n -hexadecane up to 400 MPa. Since the force field in Reference 12 was parameterized with $\eta_{\text{liq}}^{\text{sat}}$ data, the purpose of this section is to determine if the Potoff and TAMie force fields, which did not include viscosity data in their parameterization, are also reliable for estimating the η - P dependence. To provide additional insight into the consequences of using a Mie potential with $\lambda > 12$, we present results for the η - ρ dependence as well (which was not reported in Reference 12).

3.2.1. Normal alkanes

Figures 6, 7, and 8 compare the compressed liquid viscosities ($\eta_{\text{liq}}^{\text{comp}}$) for propane, n -butane, and n -octane, respectively. Each compound is simulated using the TraPPE, Potoff, and TAMie force fields at various densities. Simulation results are compared with REFPROP

correlations and TDE data, when available. All TDE data for temperatures between 288 K and 298 K are depicted. REFPROP uncertainties are assumed to be a constant percent deviation as reported in the corresponding publication. “REFPROP extrapolation” are values that are found outside of the “reference quality” range. This extrapolation is intended to guide the eye when comparing with simulation results at high densities/pressures.

Figure 6 demonstrates that the TraPPE force field has a constant negative bias even with increasing density/pressure. The TAMie force field has the most accurate η - ρ dependence, i.e., the error does not increase significantly with respect to density. By contrast, the Potoff potential demonstrates considerable over estimation of η at high densities, which is likely attributed to the overly repulsive Mie 16-6 potential at close distances. Remarkably, the Potoff force field is the most accurate at predicting the η - P dependence from saturation pressure to 1000 MPa. This can be explained as a cancellation of errors since the Potoff force field significantly over predicts both η and P at high densities. Note that the increase in Potoff deviations for the two highest pressures can potentially be explained by the large uncertainty in the REFPROP correlation and dubious extrapolation at these extreme pressures.

The results in Figures 7 and 8 for *n*-butane and *n*-octane, respectively, are similar to those in Figure 6 for propane. Specifically, the TraPPE force field under predicts η at all densities/pressures, the TAMie force field provides the most accurate η - ρ dependence, while the Potoff force field over predicts η with respect to ρ but accurately predicts the η - P trend. We conclude that Potoff should not be used to estimate the η - ρ dependence, although it is the most reliable force field for estimating the η - P dependence.

3.2.2. Branched alkanes

The trends observed in Figures 9 to 12 are consistent with the compressed liquid trends for *n*-alkanes. Specifically, TraPPE under predicts η with respect to both ρ and P . Potoff over predicts η with respect to ρ but provides a reasonable estimate of the η - P trend. As observed in Section 3.1, Potoff and TAMie are less accurate for branched alkanes than for *n*-alkanes. In particular, the Potoff η - P trends are systematically lower than the REFPROP correlations for 2-methylbutane and 3-methylpentane. However, note that the Potoff η - P trends are quite

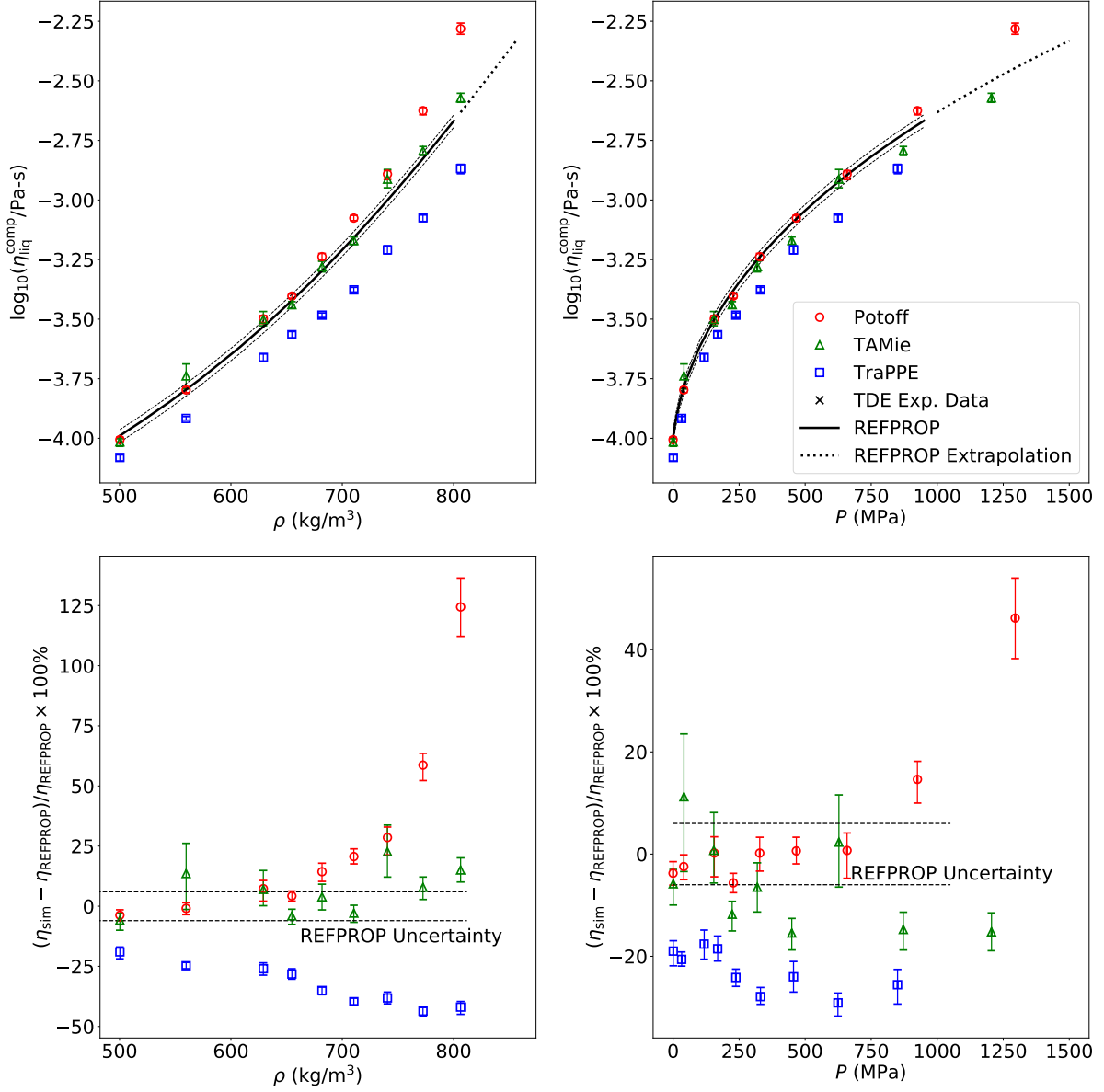


Figure 6: Compressed liquid viscosities at 293 K for propane. Top panels provide η - ρ and η - P dependence. Bottom panels present deviations between simulated (η_{sim}) and REFPROP (η_{REFPROP}) values with respect to ρ and P . Dashed lines correspond to REFPROP uncertainties. Dotted lines are extrapolation values outside of “reference quality” range. Colors/symbols denote different force fields and experimental data. Error bars represent the 95 % confidence interval estimated with bootstrap re-sampling.

reliable for 2-methylpropane and 2,2,4-trimethylpentane. These results cannot be attributed to the “short” or “long” parameter distinction, since 2-methylbutane and 2-methylpropane

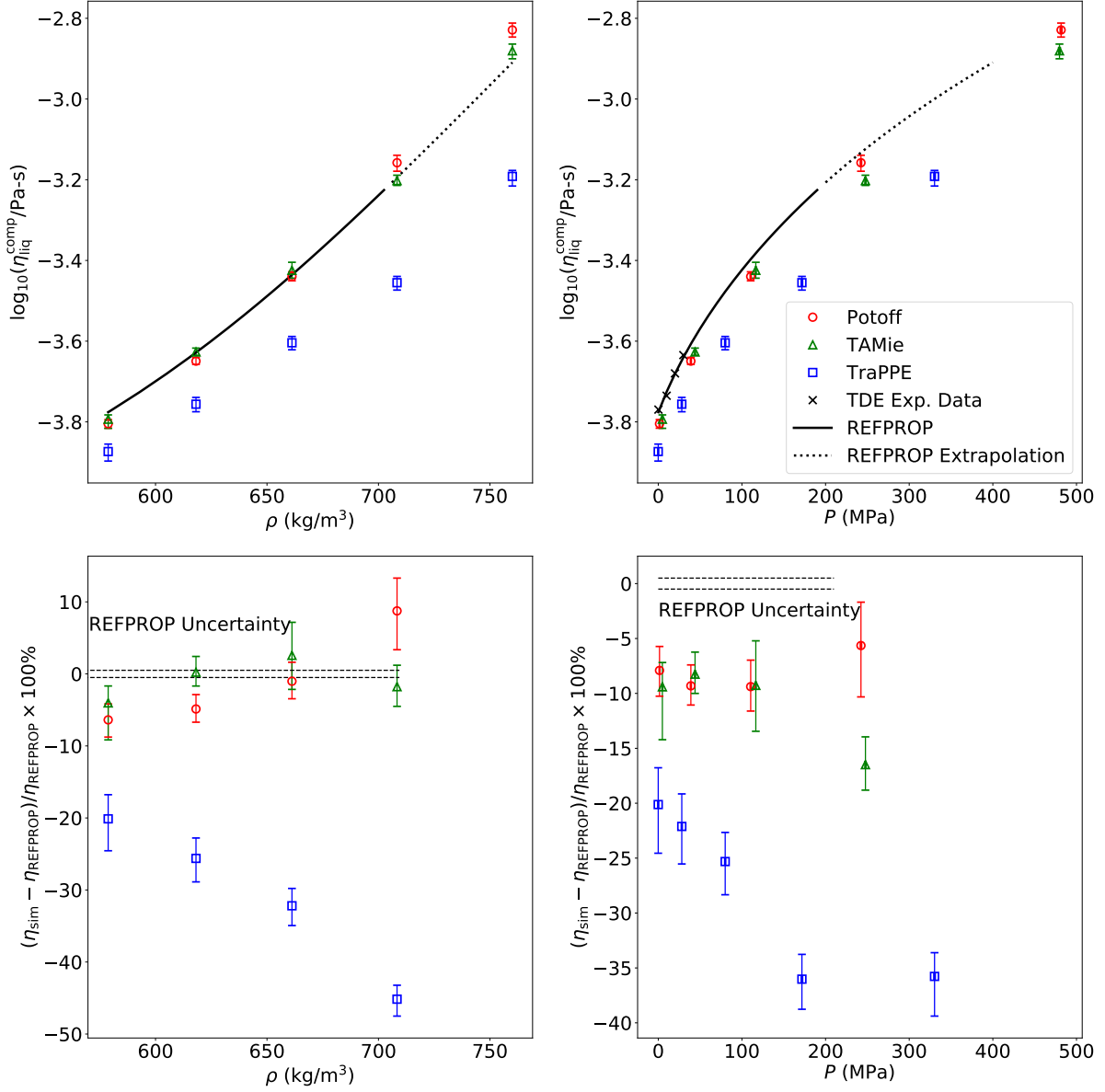


Figure 7: Compressed liquid viscosities at 293 K for *n*-butane. See caption of Figure 6 for detailed description.

both use “short” parameters while 3-methylpentane and 2,2,4-trimethylpentane both use “long” parameters.

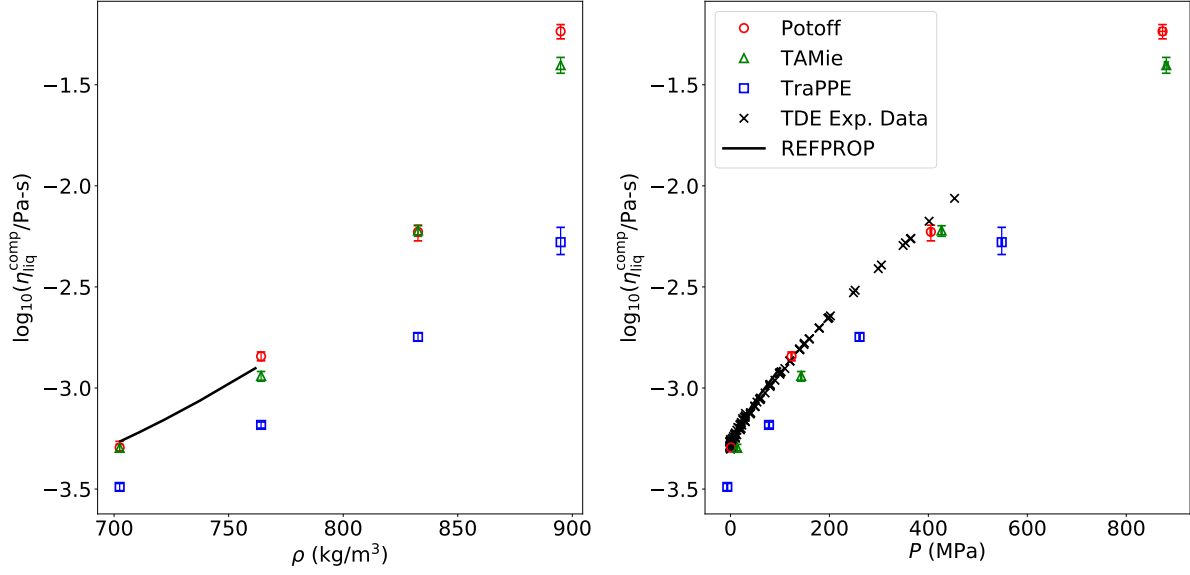


Figure 8: Compressed liquid viscosities at 293 K for *n*-octane. See caption of Figure 6 for detailed description.

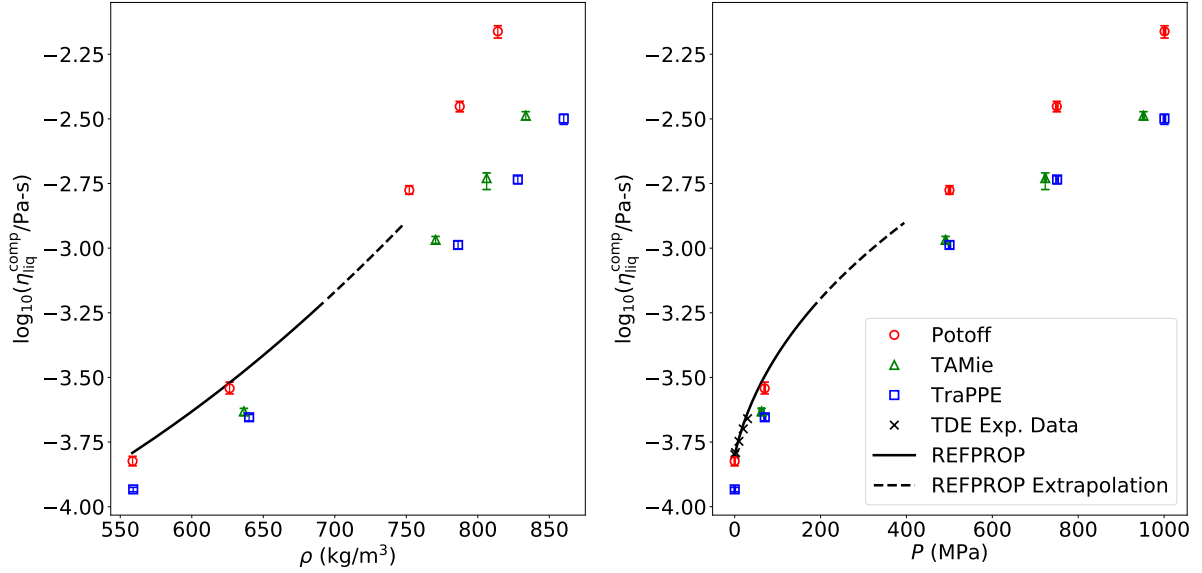


Figure 9: Compressed liquid viscosities at 293 K for 2-methylpropane. See caption of Figure 6 for detailed description.

4. Discussion/Limitations

4.1. Liquid structure

While the Potoff force field significantly over predicts the η - ρ dependence at $T = 293$ K, it does not over predict η for the highest saturated liquid densities (those near the triple

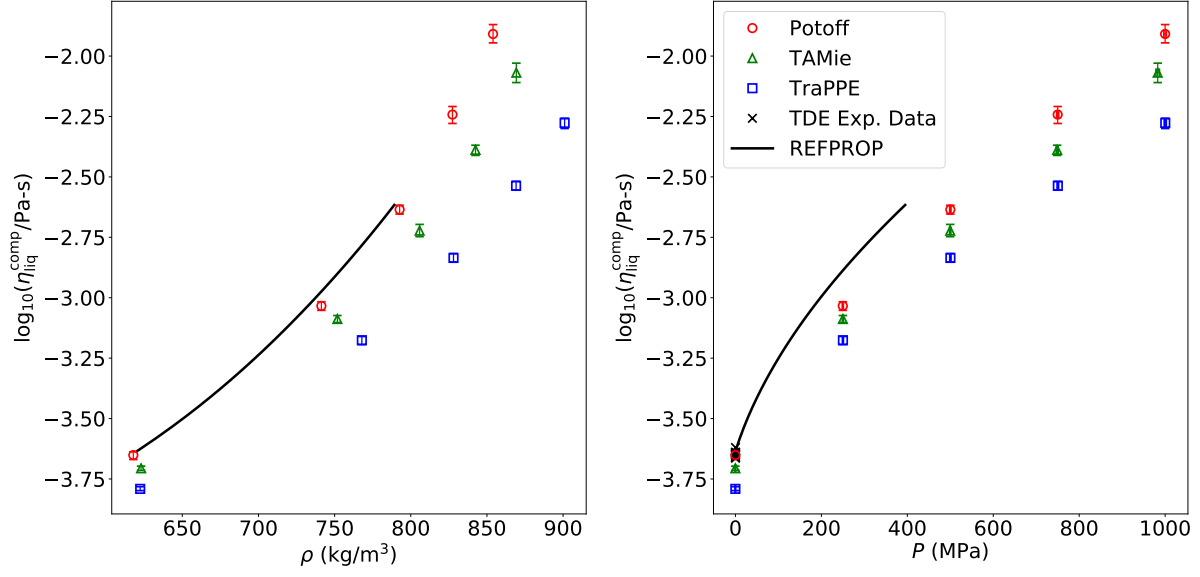


Figure 10: Compressed liquid viscosities at 293 K for 2-methylbutane. See caption of Figure 6 for detailed description.

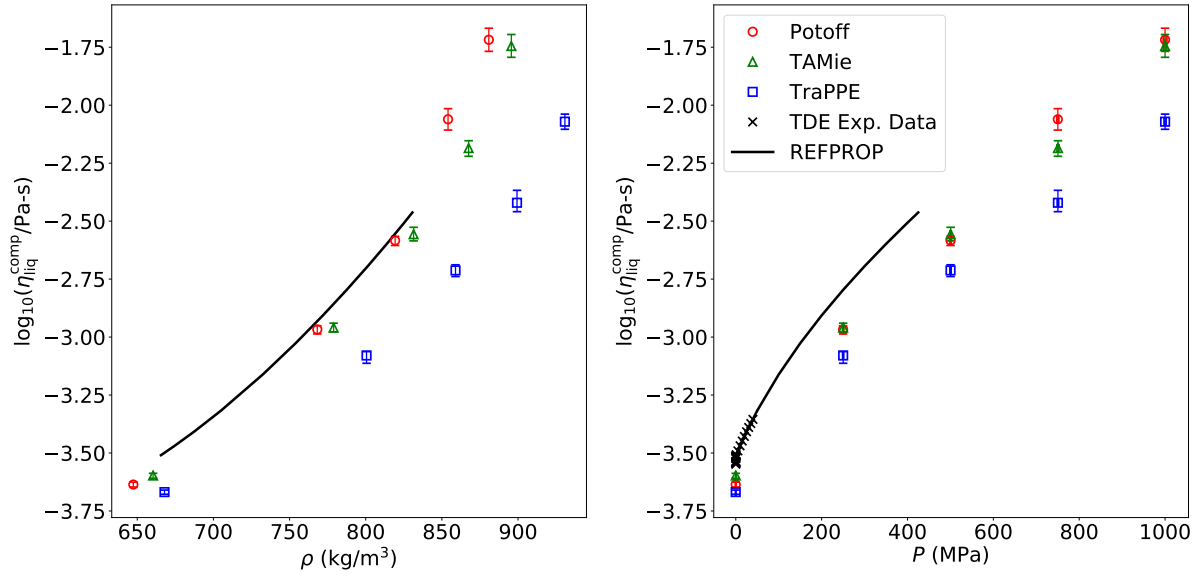


Figure 11: Compressed liquid viscosities at 293 K for 3-methylpentane. See caption of Figure 6 for detailed description.

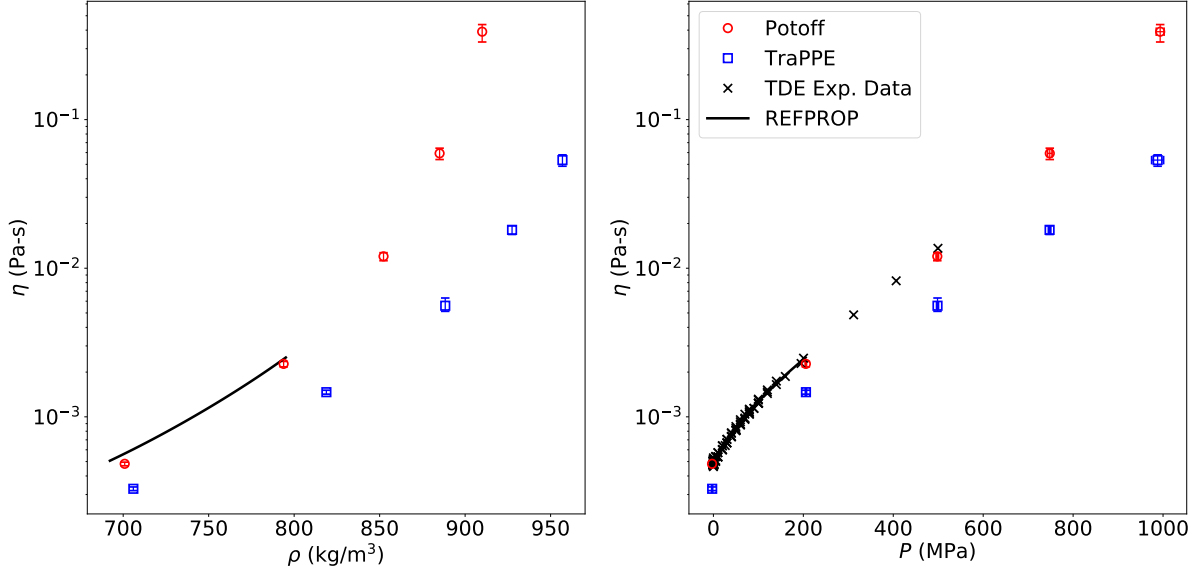


Figure 12: Compressed liquid viscosities at 293 K for 2,2,4-trimethylpentane. See caption of Figure 6 for detailed description.

point temperature) (cf. Figures 2 and 6). To better understand this seemingly inconsistent result, Figure 13 compares the radial distribution functions (RDF) for three different state points, namely, near the triple point ($T = 86$ K and $\rho = 732.63$ kg/m³) and two densities along the $T = 293$ K isotherm ($\rho = 732.63$ kg/m³ and $\rho = 806.23$ kg/m³). In order to provide a fair comparison between force fields, the RDF is plotted with respect to a reduced distance, namely, r/r_{\min} .

The top panel of Figure 13 demonstrates that the RDF shifts to the left (closer interactions) when increasing the temperature from 86 K to 293 K. Although the magnitude of this shift is similar for all three force fields, the Potoff viscosities appear to be impacted the most due to the steepness of the Mie 16-6 potential. By contrast, the bottom panel demonstrates that increasing the density at constant temperature does not shift the RDF, although it does increase the frequency of close-range interactions. Therefore, the overly repulsive Mie 16-6 potential is only problematic at high densities if there is sufficient thermal energy for the system to sample extremely close-range interactions. This explains why the Potoff force field is reliable at high densities along the saturation curve but over estimates the η - ρ dependence

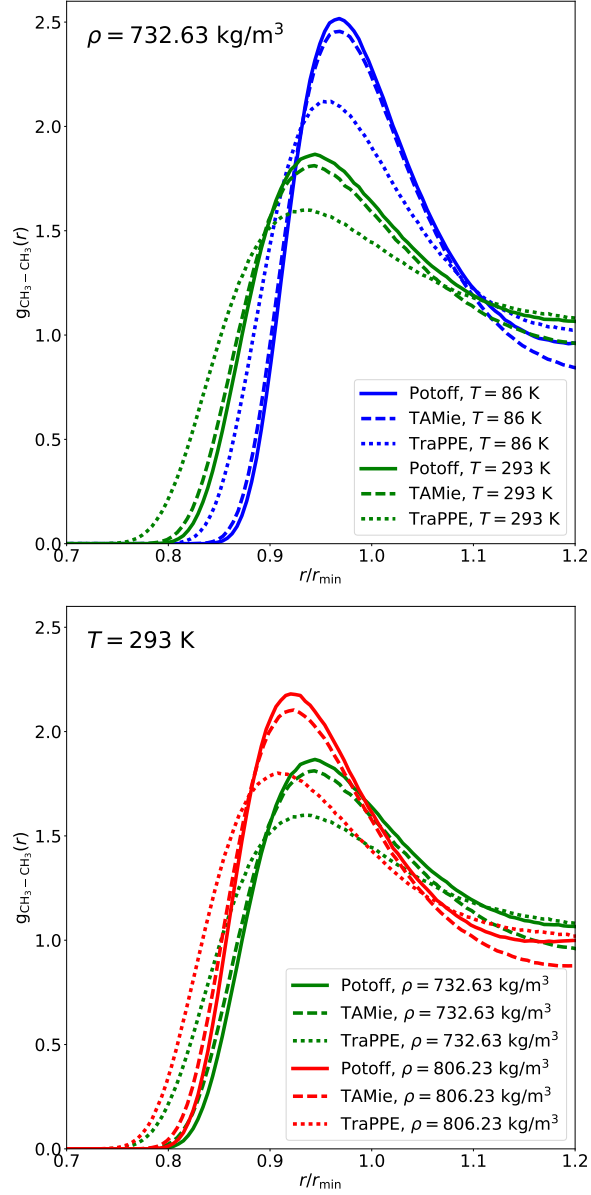


Figure 13: Comparison of radial distribution function for $\text{CH}_3\text{-CH}_3$ interactions ($g_{\text{CH}_3-\text{CH}_3}(r)$). The top panel compares two different temperatures along the triple point isochore. The bottom panel compares two different densities along the 293 K isotherm. Colors correspond to different state points while line styles denote different force fields.

at 293 K.

4.2. Finite-size effects

Previous studies have demonstrated that finite-size effects are often negligible for viscosity estimates with equilibrium molecular dynamics. Figure 14 compares simulation results for 100, 200, 400, and 800 molecule systems. While the results in Figure 14 are for propane, we observed similar results for a larger compound, specifically, 2,2,4-trimethylpentane.

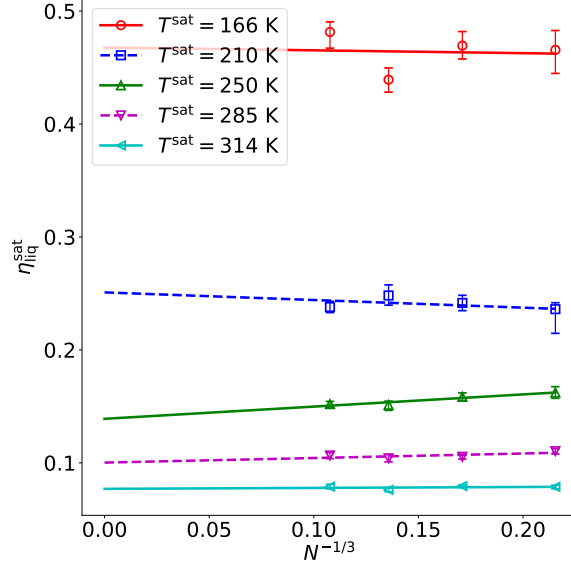


Figure 14: Finite-size effects. Simulation results were obtained for propane with the Potoff force field and $N = 100, 200, 400$, and 800 . Colors/symbols denote different saturation temperatures. The lines are obtained from a weighted linear fit with respect to $N^{-1/3}$.

Notice that the averages and uncertainties are typically quite similar for the different values of N , although some clear exceptions exist, e.g., $N = 800$ and $N = 400$ for $T = 166$ K. Although the uncertainties do not overlap in all cases, there does not appear to be a consistent trend for the average η with respect to $N^{-1/3}$. Therefore, we do not attribute the lack of overlap between certain systems to finite-size effects. Rather, this demonstrates the difficulty in obtaining completely reproducible values with the EMD Green-Kubo methodology, even when following “Best Practices.” Furthermore, note that extrapolating to $N^{-1/3} \rightarrow 0$, i.e., $N \rightarrow \infty$, can result in unrealistic estimates of η . For these reasons, we do not recommend the linear fit and extrapolation approach to correct for finite-size effects.

4.3. Cut-off distance

The choice of cut-off distance is a subtle but important decision. In this study, we implement a 1.4 nm cut-off for TraPPE, TraPPE-2, TAMie, and AUA4 but a 1.0 nm cut-off for Potoff (as recommended in Reference 18).

The “Best Practices” guide suggests that cut-off lengths could be significant but does not provide any support for this claim. To address this issue, we perform simulations of the Potoff force field using three different cut-off distances. Specifically, Figure 15 presents the Potoff viscosity values for propane, *n*-butane, *n*-octane, and *n*-dodecane using cut-offs of 1.0 nm, 1.4 nm, 1.8 nm.



Figure 15: Impact of cut-off distance.

Figure 15 demonstrates that for smaller compounds the impact of cut-off is negligible. For larger compounds, such as *n*-dodecane, a 1.0 nm cut-off leads to significant error. In fact, *n*-hexadecane and *n*-docosane were unstable with a 1.0 nm cut-off and a 2 fs time-step. Reducing the time step to 1 fs was capable of stabilizing the 1.0 nm cut-off, but would require twice the computational time. Although the 1.4 nm and 1.8 nm cut-off results are not identical, the 1.8 nm cut-off also increases the simulation wall-time by nearly a factor of two. For these reasons, the Potoff results for *n*-dodecane, *n*-hexadecane, and *n*-docosane presented previously in Figure 3 were actually obtained using a 1.4 nm cut-off.

The instability of a 1.0 nm cut-off (with 2 fs time-steps) demonstrates the importance of verifying that the cut-off distance is long enough to not impact the system dynamics. Furthermore, this demonstrates a scenario where alternative tail modifications may be preferable, e.g., force-shift or switch-force [25]. Unfortunately, these tail modifications significantly impact saturation properties, suggesting that the non-bonded parameters must be re-optimized with the tail modification. Therefore, performing simulations with a force-shift or switch-force potential for Potoff, TraPPE, TAMie, and AUA4 would likely result in inaccurate viscosities. Re-parameterizing the non-bonded interactions for a force-shift or switch-force potential is beyond the scope of this study.

4.4. $\rho_{\text{liq}}^{\text{sat}}$

The use of REFPROP $\rho_{\text{liq}}^{\text{sat}}$ instead of the force field $\rho_{\text{liq}}^{\text{sat}}$ can lead to meta-stable simulations and spurious results. Specifically, this occurs when the force field $P_{\text{vap}}^{\text{sat}}$ is less than the REFPROP $P_{\text{vap}}^{\text{sat}}$. Fortunately, this is uncommon since Potoff, TAMie, and AUA4 are quite reliable for estimating $P_{\text{vap}}^{\text{sat}}$ and TraPPE significantly over estimates $P_{\text{vap}}^{\text{sat}}$. Furthermore, even the lowest temperature simulations of propane did not appear to be below the melting point for each force field, i.e., the RDFs were liquid-like (cf. top panel of Figure 13).

There are at least four reasons why we perform simulations at the REFPROP $\rho_{\text{liq}}^{\text{sat}}$ instead of the force field $\rho_{\text{liq}}^{\text{sat}}$. First, this approach allows for a fair comparison of the force fields' ability to predict viscosity, without penalizing force fields which are less accurate at predicting $\rho_{\text{liq}}^{\text{sat}}$ or rewarding force fields that mask their deficiencies in predicting viscosity by over- or under estimating $\rho_{\text{liq}}^{\text{sat}}$. Second, this facilitates comparing force fields over the entire range of saturation temperatures, whereas this is not possible using standard simulation methods for determining vapor-liquid saturation densities, such as Gibbs Ensemble Monte Carlo (GEMC) and Grand Canonical Monte Carlo (GCMC) histogram reweighting (HR). Third, it is straightforward to, at least qualitatively, account for a systematic deviation between the force field and REFPROP $\rho_{\text{liq}}^{\text{sat}}$, e.g., a positive bias in $\rho_{\text{liq}}^{\text{sat}}$ will increase $\eta_{\text{liq}}^{\text{sat}}$. Fourth, since each of the studied force fields utilized $\rho_{\text{liq}}^{\text{sat}}$ data in their optimization, deviations between the REFPROP and force field values are small, typically less than 1 % (see Table 1 of Reference

19).

However, due to the exponential dependence of η on ρ , small differences in density can result in large deviations in viscosity. For this reason, we perform a small set of validation simulations to determine the variability caused by utilizing the REFPROP densities. Specifically, we simulate *n*-butane with Potoff, TraPPE, and TAMie and 3-methylpentane using Potoff and TraPPE. The saturated liquid densities for these validation runs were taken from the literature [18, 16, 19, 22], where Reference 16 utilized GEMC and References [18, 19, 22] used GCMC-HR.

The results using the “true” force field for *n*-butane and 3-methylpentane are found in Figures 2 and 5, respectively, as filled symbols. Note that the Potoff, TAMie, and TraPPE *n*-butane and TraPPE 3-methylpentane filled points are consistent with the respective empty points because the force field $\rho_{\text{liq}}^{\text{sat}}$ deviates from the REFPROP $\rho_{\text{liq}}^{\text{sat}}$ by less than 0.3 %. By contrast, the Potoff 3-methylpentane filled point is approximately 3 % lower than the respective empty points. This is because the Potoff force field under estimates $\rho_{\text{liq}}^{\text{sat}}$ by around 1.15 % [19]. In comparison, the Potoff S/L deviations in $\rho_{\text{liq}}^{\text{sat}}$ are between -0.12 % and -0.60 % for all other branched compounds studied. TraPPE percent deviations in $\rho_{\text{liq}}^{\text{sat}}$ are less than ± 0.6 for all compounds except for 2,2-dimethylpropane and 2,2,4-trimethylpentane, which have -1.55 % and 2.81 % deviations, respectively.

5. Conclusions

This study demonstrates the improvement that has taken place over the past two decades for predicting viscosity with molecular simulation. First, the “Best Practices” for EMD lead to more reproducible results. Second, the state-of-the-art Mie λ -6 force fields are significantly more accurate than the traditional Lennard-Jones 12-6 force fields. More specifically, the Potoff and TAMie force fields typically predict saturated liquid viscosities for *n*-alkanes to within 10 % of the REFPROP values. By contrast, the TraPPE and AUA4 models under predict saturated liquid viscosities by 20 % to 50 %, where the deviations are largest at lower temperatures. While Potoff and TAMie are also more reliable for branched alkanes, deviations are larger and demonstrate a similar temperature dependence. The key limitation

of the Potoff force field is that the choice of $\lambda = 16$ is too repulsive at close distances, which causes the viscosity to be over estimated at high densities. Due to a fortuitous cancellation of errors, the Potoff potential does provide a reliable η - P trend. Since TAMie uses $\lambda = 14$, the η - ρ trend is slightly more reliable than that of Potoff. It is important to emphasize that transport properties were not included in the training set for parameterizing the Potoff and TAMie force fields. Therefore, the results from this study demonstrate that the improved prediction of static vapor-liquid coexistence properties obtained with Mie λ -6 potentials also results in improved prediction of a transport property, namely, liquid viscosity.

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6. Supporting Information

6.1. Systems simulated

Table 7 demonstrates which compounds, force fields, and viscosity types were simulated in this study.

Table 7: Compounds, force fields, and state points. “X”: simulated, “O”: not simulated, “S” simulated with “short” parameters, “L” simulated with “long” parameters.

	TraPPE (TraPPE-2)		Potoff (S/L)		AUA4		TAMie	
Compound	$\eta_{\text{liq}}^{\text{sat}}$	$\eta_{\text{liq}}^{\text{comp}}$	$\eta_{\text{liq}}^{\text{sat}}$	$\eta_{\text{liq}}^{\text{comp}}$	$\eta_{\text{liq}}^{\text{sat}}$	$\eta_{\text{liq}}^{\text{comp}}$	$\eta_{\text{liq}}^{\text{sat}}$	$\eta_{\text{liq}}^{\text{comp}}$
ethane	X	X	X	X	X	X	X	X
propane	X	X	X	X	O	O	X	X
<i>n</i> -butane	X	X	X	X	O	O	X	X
<i>n</i> -octane	X	X	X	X	O	O	X	X
<i>n</i> -dodecane	X	O	X	O	O	O	X	O
<i>n</i> -hexadecane	X	O	X	O	O	O	X	O
2-methylpropane	X	X	S	S	O	O	X	X
2-methylbutane	X	X	S	S	O	O	X	X
2,2-dimethylpropane	X	X	S	S	X	X	O	O
2,3-dimethylbutane	X	X	S	S	O	O	X	X
2-methylpentane	X	X	L	L	O	O	X	X
3-methylpentane	X	X	L	L	O	O	X	X
2,2,4-trimethylpentane	X	X	L	L	O	O	O	O

6.2. Gromacs input files

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

6.3. Tabulated values

1. Saturation

(a) Ethane

- i. Potoff
- ii. TraPPE
- iii. AUA4
- iv. TAMie

(b) Propane

- i. Potoff
- ii. TraPPE
- iii. AUA4
- iv. TAMie

(c) Etc.

2. Compressed liquids

(a) Ethane

- i. Potoff
- ii. TraPPE
- iii. AUA4
- iv. TAMie

(b) Propane

- i. Potoff
- ii. TraPPE
- iii. AUA4
- iv. TAMie

(c) Etc.

6.4. Simulation length effects

For less viscous systems, i.e., saturation and low pressures, a 1 ns simulation is typically sufficient for the Green-Kubo integral to reach a plateau. However, even when there is an apparent plateau, systematic bias in η may still exist if the simulation is too short [5, 27]. For this reason, Figure 16 compares the Green-Kubo integral for simulations with 0.5 ns, 1 ns, 2 ns, and 4 ns. We observe that the estimated viscosity obtained from a 1 ns trajectory is consistent with that from 2 ns and 4 ns simulations. Specifically, a plateau is observed at a similar value of η despite the large fluctuations at long times. We also note that 0.5 ns simulations are typically reliable but occasionally the plateau deviates considerably. For these reasons, the results presented in this study were obtained from 1 ns simulations.

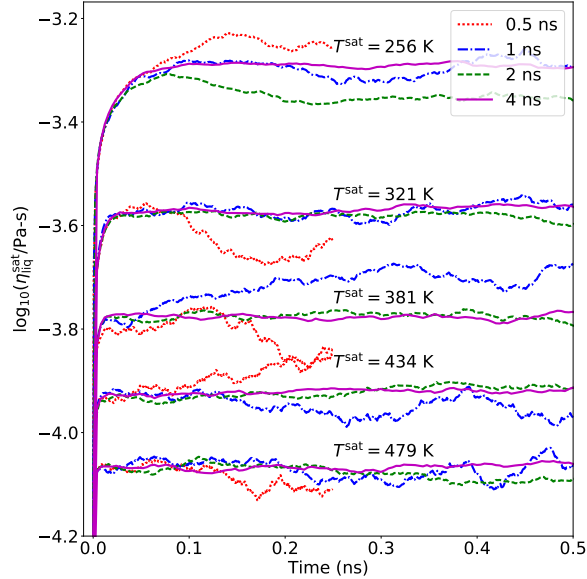


Figure 16: Simulation production time. Simulations were performed for *n*-octane using the TraPPE potential. Colors/line styles denote different simulation times (0.5 ns, 1 ns, 2 ns, and 4 ns).

For more viscous systems (greater than 0.02 Pa-s) a 1 ns simulation is too short to observe a plateau in the Green-Kubo integral. In these cases, we increased the simulation time to a value between 2 and 8 ns. Due to the increased computational cost of such simulations, we did not perform an exhaustive test with increasing simulation time. Instead, the choice of simulation time was determined primarily by the ability to detect a plateau region. Therefore,

it is possible that even longer simulations are required for the most viscous systems. Figure 17 depicts some of these highly viscous systems. Note that the total simulation time is twice the maximum time plotted. For example, an 8 ns run appears to be sufficient to detect a plateau for 2,2,4-trimethylpentane at 750 MPa, despite this system having a viscosity around 0.08 Pa-s. By contrast, a 1 ns run provides a reasonable plateau for the other two systems with viscosities near 0.02 Pa-s.

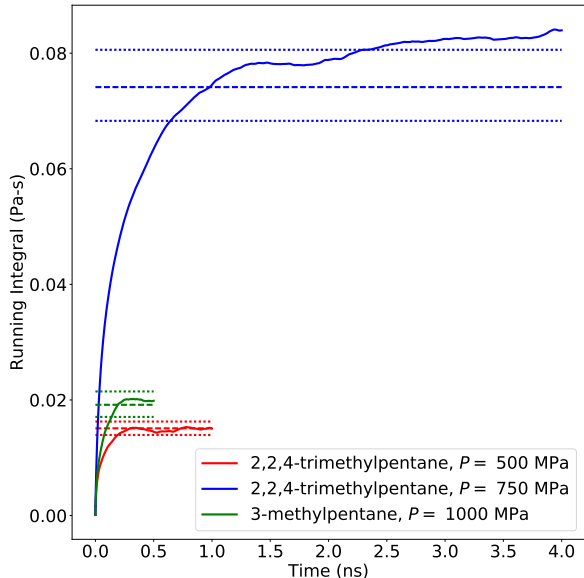


Figure 17: Green-Kubo integrals for some of the most viscous systems. Each compound was simulated with the Potoff potential. Solid lines are the average of N_{reps} replicates. Dashed lines are the estimated η value after fitting. Dotted lines represent the 95 % bootstrapped uncertainties.

6.5. Validation Runs

To validate our methodology, we attempt to replicate viscosity estimates available on the NIST Reference Simulation Data website for TraPPE-UA ethane as well as literature values for TraPPE-UA *n*-octane [6]. Figures 18 and 19 compare the ethane and *n*-octane results, respectively.

Figure 18 demonstrates that our results are more consistent with the NIST Reference Simulation Data at higher densities. Note that the NIST Reference Simulation Data are



Figure 18: Comparison with NIST Reference Simulation Data.

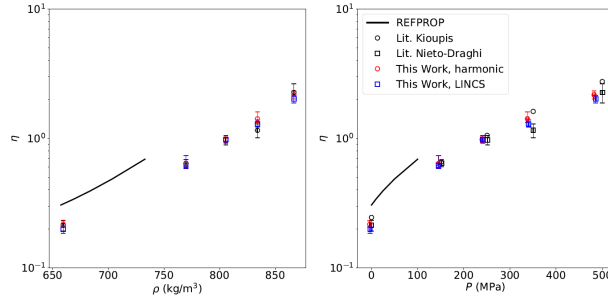


Figure 19: Comparison with Kioupis [48] and Nieto-Draghi [6]. Circle symbols denote the same harmonic potential while square symbols denote fixed bond-lengths.

obtained with the NVE ensemble, while our simulations were performed with the NVT ensemble at the average T reported by NIST.

Figure 19 demonstrates that our results agree quite well with the literature. Note that Reference 48 utilizes the same harmonic potential but performed NEMD simulations, while Reference 6 performed EMD simulations with fixed bond-lengths. Thus, the comparison between literature and “this work” should only be made for circle symbols and square symbols. Note that there are small discrepancies between the state points reported in Reference 48 and Reference 6. This should not impact our validation, but is somewhat curious.

The n -octane validation is somewhat more useful than the ethane validation for at least

three reasons. First, *n*-octane includes angle and torsional contributions that are absent in ethane. Second, the literature provides values for both rigid and flexible bonds. Third, the *n*-octane results are for fixed elevated pressures, which provides validation of our *NPT* ensemble results.

6.6. Fixed vs flexible bonds

Although static thermodynamic properties (e.g., $\rho_{\text{liq}}^{\text{sat}}$) are generally insensitive to the choice of fixed or flexible bonds, dynamic properties (e.g., η) are much more sensitive. We perform additional simulations with flexible bonds to test how sensitive the results presented in Section 3 are to the use of fixed bond-lengths. Specifically, we use the traditional harmonic bond potential:

$$u^{\text{bond}} = \frac{k_{\text{b}}}{2} (r - r_{\text{eq}})^2 \quad (9)$$

where u^{bond} is the bonded potential, k_{b} is the harmonic force constant, and r_{eq} is the equilibrium bond-length. We use an arbitrarily large value for the force constant, $k_{\text{b}} =$, as this should result in a very stiff bonded potential. Since the bond-length should not vary significantly, any deviations should not be attributed to the bond-length but rather to the contributions the bonded forces make to the viscosity.

Figure 20 demonstrates that the difference between fixed and flexible bonds is negligible in certain cases. However, there is a small, but systematic, deviation towards higher viscosities for the stiff harmonic potential.

6.7. Green-Kubo analysis

This section provides a detailed example of how we obtain estimates for η with its corresponding uncertainty. The results depicted in Figures 21 through 24 were obtained for BLANK BLANK. Figure 21 depicts a typical autocorrelation function obtained by executing the GROMACS “energy –vis.” By default, GROMACS partitions the complete simulation into twelve evenly sized time blocks. Therefore, the autocorrelation in Figure 21 is the average of twelve different time origins. GROMACS then performs a simple trapezoidal integration of neighboring points to obtain the Green-Kubo integral. The Green-Kubo integral

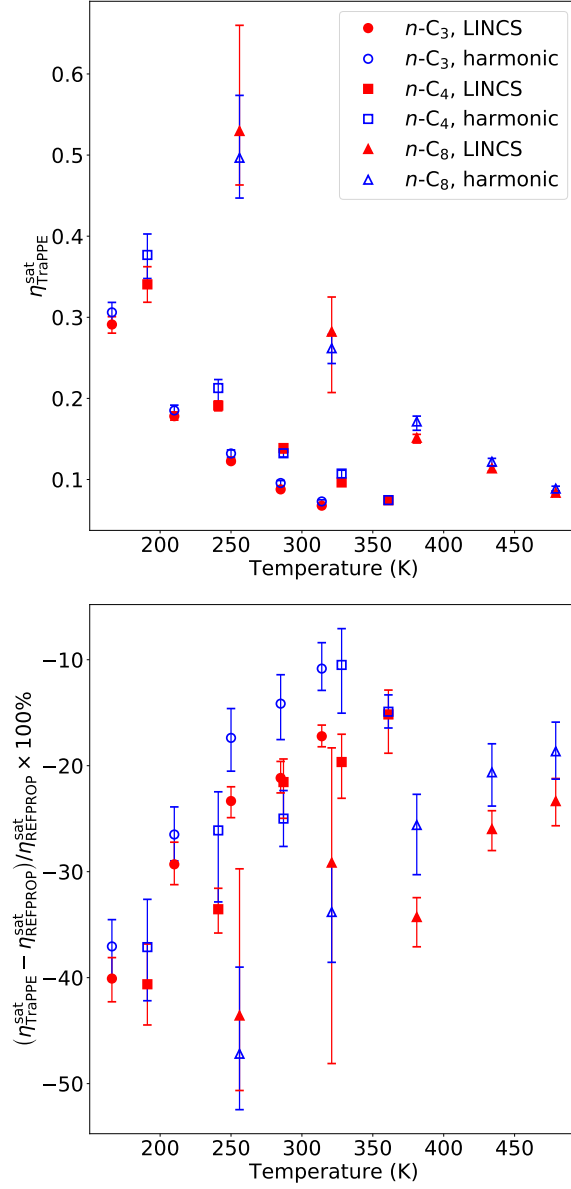


Figure 20: Fixed bond-lengths compared with an arbitrarily strong harmonic bond potential. Simulations were performed using the TraPPE-UA force field. Colors/fill denote fixed or flexible bonds while symbol shape corresponds to different compounds.

with respect to time is output in the “visco.xvg” file. Figure 22 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 22). Figure 23

shows that the fluctuations, or standard deviation, increases with time but is adequately modeled with At^b . The line labeled “cut-off” in Figures 22 and 23 is the time at which $\sigma_\eta \approx \eta^\infty$. Data beyond this time are excluded from the fit of the double-exponential function. Bootstrap re-sampling provides an estimate of the uncertainty. Figure 24 shows that, typically, the bootstrapped distribution is quite normal. The line labeled “bootstraps” in Figure 22 are the lower and upper 95 % confidence interval.



Figure 21: Autocorrelation function with respect to time.



Figure 22: Replicate simulations, average, fit to average, cut-off, and bootstrap uncertainties.



Figure 23: Standard deviation of replicate simulations with respect to time.



Figure 24: Bootstrap distribution of η .