

Supplementary Information for
Molecular Modelling of the Thermophysical Properties of Fluids:
Expectations, Limitations, Gaps and Opportunities

Marcus J. Tillotson¹, Nikolaos I. Diamantonis², Corneliu Buda³,
Leslie W. Bolton⁴, Erich A. Müller¹

¹ *Department of Chemical Engineering, Imperial College London, U.K.*

² *bp, Innovation and Engineering, Sunbury, U.K.*

³ *bp, Innovation and Engineering, Naperville, USA*

⁴ *Independent Consultant, Fleet, U.K.*

This document provides a list of some selected case studies which support the comments and appraisals provided in the main paper. The emphasis of the selection has been placed on the quality of the prediction, the limitations of the methods and the system or family of compounds which have been discussed. They are in no particular order and are not intended to be a complete nor comprehensive collection. The comments summarize the main findings, however the reader is pointed to the original references for details.

Case Studies	page
1. Prediction of viscosities and vapour-liquid equilibria for polyhydric alcohols	2
2. Molecular dynamics simulation of pure n-alkanes and their mixtures at elevated temperatures	2
3. Molecular simulation of thermodynamic properties from models with internal degrees of freedom	5
4. The use of molecular dynamics to measure thermodynamic properties of n-alkanes - case study with GROMACS	5
5. Fluid-solid phase transition of n-alkane mixtures	6
6. Comparison of Classical Force-Fields for Molecular Dynamics Simulations of Lubricants	7
7. Water-Alkane interface at various NaCl salt concentrations	8
8. Molecular dynamics simulations of CO ₂ diffusivity in n-hexane, n-decane, n-hexadecane, cyclohexane and squalane	9
9. Self diffusion coefficient and viscosity of propane	10
10. Self diffusion coefficients - force field comparison and finite boundary effects in the simulation of methane/n-hexane mixtures at high pressures	11
11. Comparison of force fields with fixed bond lengths and flexible bond lengths	12
12. Thermal conductivity of n-decane at sub/supercritical pressure	12
13. Thermodynamic and transport properties of supercritical carbon dioxide and methane	13
14. Cyclic and polycyclic compounds	13
15. Enthalpy of mixing predicted using molecular dynamics	14

16.	Phase equilibria applied to alkanes, perfluoroalkanes, alkenes and alcohols	15
17.	VLE and interfacial properties of fatty acid methyl esters from molecular dynamics simulations	15

1. Prediction of viscosities and vapour-liquid equilibria for polyhydric alcohols

This study aims to demonstrate the transferability of the TraPPE united atom (UA) force field in its ability to reproduce a wide range of properties at various state points. This force field was not originally parameterised to reproduce transport properties, however, it was shown here to yield very good predictions for the viscosities and vapour-liquid coexistence (VLE) curves for 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2-methyl-1,3-propanediol and 1,2,4-butanetriol. Quantitative agreement was found in most cases for boiling points, critical temperatures (average deviations of 2 and 1 % from experiment, respectively) and critical densities (within 5 %) for the polyhydric alcohols. Critical pressures were reproduced within 20 % of experimental values. In general, the force field tends to slightly underestimate boiling and critical temperatures and overestimate critical densities and pressures.

The viscosities for 1,2-butanediol and 1,2,4-butanetriol were within an average of 10 % from experiment while 1,4-butanediol and 2-methyl-1,3-propanediol were within 15 %. The viscosity of 1,3-butanediol was substantially overestimated by an average of 34 %.

The predictions for viscosities were satisfactory, except for 1,3-butanediol. Since the VLE of 1,3-butanediol was accurately predicted this suggests that the intermolecular interactions and conformational distributions are well modelled. It was suggested that the overestimation of the viscosity of 1,3-butanediol compared to experiment is due to a torsional potential with unrealistically high barrier heights. This could be explained because the torsional potential affects viscosity more than it affects the VLE. The source of error in the viscosity calculation is, therefore, not due to the non-bonded terms in the force field, but possibly due to the barrier heights in one or more of the torsional parameters.

The results demonstrate the transferability of the TraPPE-UA force field to predict multiple properties and state points, as well as the usefulness of simulation for explaining bulk properties from molecular level observations.

References

- S. Kelkar, J. L. Rafferty, E. J. Maginn and J. Ilja Siepmann, Prediction of viscosities and vapor-liquid equilibria for five polyhydric alcohols by molecular simulation, *Fluid Phase Equilib.*, 2007, 260, 218–231.
- P. A. Gordon, M. Schiller, C.-P. C. Kao, S. Bair, D. G. Friend, Benchmarks for the Third Industrial Fluid Properties Simulation Challenge, *Fluid Phase Equilib.*, 2007, 260, 164-168.

2. Molecular dynamics simulation of pure n-alkanes and their mixtures at elevated temperatures

Papavasileiou *et al.* investigated the liquid density, surface tension and viscosities of higher *n*-alkanes and their mixtures using molecular dynamics (MD) simulation over a broad temperature range, from 323.15 to 573.15 K, with several force fields; TraPPE-UA – a well

established united atom potential, L-OPLS – an all-atom (AA) optimised potential for liquid simulations re-parameterised for long *n*-alkanes, Lipid14 - an updated AMBER force field validated in the simulation of lipid bilayers, MARTINI – a coarse grained (CG) simulation.

The TraPPE-UA force field most accurately reproduced the liquid density values in comparison to Lemmon and Huber equation of state (EoS) reference values. The MARTINI force field displayed the correct temperature relationship but provided overestimated values for liquid density. This is likely because the MARTINI force field parameterisation has been optimised at ambient temperature 300 K and pressure 1 bar (conditions commonly found in biological systems) to reproduce the free energies of vaporisation, hydration and partitioning between organic and water phases. As the *n*-alkane chain length increases to *n*-C₂₈ the overestimation is not so pronounced and MARTINI results agreed better with experiment.

The AA Lipid14 and L-OPLS force fields were very successful at predicting liquid densities at the lower end of the predicted range. The value was within 0.2 and 1 % of the experiment for *n*-C₁₂ using the Lipid14 and L-OPLS force fields respectively at 323.15 K. However, as the temperature rises there were significant deviations from the reference data for both force fields. They underestimated the experiment values at 573.15 K by an average of 25 %. Interestingly, both force fields displayed the same temperature dependence in liquid density prediction. The trans-dihedral content is reduced with temperature, giving rise to chain folding. The *n*-alkanes adopt a less extended configuration with temperature increase, as demonstrated for the TraPPE-UA, L-OPLS and Lipid14 force fields, by a decrease in the mean squared radius of gyration and mean squared end-to-end vector. In contrast, the MARTINI coarse grained description adopts a four-to-one mapping, where four heavy atoms are represented by a single bead. As a result, there are no dihedral contributions to the potential energy and, therefore, no conformational temperature dependence was observed. However, MARTINI offers the CG advantages in terms of computational efficiency.

The cut-off for the Lennard-Jones (LJ) potential can significantly affect the calculated values for surface tension, particularly for inhomogeneous systems containing vapour-liquid (VL) interfaces. This is due to the truncation of dispersion forces leading to incorrect estimates of these properties. To compensate, larger cut-offs or lattice-based methods such as LJ-Particle Mesh Ewald (LJ-PME) can be utilised. The TraPPE-UA force field with a LJ potential adjusted for long cut-off (2.3 nm) interactions yielded the best agreement with experiment with an average absolute deviation (AAD) of 4 % for the interfacial tension of *n*-C₁₂. The MARTINI calculation performed similarly with an AAD of 6 %. L- OPLS and Lipid14 produced less good predictions, with underestimations of 34 and 39 % for average surface tension, respectively. The LJ-PME method provided a less good fit for TraPPE-UA with 10 % overestimated values compared to experiment. On the other hand, the L- OPLS and Lipid14 results were improved with an average underestimation of 30 and 34 %, respectively. Agreement was excellent with experiment at 323.15 K but this worsens with increasing temperature, the trend resembling the decay in density predictions. For *n*-C₂₈, the best prediction for surface tension was also from the TraPPE-UA force field with LJ potential adjusted for long range cut-off. MARTINI results were 4 % underestimated on average from experiment. For L-OPLS and Lipid14 the deviations were similar but less pronounced in comparison to *n*-C₁₂ predictions. Similar trends were obtained for the *n*-C₁₂/*n*-C₂₈ binary mixture where TraPPE-UA with large cut-offs produced the best interfacial tension values. The MARTINI force field is a good alternative that offers computational efficiency for systems of large size without the need for cutoff adjustment. L-OPLS and Lipid14 provided the least good fit for interfacial tension of the binary mixtures, especially with increasing temperature

regardless of the LJ long interaction treatment. The combination of TraPPE-UA with long LJ cutoff, 2.3 nm, provided the best results for the interfacial tension of the *n*-alkanes studied and their binary mixtures. The poor performance of L-OPLS and Lipid14 means their use should be restricted to the prediction of interfacial tensions at low temperatures.

Lipid14 and L-OPLS performed the best but overestimated the viscosity at the lowest temperature whilst providing very good results in the 423.15 - 498.15 K temperature range. This is counterbalanced by their increased computational demands. As a result, their use should be limited to relatively small system sizes. The coarser representation of the TraPPE-UA produced poor viscosity predictions in all *n*-alkane systems. MARTINI led to a less accurate capture of viscosities with predictions $\sim 17\%$ AAD from experiment in all cases. As chain length increases the predicted viscosities from TraPPE-UA and MARTINI become worse. This demonstrates that an all-atom representation is required for the description of viscosities since the accurate representation of hydrogen atoms are contributing factors for this property. In addition, L-OPLS and lipid14 have torsional potential terms that produce temperature dependence trends that follow the same values as experimental viscosities.

The underestimated values for surface tension from both AA force fields indicates that the interactions between molecules at the surface is not sufficiently strong. This is likely as a result of non-polarisable force fields. The coarser representations of the TraPPE-UA potential, with a LJ potential adjusted for long cut-off (2.3 nm), and the MARTINI model yielded more accurate agreement for surface tension.

All models qualitatively reproduced the temperature dependence of the properties. The TraPPE-UA force field gave the most accurate and consistent density values over the entire temperature range. TraPPE-UA and MARTINI were the best for the calculation of surface tension. L-OPLS and Lipid14 were the most accurate for viscosities compared to the other models.

Overall, these widely used force fields are suitable candidates for the study of pure *n*-alkane properties and in their mixed states. However, careful consideration needs to be made regarding the best use over the range of temperatures and different properties investigated. There is not a single outstanding force field over the entire range of temperatures and that can be applied to all properties. This is unsurprising considering the different levels of atomic detail and parametrisation strategies used to represent these force fields. The performance of these force fields, therefore, is largely due to the parameterisation philosophy, i.e. it correlates strongly with the quantities under the conditions used in the fitting process.

References

K. D. Papavasileiou, L. D. Peristeras, A. Bick and I. G. Economou, Molecular Dynamics Simulation of Pure *n*-Alkanes and Their Mixtures at Elevated Temperatures Using Atomistic and Coarse-Grained Force Fields. *J. Phys. Chem. B*, 2019, **123**, 6229-6243.

T. M. Koller *et al.* Liquid Viscosity and Surface Tension of *n*-Dodecane, *n*-Octacosane, Their Mixtures and a Wax between 323 and 573 K by Surface Light Scattering. *J. Chem. Eng. Data*, 2017, **62**, 3319-3333.

T. Darden, D. York, L. Pedersen, Particle Mesh Ewald: An N-Log(N) Method for Ewald Sums in Large Systems, *J. Chem. Phys.* 1993, **98**, 1008910092.

J. J. Potoff and D. A. Bernard-Brunel, Mie potentials for phase equilibria calculations: Application to alkanes and perfluoroalkanes, *J. Phys. Chem. B*, 2009, **113**, 14725–14731.

3. Molecular simulation of thermodynamic properties from models with internal degrees of freedom

The paper by Schappals *et al.* identified statistical and systematic errors in a round robin study. The same set of simulation tasks were given to independent working groups, using different molecular simulation codes; TOWHEE, Tinker, NAMD, *ms2*, LAMMPS, IMC, GROMACS and DL_POLY. The properties of density and potential energy, u , as a function of temperature and pressure were solved for a set of four alkanes in the liquid state, namely, ethane, propane, *n*-butane and iso-butane, using three different force fields. The main research question is, how reproducible is the information on a quantity only accessible by computer simulation, if different codes are used? A similar study by Lejaeghere *et al.* of quantum chemical density function theory (DFT) simulations concluded that the results from different codes is close to reaching a satisfactory level. However, the collected data from molecular simulation showed deviations, obtained by the different groups, that far exceeded the statistical uncertainty of individual results. Deviations in results were distinctly larger for more complex force fields.

References

M. Schappals *et al.*, Round Robin Study: Molecular Simulation of Thermodynamic Properties from Models with Internal Degrees of Freedom. *J. Chem. Theory Comput.*, 2017, **13**, 4270–4280.

K. Lejaeghere *et al.* Reproducibility in density functional theory calculations of solids. *Science*, 2016, **351**, 6280, 1394.

4. The use of molecular dynamics to measure thermodynamic properties of n-alkanes - case study with GROMACS

In Caleman *et al.*, MD simulations were employed over a broad temperature range (273 to 460 K) to examine the performance of several force fields for the reproduction of liquid properties for *n*-alkanes. This included liquid density and important secondary derivative thermodynamic properties such as heat capacity, thermal expansion coefficient, isothermal compressibility.

The OPLS-AA and CHARMM force fields were very accurate in reproducing liquid densities of *n*-hexane, *n*-decane and *n*-dodecane, indicating that these force fields, originating from the world of biomolecular simulations, are suitable for predicting the properties of *n*-alkanes in the pure state over the temperature range 278 - 340 K at 1 atm. However, the calculated liquid densities deviated from experimental values at temperatures > 340 K. In addition, the calculated secondary derivative properties deviated significantly from experiment.

Fluctuation properties proved more difficult to predict than simple linear averages (density) using MD simulation. Here the properties were computed from a single MD trajectory, which requires a long computation time for the system to reach equilibrium. It may be that even longer equilibration times are needed. Even then, if the system becomes 'stuck' in a metastable state it may not be able to sample a reasonable amount of configurational space. This can result in values that are far from the experimental data. The study by Payal *et al.* ran integrals that appear to be converged within the time scale of the simulation. Calculated viscosity values were still overestimated by 10-15 % from experiment using TraPPE-UA and TTK-AA force field models. End-to-end distances for *n*-decane and *n*-hexadecane were similar for the two force fields indicating that molecular configurations were indistinguishable. Therefore, as

enough simulation time was permitted for the adequate sampling of configurational space, errors were then attributed to the quality of inter-atomic potential parameters and differences in the dynamical characteristics of the fluids.

References

C. Caleman, P. J. van Maaren, M. Hong, J. S. Hub, L. T. Costa and D. van der Spoel, Force field benchmark of organic liquids: Density, enthalpy of vaporization, heat capacities, surface tension, isothermal compressibility, volumetric expansion coefficient, and dielectric constant. *J. Chem. Theory Comput.*, 2012, **8**, 61–74.

R. S. Payal, S. Balasubramanian, I. Rudra *et. al.* Shear viscosity of linear alkanes through molecular simulations: Quantitative tests for *n*-decane and *n*-hexadecane, *Mol Simul.*, 2012, **38**, 14-15, 1234-1241.

5. Fluid-solid phase transition of *n*-alkane mixtures

A coarse-grained model employing the statistical associating fluid theory (SAFT) force field was used in the calculation of self-diffusion coefficient of linear alkanes, up to *n*-C₃₀H₆₂. When the self-diffusion of tetracosane, *n*-C₂₄, was modelled for the fluid and the solid phases, a change in slope around the freezing point was captured indicating the appearance of an arrested state.

Neither atomistic nor CG models were in qualitative agreement with the experimental results, showcasing a limitation in the direct replacement of simulation for the experimental evaluation of the melting point. A change in slope in the diffusion coefficient with temperature was observed with the CG simulation at temperatures below the expected freezing point of the model. This suggests a slowdown of the fluid dynamics at the state point where a solid would be expected, i.e. the molecules experience an arrestment in their mobility, consistent with the current theory of glass-forming fluids.

It was shown that upon the approach to freezing, the heavier components in a polydisperse *n*-alkane mixture restrict their movement first whilst lighter ones retain their fluidity which helps fluidize the mixture. This is in line with the observation that the wax appearance temperature for mixtures is not an individual temperature, rather a range of well-defined temperatures initiated by the slowing down of molecular movement. Furthermore, it is not possible to deduce the wax appearance temperature from pure component properties since a range of light and heavy chains have slightly different diffusivity in a mixture than in pure forms. The results suggest the formation of an arrested gel state upon the decrease of temperature that precedes the crystalline process.

References

S. Shahrudin, G. Jiménez-Serratos, G. J. P. Britovsek, O. K. Matar and E. A. Müller, Fluid-solid phase transition of *n*-alkane mixtures: Coarse-grained molecular dynamics simulations and diffusion-ordered spectroscopy nuclear magnetic resonance, *Sci. Rep.*, 2019, **9**, 1–9.

6. Comparison of Classical Force-Fields for Molecular Dynamics Simulations of Lubricants

Lubricants are useful systems to study since they contain relatively large complex molecules and are typically operated at high temperature and high pressure (HTHP) conditions. As such these molecules and conditions present a challenging test for most MD force fields. Also, simulation can provide insights into molecular behaviour of important lubricant systems. The study by Ewen *et. al.* provided benchmark testing of a large number of AA and UA force fields for *n*-hexadecane using equilibrium molecular dynamics (EMD) at ambient and HTHP conditions. This is an important model lubricant with a large range of industrial applications. The two best force fields for each molecular description were taken forward for the confined non-equilibrium molecular dynamics (NEMD) simulation for the structure and friction of steric acid adsorbed onto iron oxide and separated by a layer of *n*-hexadecane.

Probably the most significant properties in the description of tribological systems are density and viscosity since they are inherently linked to lubricant hydrodynamics. In an MD force field, liquid density is mainly governed by non-bonded LJ and Coulombic interactions, whilst viscosity is largely influenced by the molecular 'stiffness' of the torsional potential. UA force fields are reported to reproduce accurate densities; however viscosities are under-predicted compared to experiment. For example, under ambient conditions, the TraPPE-UA force field provided a viscosity prediction for C₁₀ of -20 % which rises to -50 % for longer C₁₆ molecules. It has also been shown that some AA force fields predict significantly elevated melting points for long chain alkanes that leads to overestimated density and viscosity values.

Important variations were observed for the predicted density values of *n*-hexadecane at different temperature and pressure conditions. The OPLS-AA and AMBER-AA force fields over-predicted the density at ambient conditions by 11 % and 14 %, respectively. This was attributed to crystallisation because of an overestimation of the melting point. Crystallisation did not occur at 423 K and 60.8 MPa where the densities were closer to experiment, with an average under-prediction for OPLS-AA and AMBER-AA of around 4 %. OPLS-AA over-predicted the density again at 423 K and 202.7 MPa suggesting crystallisation. The form of OPLS-AA with updated non-bonded and torsional parameters for long chain molecules, L-OPLS-AA, was significantly improved with no observed crystallisation events. The density predictions were the most accurate of all the AA force fields, within 5 % for all conditions simulated. The predictions made with the UA force fields were generally more accurate, within 5 % of experiment for all conditions simulated. This is probably because of a parameterisation process that includes a more comprehensive range of molecules, up to C₃₂. The TraPPE-UA version using the 16-6 Mie potential for van der Waals interactions was less accurate for density predictions compared to the original 12-6 LJ form.

The viscosity predictions were much less accurate for all force fields. This is to be expected since transport properties, unlike density, are not included in the parameterisation of classical force fields. The UA force fields were generally less accurate with a consistent under-prediction of between 10 and 60 % depending on conditions. The values become worse at 423 K and 202.7 MPa where the molecular 'roughness' has a greater impact on the viscosity prediction. This suggests that the physical representation of hydrogen atoms may not be as important at ambient conditions but more so for the viscosity prediction of long chain molecules at high pressure conditions. Here the molecules become forced together causing steric clashes between the hydrogen atoms on neighbouring molecules. The consistently under-predict of the viscosity by the UA force fields suggests that the molecules move past each other

more easily in confined liquids than if an AA atom force field was used. This is likely to have a detrimental effect on the simulated friction coefficients for the interest of tribological situations.

The TraPPE-UA force field prediction for viscosity at ambient conditions was significantly improved using the 16-6 Mie potential; -10 % compared to -30 % for the 12-6 non-bonded LJ potential. However, it still provided an under-prediction for viscosity by 35 % at 423 K and 202.7 MPa. Despite the improvement at ambient conditions, a lack of compatibility of the different functional form with other functional groups or surfaces is an important consideration for modelling the hydrodynamics of a base oil.

The under-predictions of viscosity values from UA force fields makes them less accurate for the simulation of tribological systems. However, they will continue to be useful for capturing the trends in large, complex systems due to their relatively low computational expense. It is considered that AA force fields, in particular the L-OPLS-AA force field, are best suited for the MD simulation of long-chain linear molecules if sufficient computational resources are available.

References

J. Ewen, C. Gattinoni, F. Thakkar, N. Morgan, H. Spikes, D. Dini, A Comparison of Classical Force-Fields for Molecular Dynamics Simulations of Lubricants, *Materials*, 2016, 9, 8, 651–17.

R. S. Payal, S. Balasubramanian, I. Rudra, K. Tandon, I. Mahlke, D. Doyle, R. Cracknell, Shear viscosity of linear alkanes through molecular simulations: Quantitative tests for n-decane and n-hexadecane, *Mol. Simulat.* 2012, 38, 1234–1241.

K. Murzyn, M. Bratek, M. Pasenkiewicz-Gierula, Refined OPLS All-Atom Force Field Parameters for n-Pentadecane, Methyl Acetate, and Dimethyl Phosphate, *J. Phys. Chem. B.*, 2013, 117, 16388–16396.

S. W. I. Siu, K. Pluhackova, R. A. Bockmann, Optimization of the OPLS-AA Force Field for Long Hydrocarbons, *J. Chem. Theory Comput.*, 2012, 8, 1459–1470.

7. Water-Alkane interface at various NaCl salt concentrations

In a classical molecular dynamics simulation to examine the molecular properties of water-alkane interface at various salt, NaCl, concentrations, a variety of different force field combinations were investigated. A comparison was made between the simulations' and experimental surface/interfacial tension values for water-vapour, decane-vapour and water-decane interfaces.

The salinity dependence on surface/interfacial tension is accurately captured using the Smith and Dang parametrisation of NaCl. The overall trend of surface tension variation with NaCl concentration is well captured by all force fields within the classical MD simulation. This implies that the accurate modelling of interfaces containing electrolytes depends more on the parametrisation of the ion, rather than the water model. The treatment of long-range dispersion forces is important for the accurate reproduction of liquid-vapour densities.

References

T. R. Underwood and H. C. Greenwell, The Water-Alkane Interface at Various NaCl Salt Concentrations: A Molecular Dynamics Study of the Readily Available Force Fields, *Sci. Rep.*, 2018, 8, 1–11.

M. Sega, & C. Dellago, Long-range dispersion effects on the water/vapor interface simulated using the most common models, *J. Phys. Chem. B*, 2017, 121, 3798–3803.

M. Schlossman, Liquid-liquid interfaces: studied by X-ray and neutron scattering. *Current Opinion in Colloid & Interface Science*, 2002, 7, 235–243.

J. C. Neyt, et al., How does the electronic continuum model perform in the prediction of the surface tension of salt solutions?, *Chem. Phys. Lett.*, 2014, 595, 209–213.

8. Molecular dynamics simulations of CO₂ diffusivity in *n*-hexane, *n*-decane, *n*-hexadecane, cyclohexane and squalane

In this study by Moulton *et al.*, three force field models, TraPPE-UA, OPLS-AA and L-OPLS, were used in the representation of hydrocarbons; *n*-hexane, *n*-decane, *n*-hexadecane, cyclohexane and squalane (C₃₀H₆₂, often used in personal care cosmetics and produced by the hydrogenation of squalene). The L-OPLS description is a re-optimised form of OPLS where parameters of the *n*-alkane are fitted to;

- the torsional parameters of gas-phase ab-initio energy profiles
- the energy parameter of the LJ potential for methylene hydrogen atoms
- the partial charges.

The pressure dependence on diffusivity of CO₂ (D_{CO_2}) in *n*-alkane liquids was qualitatively reproduced using TraPPE-UA, OPLS-AA and L-OPLS force fields.

All force fields resulted in accurate density predictions for the lower temperature values (298.15 and 323.15 K) with an AAD of 0.5 %, while at 423.15 K the deviation was ~ 4 %. Specifically, for the *n*-alkanes, L-OPLS reproduced the viscosities and densities more accurately (AAD ~ 7.5 %) than OPLS or TraPPE-UA, with L-OPLS and OPLS showing similar behaviour. Despite the TraPPE-UA being the most computationally efficient model due to the united atom representation and absence of electrostatic contributions, it provided the least accurate results for viscosity of *n*-hexane with an AAD from experiment in the range of 16-38 % over all temperatures and pressures. This resulted in a poor performance for TraPPE-UA in the calculation of the CO₂ diffusion coefficient in *n*-hexane. Similar results for densities and viscosities were obtained with the remaining hydrocarbons, except for OPLS which showed an early gel-to-liquid phase transition for *n*-hexadecane as indicated by very high (by 2 orders of magnitude) viscosities at 298.15 K, i.e. the OPLS-AA torsional parameters predicted this phase transition for long *n*-alkanes at temperatures well above the T_m .

The AA force fields (OPLS) seem to do better than the UA force field, possibly because TraPPE-UA lacks the electrostatic contributions that are important in the description of liquid density and viscosity. For the D_{CO_2} in the hydrocarbons measured, the L-OPLS force field was found to be the most accurate. This suggests that the optimisation of the torsional potential in L-OPLS is crucial for the accurate prediction of the transport properties for long chain molecules. The D_{CO_2} obtained from all force field tested was shown to deviate significantly from Stokes-Einstein behaviour, in agreement with experimental measurements.

All three models represented the pressure dependence of the diffusion coefficient of CO₂ in hydrocarbons qualitatively, i.e. the correct trend from experimental data is captured, showing that the CO₂ diffusion coefficient in hydrocarbons decreases as the pressure increases, which is typical for gases dissolved in liquids. There is a strong dependence of D_{CO_2} on hydrocarbon

molecular size because the motion of CO₂ molecules is more hindered by the solvent molecules with higher carbon number, as expected. The L-OPLS force field was found to be the most accurate. Therefore, the optimised torsion parameters for long chain molecules can be considered important for the accurate description of the transport properties.

Atomistic MD simulations showed there is a strong dependency for the D_{CO_2} on the solvent size. This is as expected since an increase in the number of carbon atoms in the molecules comprising the solvent results in the hindered motion of CO₂ molecules. Overall, the TraPPE-UA force field was found to be the least accurate for the hydrocarbons studied. Despite the computational efficiency of the UA representation, the absence of electrostatic contributions affected the results. L-OPLS was the most accurate as a result of the optimised torsional potentials and charges that provide improved liquid density and viscosity predictions compared to the original OPLS-AA force field. OPLS-AA showed early gel-to-liquid transitions. The different force fields predicted different microscopic properties, seen in the mean square radius of gyration and pair correlation function between CO₂ and *n*-alkanes. This results in the different macroscopic properties of density, viscosity and diffusion coefficient for each different force field.

References

- O. A. Moutos, I. N. Tsimpanogiannis, A. Z. Panagiotopoulos, J. P. M. Trusler and I. G. Economou, Atomistic Molecular Dynamics Simulations of Carbon Dioxide Diffusivity in *n*-Hexane, *n*-Decane, *n*-Hexadecane, Cyclohexane, and Squalane, *J. Phys. Chem. B*, 2016, 120, 12890-12900. DOI: 10.1021/acs.jpcc.6b04651.
- S. P. Cadogan, B. Mistry, Y. Wong, G. C. Maitland and J. P. M. Trusler, Diffusion Coefficients of Carbon Dioxide in Eight Hydrocarbon Liquids at Temperatures between (298.15 and 423.15) K at Pressures up to 69 MPa, *J. Chem. Eng. Data*, 2016, 61, 3922–3932.
- O. A. Moutos, G. A. Orozco, I. N. Tsimpanogiannis, A. Z. Panagiotopoulos and I. G. Economou, Atomistic molecular dynamics simulations of H₂O diffusivity in liquid and supercritical CO₂, *Mol. Phys.*, 2015, 113, 2805–2814.
- S. W. I. Siu, K. Pluhackova, R. A. Böckmann, R. A., Optimization of the OPLS-AA force field for long hydrocarbons. *J. Chem. Theory Comput.* 2012, 8, 14591470.G.
- L. Pollack, J. J. Enyart, Atomic test of the Stokes-Einstein law. II. Diffusion of Xe through liquid hydrocarbons, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1985, 31, 980984.
- B. A. Kowert, N. C. Dang, Diffusion of dioxygen in *n*-alkanes. *J. Phys. Chem. A.*, 1999, 103, 779781.
- K. Rajagopal, L. L. P. R. Andrade, M. L. L. Paredes, High- pressure viscosity measurements for the binary system cyclohexane + *n*-hexadecane in the temperature range of (318.15 to 413.15) K, *J. Chem. Eng. Data*. 2009, 54, 29672970.

9. Self-diffusion coefficient and viscosity of propane

Higgoda *et. al.* presents an enhancement to molecular dynamics force fields for the determination of viscosity and the self-diffusion coefficient. This was demonstrated using propane as an example system. A semi rigid version of propane, with rigid bonds and flexible angles and dihedrals, was developed to determine these dynamical properties over a broad density range; from superheated vapour to the gas state and supercritical region up to the compressed liquid state. A simplified, pair-specific, AA, *ab initio*-based force field (AI-FF) was derived from quantum calculations in the limit of zero density. The calculations were compared with the commonly used effective semi-rigid TraPPE-UA force field and the flexible OPLS-AA force field. The AI-FF showed improved predictions in most of the studied fluid

regions. The AI-FF for C₃H₈ demonstrates transferability to the compressed liquid state, where dynamical properties provided deviations within 10 % of experimental data. The fully flexible OPLS-AA force field poorly represents viscosities at low pressures. This can be attributed to the quality of the force field rather than the flexibility of the model since the discrepancies are improved at higher pressures. The TraPPE-UA force field shows decreasing suitability at larger densities. These results demonstrate that the calculated self-diffusion coefficients and viscosities are strongly influenced by the interplay between the molecular representation and the intermolecular, intramolecular potentials of the models.

References

U. A. Higgoda, R. Hellmann, T. M. Koller and A. P. Fröba, Enhancement of the predictive power of molecular dynamics simulations for the determination of self-diffusion coefficient and viscosity demonstrated for propane, *Fluid Phase Equilib.*, 2019, 496, 69–79.

E. Vogel, S. Herrmann, New formulation for the viscosity of propane, *J. Phys. Chem. Ref. Data* 45, 2016, 043103.

10. Self-diffusion coefficients - force field comparison and finite boundary effects in the simulation of methane/*n*- hexane mixtures at high pressures

Self-diffusion coefficient predictions have been strongly correlated to the simulation box size. The limitations caused by the size of the simulation box are based on long-range coulombic and hydrodynamic interactions. Correcting for these systematic errors is important for any comparison between simulation and experiment. Analytic corrections can attenuate the system size effect. The correction factor scales with $N^{-1/3}$, where N is the number of particles.

Most of the commonly used force-fields for hydrocarbons, e.g., OPLS, GROMOS, TraPPE and NERD, are parameterised to reproduce thermodynamic and phase equilibrium properties satisfactory. Very often this translates to the reproduction of accurate transport properties even without the finite-size correction factor. However, it has been noted that the dimensions of the simulation box can still greatly influence the self-diffusion coefficient results. In contrast, viscosities showed no significant system size dependency. Various molecular representations, UA or AA, and different force fields produce biased results due to caging effects and dihedral representations, respectively.

References

T. J. P. dos Santos, C. R. A. Abreu, B. A. C. Horta and F. W. Tavares, Self-diffusion coefficients of methane/*n*-hexane mixtures at high pressures: An evaluation of the finite-size effect and a comparison of force fields. *J. Supercrit. Fluids*, 2020, 155, 104639.

I. C. Yeh and G. Hummer, System-size dependence of diffusion coefficients and viscosities from molecular dynamics simulations with periodic boundary conditions, *J. Phys. Chem. B*, 2004, 108, 15873–15879.

11. Comparison of force fields with fixed bond lengths and flexible bond lengths

Fischer *et al.* studied the influence of the way bonds are modelled on the transport properties of liquids. Force fields with harmonic bond length potentials were found to give equivalent results to models with rigid bond lengths for pressure, viscosity, self-diffusion coefficient and thermal conductivity. Vibration of bonds seemed to have no significant effect on transport properties or phase equilibria.

The thermal conductivity predicted by the force field with rigid bond lengths had an offset compared to the harmonic bond length models. This can be approximated through an analytic correction term.

Bond length flexibility details are not very important for the calculations of most transport properties; (liquid phase) pressure, shear viscosity and self-diffusion coefficient. For thermal conductivity, a force field for flexible bond lengths is conceptually different to one with rigid bond lengths. To account for the difference, a 'corrected rigid bond' term is applied which makes rigid bond models comparable to models with flexible bond lengths. For thermodynamic (equilibrium) properties, bond length flexibility parameters are certainly not relevant, as the internal degrees of freedom do not make a difference.

Introducing force fields with potentials for harmonic bond lengths leads to transport property results that were in good agreement to the results obtained with rigid bond lengths within suitable values of bond energy constants, k_1 . Suitable values for k_1 are in the range of those used by fully flexible UA force fields such as CHARMM and GROMOS.

References

M. Fischer, G. Bauer, J. Gross, Force Fields with Fixed Bond Lengths and with Flexible Bond Lengths: Comparing Static and Dynamic Fluid Properties, *J. Chem. Eng. Data*, 2020, 65, 15831593.

Z. Liang, H.-L. Tsai, The vibrational contribution to the thermal conductivity of a polyatomic fluid, *Mol. Phys.*, 2010, 108, 17071714.

12. Thermal conductivity of *n*-decane at sub/supercritical pressure

Four different UA force fields and four AA force fields were used to predict the thermal conductivity of *n*-decane at sub/supercritical pressures using EMD and reverse non-equilibrium molecular dynamics (RNEMD) methods. It was found that the UA models were more accurate in the predictions than AA models and that EMD methods showed better accuracy than RNEMD methods with the same UA force fields. The SKS force field gave the best prediction accuracy.

References

X. Yang, Y. Gao, M. Zhang, Comparison of atomic simulation methods for computing thermal conductivity of *n*-decane at sub/supercritical pressure, *J. Mol. Liq.*, 2021, 342, 117487.

13. Thermodynamic and transport properties of supercritical carbon dioxide and methane

Results show that force fields originally parameterised to reproduce vapour-liquid coexistence curves were effective at the prediction of other thermodynamic properties for CO₂ and CH₄ over an extended temperature and pressure range. Overall, it was found that the results from molecular simulation were more accurate and consistently better than predictions from a commonly used equations of state (cubic Peng-Robinson EoS). The viscosities and thermal conductivities of CO₂ and CH₄ were obtained by molecular dynamics and the Green-Kubo formalism. The Einstein relationship was used to provide self-diffusion coefficient predictions. The temperature range investigated was between 273.15 and 573.15 K and pressures up to 800 MPa. Seven different models were compared for CO₂ and three different models for CH₄ to investigate property prediction difference due to the force field nature and parameterisation. The simulation results showed good agreement with experiment data, except for thermal conductivities at low density. The flexible TraPPE description of CO₂ was able to estimate transport properties with accuracies comparable to rigid molecules. However, higher deviations from experimental data occurred for thermal conductivity. The use of a correction term to account for vibrational modes in rigid models generally improved predictions of thermal conductivity. Here, the explicit account of vibrational and bending degrees of freedom for the CO₂ flexible model lead to less accurate results.

References

- C. G. Aimoli, E. J. Maginn and C. R. A. Abreu, Force field comparison and thermodynamic property calculation of supercritical CO₂ and CH₄ using molecular dynamics simulations, *Fluid Phase Equilib.*, 2014, 368, 80-90.
- C. G. Aimoli, E. J. Maginn and C. R. A. Abreu, Transport properties of carbon dioxide and methane from molecular dynamics simulations, *J. Chem. Phys.*, 2014, 141, 1–13.

14. Cyclic and polycyclic compounds

The study by Yiannourakou *et. al.* uses force field-based Gibbs ensemble Monte Carlo (GEMC) molecular simulation in the prediction of VLE properties (normal boiling point, liquid density and vapour pressure) for polycyclic compounds of up to 30 carbon atoms. The use of a UA force fields allowed for computation efficiency in the simulation of larger molecules (~400 g/mol) whilst maintaining a good representation of molecular structure. The TraPPE-UA force field was modified to consider fully flexible bond stretching and additional parameterisation for alkylated polycyclic compounds with saturated and/or aromatic rings. The improvements are likely to benefit a large range of applications including fuels, lubricants and speciality chemicals. The VLE of cyclic and polycyclic compounds, with or without side chains and bridging chains, were predicted using new UA types for ternary and quaternary carbons in naphthenes and aromatics. Existing TraPPE-UA parameters were used for other linear and branched alkyl molecular fragments. Comparisons made with experimental data revealed an AAD for normal boiling temperature of 6.4 K and liquid densities within 0.91 %. No noticeable increased deviations were observed with increasing molecular weight.

The modified force field provided an excellent performance for the VLE properties for a data set that covered a wide range of molecular size and conformations. There was no systematic drift with respect to chemical family or molecular size for the predicted normal boiling points

or liquid densities, covering a wide range. This indicates a feasible route for the prediction of transport properties of naphthene and polyaromatic compounds by molecular dynamics. However, it is expected that additional optimisation of the intramolecular parameters is required for the prediction of dynamic properties.

The VLE of thiophene molecules were also well predicted in this study. Sulfur containing polycyclic compounds, present in sour forms of crude oil, include sulfur-bearing thiophenes. Other non-hydrocarbon polycyclic compounds include oxygen-bearing (furan), and nitrogen-bearing (pyridine) cycles. These molecules have small or moderate permanent dipole moments. It is known that the electrostatic interactions are important in the interactions with other molecules, particularly with strongly polar ones such as water. Several force fields contain explicit electrostatic energy terms using atom-centred charges, for AA models, or off-atom charges in the case of anisotropic united atom (AUA) models. The parametrisation of these force fields in a transferable way has proven challenging since classical electrostatic point charges do not describe the polarisability of these polyaromatic molecules. It is suggested that the investigation of stereoisomers, such as the cis-trans conformation of decalin, may also require a type of AUA force field as well as the introduction of electrostatic charges.

References

M. Yiannourakou, P. Ungerer, V. Lachet, B. Rousseau, & J. M. Teuler, United atom forcefield for vapor-liquid equilibrium (VLE) properties of cyclic and polycyclic compounds from Monte Carlo simulations, *Fluid Phase Equilib.*, 2019, 481, 28–43.

15. Enthalpy of mixing predicted using molecular dynamics

In this study by Dai *et. al.*, the accuracy of predicting the Enthalpy of mixing (EOM) for binary mixtures of molecular liquids was examined using the OPLS and TIP4P force fields. The results indicated that the predicted EOM values were qualitatively correct but deviated from experimental data. The calculated EOM values were generally larger than the experimental data, meaning that the predicted mixtures were less miscible. The overestimation of EOM values indicates an underestimation of inter-molecular interactions between unlike molecules in the mixture. The accuracy of prediction is affected by the force field quality in representing interactions among different molecules. The missing energies are likely to be due to polarisation effects. Using methanol/benzene and ethanol/benzene mixtures, they demonstrated that non-additive interaction terms between polarisable atoms can significantly improve the quality of the predictions. Charge-dependent LJ parameters are required to represent the polarisation effects accurately.

References

J. Dai, X. Li, L. Zhao and H. Sun, Enthalpies of mixing predicted using molecular dynamics simulations and OPLS force field, *Fluid Phase Equilib.*, 2010, 289, 156–165.

A. Warshel, M. Kato, A.V. Pisliakov, Polarizable Force Fields: History, Test Cases, and Prospects, *J. Chem. Theory Comput.* 3, 6, 2007, 2034–2045.

16. Phase equilibria applied to alkanes, perfluoroalkanes, alkenes and alcohols

In this range of studies by Potoff *et. al.*, an improvement in the predicted vapour pressures for *n*-alkanes, whilst simultaneously reproducing high accuracy of saturated liquid densities, was found by varying the repulsive exponent of the LJ potential in a UA model. Saturated liquid densities were predicted to within 1 % of experiment and vaporisation pressures to within 3 and 6 % of experiment for *n*-alkanes and perfluoroalkanes, respectively. Their results suggest that while liquid densities are controlled primarily by the particle diameter and depth of the potential minimum, the predicted vapour pressure is a function of the range of the intermolecular interactions, i.e. by increasing the steepness of the potential in the repulsive region, the magnitude of the potential in the region between r_{\min} (the radius at which the interaction potential is a minimum) and 5.5 Å was also increased, effectively increasing the range of interactions between pseudoatoms. Increasing this range of interactions leads to reductions in vapour pressure, as the cohesive energy in the gas phase increases. This approach significantly improved the reproduction of vapour pressures without the need for treating bond lengths, or displacing interaction sites from atomic nuclei. In future force field development, the vapour pressure should be considered in order to reproduce the range on interactions between atoms correctly. In polar molecules, the range of interactions could be altered through modifications to the magnitude of partial charge distributions, rather than through the variable repulsion exponent.

The performance of modified LJ parameters for the TraPPE-UA force field of pure alcohols was very satisfactory, in general, for the prediction of thermophysical properties.

References

J. J. Potoff and D. A. Bernard-Brunel, Mie potentials for phase equilibria calculations: Application to alkanes and perfluoroalkanes, *J. Phys. Chem. B*, 2009, 113, 14725–14731.

J. J. Potoff and G. Kamath, Mie potentials for phase equilibria: Application to alkenes, *J. Chem. Eng. Data*, 2014, 59, 3144–3150. 3.
154

B. Chen, J. J. Potoff and J. I. Siepmann, Monte Carlo calculations for alcohols and their mixtures with alkanes. Transferable potentials for phase equilibria. 5. United-atom description of primary, secondary, and tertiary alcohols, *J. Phys. Chem. B*, 2002, 105, 3093–3104.

17. VLE and interfacial properties of fatty acid methyl esters (FAMEs) from molecular dynamics simulations

The vapour-liquid phase envelope of methyl esters was accurately predicted using the UA approach with the TraPPE-UA force field. Density profiles, coexistence densities, vapour pressures, surface, entropies and enthalpies, interfacial thickness as a function of temperature as well as the boiling temperature and the critical temperatures, densities and pressures were also calculated for each member of the series. The results were found to compare well with results from experimental data taken from the literature.

This demonstrates the TraPPE-UA force field was able to predict, in a transferable manner, the phase equilibria and interfacial properties of methyl esters. The simulated surface tension values are important as no experimental data is available for FAMEs at temperatures > 360 K.

Excellent agreement was found for surface tension at low temperatures and for vapour-liquid coexistence densities and vapour pressures in a wide range of temperatures.

References

E. Feria, J. Algaba, J. M. Míguez, A. Mejía, P. Gómez-Álvarez and F. J. Blas, Vapour-liquid phase equilibria and interfacial properties of fatty acids methyl esters from molecular dynamics simulations, *Phys. Chem. Chem. Phys.*, 2020, 22, 4974–4983.