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A Multi-scale Computational Framework for Property Prediction of Fluid Mixtures

March 7-9, 2023




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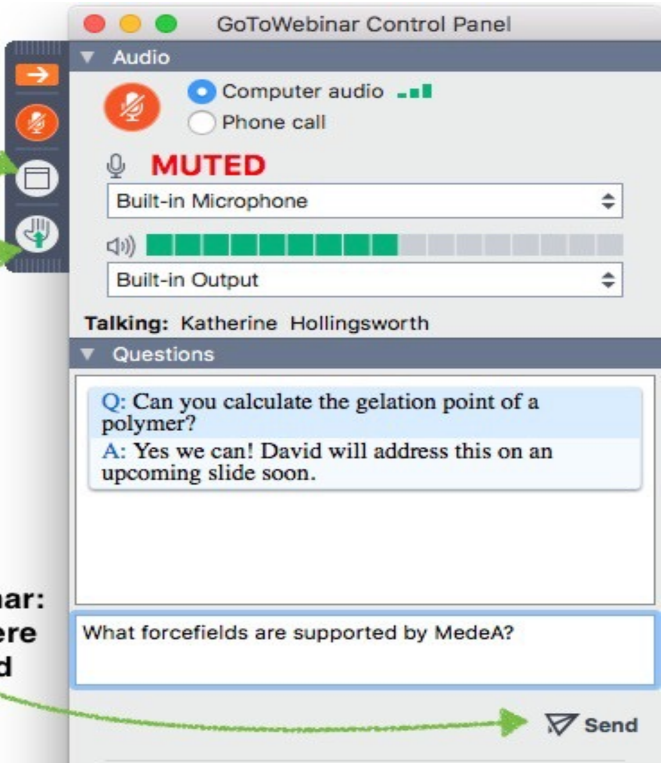

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Webinar Speakers

Katherine Hollingsworth

Presenter: Dr. Marianna Yiannourakou

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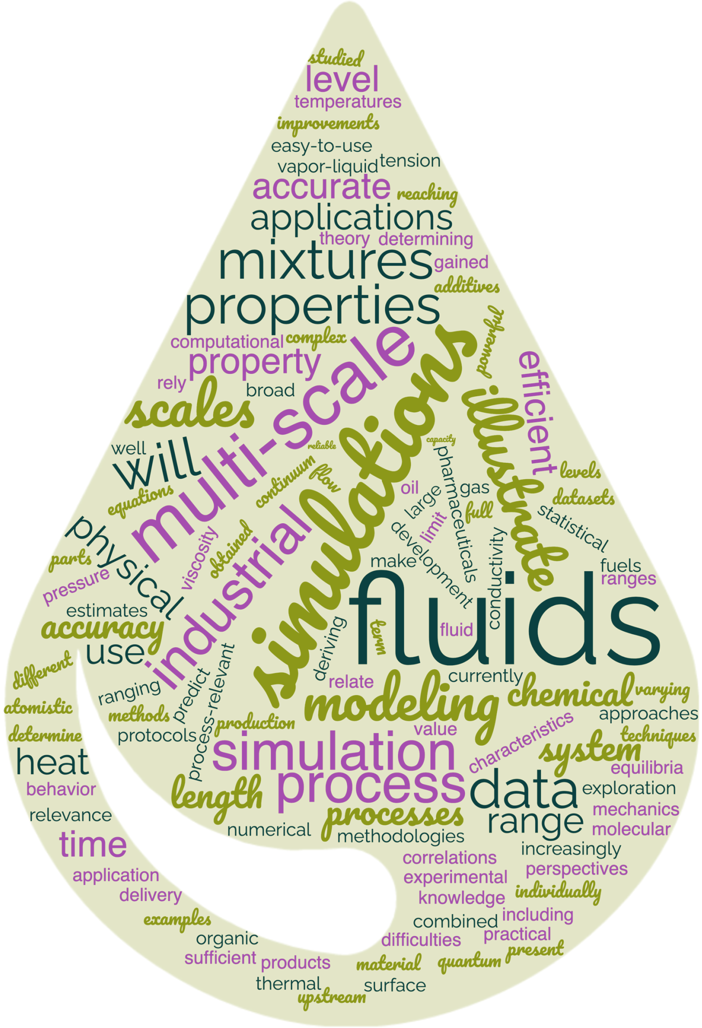
A Multi-scale Computational Framework for Property Prediction of Fluid Mixtures

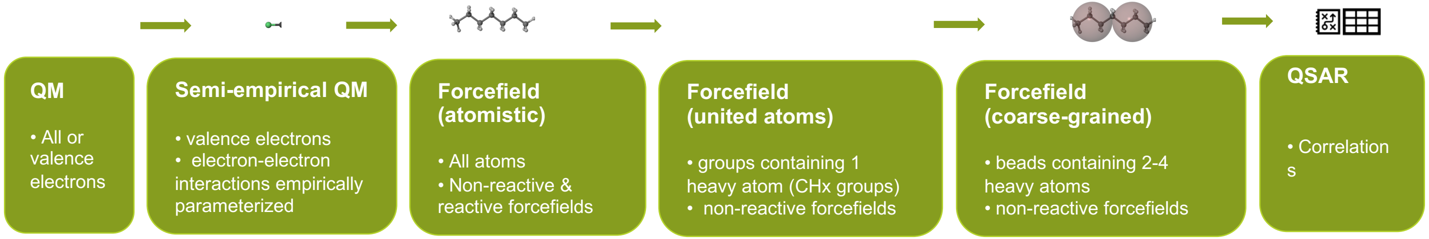
March 7-9, 2023



How can molecular modeling help?

- What properties can be calculated using molecular modeling?
- How are the properties calculated?
- What is the expected accuracy for property prediction of fluid mixtures, using molecular modeling?
- What input is required?
- What is the computation cost and human effort for the computations?

Tools: Different levels of description



- Simulations at different levels of theory, using corresponding models can be used to study phenomena that occur at different time/length scales
- Selection of the appropriate level of theory and methods depends on:
  - Property or phenomenon of interest
  - Expected accuracy
  - Method coverage
- Information from one level can be passed on to the next

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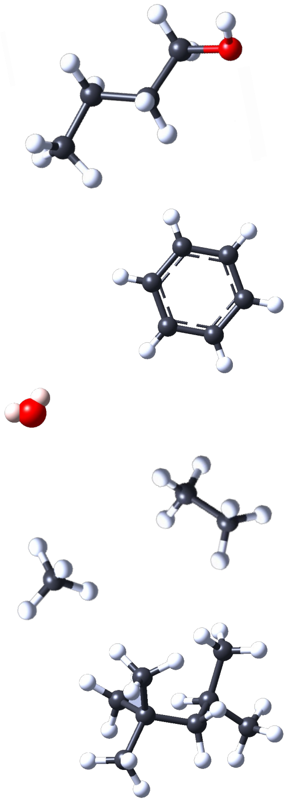
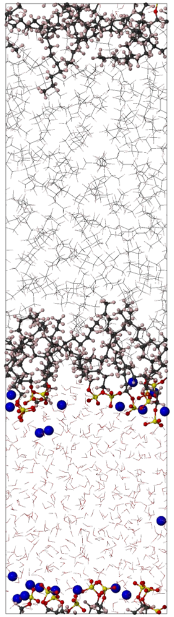
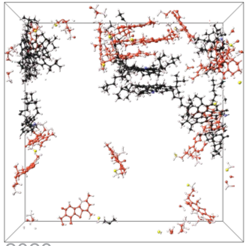
Fluids

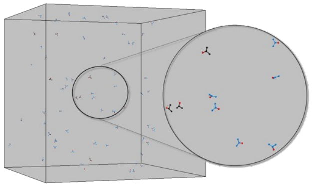


	Pure Compounds’ Properties
1	Density
2	Saturation Pressure
3	Vaporization Enthalpy
4	Chemical potential / Fugacity
5	Cohesive Energy Density
6	Joule-Thomson Coefficient
7	Speed of Sound
8	Heat Capacity
9	Compressibility Factor
10	Normal Boiling Point Temperature
11	Critical Point (density, pressure, temperature)
12	Heat of Formation
13	IR Spectra
14	UV-Vis Spectra
15	Multipole moments (dipole, quadrupole, etc)
16	Self Diffusion Coefficient
17	Thermal Conductivity
18	Viscosity
19	Surface Tension
20	Acentric factor
21	Thermal expansion coefficient

	Mixtures’ Properties
1	Density
2	Equilibrium Pressure
3	Chemical Potential / Fugacity
4	Composition
5	Equilibrium constants
6	Henry solubility constant
7	Azeotrope
8	Joule-Thomson Coefficient
9	Speed of Sound
10	Heat Capacity
11	Self Diffusion Coefficient
12	Thermal Conductivity
12	Viscosity
13	Thermal expansion coefficient







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Calculating fluid mixtures properties from molecular simulations

All-atom / United-Atom / Coarse-Grained Forcefields

- VLE
- Henry Solubility constants
- Diffusivity coefficients
- Viscosity
- Surface Tension

Fluid Phase Equilibria 560 (2022) 113478

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journal homepage: www.elsevier.com/locate/fluid

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Molecular simulations for improved process modeling of an acid gas removal unit

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[b] TotalEnergies S.E., Exploration Production, Development and Support to Operations, Liquefied Natural Gas – Acid Gas Entity, CCUS R&D Program, Paris, 92078 France
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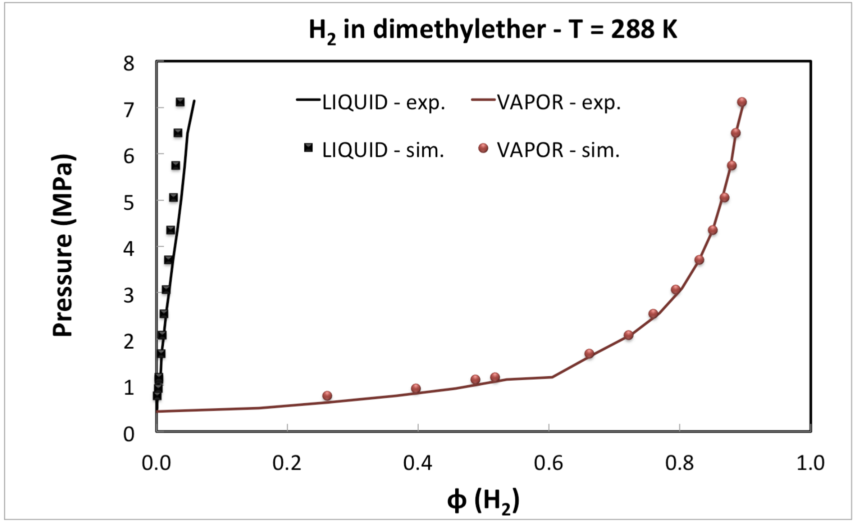
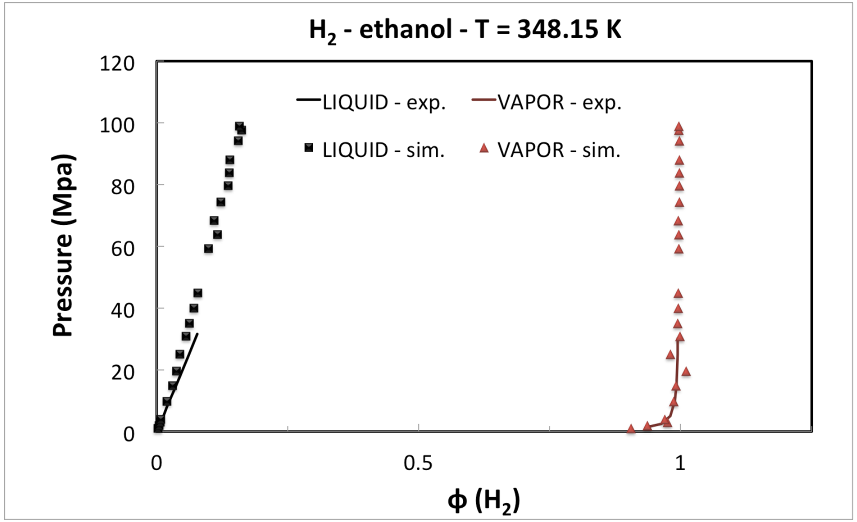
Forcefields (FF)

1. All-atom (AA, non-reactive) FFs for organics (and some inorganics), e.g.:
   - PCFF+ (used in the MD examples shown here)
   - PCFF+ has a coverage of 97% of the compounds contained in the DIPPR's Project 801 Database
2. United-Atom (UA, non-reactive) FFs for organics, e.g.:
   - AUA+ (used in the MC examples here)
   - Several popular models for small molecules, such as H_2S, CO_2, H_2O, CH_4
3. SAFT-γ Mie (CG, non-reactive) FFs for organics:
   - Developed from SAFT EOS
   - Coverage of 6000+ compounds and possibility to parametrize from both bottom-up and top-bottom approaches: www.bottledsaft.org

Vapor Liquid Equilibria - Mixtures

MedeA GIBBS simulations





Yiannourakou et al., Mol. Sim. 39, p. 1165-1211 (2013)

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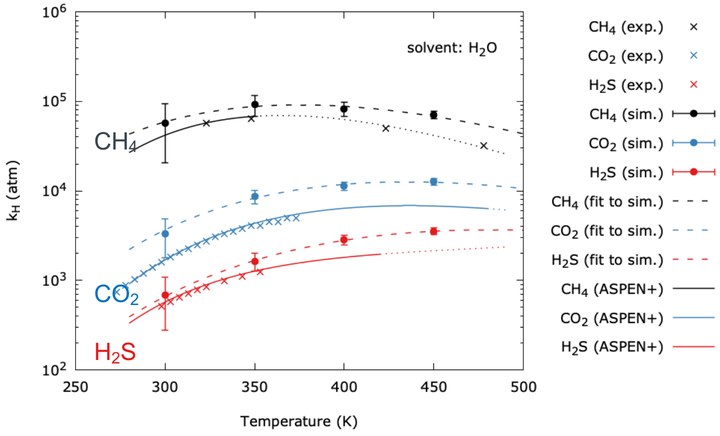
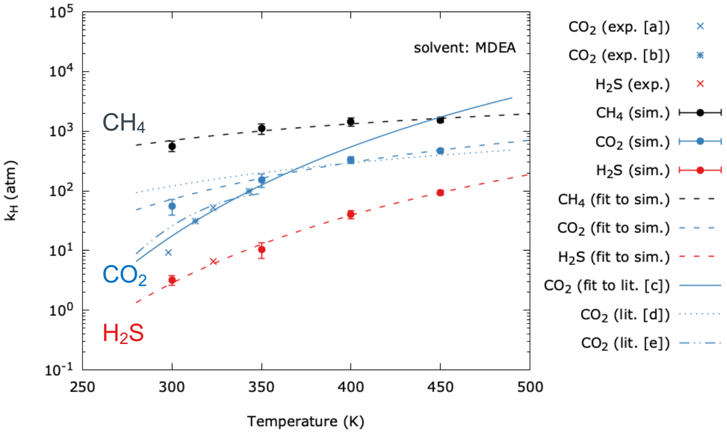
Henry Solubility Constant

- Simulations accurately predict Henry solubility constants ranking and temperature dependence
- Semi-quantitative agreement is achieved (order of magnitude) for all three solutes in water

Yiannourakou *et al*, *Molecular simulations for improved process modeling of an acid gas removal unit*, FPE 560, p. 113478 (2022)



Monte Carlo simulations in the Gibbs Ensemble (*MedeA GIBBS*)



Monte Carlo simulations in the Gibbs Ensemble (*MedeA GIBBS*)

Left plot:

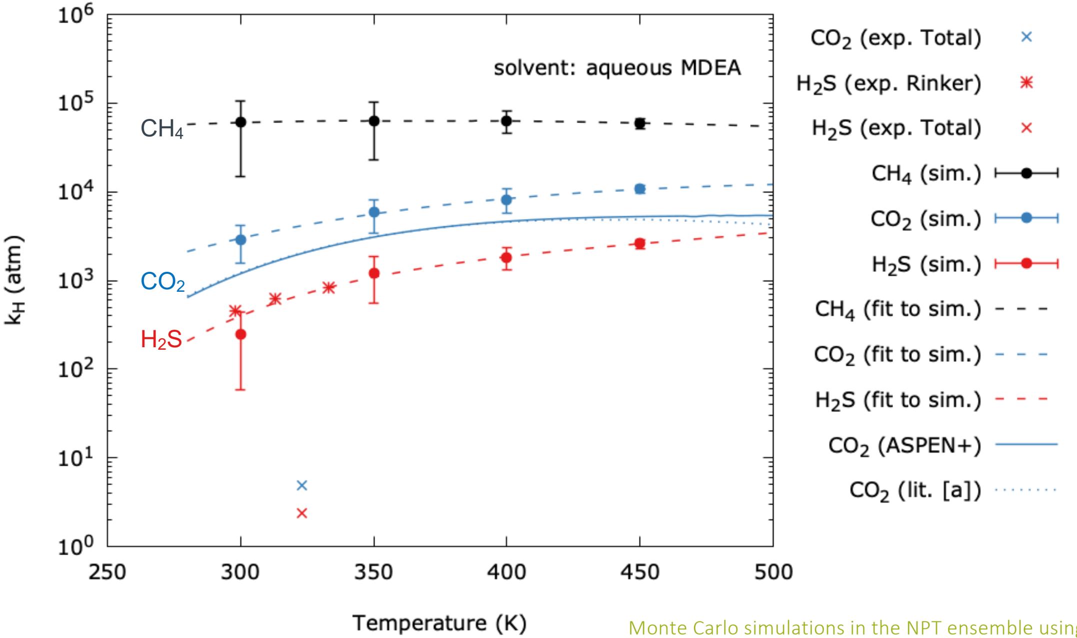
- Exp. data for CO_2/H_2S/ CH_4 from:
  - Gillespie *et al.*, Gas Processors Association. (1982)
  - Carroll *et al.*, J. Phys. Chem. Ref. Data 20, p. 1201 (1991); Crovetto *et al.*, J. Phys. Chem. Ref. Data 20, p. 575 (1991); *Prini et al.*, J. Phys. Chem. Ref. Data 18, p. 1231 (1989)
  - Iliuta *et al.*, J. Chem. Eng. Data 52, p. 2 (2007); Sander, Atmos. Chem. Phys. 15, p. 4399 (2015)
- CO_2 / CH_4 / H_2S (ASPEN+): ASPEN+

Right plot:

- Exp. data for CO_2 [a] / H_2S from: TotalEnergies, Internal data (2019)
- Exp. data for CO2 [b]: Skylogianni *et al.* (2020)
- CO_2 (lit [c]): Skylogianni *et al.* (2020)
- CO_2 (lit [d]): Zhang & Chen (2011)
- CO_2 (lit [e]): TotalEnergies, Internal data (2019)

Henry Solubility Constant

- Aqueous solution of MDEA: 30% wt
- Simulations results for H_2S are in agreement with experiments reporting measuring only physisorption of H_2S in MDEA, using a protonated MDEA solution
- Simulation results for CO_2 overpredict the Henry constant (underestimate the solubility) of CO_2 in MEDEA but accurately predict the temperature dependence of the Henry constant



Monte Carlo simulations in the NPT ensemble using Widom test insertions (*MedeA GIBBS*)

- Exp. TOTAL: TotalEnergies (2019) – unpublished work
- Exp. Sandal: Rinker *et al.*, The Canadian J. of Chem. Eng. 78 (2000)
- CO_2 (ASPEN+): ASPEN+
- CO_2 (lit): Zhang *et al.*, Ind. & Eng. Chem. Res. 50, p. 163 (2011)

Yiannourakou *et al*, *Molecular simulations for improved process modeling of an acid gas removal unit*, FPE 560, p. 113478 (2022)

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Diffusivity

Self-Diffusion Coefficient

- Run NVE simulations and calculate the Mean Squared Displacement of the molecules

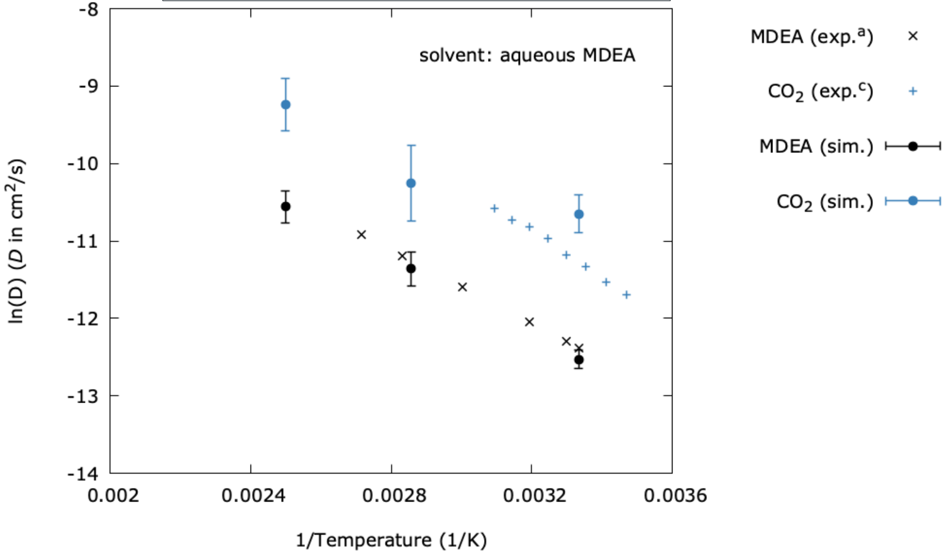
$$MSD = \left\langle \left(r(t) - r(t_0) \right)^2 \right\rangle$$

r(t) and *r(t_0)* are the position vectors of the gas molecule i at times t and t_0, respectively; Brackets <> denote the ensemble average over time origins, providing the mean square displacement (MSD)

- Calculate the self-diffusion coefficient of the molecules through their MSD

$$D = \frac{1}{6} \cdot \frac{\left\langle \left(r(t) - r(t_0) \right)^2 \right\rangle}{t}$$

Yiannourakou *et al.*, FPE 560, p. 113478 (2022)



Equilibrium molecular dynamics simulations in the NVE ensemble (*MedeA LAMMPS*)

- Exp. MDEA (a): Snijder et al., *Journal of Chemical & Engineering Data*. 38, p. 475-480 (1993)
- Exp. CO_2 (c): Al-Ghawas et al., *Journal of Chemical & Engineering Data* 34, p. 385-391 (1989)

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Viscosity of water, MDEA and an aqueous solution of MDEA

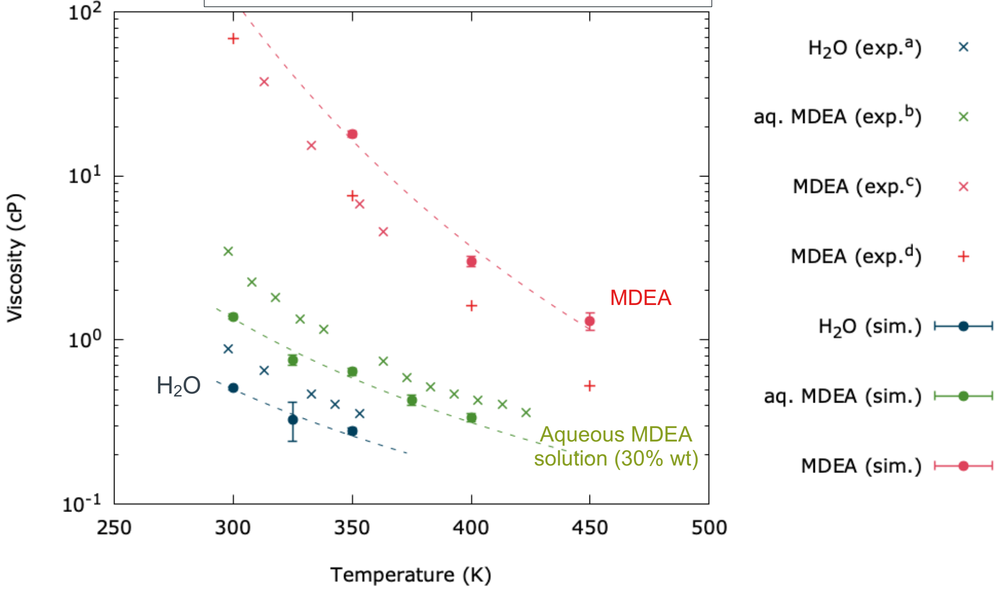
- The Green-Kubo method is used for the calculation of viscosity during equilibrium molecular dynamics (EMD) simulations

$$\eta = \frac{V}{kT}\int_0^{\infty}\langle P_{ij}(0)P_{ij}(t)\rangle dt$$

where V is the volume of the cell, k the Boltzmann's constant, T is the temperature, P_{ij}, i, j = x, y, z are components of the shear stress tensor

- Calculated viscosities of MDEA and the aqueous solution of MDEA (30% wt) predict the temperature dependence of the viscosity

Yiannourakou *et al.*, FPE 560, p. 113478 (2022)



Equilibrium molecular dynamics simulations in the NVE ensemble (*MedeA LAMMPS*)

- Exp. H_2O (a): Teng et al., J. Chem. Eng. Data 39, p. 290 (1994)
- Exp. aqueous MDEA solution (30% wt) (b): Arachchige et al., Ann. Trans. Of the Nordic Rheol. Soc. 22 (2014)
- Exp. MDEA (c): Yusoff et al., J. Ind. & Eng. Chem. 20, p. 3349 (2014)
- Exp. MDEA (d): Wilding et al., Dippr project 801, FPE 150-151, p. 413 (1998)

Surface Tension of water, methanol and their mixtures

- Calculation of surface tension during MD simulations in the NVT ensemble

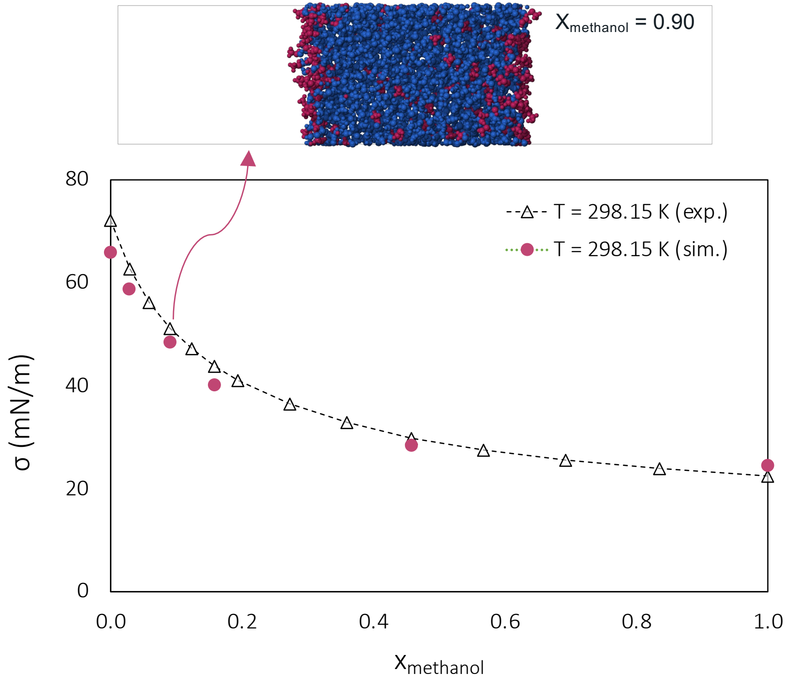
$$\gamma = 0.5L\left\{\langle\sigma_z\rangle - \frac{1}{2}\left[\langle\sigma_x\rangle + \langle\sigma_y\rangle\right]\right\}$$

where *L* is the cell length in the direction normal to the interface and brackets <> denote the time average

- Qualitatively and quantitatively, the results agree well with experimental data

- Simulation details:
  - Forcefield: pcff+ (v2023)
  - Each point is the average of five (5) consecutive simulations of duration 1 ns each
  - System size: 2,000 molecules (water & ethanol)
  - T = 298.15 K
  - r_{cut} = 15 Å
  - tstep = 1 fs

Equilibrium molecular dynamics simulations in the NVT ensemble (*MedeA LAMMPS*)



Exp. data from: G. Vasquez et al., J. Chem. Eng. Data 40, p. 611-614 (1995)

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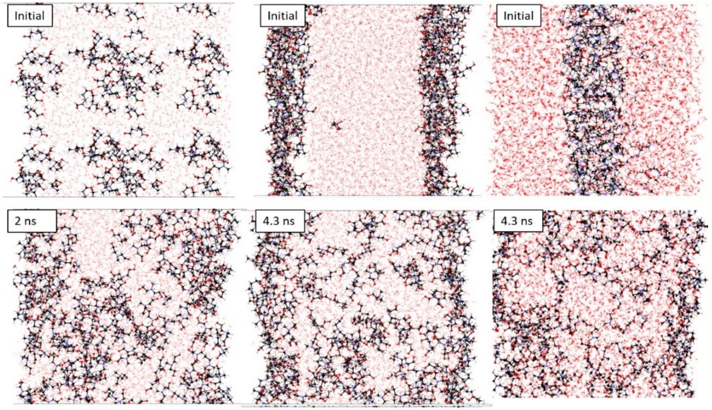
Surface Tension of water, MDEA and an aqueous MDEA solution

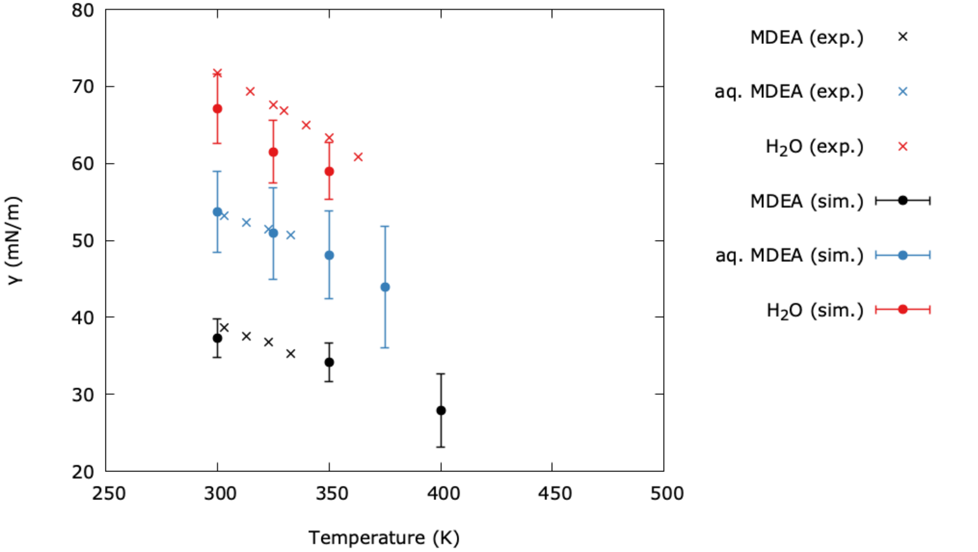
- Calculation of surface tension during MD simulations in the NVT ensemble

$$\gamma = 0.5L\left\{\langle\sigma_z\rangle - \frac{1}{2}\left[\langle\sigma_x\rangle + \langle\sigma_y\rangle\right]\right\}$$

where L is the cell length in the direction normal to the interface and brackets <> denote the time average

- Qualitatively and quantitatively, the results agree well with experimental data for MDEA, H_2O and the aqueous solution of MDEA (30% wt)





Yiannourakou *et al.*, FPE 560, p. 113478 (2022)

Equilibrium molecular dynamics simulations in the NVT ensemble (*MedeA LAMMPS*)

- Exp. MDEA: Wilding et al., Dippr project 801, FPE 150-151, p. 413 (1998)
- Exp. aqueous MDEA solution (30% wt): Muhammad et al., J. Chem. & Eng. Data 53, p. 2226 (2008)
- Exp. H_2O: Vargaftik, Volkov, & Voljak, 1983

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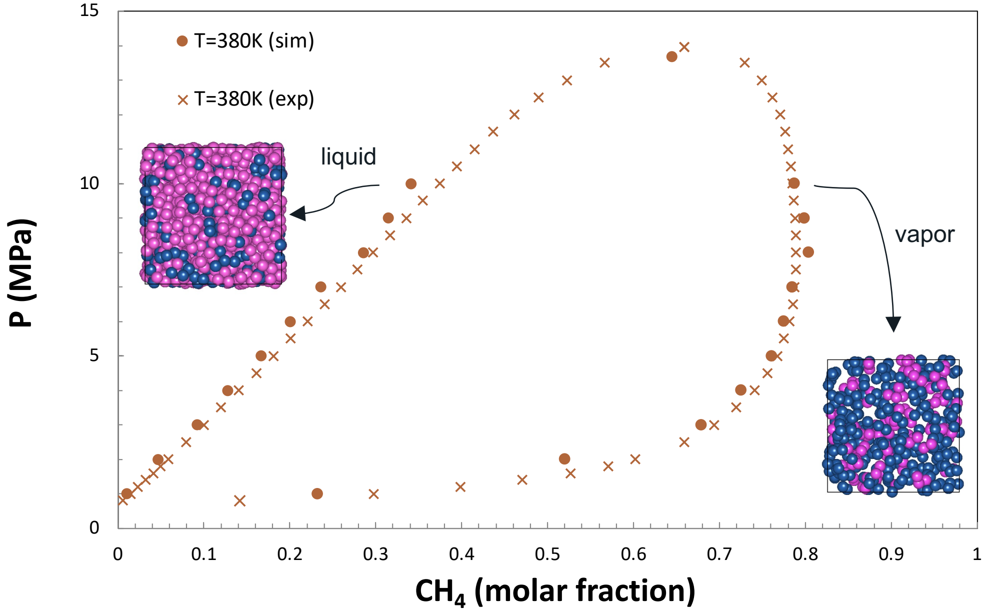
VLE of mixtures – Coarse grained models

methane / n-pentane

- T = 380 K
- P ∈ [1,10] MPa
- Isobaric GEMC simulations
- 40 million steps
- 800-1000 molecules
- methane: 1 bead
- n-pentane: 2 beads

MedeA GIBBS simulations

Mie FF, parameters from: C. Herdes *et al.*, Fluid Phase Equilibria **406**, 91-100 (2015)



Exp. Data from: V.M. Berry and B.H. Sage, "Phase Behavior in Binary and Multicomponent Systems At Elevated Pressures: n-Pentane and Methane-n-Pentane"

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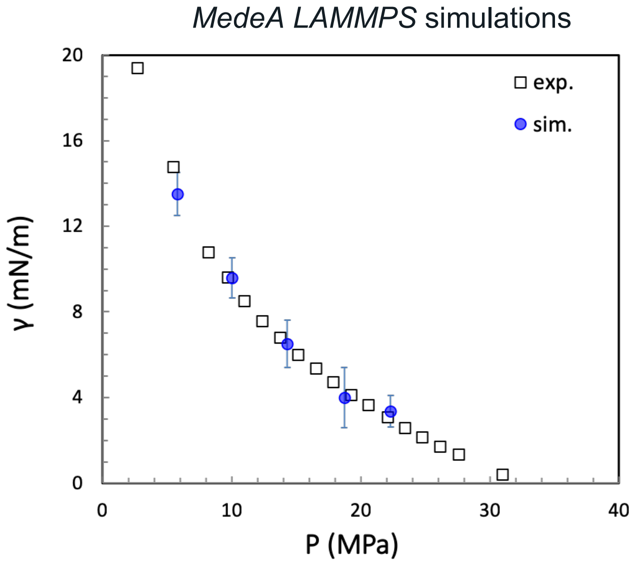
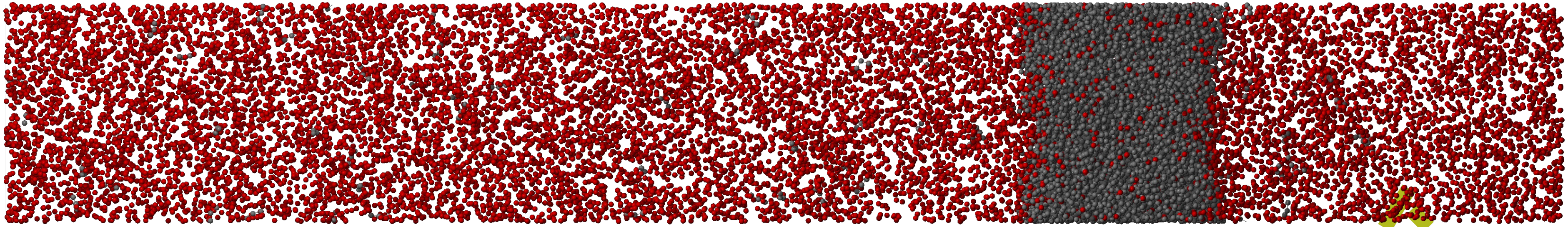
Interface Tension – Coarse-grained description

methane / n-decane

- T = 366.48 K
- P ∈ [5,25] MPa
- tstep = 0.01 ps
- t = 5 ns



Reproduction of work from:
C. Herdes *et al.*, Fluid Phase Equilibria **406**, 91-100 (2015)



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Calculating fluid mixtures properties from correlations

- Density

Compositional Modeling of Crude Oils Using C_{10}–C_{36} Properties Generated by Molecular Simulation

Philippe Ungerer*, Marianna Yiannourakou, Alexander Mavromaras, and Julien Collell

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Publication Date: March 4, 2019
https://doi.org/10.1021/acs.energyfuels.8b04403
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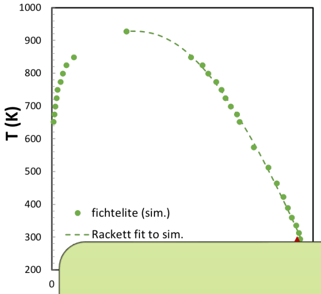
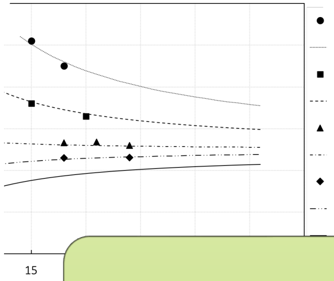
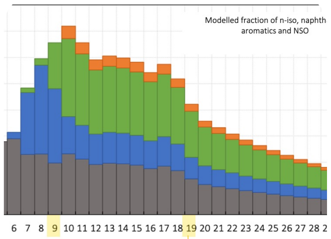
Summary



Calculation of pure-compound properties



Calculation of correlations for pure-compounds

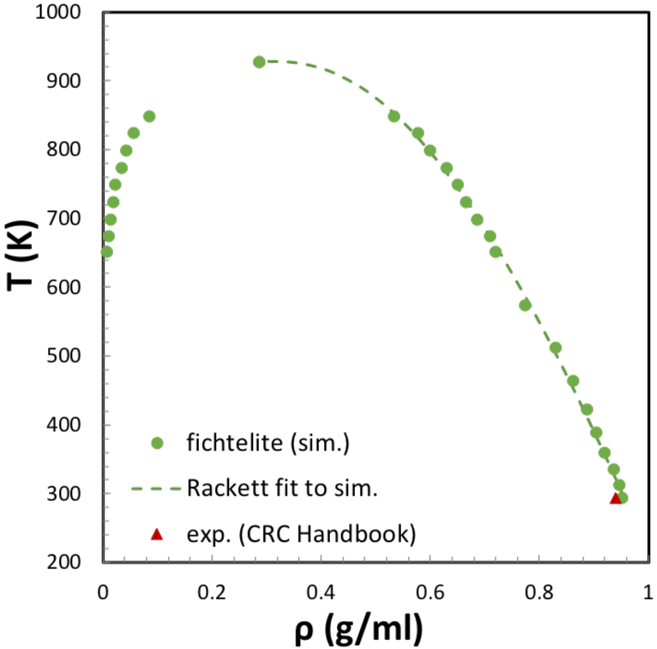


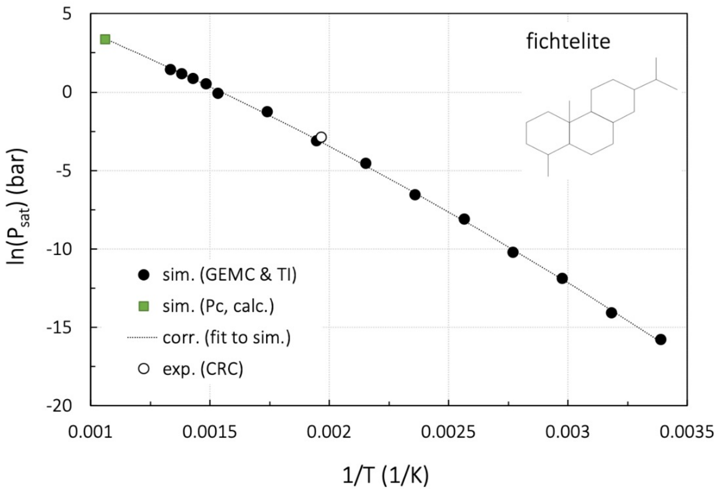
Use of correlations for computing properties of oil samples (multi-component)

Vapor Liquid Equilibrium (VLE) of pure compounds

Fichtelite

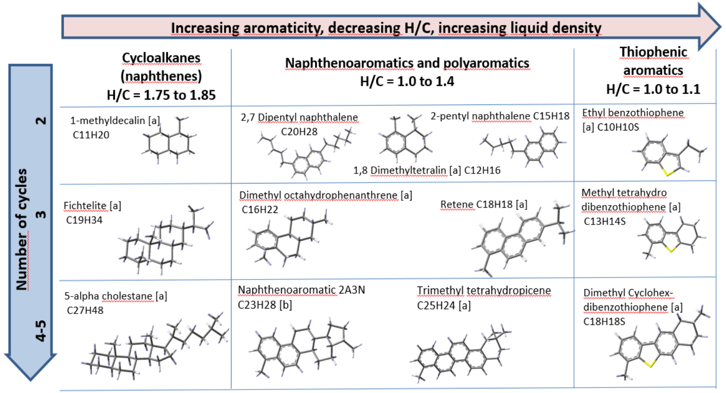
T_C (K)	ρ_C (g/ml)	P_C (bar)	T_b (K)	ω
928	0.285	21.6	644	0.291



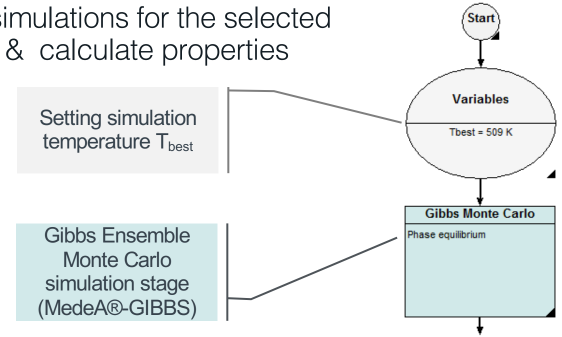


Fitting equations for pure compounds (density)

1 Select representative members of a chemical family



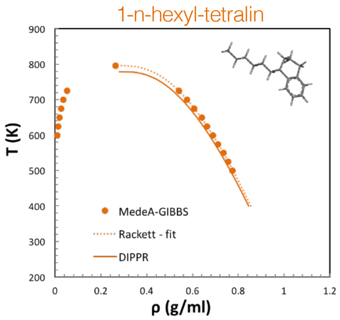
2 Run MC simulations for the selected members & calculate properties

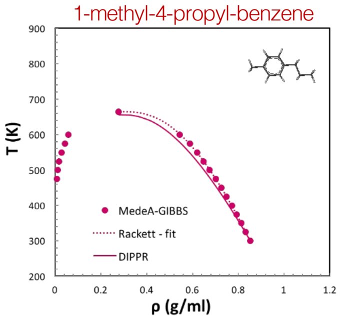


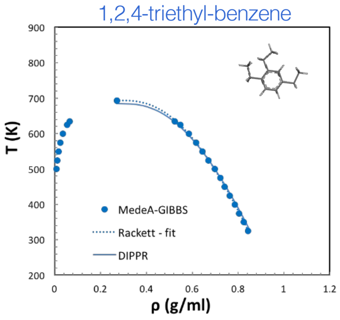
3 Fit engineering equations on calculated properties (compound specific)

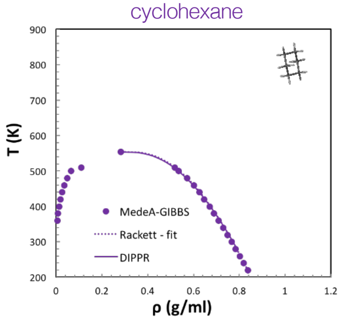
e.g. Rackett Eq.: $V^{sat} = V_c Z_c^{(1-T_r)^A}$

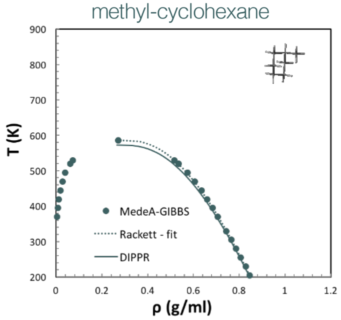
Yiannourakou et al., FPE 481, p. 28-43 (2019)

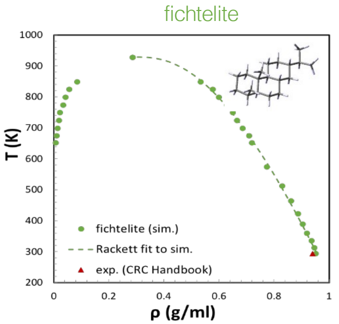












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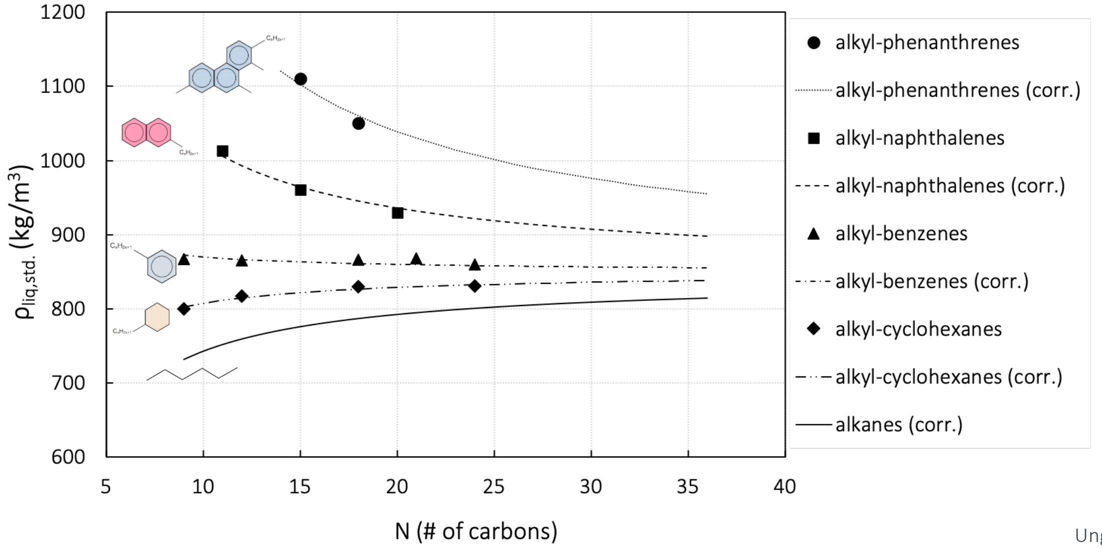
Correlations for fitting equations (pure compounds - density)

4 Create correlations for parameters of engineering equations (family specific)

e.g. Correlations for Z_C and A parameters of the Rackett equation for a specific family with the number of C atoms (N_C)

$$Z_C = a \cdot N_C{}^b \qquad A = a \cdot N_C{}^2 + b \cdot N_C + c$$

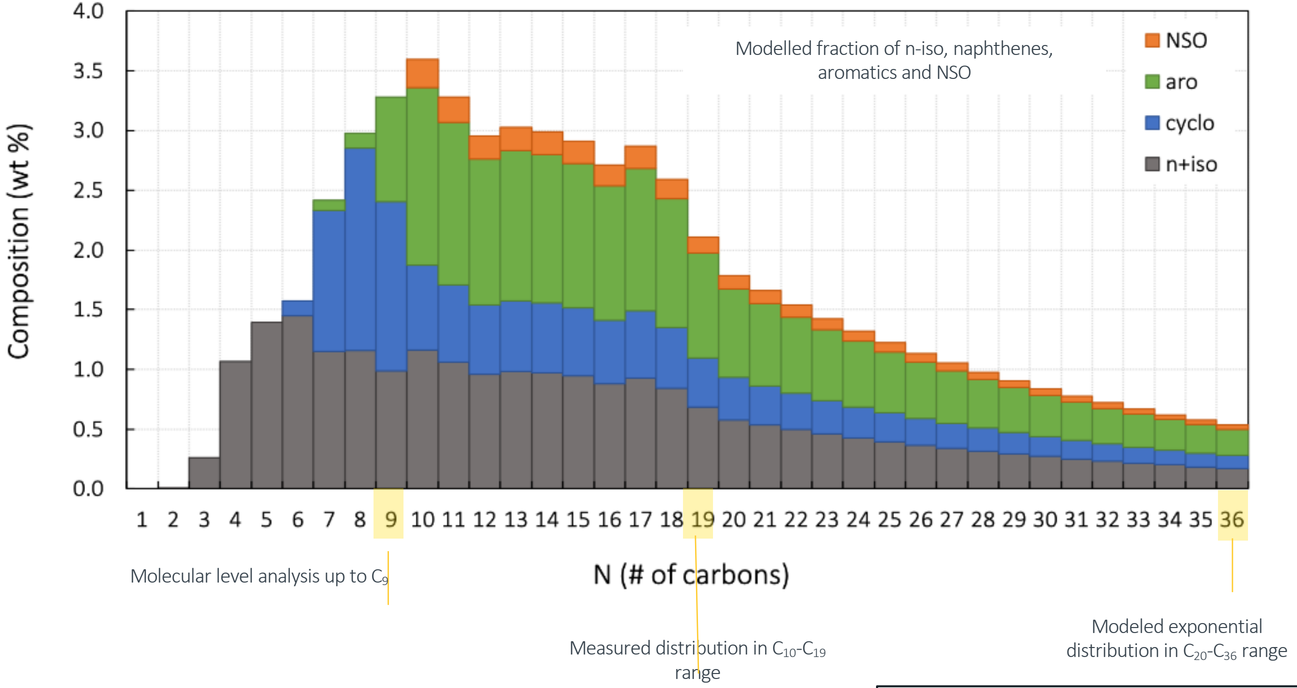
5 Use correlations to predict properties for other members of a chemical family



Ungerer et al., Energy Fuels 33, 2967-2980 (2019)

Properties of mixtures with continuous distribution of composition, from pure compound properties

6 Use existing experimental information to create models of the mixtures (e.g. Stock Tank Oil)



Ungerer et al., Energy Fuels 33, 2967-2980 (2019)

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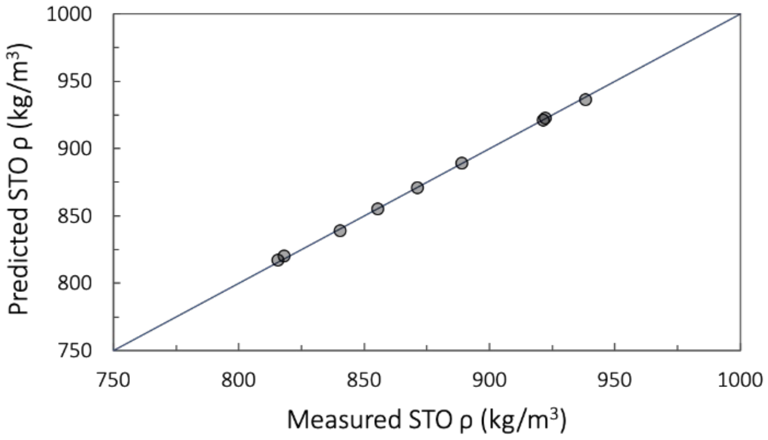
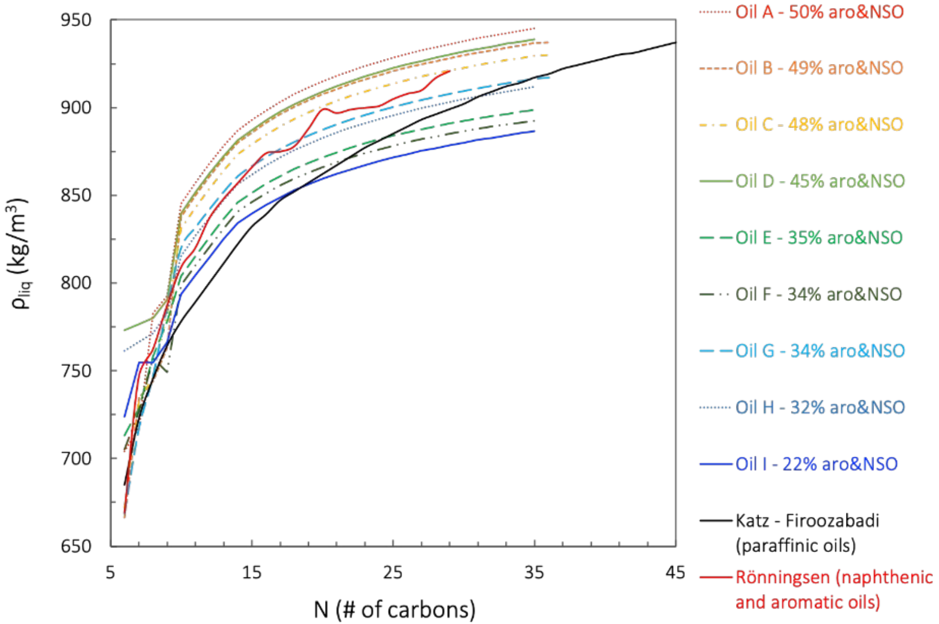
Properties of mixtures with continuous distribution of composition, from pure compound properties

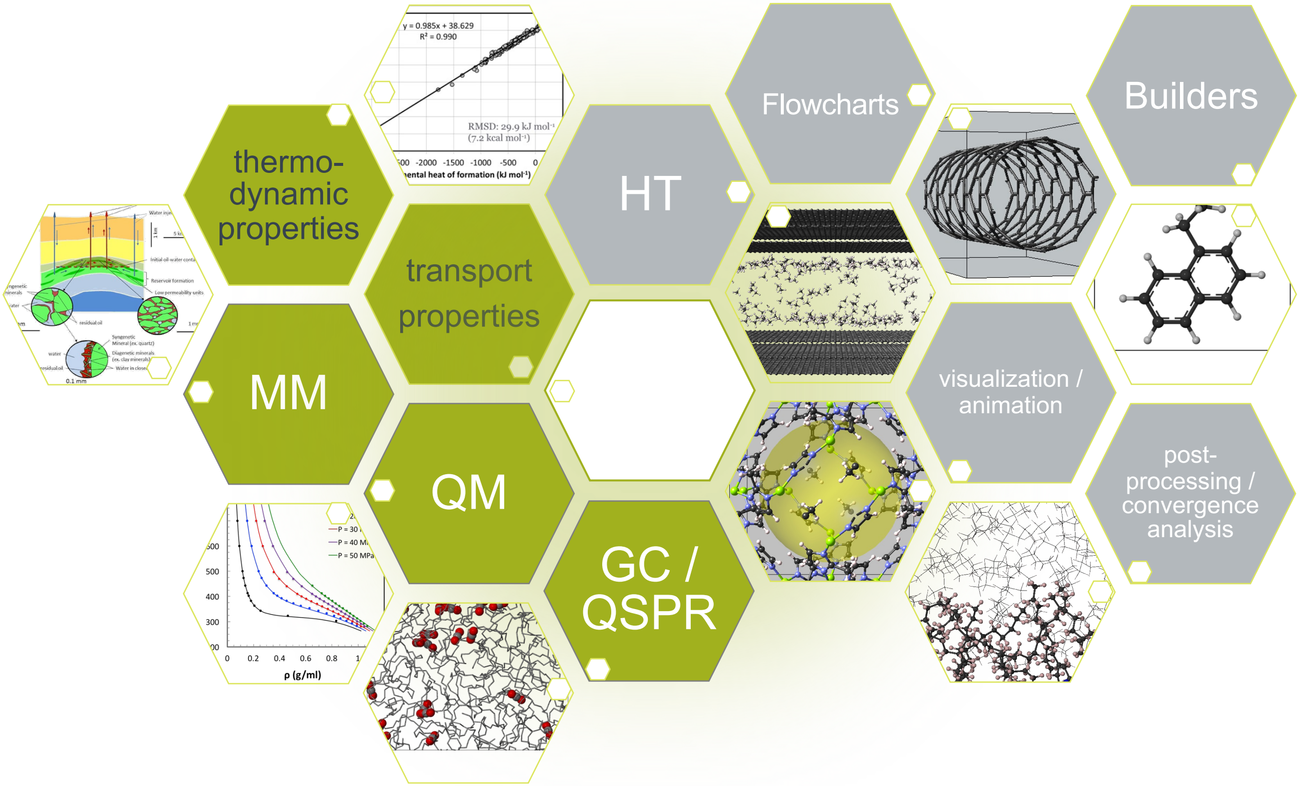
7 Calculate Mixture properties, from pure compound data, e.g. density of STO (Stock Tank Oil)





Ungerer et al., Energy Fuels 33, 2967-2980 (2019)

Conclusions – Perspectives



Conclusions – Perspectives

Direct simulations can be employed for computing fluid mixtures' properties such as: VLE, diffusivity, viscosity, surface tension, etc

Depending on the property of interest and method, different accuracies may be achieved. Expected accuracies can be estimated

The use of robust workflows with automated prost-processing and HT capabilities is increasing substantially the efficiency of molecular modeling

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Conclusions – Perspectives

PCFF+ (AA) forcefield achieves very high coverage of organic (and some inorganic) compounds, while demonstrating also high accuracy; these forcefields are particularly useful for MD simulations

Extending UA and CG forcefields to reach higher coverage is meaningful to be able to treat many families of (organic) compounds; these forcefields are very useful particularly for MC simulations to study VLE

New forcefield types, such as Machine Learned forcefields (MLPs), may be quite interesting to explore, particularly when reactions are occurring

Conclusions – Perspectives

Consistent prediction of properties of pure compounds is achieved, from molecular simulation; these data may also be used as pseudo-experimental data

Creation of correlations for estimation of properties of pure compounds is feasible, based on molecular simulation results

Use of pure compound properties and available experimental data to optimize composition and predict properties of multi-component mixtures (e.g. oil) is feasible

Use of simulation results not only for property prediction but also for understanding the influence of phenomena that occur at the nanoscale on the macroscopic properties of a system is highly valuable

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Computational effort

Property	Property Symbol	Method used	Computational time estimate
Vapor Liquid Equilibrium (VLE) • Density • Saturation Pressure • Vaporization Enthalpy	$\rho(T)$ $P_{sat}(T)$ $\Delta H_{vap}(T)$	MM (Monte Carlo)	hours/couple of days on 4-12 cores
Henry Solubility Constant	$k_H(P,T)$	MM (Monte Carlo)	hours/couple of days on 4-12 cores
Solubility		MM (Monte Carlo)	hours/couple of days on 4-12 cores
Viscosity	$\eta(P,T)$	MM (molecular dynamics)	hours/days on 16-32 cores
Diffusivity	$D(P,T)$	MM (molecular dynamics)	hours/days on 16-32 cores
Thermal Conductivity	$\lambda(P,T)$	MM (molecular dynamics)	hours/days on 16-32 cores
Surface Tension	$\gamma(P,T)$	MM (molecular dynamics)	days on 16-32 cores
Reaction Kinetics	$\Delta G^{\#}(T)$, $k(T)$, $r(T)$	QM & MM (molecular dynamics)	hours/days on 16-32 cores

MM: molecular mechanics, QM: quantum mechanics, FF: ForceField

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Credits

- **LAMMPS**:
  - S. Plimpton, *Fast Parallel Algorithms for Short-Range Molecular Dynamics*, J Comp Phys, 117, 1-19 (1995), www.lammps.sandia.gov
  - A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, S. J. Plimpton, *LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales*, Comp. Phys. Comm. 271, p. 10817 (2022).

- **GIBBS**: License IFP-EN – LCP (CNRS – Université Paris Sud)
  - P Ungerer, C Beauvais, J Delhommelle, A Boutin, B Rousseau, AH Fuchs, The Journal of Chemical Physics 112 (12), 5499-5510
  - E. Bourasseau, M. Haboudou, A. Boutin, A.H. Fuchs, P Ungerer, The Journal of chemical physics 118 (7), 3020-3034
  - A.D. Mackie, .B Tavitian, A. Boutin, A.H. Fuchs, Molecular Simulation 19 (1), 1-15
  - M. Lagache, P. Ungerer, A. Boutin, A.H. Fuchs, Physical Chemistry Chemical Physics 3 (19), 4333-4339
  - E. Bourasseau, P. Ungerer, A. Boutin, A.H. Fuchs, Molecular Simulation 28 (4), 317-336
  - N. Ferrando, A. Boutin and V. Lachet, Journal of Physical Chemistry **114**: 8680-8688, (2010).

- ***MedeA*®**: *Materials Exploration and Design Analysis*; Materials Design, Inc. 2023. www.materialsdesign.com

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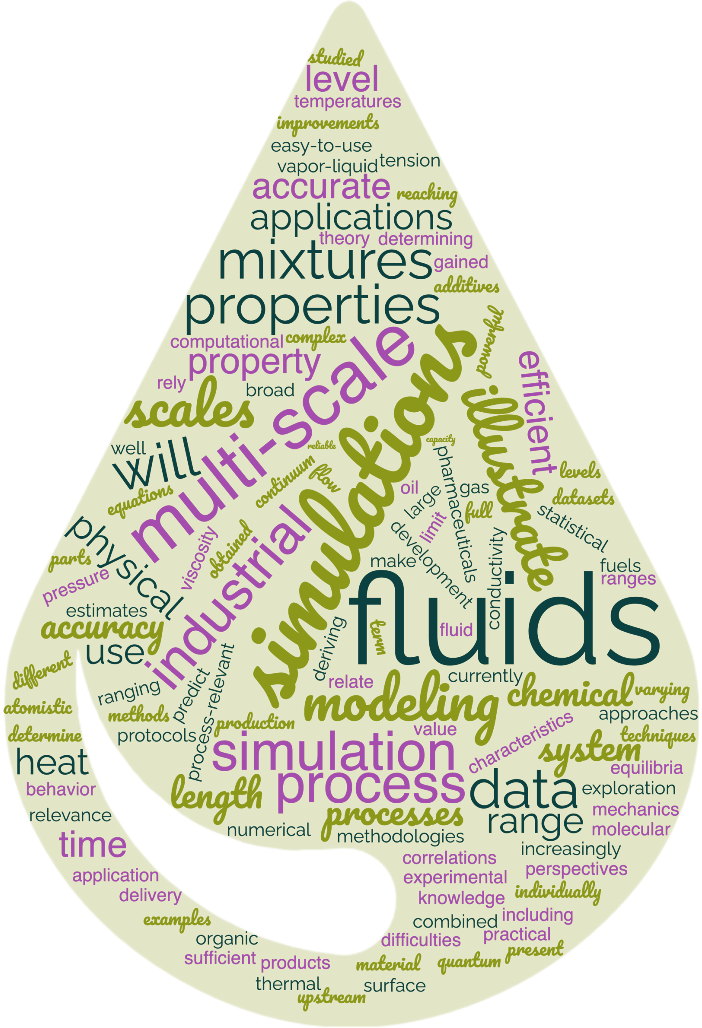
A Multi-scale Computational Framework for Property Prediction of Fluid Mixtures

March 7-9, 2023



MedeA Modules Used

MedeA Environment: Materials Modeling and Simulation Environment

MedeA Molecular Builder: Create 3D molecular models. Import and edit molecular systems or build them stepwise using the *MedeA* molecular fragment library.

MedeA Amorphous Materials Builder: Create condensed phase models based on system chemical composition and target density. It eliminates lengthy mixing and amorphization simulations through realistic sampling of the translational, rotational, and conformational degrees of freedom of component species.

MedeA GIBBS: *MedeA GIBBS* focuses on the prediction of fluid properties in various equilibrium conditions such as molecular liquids of complex structure, sorption in natural and industrial adsorbents, solubility of small compounds in polymer materials, and ion exchange.

MedeA LAMMPS: *MedeA LAMMPS* focuses on the efficient execution of computational tasks using computational hardware ranging from massively parallel facilities to laboratory-scale workstations and gpu-enabled clusters.

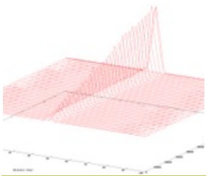
MedeA Modules Used

***MedeA* Thermal Conductivity:** Calculate lattice thermal conductivity with Green-Kubo or non-equilibrium MD Müller-Plathe

***MedeA* Viscosity:** Calculate viscosity with Green-Kubo or non-equilibrium MD Müller-Plathe

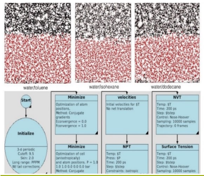
***MedeA* Surface Tension:** Calculate surface tension of fluid slabs

***MedeA* Diffusion:** Automatically calculate diffusivity from mean square displacement



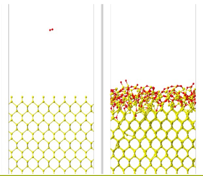
MT, Deformation

Mechanical, Thermal
Plastic deformation



Transport

Diffusion, Viscosity, Thermal conductivity, Surface Tension



Deposition,

Growth, Oxidation, and Etching

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https://www.materialsdesign.com/webinars/recorded/acid-gas-removal-2021

The Innovative Force of High-Performance Computing in Materials Science:

https://www.materialsdesign.com/webinars/recorded/NVIDIA-HPC-in-Materials-Science

Development of New Solvents for CO2 Capture Using Molecular Simulations:
https://www.materialsdesign.com/webinars/recorded/acs-c02-capture

Predicting Petroleum Fraction Thermophysical Properties - Advances in Molecular Simulation:

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Question and Answer Session

Dr. Marianna Yiannourakou

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Questions about Materials Design Webinars

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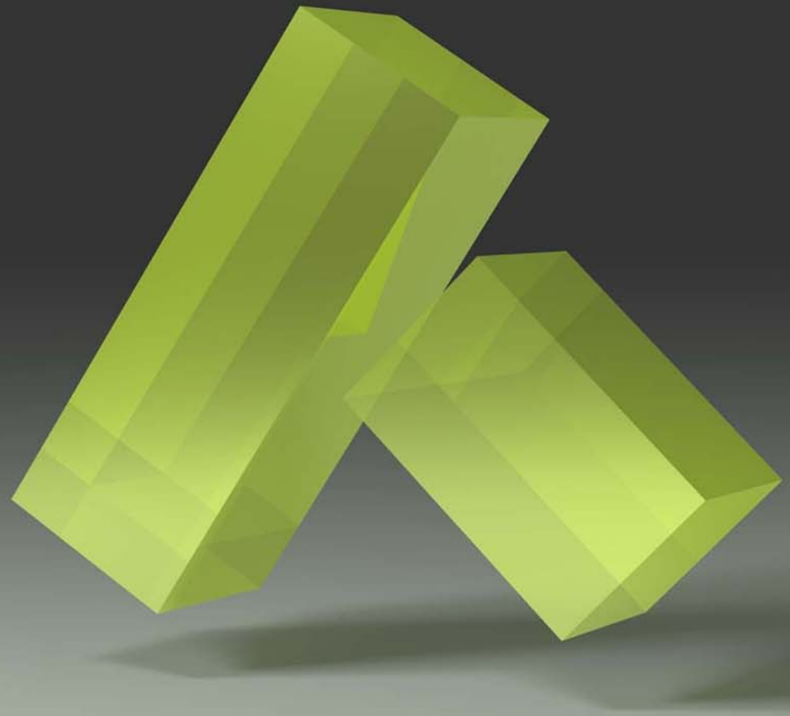

MedeA

Innovation by Simulation