



New Horizons in Atomistic Simulation, York, January 5, 2018

Computational molecular engineering in interfacial thermodynamics

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In collaboration with:

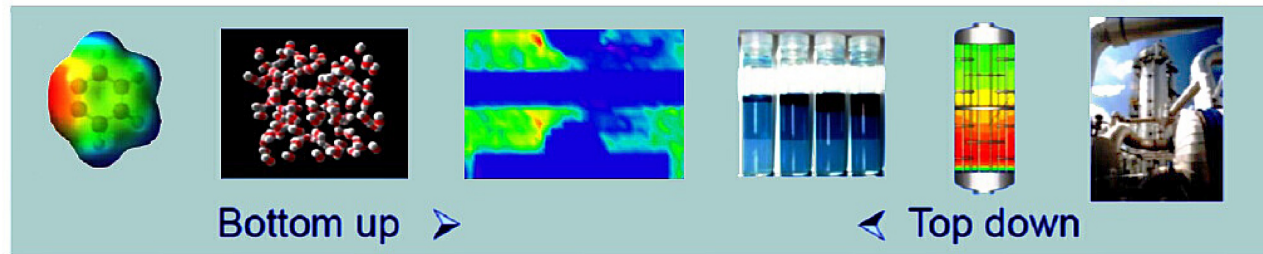
Wolfgang Eckhardt, Munich
Hans Hasse, Kaiserslautern
Peter Klein, Kaiserslautern
Philipp Neumann, Hamburg
Simon Stephan, Kaiserslautern
Katrín Stöbener, Kaiserslautern
Jadran Vrabec, Paderborn
Stephan Werth, Kaiserslautern



**Computational
Molecular Engineering**



Computational molecular engineering

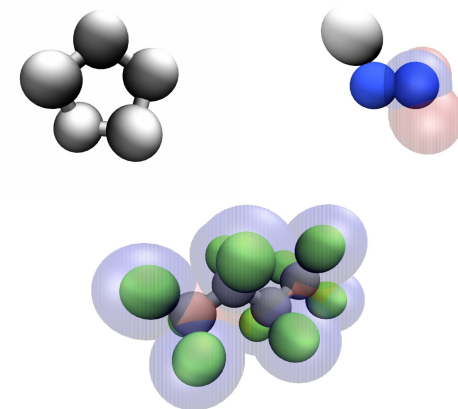


Physical Chemistry
(qualitative validity)



Chemical Engineering
(quantitative reliability)

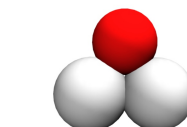
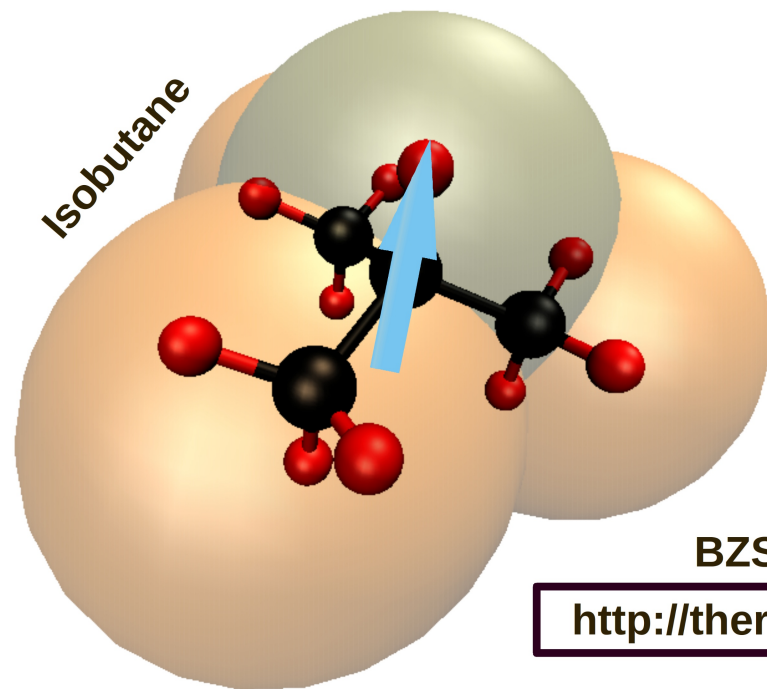
- Realistic representation of pairwise intermolecular interactions
- Short-range repulsion and dispersion as well as long-range electrostatics (multipoles)
- Models with free parameters, adjusted to thermodynamic data
- Reliable interpolation, extrapolation and prediction of fluid properties



**Computational
Molecular Engineering**



Molecular models of the Boltzmann-Zuse Society

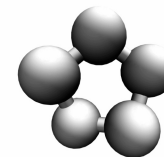


Ethylene oxide

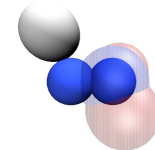


1,2-Dichloroethane

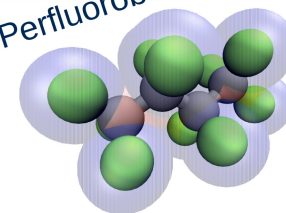
Cyclopentane



Methylhydrazine



Perfluorobutane



BZS Molecular Model Database

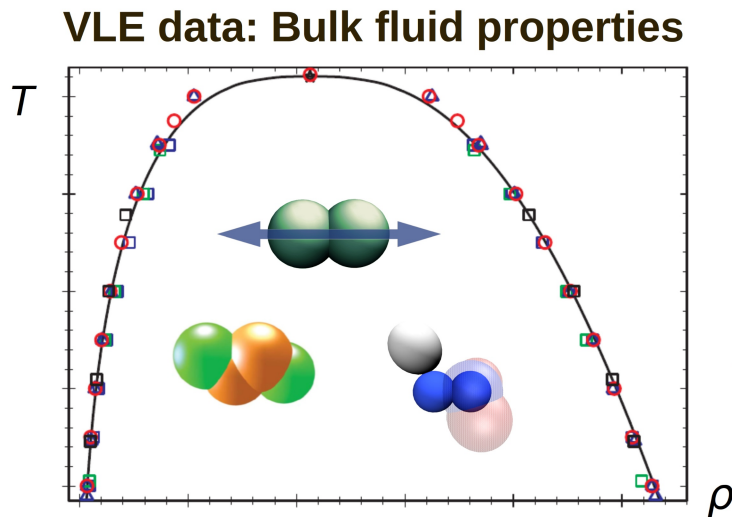
<http://thermovm.mv.uni-kl.de/moleculeDB/>



Computational
Molecular Engineering

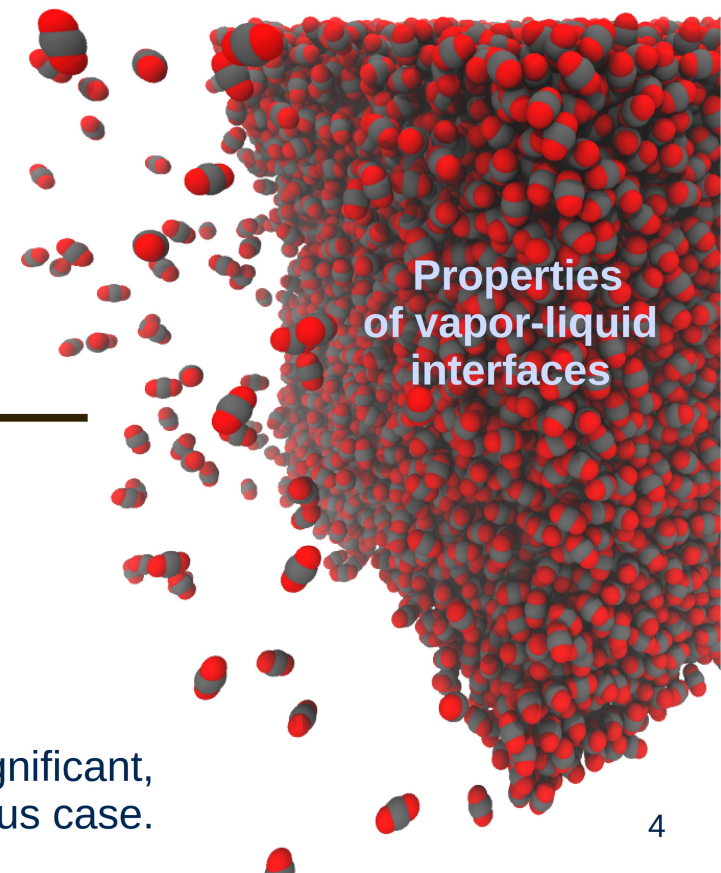
(Model parameters adjusted to vapor-liquid equilibrium data)

Molecular simulation of interfacial properties



prediction
(model property)

validation
(model accuracy)



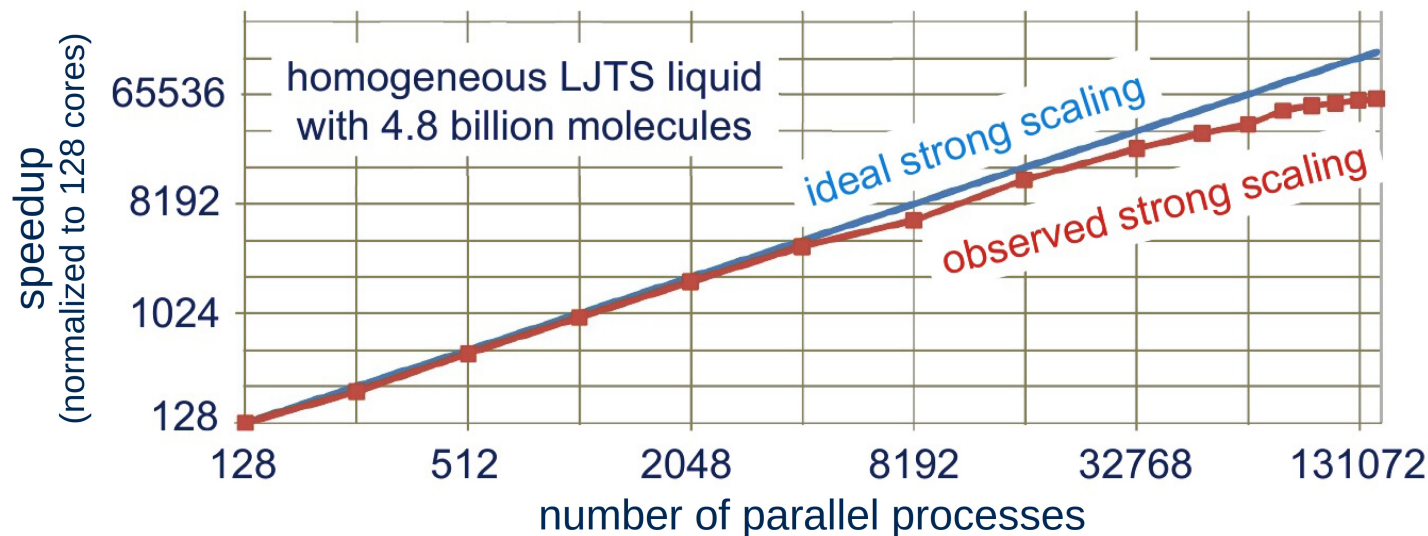
Molecular simulation of heterogeneous systems:

- Greater length scale and greater time scale required.
- Long-range contribution from dispersion becomes significant, whereas it can be handled trivially in the homogeneous case.

Massively-parallel molecular dynamics

<http://www.ls1-mardyn.de/>

(large systems 1: molecular dynamics)^{1,2}



SkaSim



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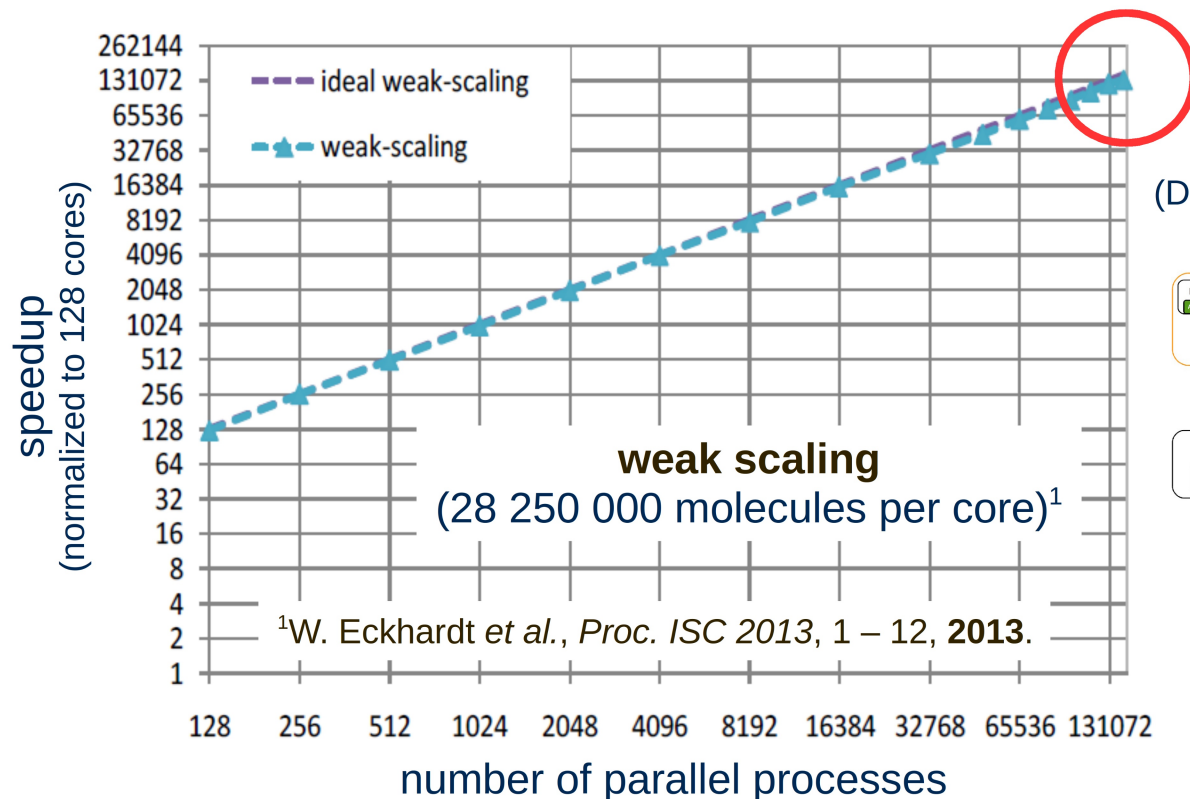


Computational
Molecular Engineering

¹C. Niethammer *et al.*, *J. Chem. Theory Comput.* 10(10), 4455 – 4464, **2014**.

²W. Eckhardt *et al.*, *Proc. ISC 2013*, LNCS 7905, 1 – 12, **2013**.

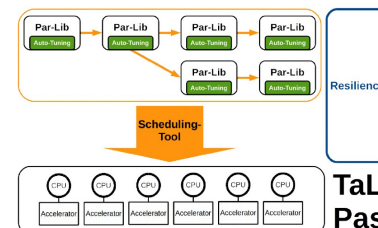
Massively-parallel molecular dynamics



$N = 4\,125\,000\,000\,000$

SuperMUC (146 000 Cores)¹

(December 2017: $N > 20\,000\,000\,000\,000$)



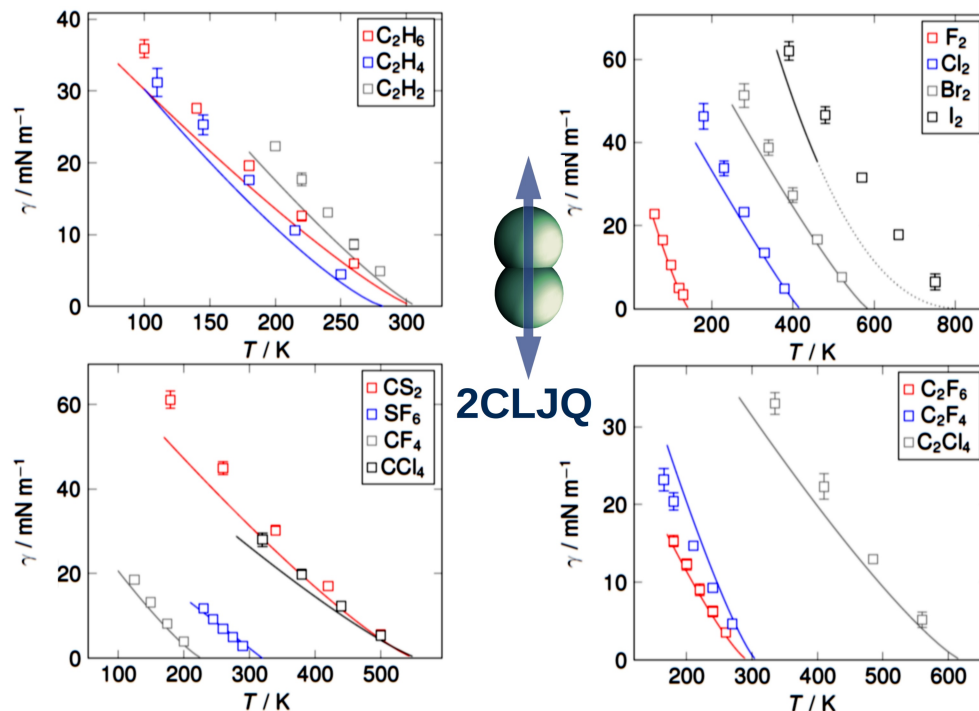
TUM
TECHNISCHE
UNIVERSITÄT
MÜNCHEN



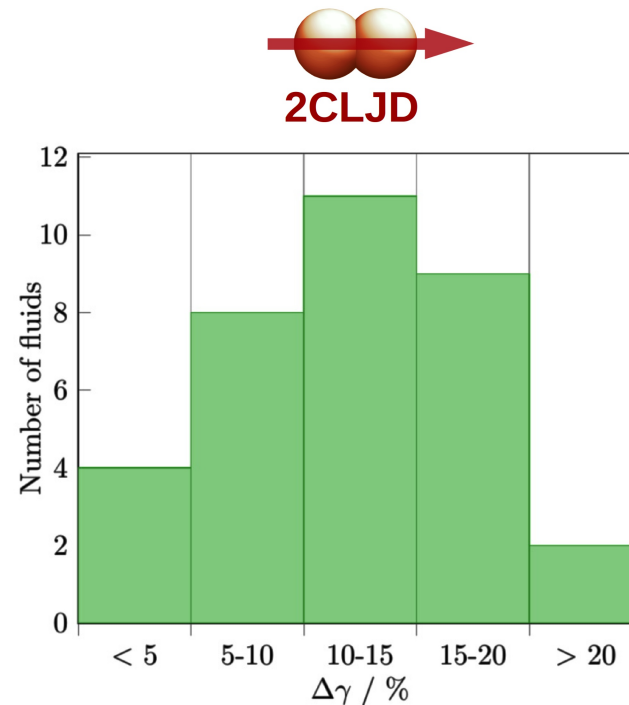
**Computational
Molecular Engineering**

Surface tension predicted by molecular models

2 LJ sites + quadrupole¹



2 LJ sites + dipole²



¹S. Werth et al., *Chem. Eng. Sci.* 121, 110 – 117, **2015**; ²S. Werth et al., *J. Chem. Phys.* 144, 054702, **2016**.



Surface tension predicted by molecular models

Non-polar: LJ

Neon (Ne), Argon (Ar)
Krypton (Kr), Xenon (Xe)
Methane (CH₄)

Dipolar: 2CLJD

Carbon monoxide (CO)
R11 (CFCl₃)
R12 (CF₂Cl₂)
R13 (CF₃Cl)
R13B1 (CBrF₃)
R22 (CHF₂Cl)
R23 (CHF₃)
R41 (CH₃F)
R123 (CHCl₂-CF₃)
R124 (CHFCl-CF₃)
R125 (CHF₂-CF₃)
R134a (CH₂F-CF₃)
R141b (CH₃-CFCl₂)
R142b (CH₃-CF₂Cl)
R143a (CH₃-CF₃)
R152a (CH₃-CHF₂)
R40 (CH₃Cl)
R40B1 (CH₃Br)
Methyl iodide (CH₃I)
R30B1 (CH₂BrCl)
R20 (CHCl₃)
R20B3 (CHBr₃)
R21 (CHFCl₂)
R32 (CH₂F₂)
R30 (CH₂Cl₂)

12 %

Dipolar: 2CLJD (contd.)

R30B2 (CH₂Br₂)
Methylene iodide (CH₂I₂)
R12B2 (CBr₂F₂)
R12B1 (CBrClF₂)
R10B1 (CBrCl₃)
R161 (CH₂F-CH₃)
R150a (CHCl₂-CH₃)
R140 (CHCl₂-CH₂Cl)
R140a (CCl₃-CH₃)
R130a (CH₂Cl-CCl₃)
R160B1 (CH₂Br-CH₃)
R150B2 (CHBr₂-CH₃)
R131b (CH₂F-CCl₃)
R123B1 (CHClBr-CF₃)
R112a (CCl₃-CF₂Cl)
R1141 (CHF=CH₂)
R1132a (CF₂=CH₂)
R1140 (CHCl=CH₂)
R1122 (CHCl=CF₂)
R1113 (CFCl=CF₂)
R1113B1 (CFBr=CF₂)

Quadrupolar: 2CLJQ

Fluorine (F₂)
Chlorine (Cl₂)
Bromine (Br₂)
Iodine (I₂)
Nitrogen (N₂)
Oxygen (O₂)
Carbon dioxide (CO₂)

20 %

Quadrupolar: 2CLJQ (contd.)

Carbon disulfide (CS₂)
Ethane (C₂H₆)
Ethylene (C₂H₄)
Acetylene (C₂H₂)
R116 (C₂F₆)
R1114 (C₂F₄)
R1110 (C₂Cl₄)
Propadiene (CH₂=C=CH₂)
Propyne (CH₃-C≡CH)
Propylene (CH₃-CH=CH₂)
R846 (SF₆)
R14 (CF₄)
R10 (CCl₄)
R113 (CFCl₂-CF₂Cl)
R114 (CF₂Cl-CF₂Cl)
R115 (CF₃-CF₂Cl)
R134 (CHF₂-CHF₂)
R150B2 (CH₂Br-CH₂Br)
R114B2 (CBrF₂-CBrF₂)
R1120 (CHCl=CCl₂)

Multi-site models

Isobutane (C₄H₁₀)
Cyclohexane (C₆H₁₂)
Methanol (CH₃OH)
Ethanol (C₂H₅OH)
Formaldehyde (CH₂=O)
Dimethylether (CH₃-O-CH₃)
Acetone (C₃H₆O)

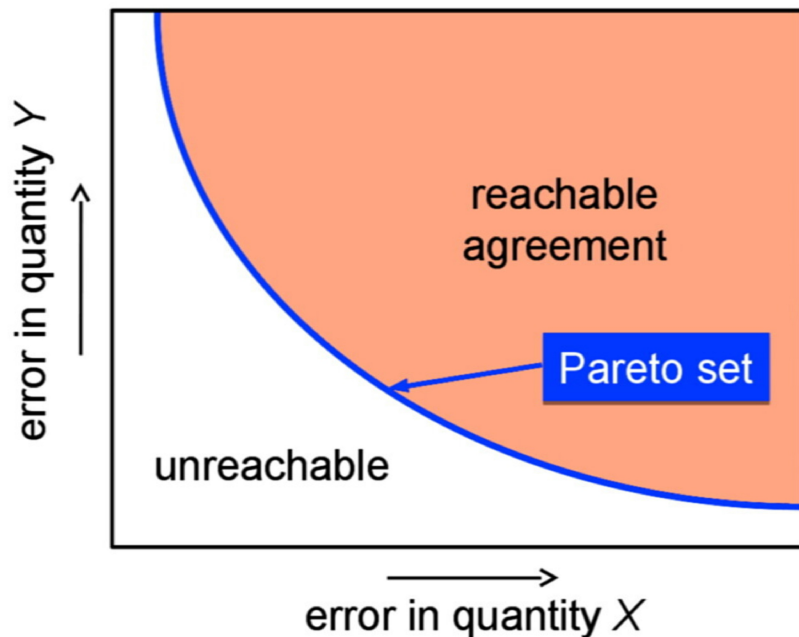
22 %

Multi-site models (contd.)

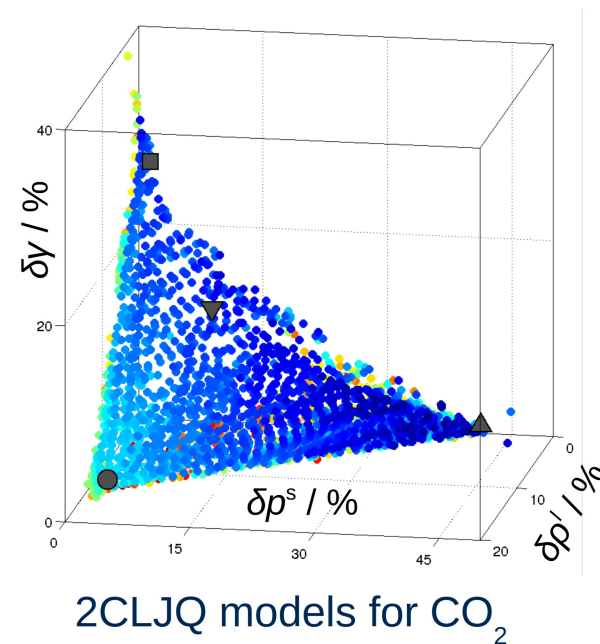
Ammonia (NH₃)
Methylamine (NH₂-CH₃)
Dimethylamine (CH₃-NH-CH₃)
R227ea (CF₃-CHF-CF₃)
Sulfur dioxide (SO₂)
Ethylene oxide (C₂H₄O)
Dimethylsulfide (CH₃-S-CH₃)
Hydrogen cyanide (HCN)
Acetonitrile (NC₂H₃)
Thiophene (SC₄H₄)
Nitromethane (NO₂CH₃)
Phosgene (COCl₂)
Benzene (C₆H₆)
Toluene (C₇H₈)
Chlorobenzene (C₆H₅Cl)
Dichlorobenzene (C₆H₄Cl₂)
Cyclohexanol (C₆H₁₁OH)
Cyclohexanone (C₆H₁₀O)
Cyanogen (C₂N₂)
Cyanogen chloride (CClN)
Formic acid (CH₂O₂)
Ethylene glycol (C₂H₆O₂)
Water (H₂O)
Hydrazine (N₂H₄)
Methylhydrazine (CH₆N₂)
Dimethylhydrazine (C₂H₈N₂)
Perfluorobutane (C₄F₁₀)
Ethyl acetate (C₄H₈O₂)
Hexamethyldisiloxane (C₆H₁₂OSi₂)
Octamethylcyclotetrasiloxane (C₈H₂₄O₄Si₄)

Multicriteria optimization

Pareto optimality criterion



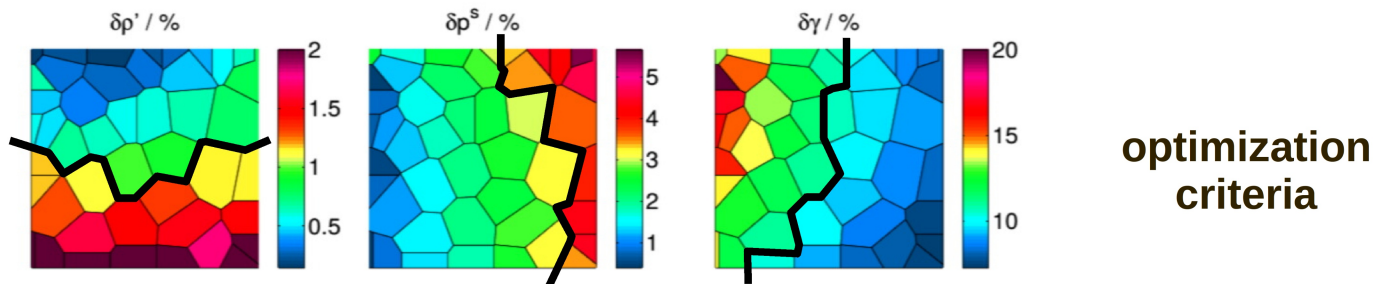
Multiple objectives



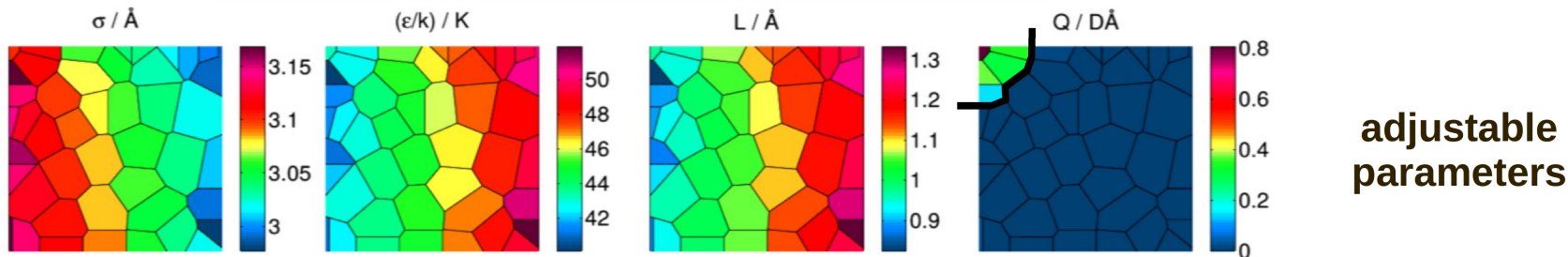
Prerequisite: Thermodynamic properties of the **model class** have been characterized.

Multicriteria optimization of molecular models

Self-organized patch plots¹ visualizing the Pareto front and the Pareto-optimal models:



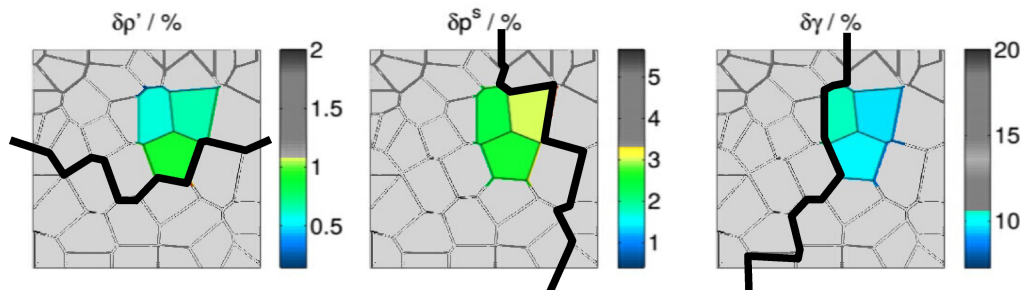
Pareto-optimal 2CLJQ models for oxygen



¹K. Stöbener et al., *Fluid Phase Equilib.* 411, 33 – 42, 2016.

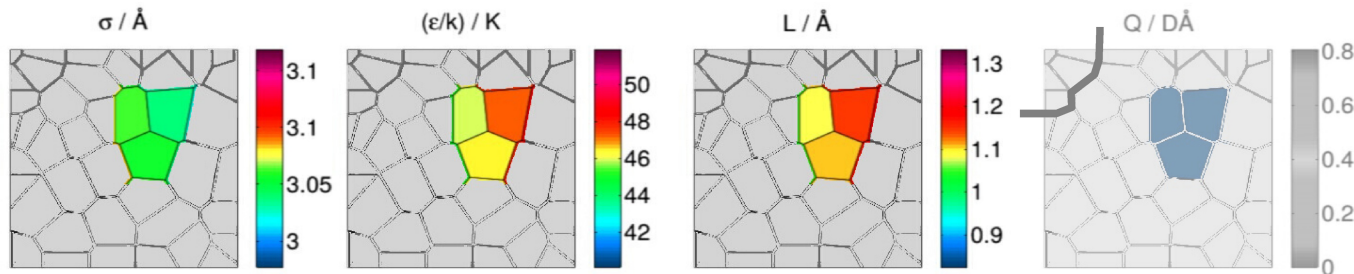
Multicriteria optimization of molecular models

Self-organized **patch plots**¹ visualizing the Pareto front and the Pareto-optimal models:



optimization
criteria

Pareto-optimal 2CLJ models satisfying all constraints



adjustable
parameters

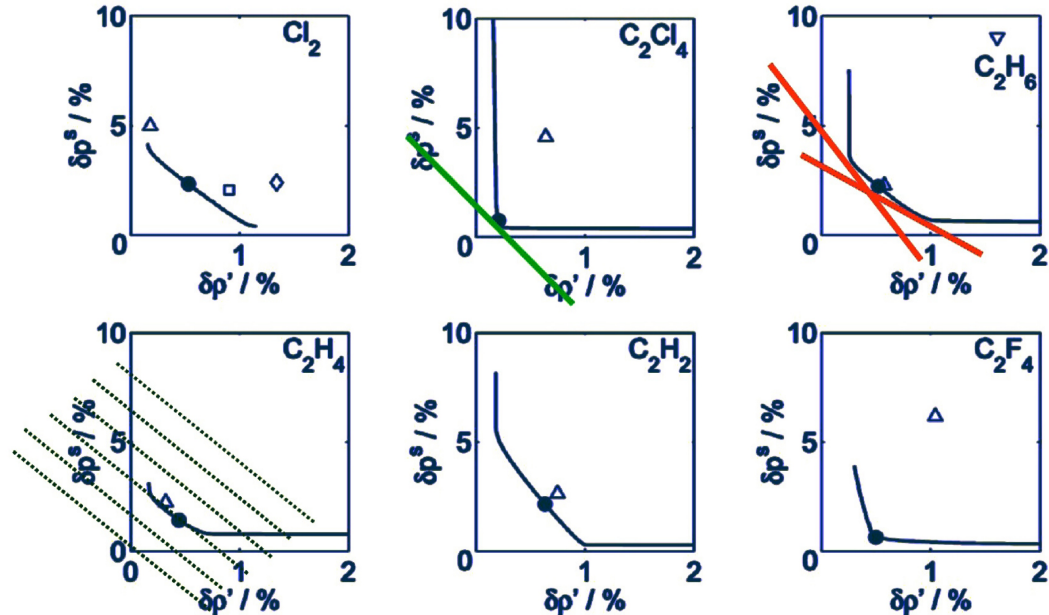
¹K. Stöbener et al., *Fluid Phase Equilib.* 411, 33 – 42, **2016**.

Model resiliency with respect to priority shifts

Pareto knee:

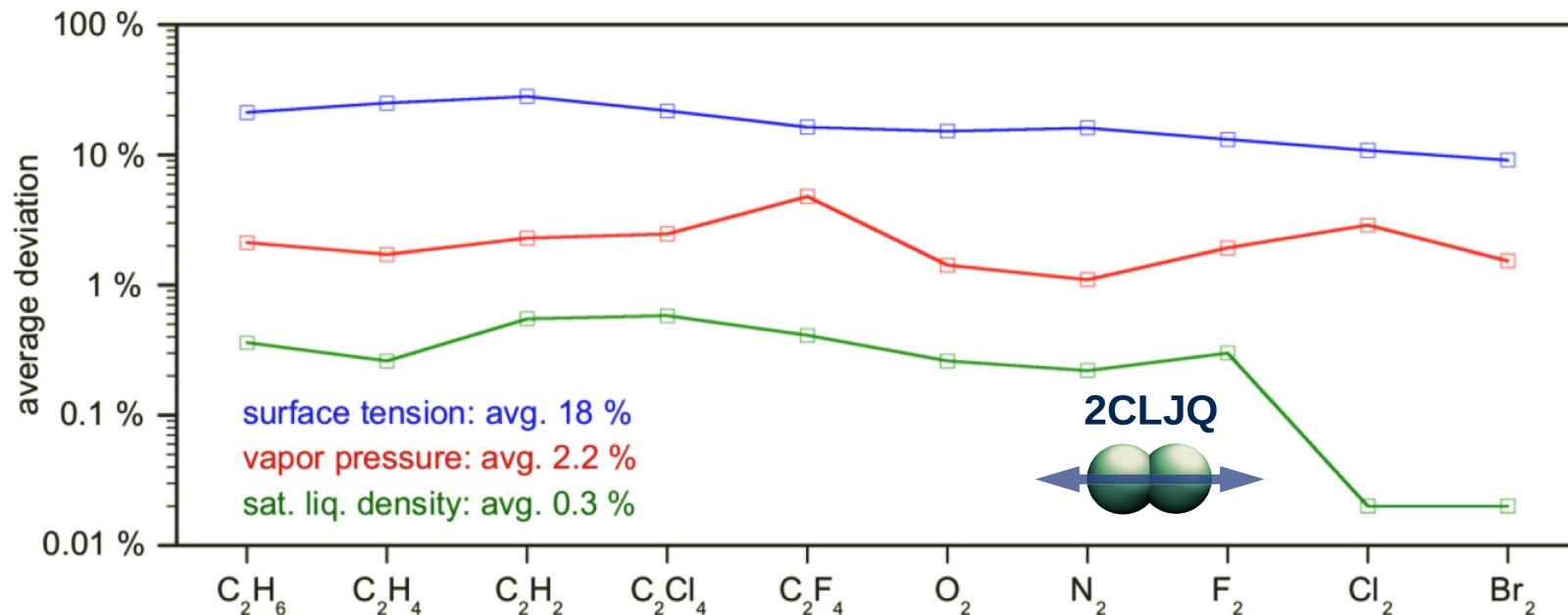
- Position where the curvature of the Pareto front becomes maximal, or
- central point of a possibly non-convex region between maximally curved parts.

The quality of models corresponding to the Pareto knee are relatively robust even if design priorities vary significantly.



Scalarizations based on linear combinations of optimization criteria are inadequate for concave regions of the Pareto front. A systematic exploration is needed to find the Pareto knee.

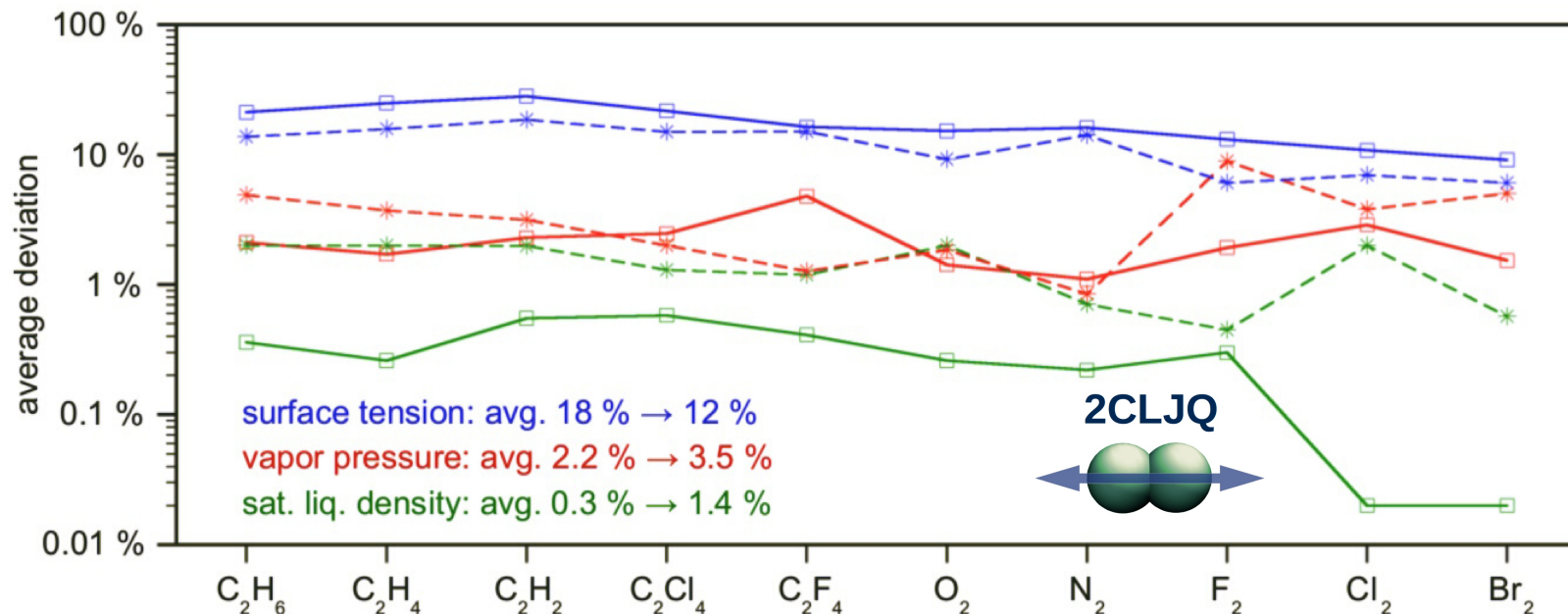
Model reparameterization for quadrupolar fluids^{1, 2}



¹J. Vrabec, J. Stoll, H. Hasse, *J. Phys. Chem. B* 105(48), 12126–12133, **2001**;

²S. Werth, K. Stöbener, P. Klein, K.-H. Küfer, M. Horsch, H. Hasse, *Chem. Eng. Sci.* 121, 110–117, **2015**.

Model reparameterization for quadrupolar fluids¹⁻³



¹J. Vrabec, J. Stoll, H. Hasse, *J. Phys. Chem. B* 105(48), 12126–12133, **2001**;

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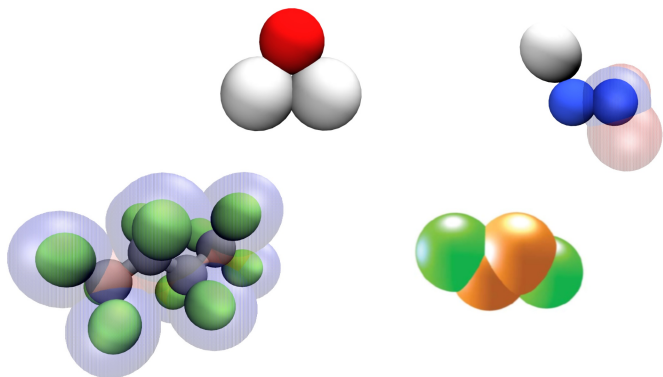
³K. Stöbener, P. Klein, M. Horsch, K.-H. Küfer, H. Hasse, *Fluid Phase Equilib.* 411, 33–42, **2016**.

Paradigm shift in molecular modeling

Molecular model development as an “art” conducted by experts only

- Only a very limited community of people is qualified to design molecular models;
- for each fluid, an expert develops a model, which can be found in the literature;
- the way in which the model was designed and optimized is usually not disclosed.

Users need a background in molecular thermodynamics to assess the model quality, and even then, they **cannot actively contribute** to adjusting the model without repeating the expert work.



BZS Molecular Model Database

<http://thermovm.mv.uni-kl.de/moleculeDB/>



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Molecular modeling as a “technology” accessible to all engineers

- Properties of the model class have been characterized (by previous expert work);
- on this basis, models are flexibly parameterized at the level of engineering practice.

Users who typically do not have a scientific background in molecular simulation methods are enabled to **actively guide** molecular modeling and simulation practice according to their needs.



Engineering Department
American University of Iraq, Sulaimani (AUIS)



**Computational
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Peter Klein
Philipp Neumann

Simon Stephan
Katrin Stöbener
Jadran Vrabec
Stephan Werth

BMBF

