Thermodynamik Kolloquium, Bayreuth, 4.10.2010

Molekulare Modellierung und Simulation physikalisch-chemischer Eigenschaften von Fluiden für industrielle Anwendungen

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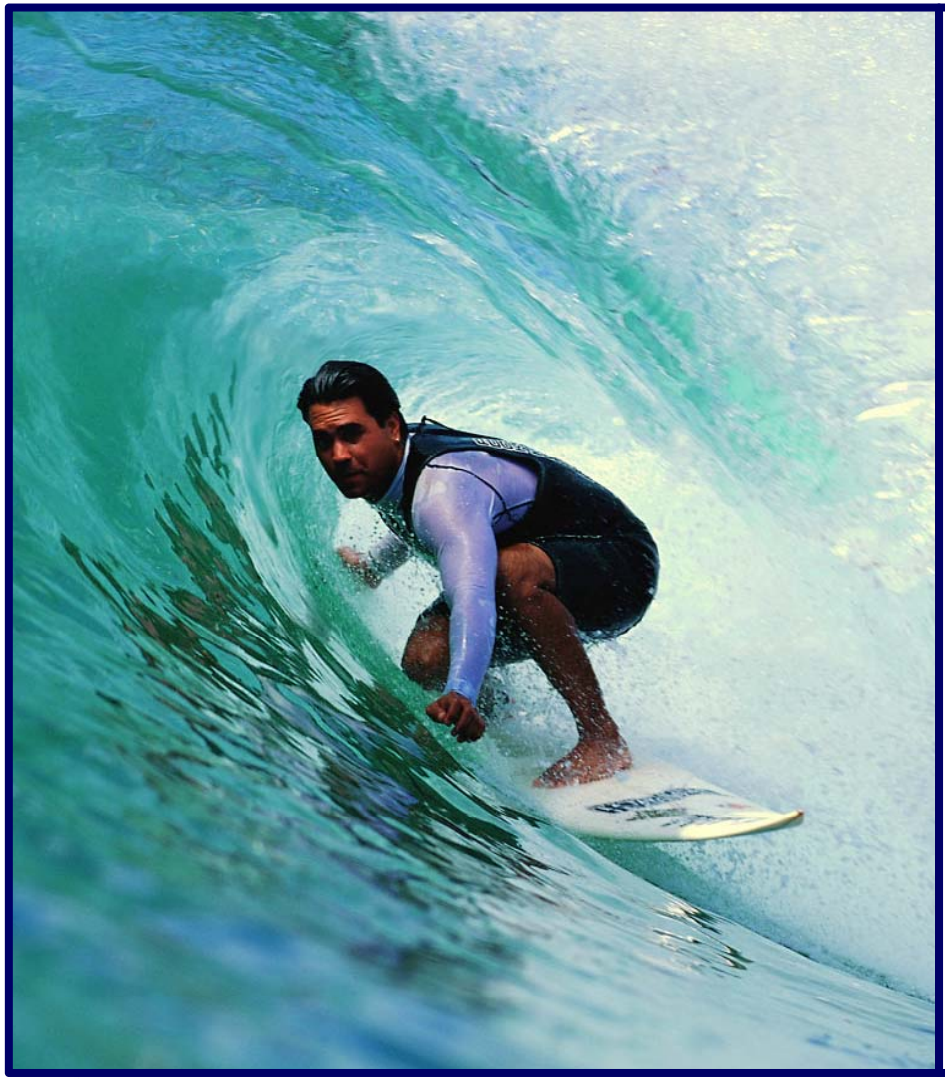
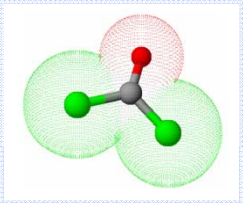
SPP 1155 DFG
Deutsche Forschungsgemeinschaft TFB 66
BASF The Chemical Company
Universität Paderborn Die Universität der Informationsgesellschaft
Computational Molecular Engineering

Industrially Important Hazardous Chemicals

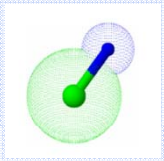


Industrially Important Hazardous Systems

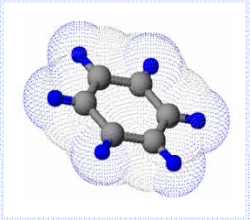
Phosgene Group



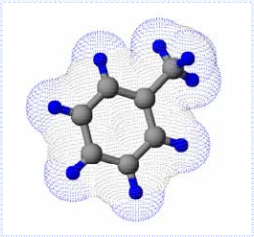
CCl_2O



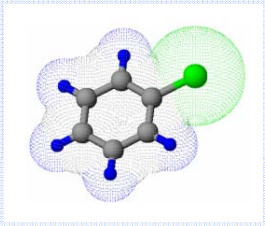
HCl



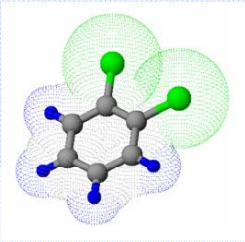
C_6H_6



$C_6H_5\text{-}CH_3$

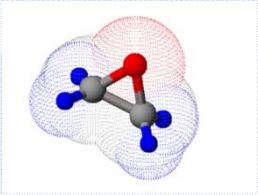


$C_6H_5\text{-}Cl$

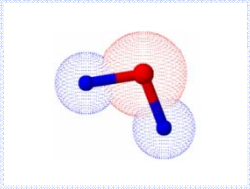


$o\text{-}C_6H_4\text{-}Cl_2$

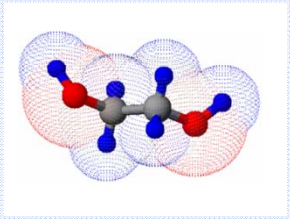
Ethylene Oxide Group



C_2H_4O



H_2O



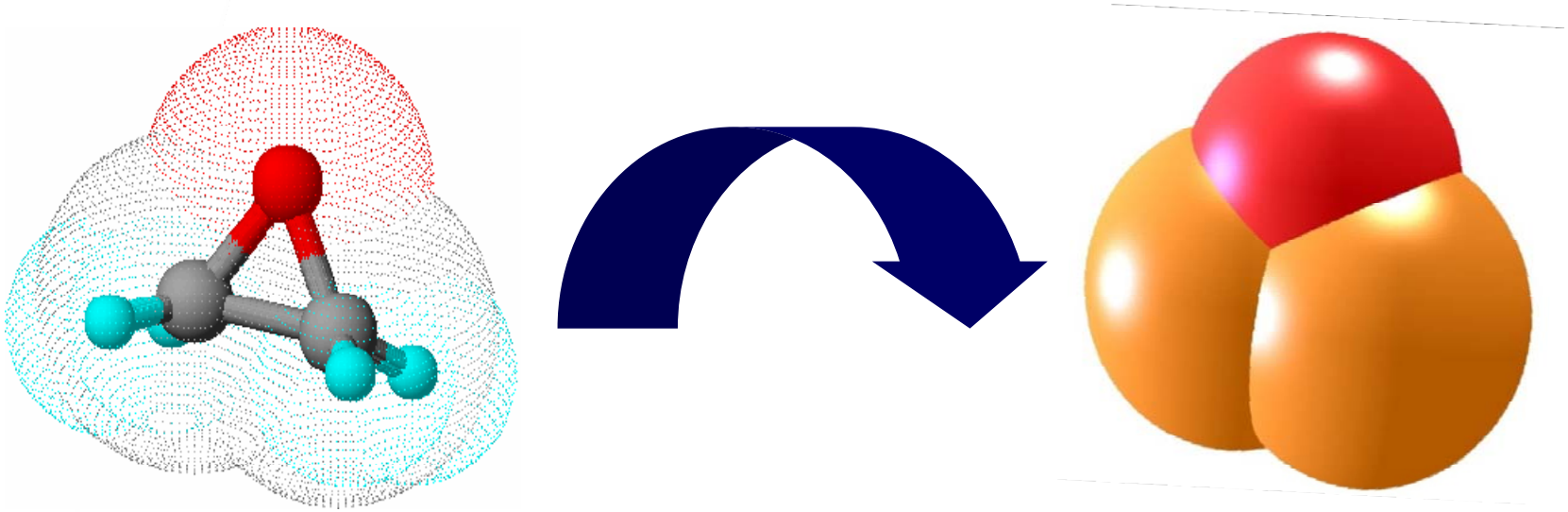
$HO(CH_2)_2OH$

- high economic interest
- difficult experiments
- few reliable data
- need for predictive modeling and simulation

- Excellent test cases for molecular modeling and simulation

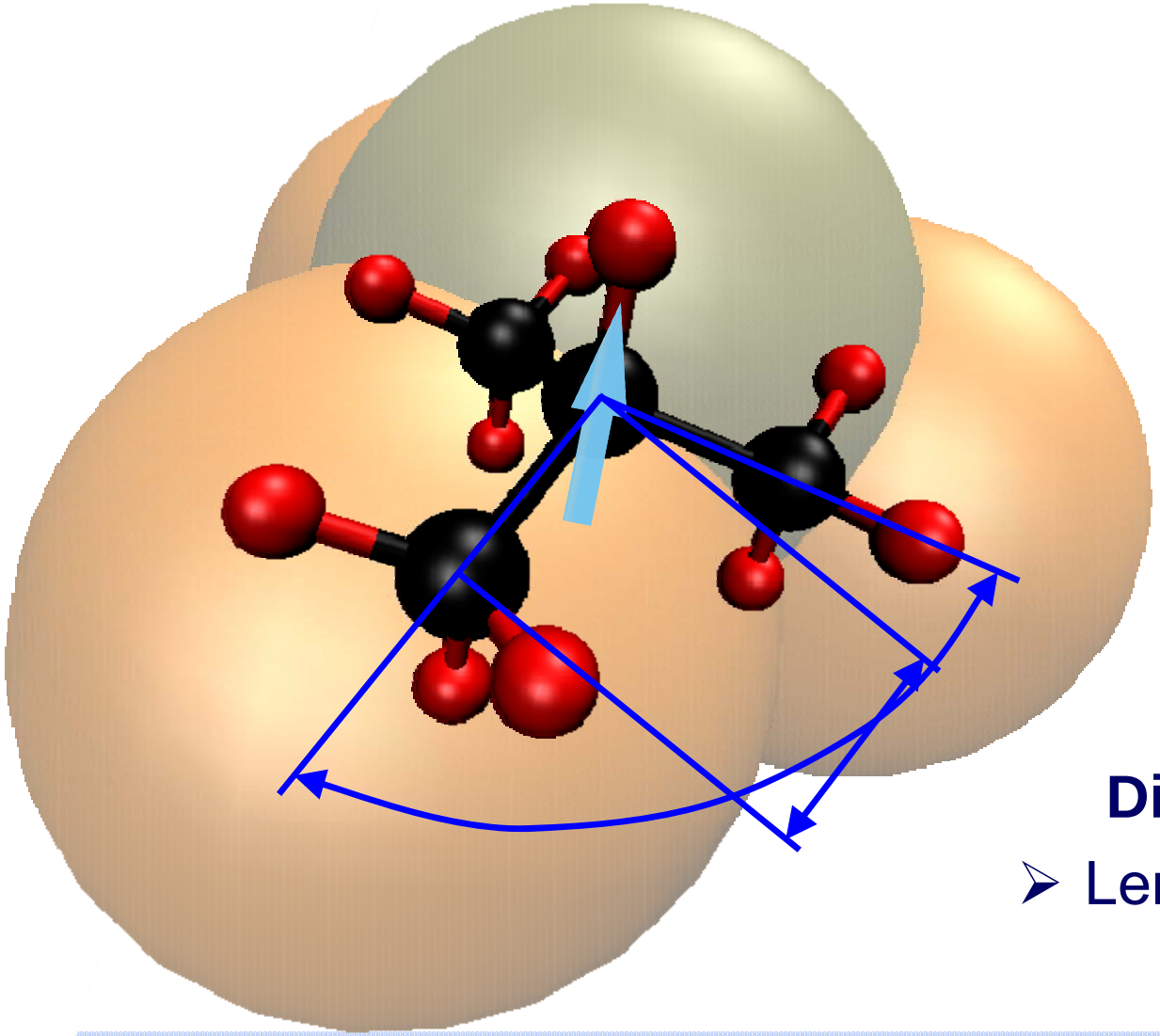
Molecular Model Type

Example: Ethylene Oxide



- Multicenter Lennard-Jones + electrostatic sites
- Rigid
- United atom approach

Molecular Model Development



Geometry:

- bond lengths
- bond angles
- **QM**

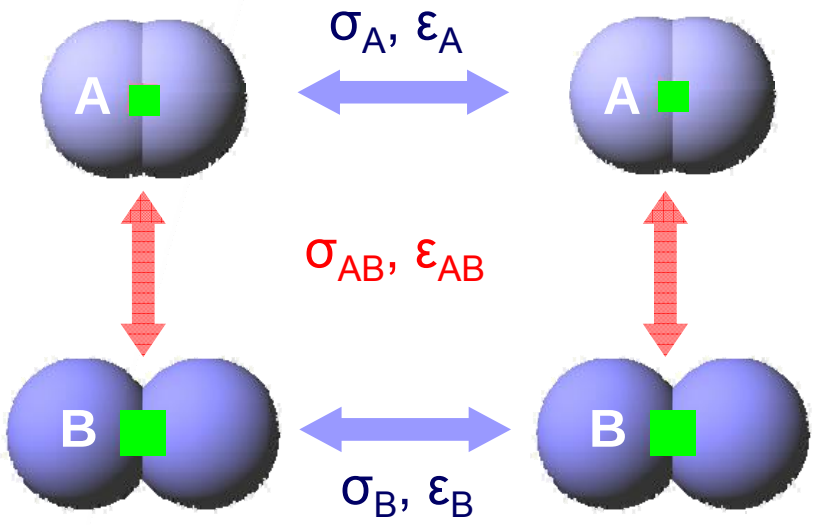
Electrostatics:

- partial charges
- dipoles
- quadrupoles
- **QM / VLE**

Dispersion, Repulsion:

- Lennard-Jones potentials
- **VLE**

Molecular Modelling of Mixtures



Predictions $\xi = 1$

or

State-independent parameter ξ fitted to **one** experimental data point *p(T,x)* oder *H(T)*

Unlike interaction A-B:

- Electrostatics fully predictive
- Lennard-Jones parameters from combination rules

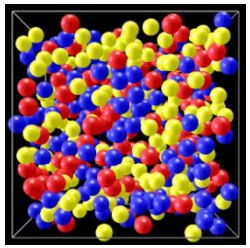
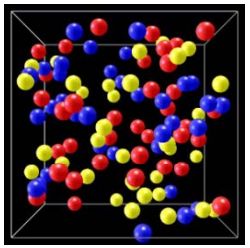
Modified Lorentz-Berthelot

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2$$

$$\varepsilon_{AB} = \xi \cdot \sqrt{\varepsilon_A \varepsilon_B}$$

From Molecular Models to Physico-Chemical Properties

- **Methods**

  - Grand Equilibrium (VLE simulation)

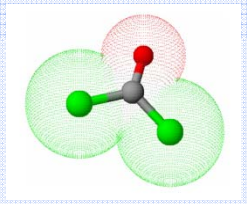
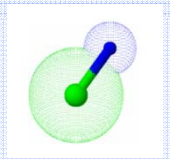
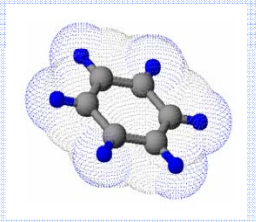
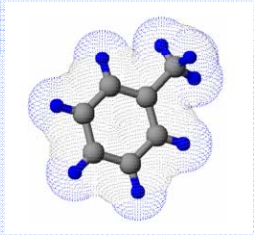
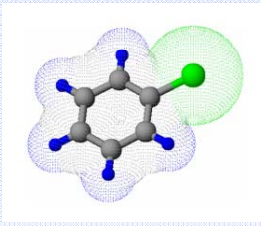
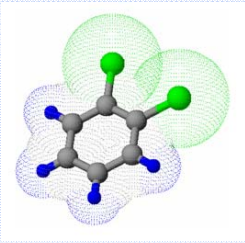
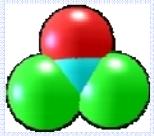
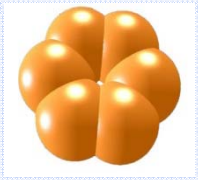
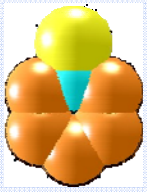
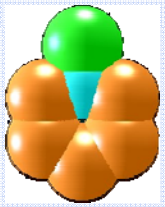
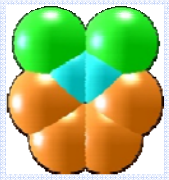
- **Software**

  - *ms2* (simulation of thermodynamic properties)

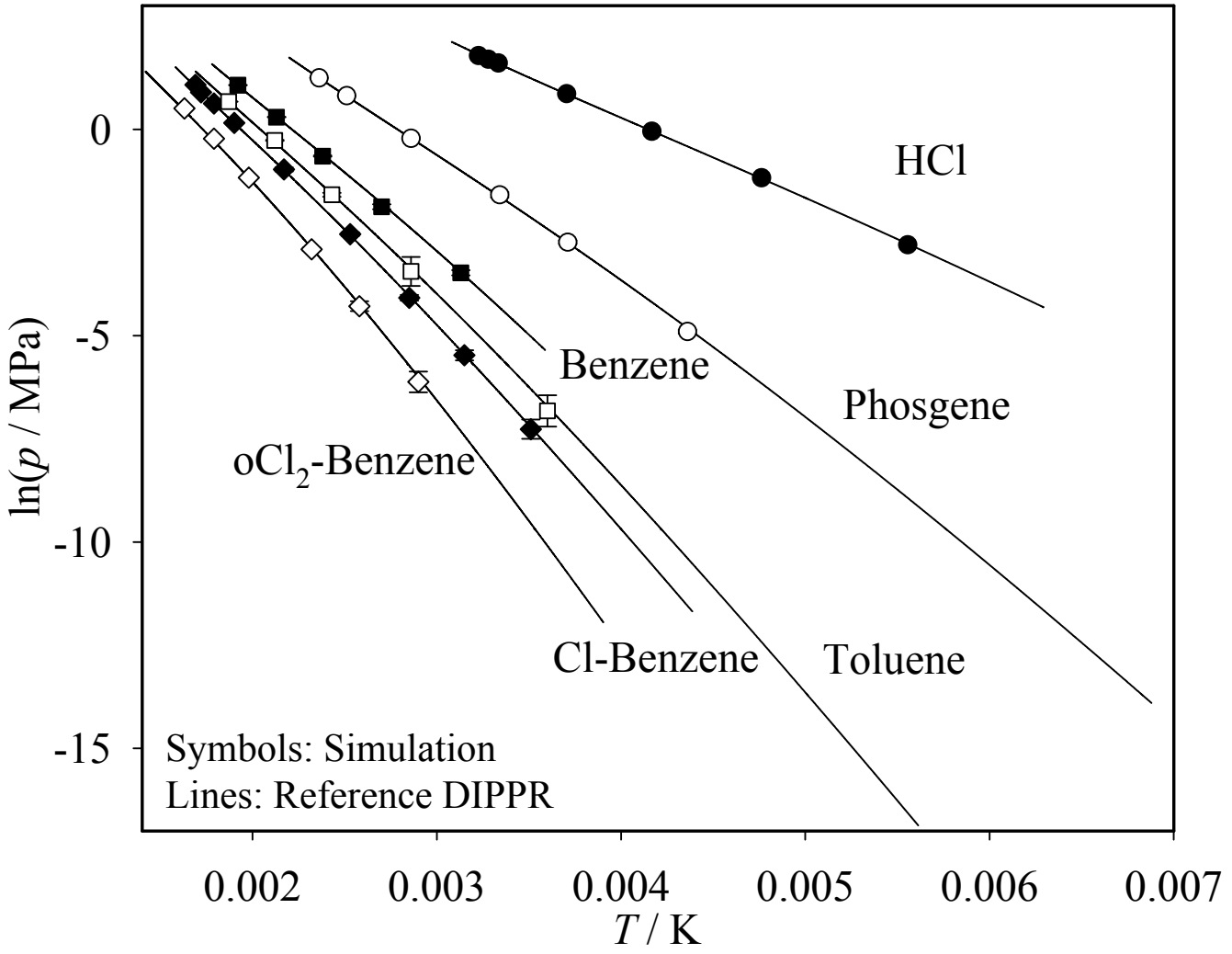
- **Hardware**

  - Parallel computing

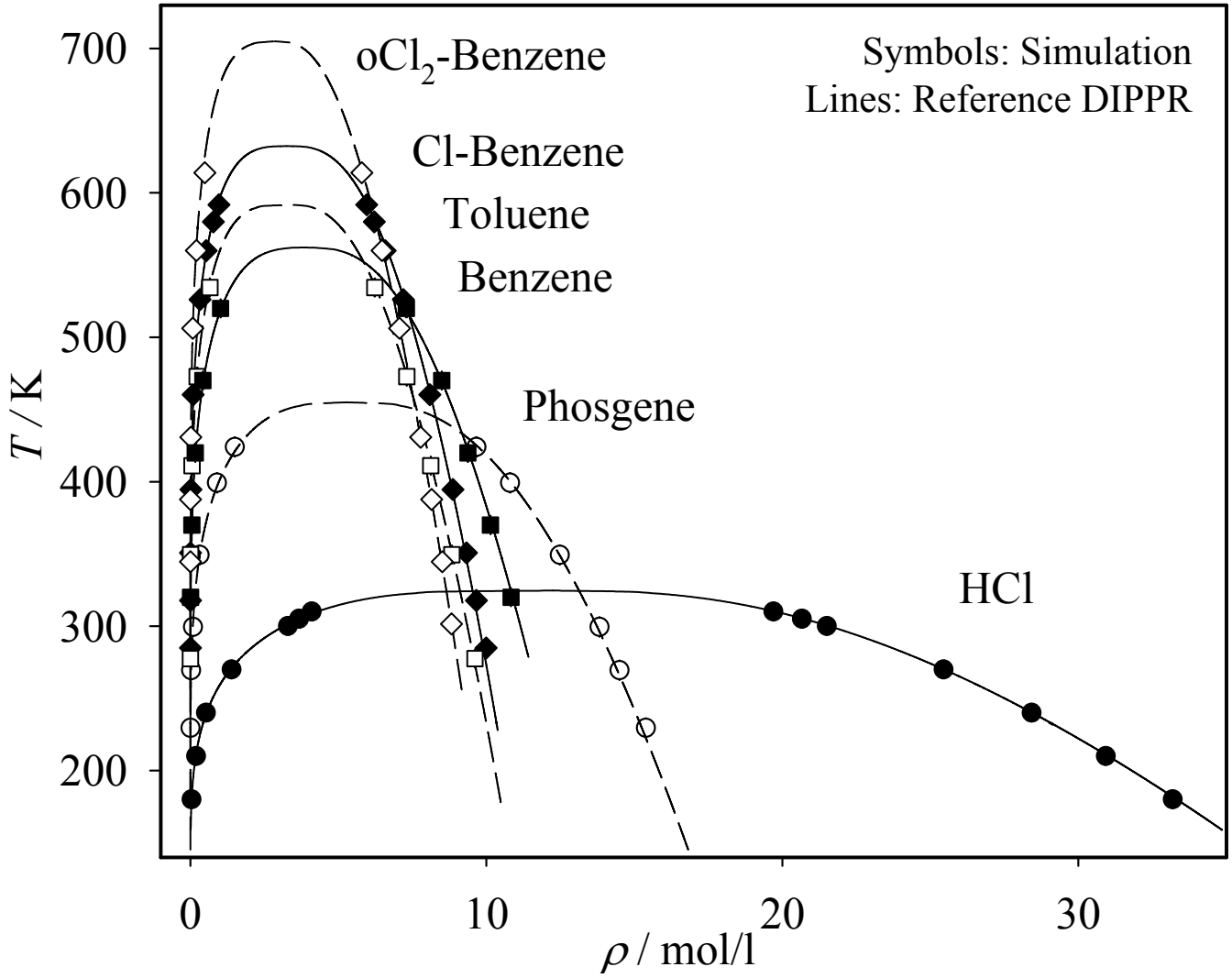
Phosgene Group: Pure Component Models

Phosgene	Hydrogen Chloride	Benzene	Toluene	Chloro-Benzene	o-Dichloro-Benzene
					
CCl_2O	HCl	C_6H_6	$C_6H_5\text{-}CH_3$	$C_6H_5\text{-}Cl$	$o\text{-}C_6H_4\text{-}Cl_2$
					

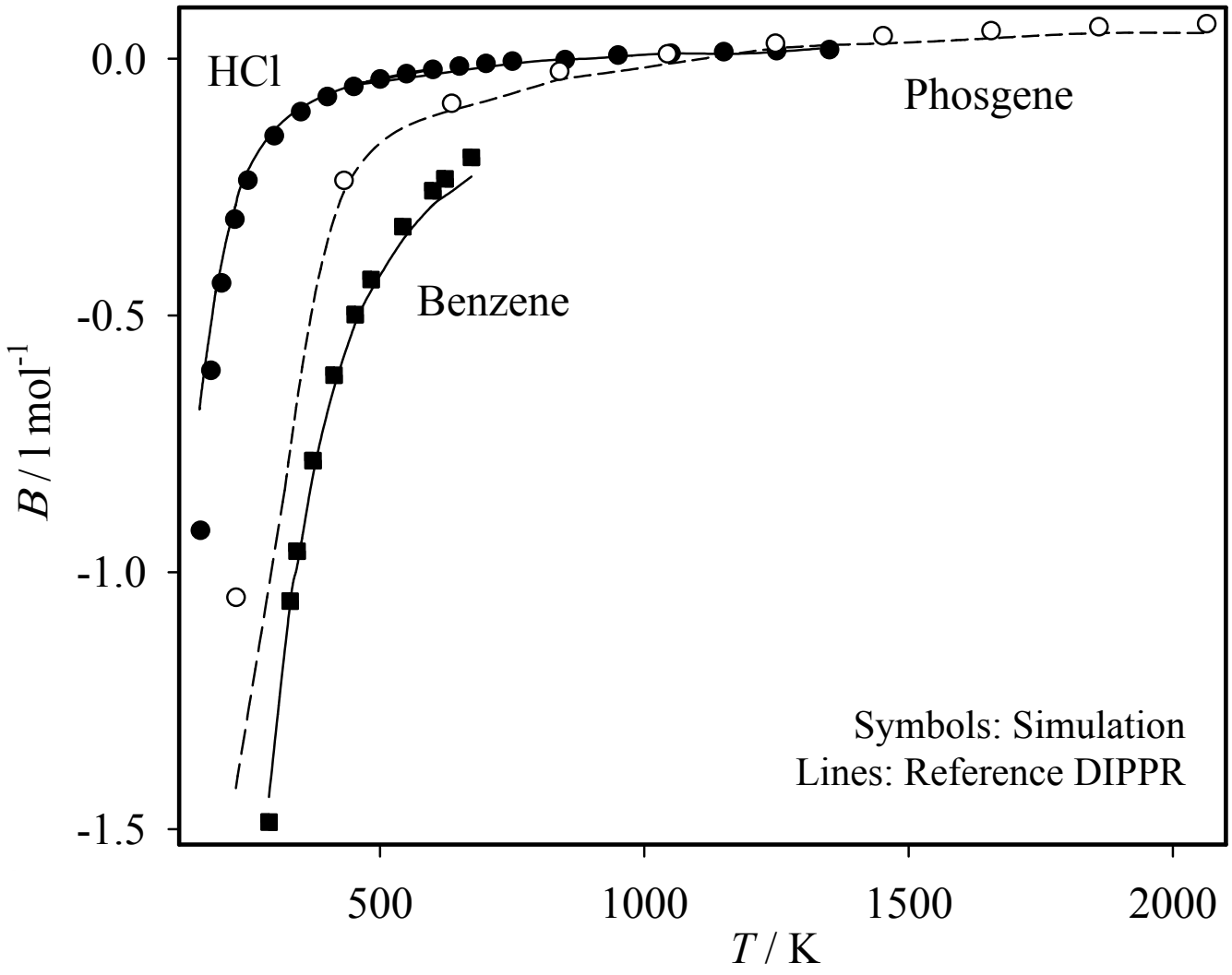
Vapor Pressures



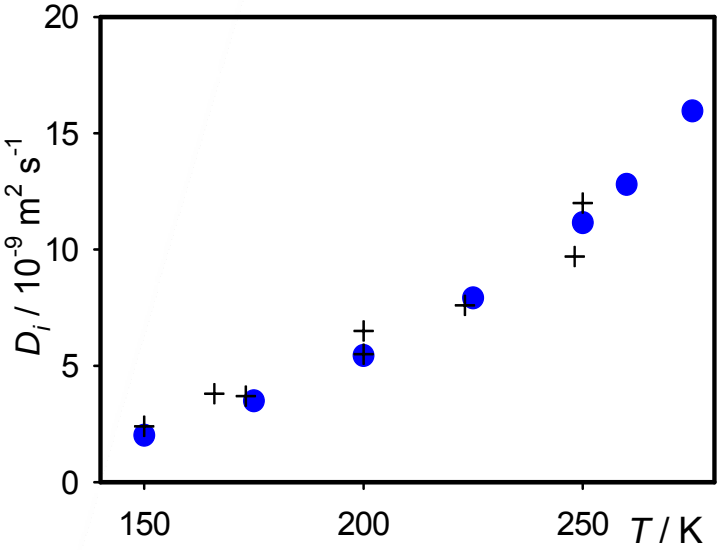
Saturated Densities

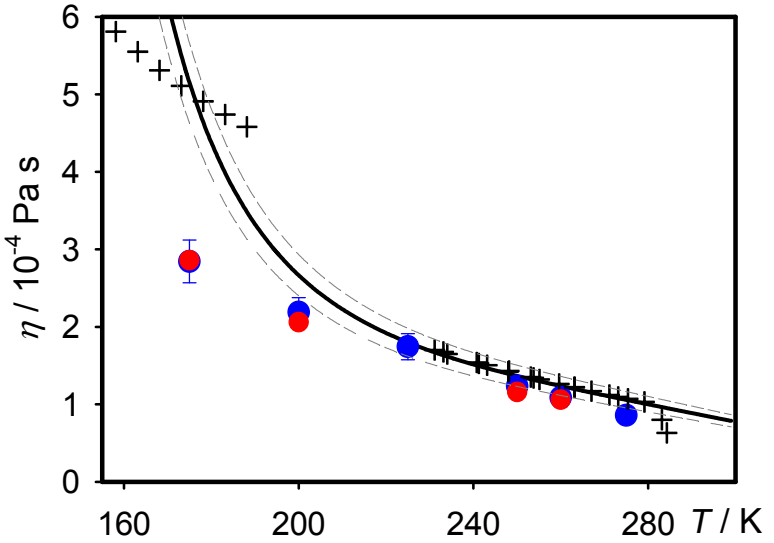


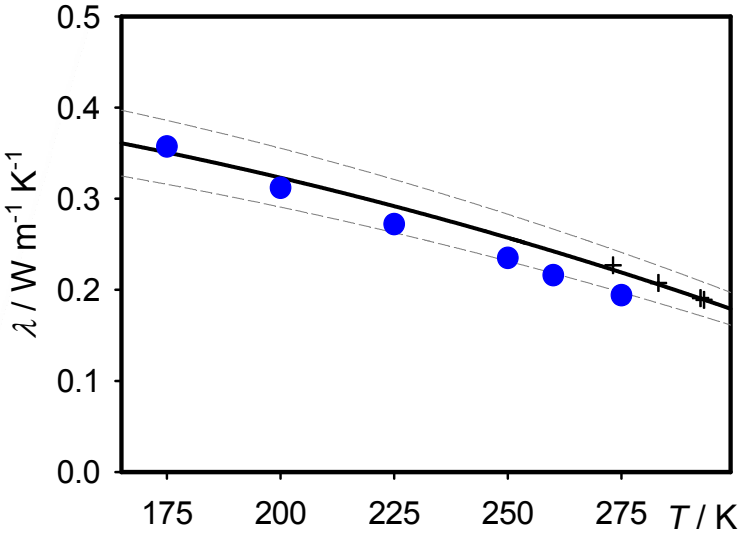
Predictions: Second Virial Coefficients



Predictions: Transport Properties of Liquid HCl





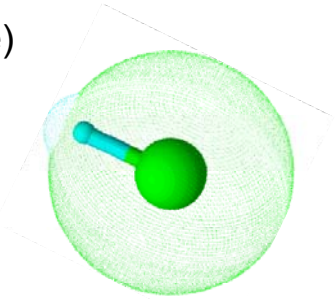


Prediction EMD Simulation

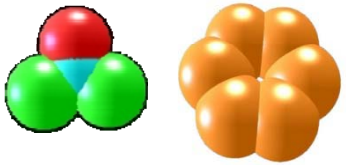
Prediction NEMD Simulation

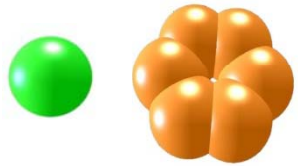
\+ Experiment (Literature)

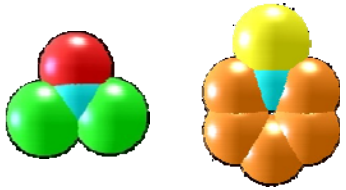
All Data @ 0.1 MPa

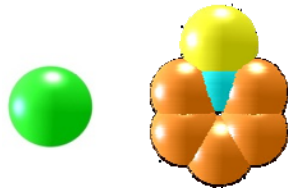


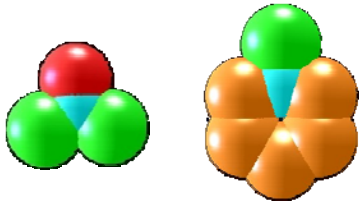
Phosgene Group: Studied Binary Mixtures

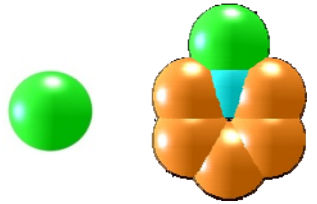
Phosgene + Benzol 

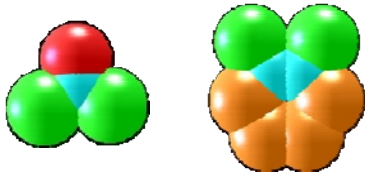
HCl + Benzene 

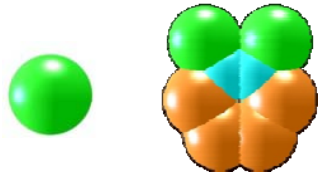
Phosgene + Toluol 

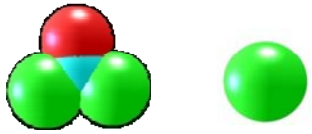
HCl + Toluene 

Phosgene + Cl-Benzene 

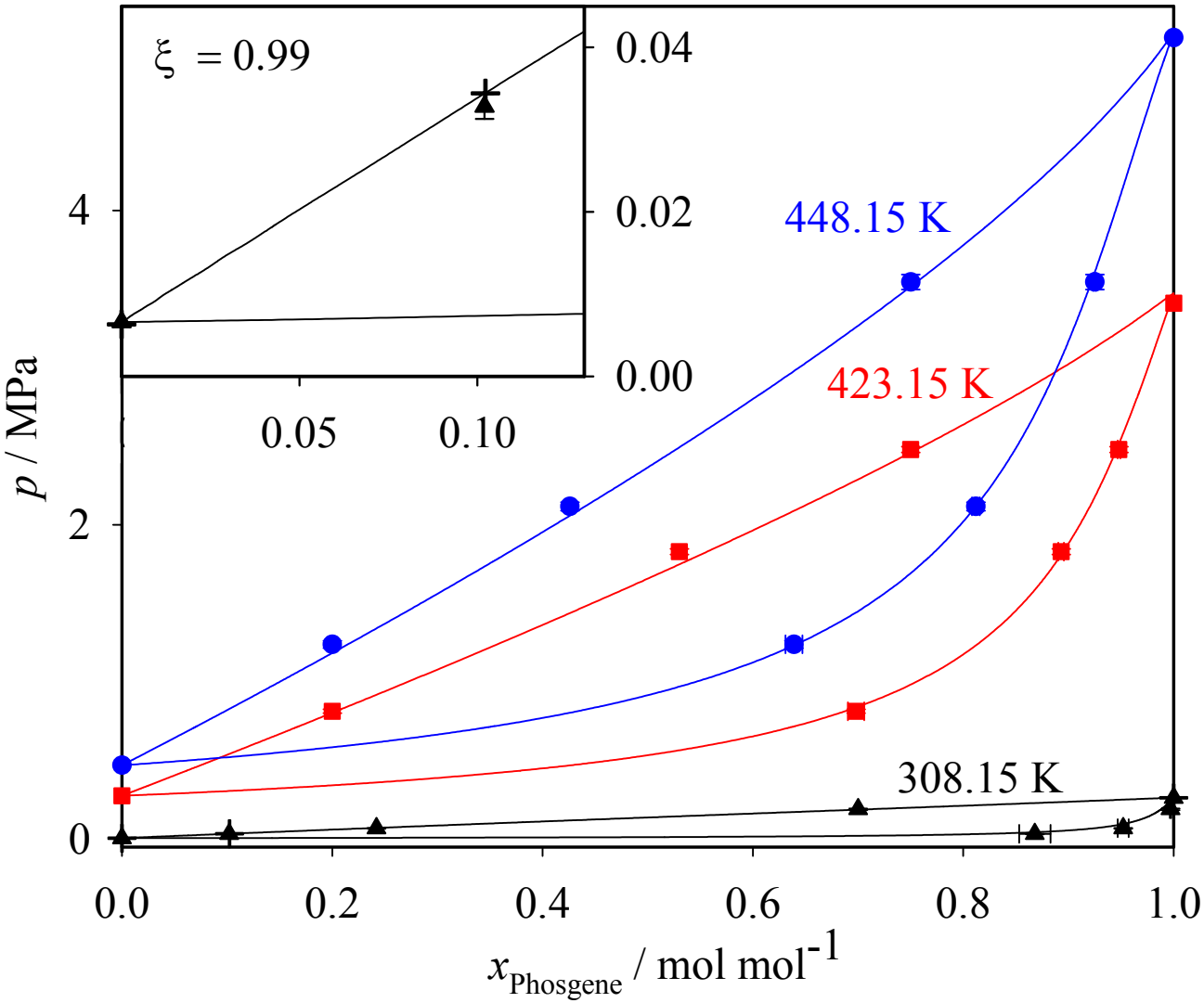
HCl + Cl-Benzene 

Phosgene + o-Cl_2-Benzene 

HCl + o-Cl_2-Benzene 

Phosgene + HCl 

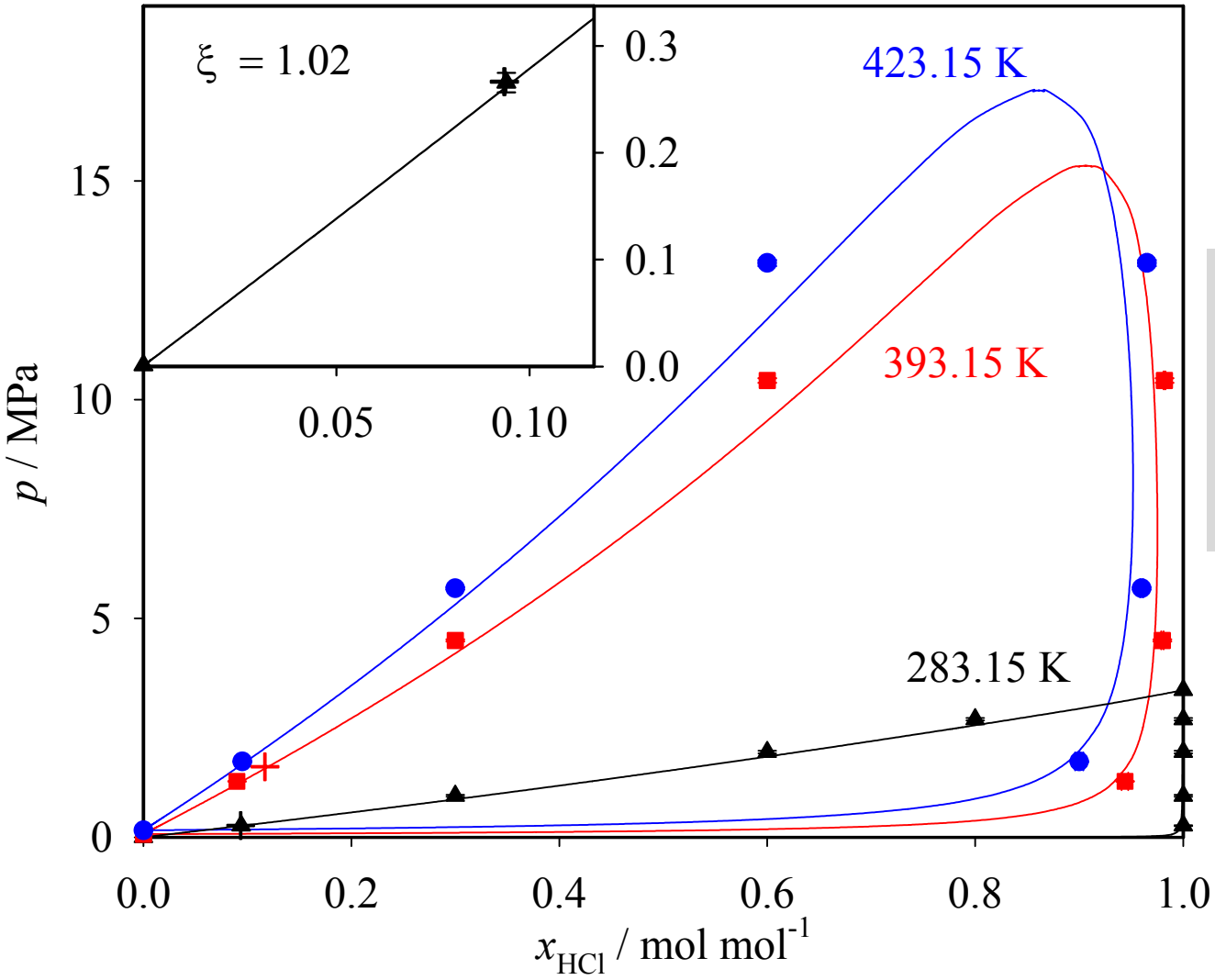
Vapor-Liquid Equilibrium Phosgene + Toluene



Case:
Molecular simulation and EOS agree well

Symbols: simulation (full)
experiment (cross)
Lines: Peng-Robinson EOS

Vapor-Liquid Equilibrium HCl + Chlorobenzene

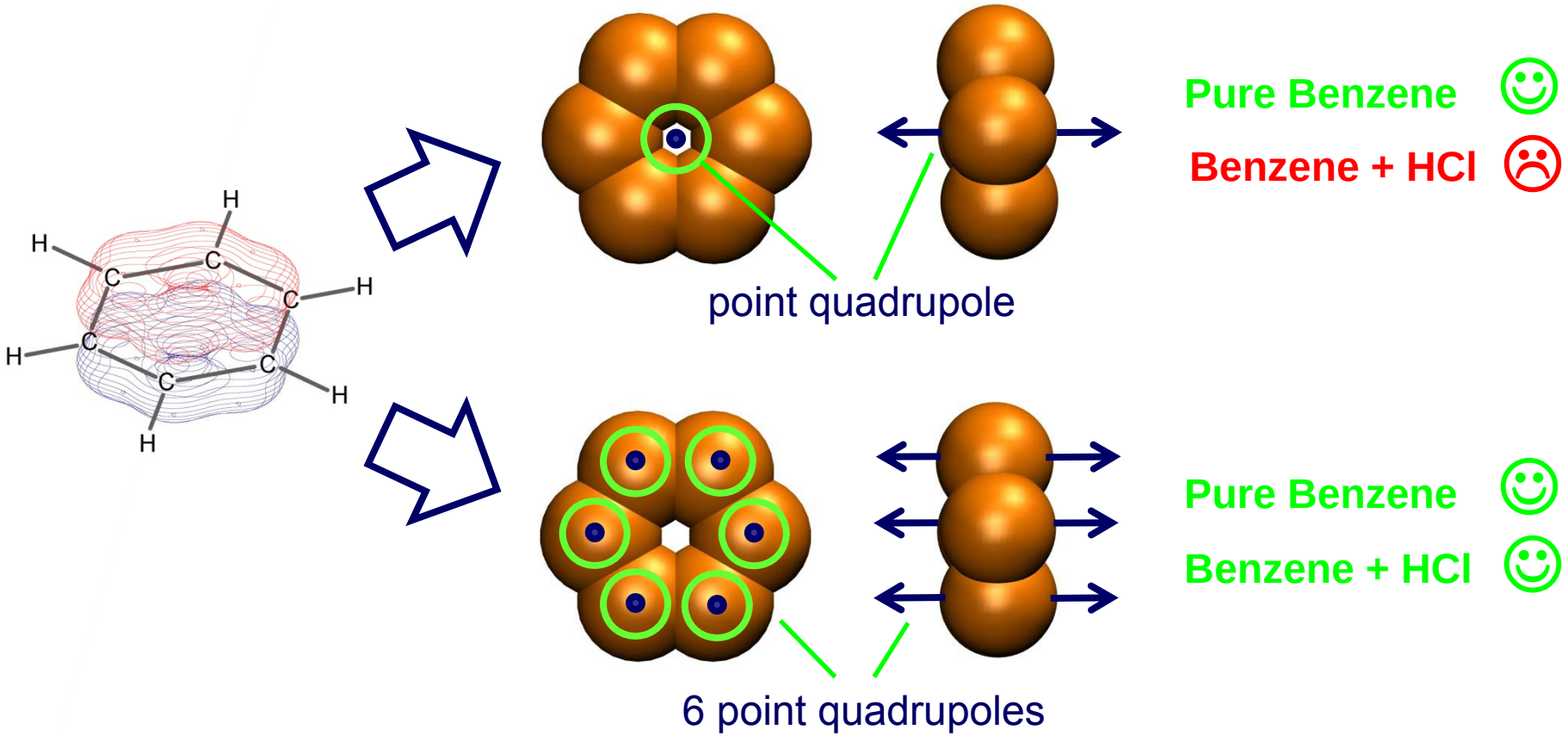


Case:

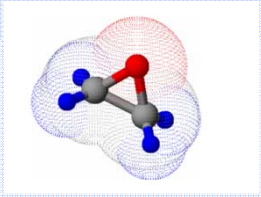
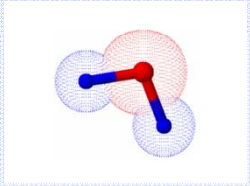
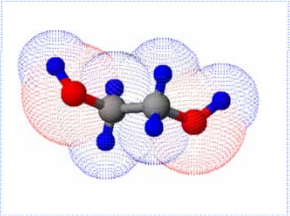
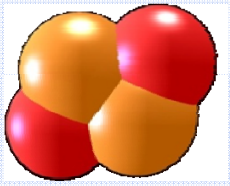
- good predictions both by molecular simulation and EOS
- deviations upon approaching critical point

Symbols: simulation (full)
experiment (cross)
Lines: Peng-Robinson EOS

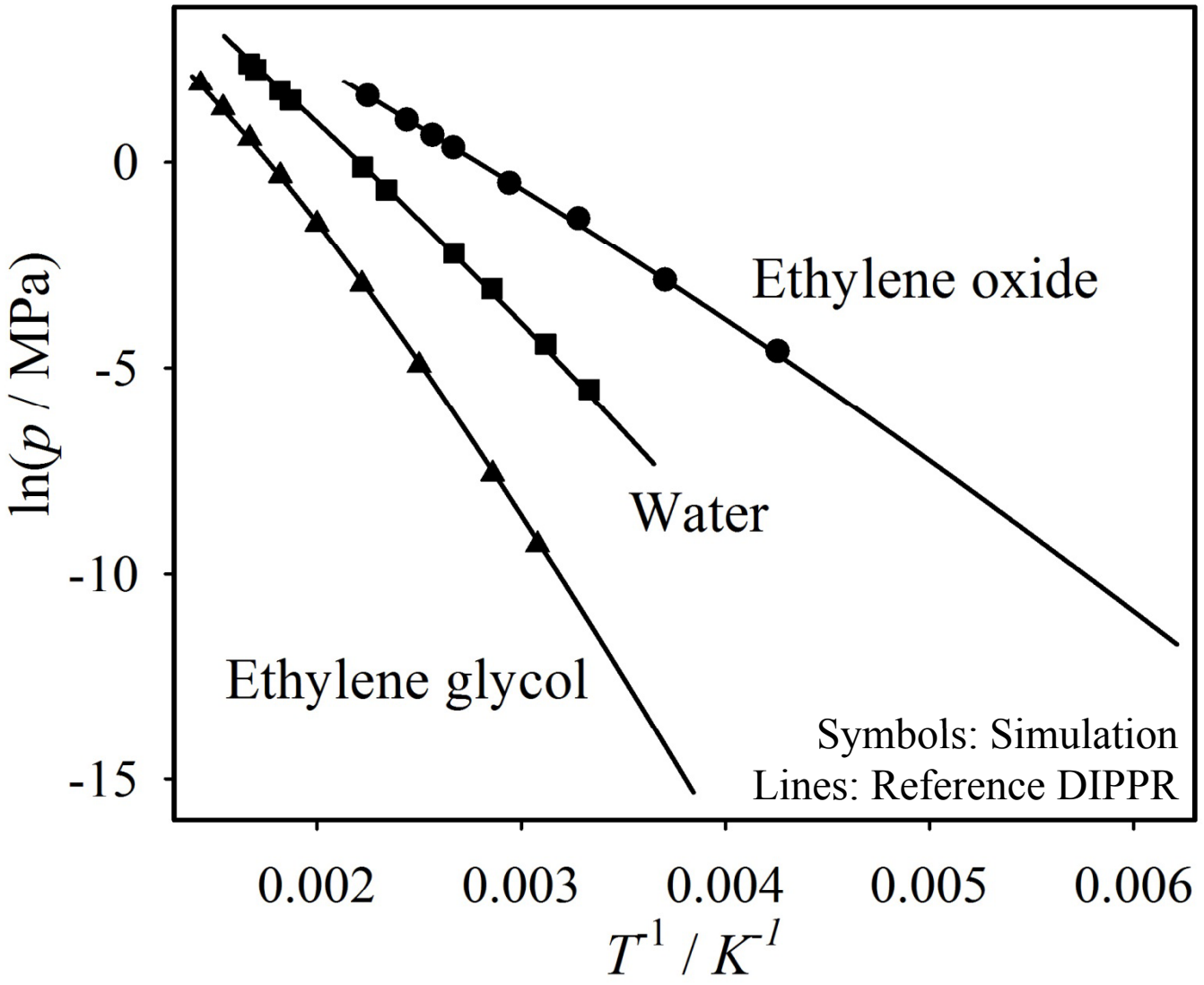
Pitfalls: Modeling Benzene



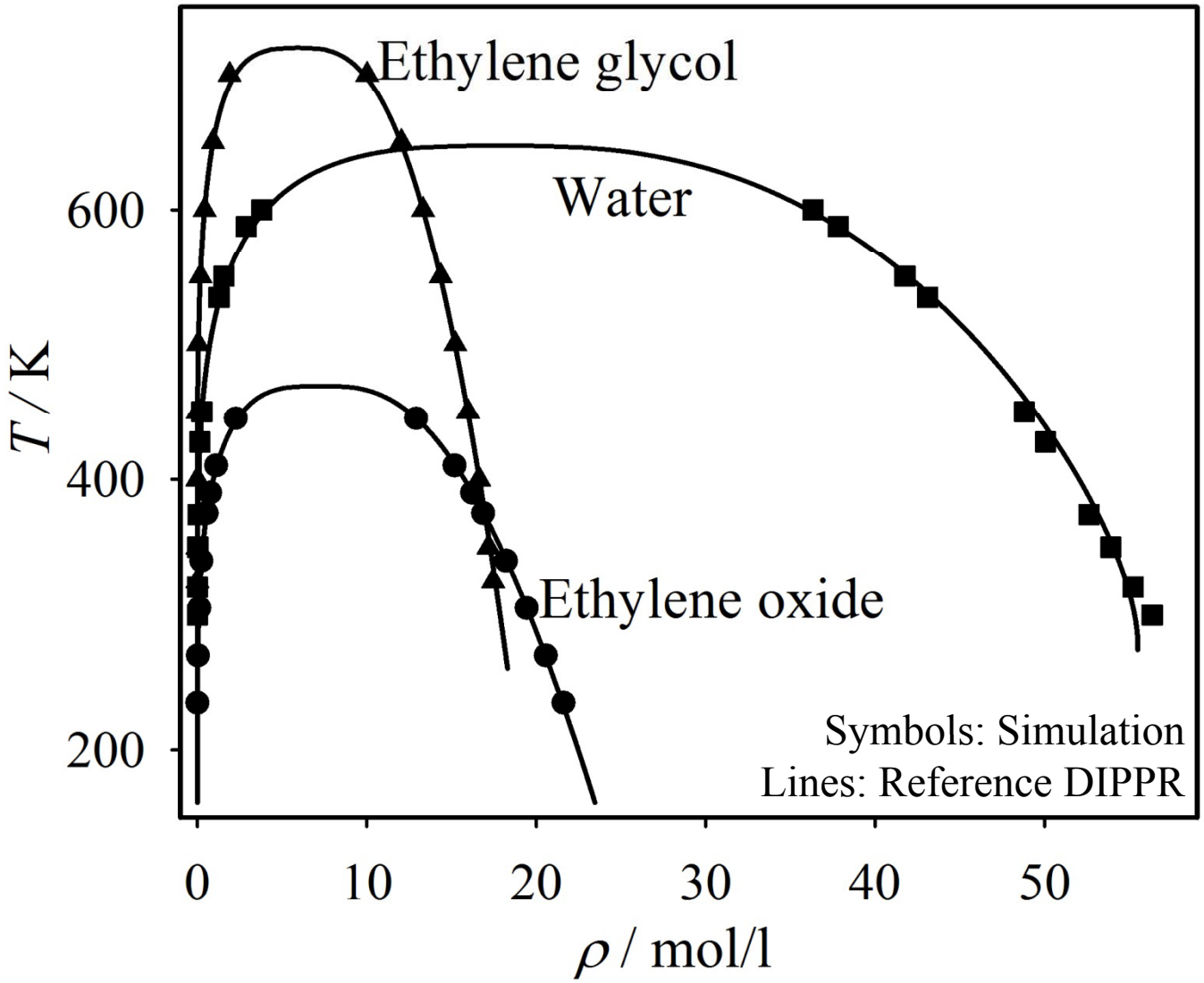
Ethylene Oxide Group: Pure Component Models

Ethylene Oxide	Water	Ethylene Glycole
		
C_2H_4O	H_2O	$HO(CH_2)_2OH$
		

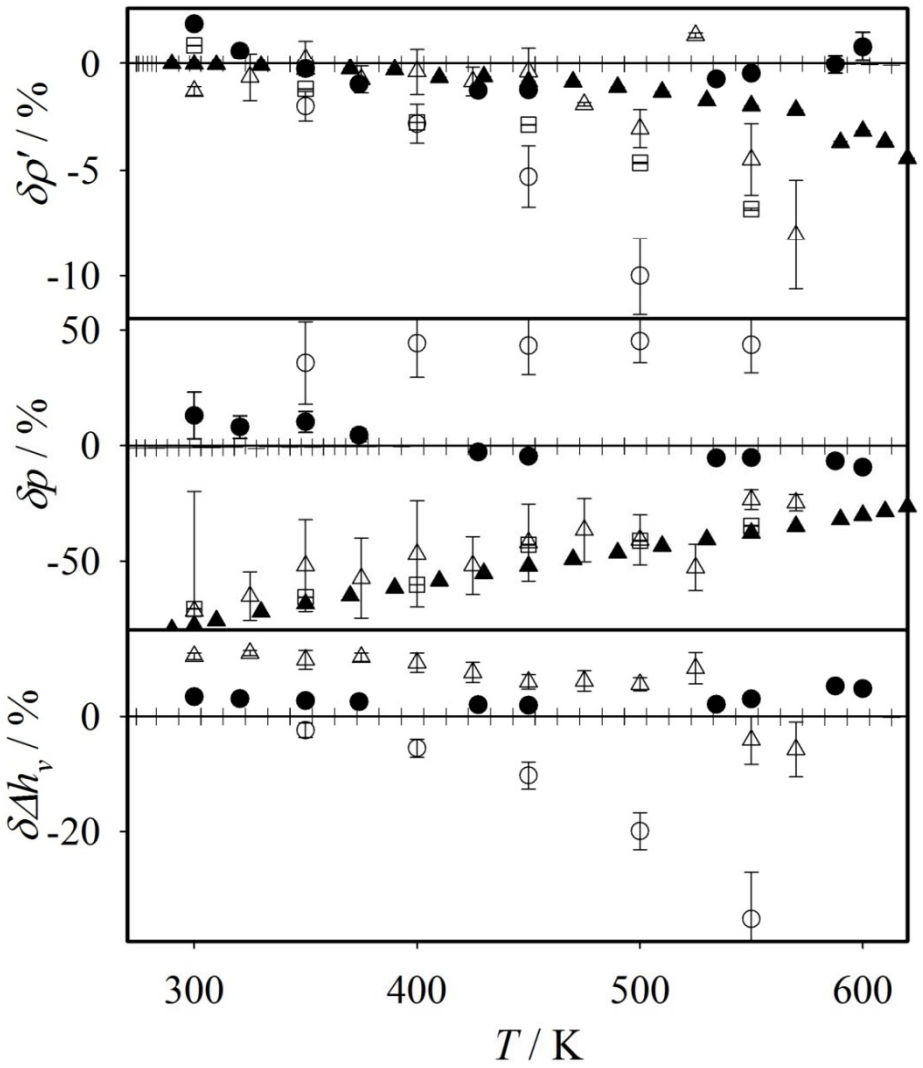
Vapor Pressures



Saturated Densities



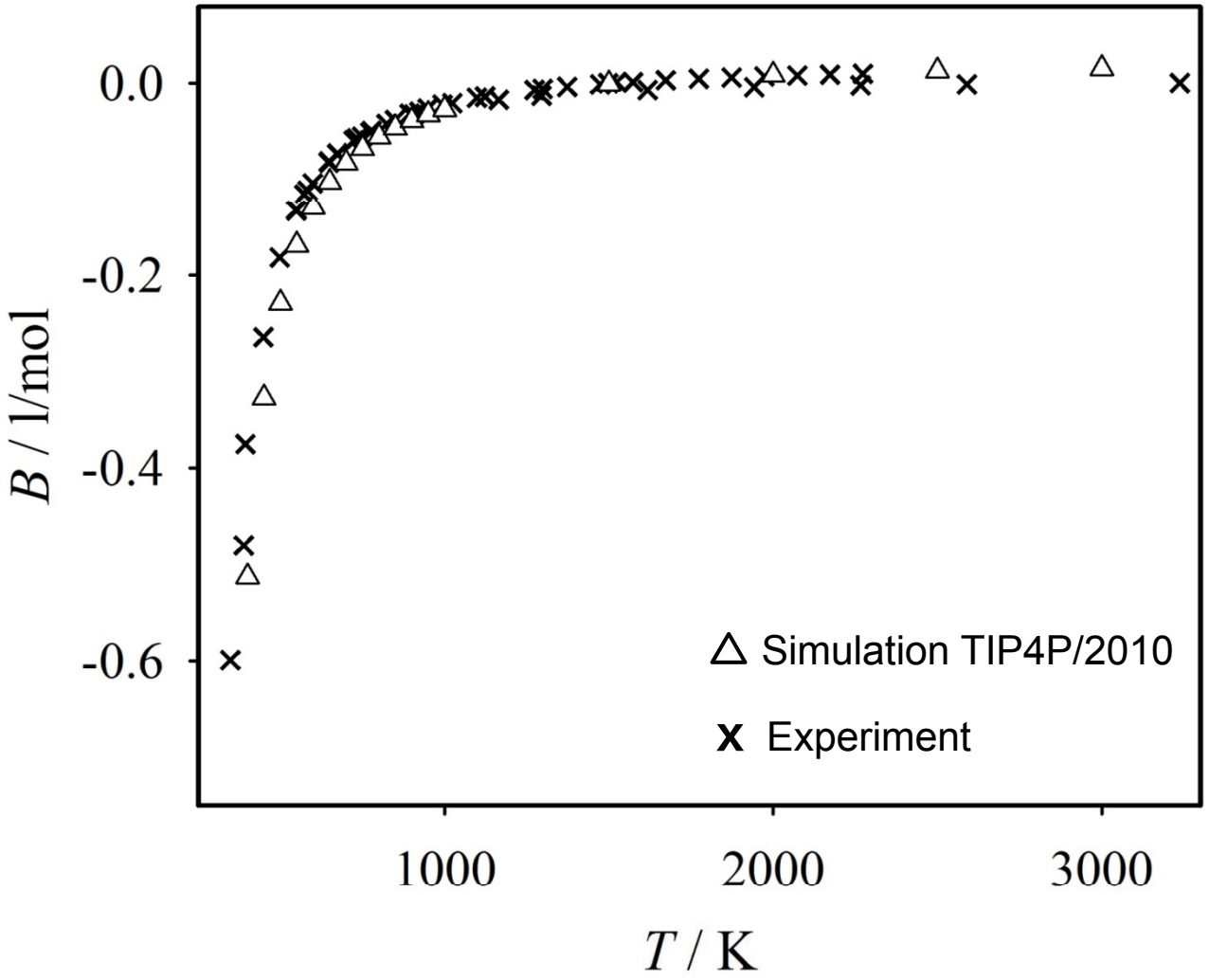
Predictions of Vapor-Liquid Equilibrium of Water



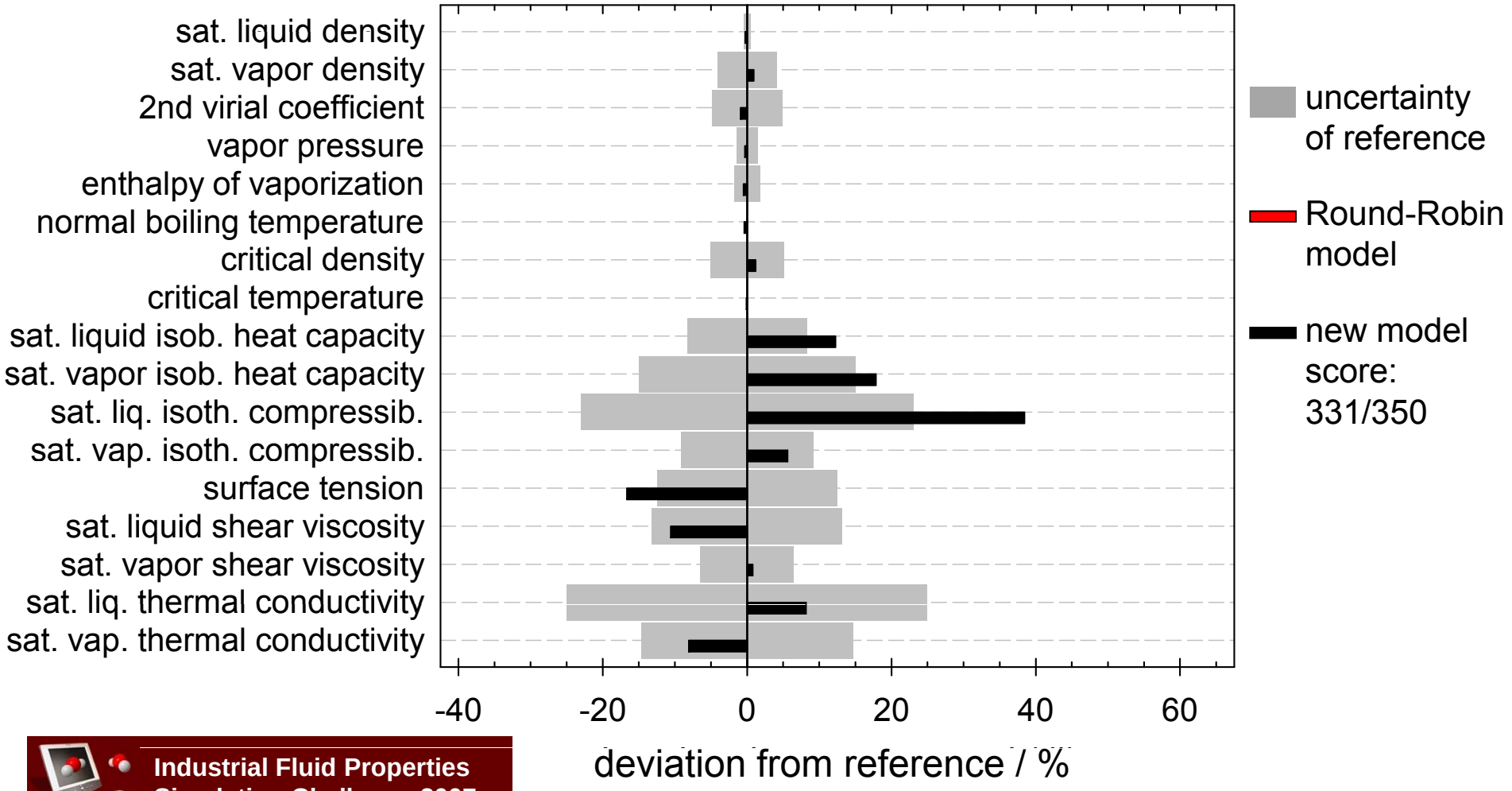
Relative deviation from reference data:

- ● TIP4P/2010 (present work)
- ▲ TIP4P/2005 (data of Vega et al.)
- ○ TIP4P (data of Lisal et al.)
- △ TIP4P-Ew (data of Baranyai et al.)
- □ SPC/E (data of Guissani et al.)

Second Virial Coefficient of Water



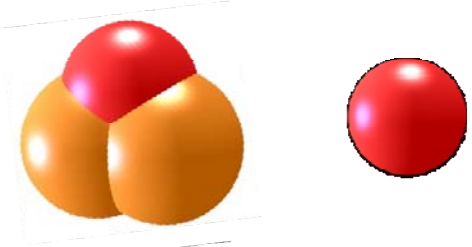
Ethylene Oxide: Predictions of various properties



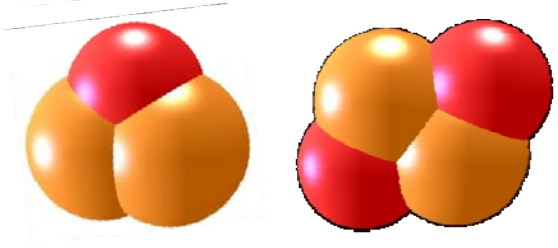
Industrial Fluid Properties Simulation Challenge 2007

Ethylene Oxide Group: Studied Mixtures

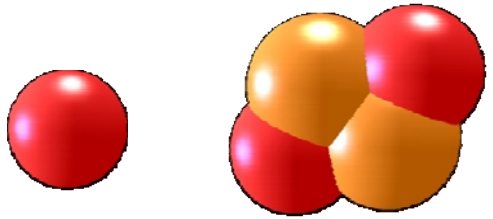
Ethylene Oxide + Water



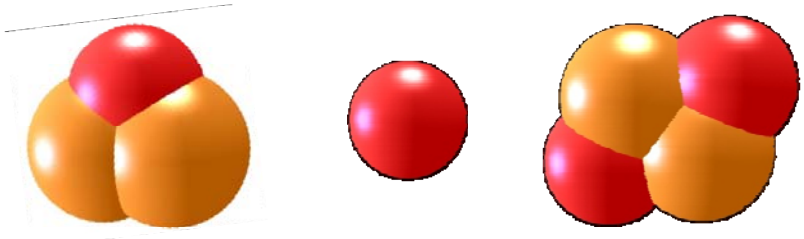
Ethylene Oxide + Ethylene Glycol



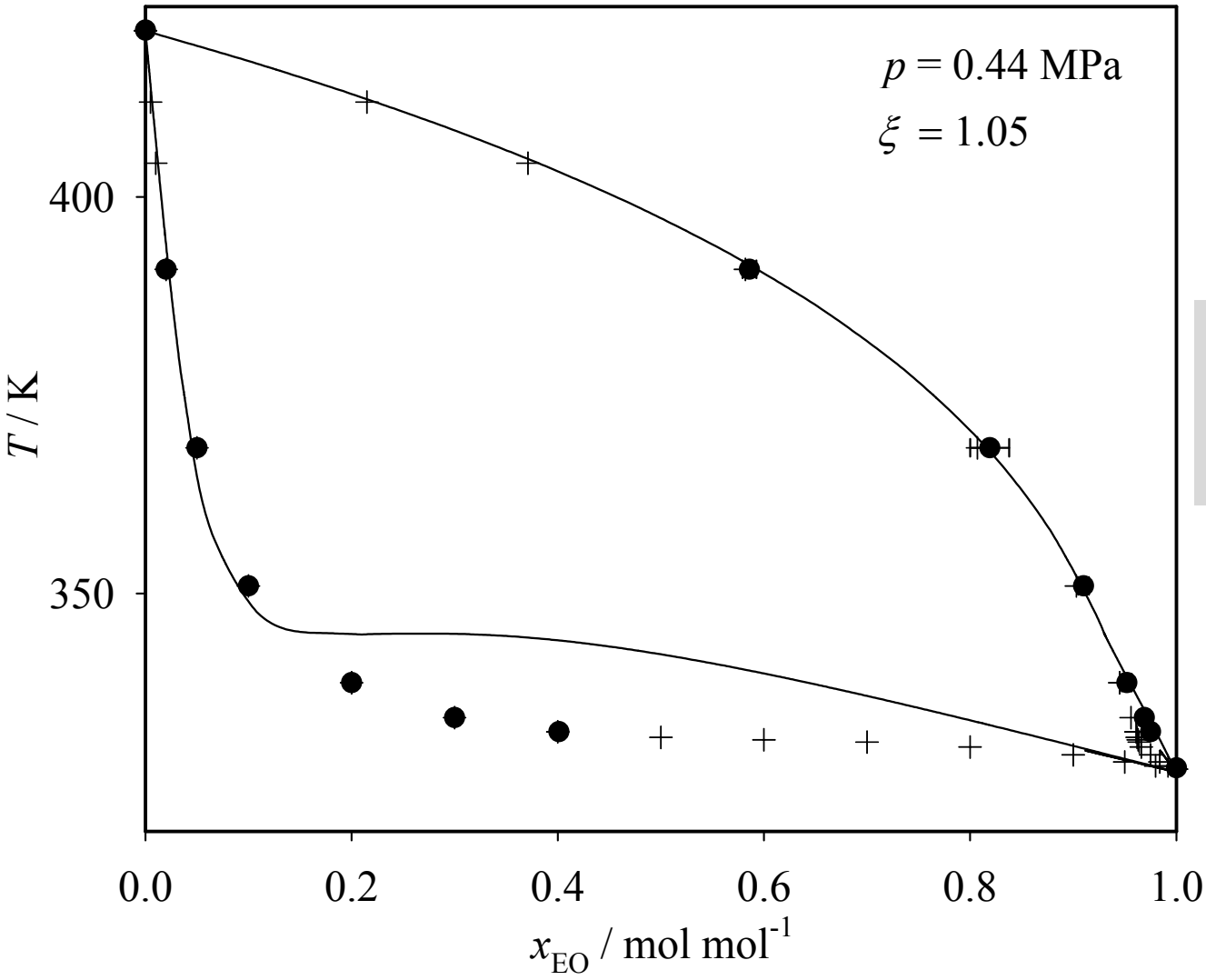
Water + Ethylene Glyol



Ethylene Oxide + Water +
Ethylene Glycol



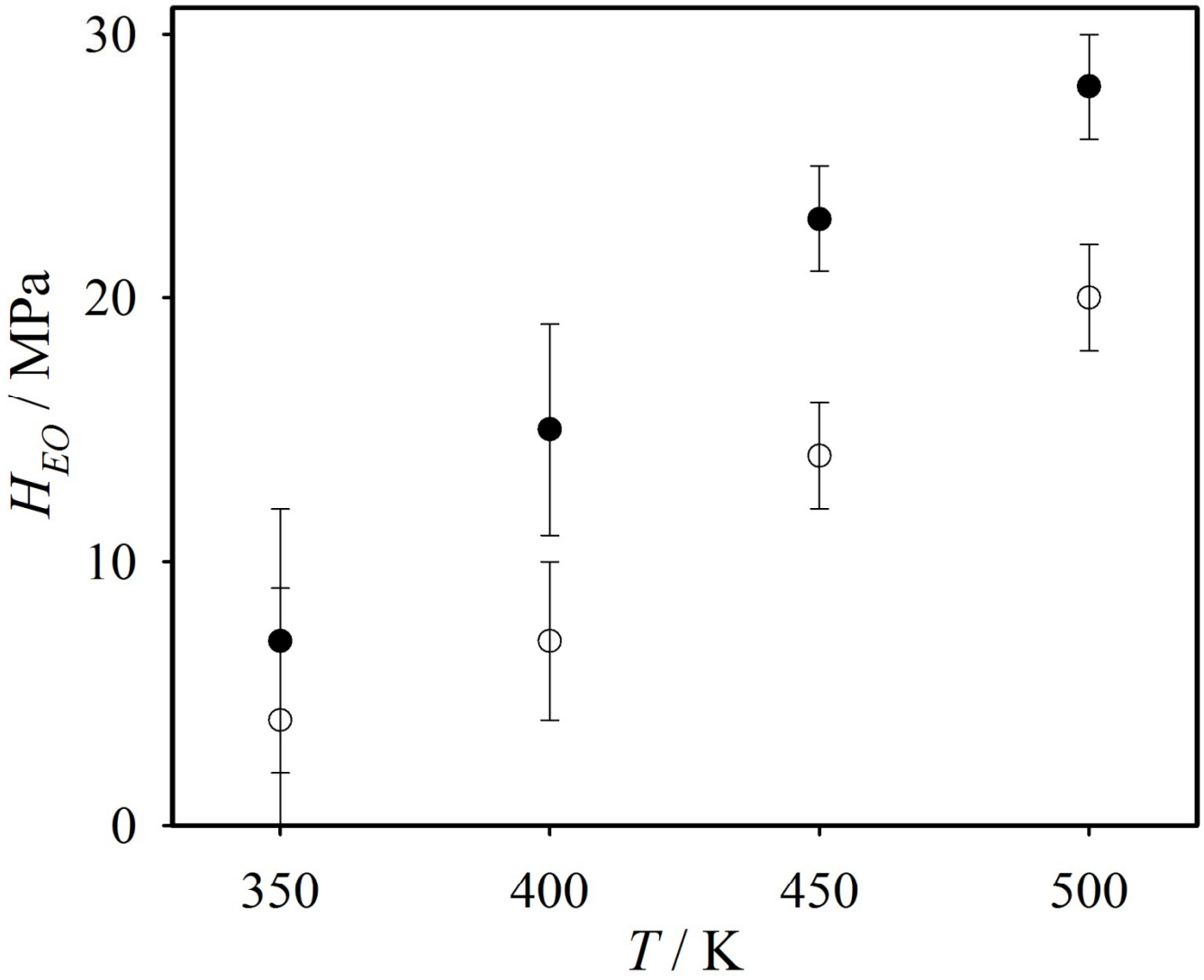
Vapor-Liquid Equilibrium Ethylene Oxide + Water



Case:
- good predictions by molecular simulation
- wrong prediction by EOS

\+ Experiment
● Simulation
—— Peng-Robinson EOS

Henry's Law Constants of Ethylene Oxide



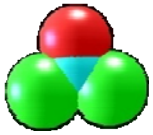
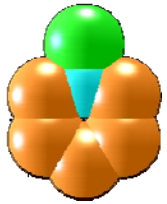
Symbols: Simulation:

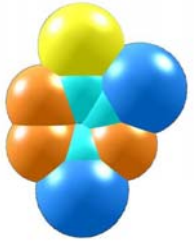
Solvent:

- ● Water (W)
- ○ Water (W) + Ethylene Glycole (EG) mass ratio W/EG = 6

Application to Reaction Kinetic Studies

Phosgeneation, Liquid Mixture (110 °C, 1 bar)



Phosgene + **Cl-Benzene** + **HCl** + **2,4-Diaminetoluene**

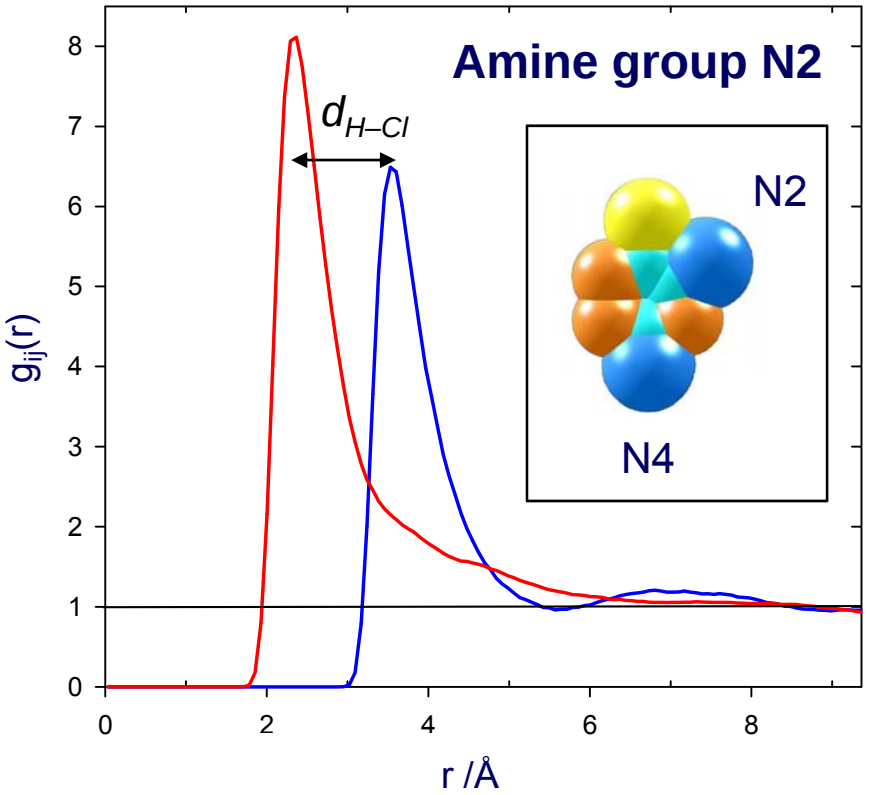
50 mol% 40 mol% 7 mol% 3 mol%

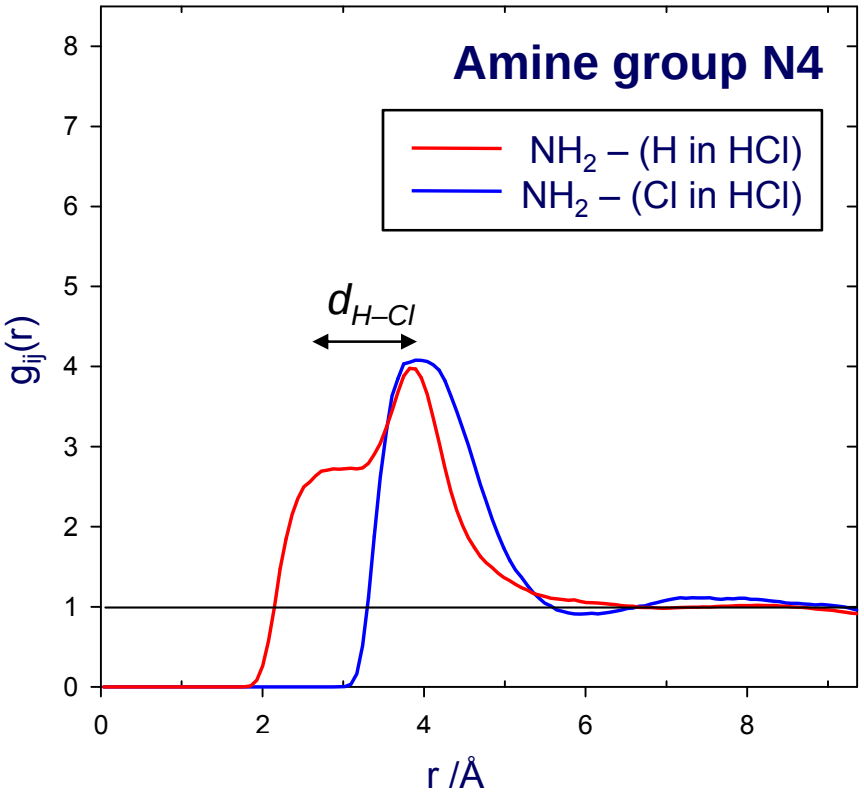
Study of radial pair distribution (RDF)

$$g_{ij}(r) = \frac{local\ concentration\ c_j}{overall\ concentration\ c_j}$$

Radial Distribution Functions: Amine Groups – HCl

Important for Formation of Undesired Hydrochlorides





- Deviations between overall and local concentration up to a factor of 8
- HCl likes amine group N2 than amine group N4
- HCl preferentially docks with the proton at amine group N2, that preference is not as strong for amine group N4

Summary

- ✓ Molecular modeling and simulation of industrially relevant hazardous fluids
- ✓ Thermodynamic properties of pure components and mixtures
- ✓ Systems with Phosgene and Ethylene Oxide:
  - ➢ Economically important
  - ➢ Experiments difficult / only few reliable data
  - ➢ Incentive for molecular simulations
- ✓ Comparison of molecular simulations with experiments and EOS
- ✓ Molecular simulation: valuable independent predictive method
- ✓ Link to reaction engineering by RDF and local concentrations
- ✓ Potential of molecular modeling and simulation is recognized in industry

Acknowledgment

- **DFG Priority Program 1155:**
  Molecular Modelling and Simulation in Process Engineering
- **DFG TFB 66:**
  Molecular Modelling and Simulation for Prediction of
  Fluid Properties für Industrial Applications

SPP 1155 DFG

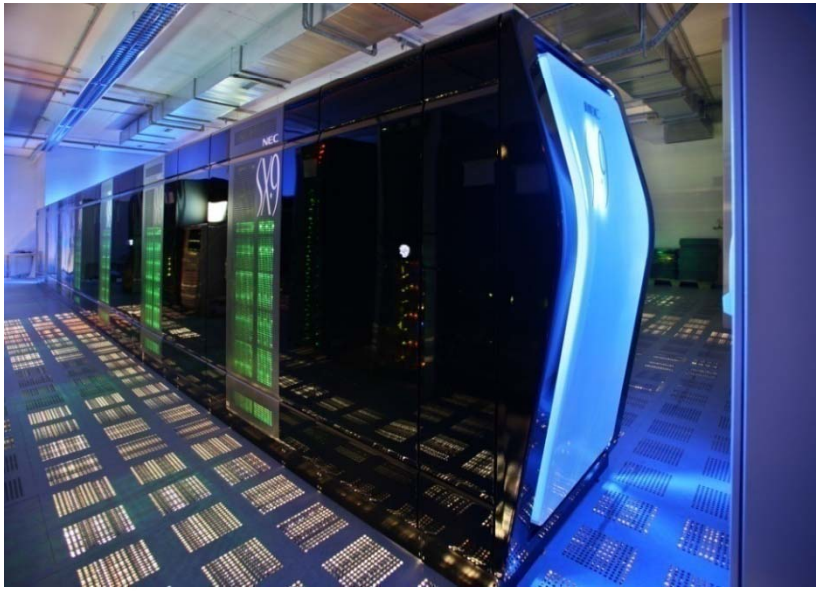
Deutsche Forschungsgemeinschaft DFG

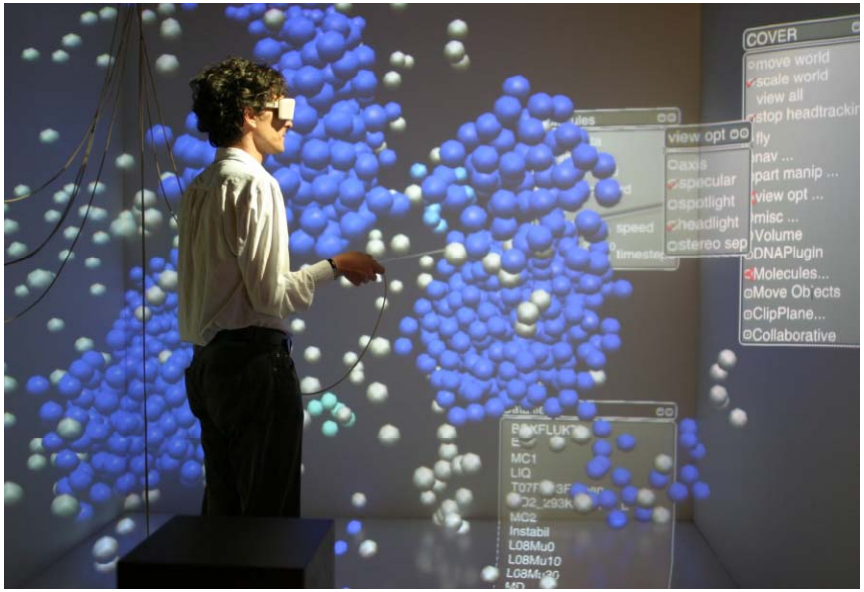
Computational
Molecular Engineering

IMEMO Project

Innovative HPC methods for massively scaling molecular simulation

@ BMBF Program: HPC software for massively parallel hardware





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