Molecular Modeling and Simulation of Thermodynamic Properties of Fluids for Industrial Applications

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Scales relevant to thermodynamics
Molecular simulation

- **Molecular dynamics (MD)**
  - deterministic system
  - static and dynamic properties
  - straightforwardly applicable to non-equilibria

- **Monte-Carlo (MC)**
  - statistical approach
  - energetic acceptance criteria
  - only static properties
Industrially important hazardous systems

**Phosgene group**

- $\text{CCl}_2\text{O}$
- $\text{HCl}$
- $\text{C}_6\text{H}_6$
- $\text{C}_6\text{H}_5\text{-CH}_3$
- $\text{C}_6\text{H}_5\text{-Cl}$
- $\text{o-C}_6\text{H}_4\text{-Cl}_2$

**Ethylene Oxide group**

- $\text{C}_2\text{H}_4\text{O}$
- $\text{H}_2\text{O}$
- $\text{HO(CH}_2\text{)}_2\text{OH}$

- 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, e.g. for Ethylene Oxide

- Rigid, non-polarizable
- Multicenter Lennard-Jones + electrostatic sites
- United atom approach
- Development based on quantum chemical and VLE data
Molecular properties from quantum chemistry

**Geometry**
- Hartree-Fock with small basis set (e.g. 6-31G) or DFT methods

**Electrostatics from electron density distribution**
- Møller-Plesset2 with medium, polarizable basis set (e.g. 6-311+G**)  
  - Embedded in a dielectric cavity (COSMO) to account for a liquid (dense) phase

**Dispersion and repulsion**
- At least dimers have to be regarded
- CCSD(T) or Møller-Plesset2 with large basis set (TZV or QZV)
- Large computational effort due to large basis set and accurate electron correlation

Better to be optimized to VLE data
Optimization to experimental VLE data

- Lennard-Jones parameters optimized to saturated liquid density and vapor pressure

- Optimization result:

\[ \delta \rho' = 0.4\% \]

\[ \delta \rho = 1.5\% \]
Deviations from reference values

- sat. liquid density
- sat. vapor density
- 2nd virial coefficient
- vapor pressure
- enthalpy of vaporization
- normal boiling temperature
- critical density
- critical temperature
- sat. liquid isob. heat capacity
- sat. vapor isob. heat capacity
- sat. liq. isoth. compressib.
- sat. vap. isoth. compressib.
- surface tension
- sat. liquid shear viscosity
- sat. vapor shear viscosity
- sat. liq. thermal conductivity
- sat. vap. thermal conductivity

- deviation from experiment / %
- -40 -20 0 20 40 60

Industrial Fluid Properties Simulation Challenge 2007

new model
uncertainty of reference
# Phosgene group: pure component models

<table>
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Vapor pressure

\[
\ln(p / \text{MPa}) = -kT
\]

- HCl
- Benzene
- Phosgene
- oCl₂-Benzene
- Cl-Benzene
- Toluene

● Simulation
── DIPPR correlations
Saturated densities

- Simulation
- DIPPR correlations

Chemicals and their saturated densities:
- oCl₂-Benzene
- CI-Benzene
- Toluene
- Phosgene
- Benzene
- HCl

Temperature (T/K) vs. density (ρ / mol/l) chart.
Molecular modeling of mixtures

Unlike interaction A-B:
- Electrostatics fully predictive
- Lennard-Jones parameters from combination rules

Predictions

\[ \xi = 1 \]

or

State-independent parameter \( \xi \) fitted to one experimental data point \( \rho(T,x) \) oder \( H(T) \)

Modified Lorentz-Berthelot

\[
\begin{align*}
\sigma_{AB} &= \frac{\sigma_A + \sigma_B}{2} \\
\varepsilon_{AB} &= \xi \cdot \sqrt{\varepsilon_A \varepsilon_B}
\end{align*}
\]
Vapor-liquid equilibria of mixtures

- Applied to >360 binaries, >35 ternaries and one quaternary
Phosgene group: studied binary mixtures

Phosgene + Benzol

Phosgene + Toluol

Phosgene + Cl-Benzene

Phosgene + o-Cl₂-Benzene

Phosgene + HCl
Vapor-liquid equilibrium of HCl + Chlorobenzene

\[ \xi = 1.02 \]

Case:
- Good predictions both by molecular simulation and EOS
- Deviations upon approaching critical point

Graph:
- ρ / MPa vs. \( x_{\text{HCl}} / \text{mol mol}^{-1} \)
- Experiment +
- Simulation ●
- Peng-Robinson EOS —
Ethylene Oxide group: studied binary mixtures

- Ethylene Oxide + Water
- Ethylene Oxide + Ethylene Glycol
- Water + Ethylene Glycol
Vapor-liquid equilibrium of Ethylene Oxide + Water

\[ \xi = 1.2 \quad k_{ij} = -0.1 \]

\[ T / K \]
\[ x_{EO} / \text{mol mol}^{-1} \]

Case:
- good predictions by molecular simulation
- wrong prediction by EOS
Shear viscosity of Methanol + Water

- TIP4P/2005 Water model by Vega et al.
- Methanol model, this work

![Graph showing shear viscosity of Methanol + Water at 5°C and 25°C, 0.1 MPa.](image)
Self-diffusion coefficients of Methanol + Water

- TIP4P/2005 Water model by Vega et al.
- Methanol model, this work

![Graph showing self-diffusion coefficients of Methanol and Water at different temperatures and mole fractions of Methanol.](image)

- 0.1 MPa
- 25 °C
- 5 °C

Experiment
Simulation
ms2: molecular simulation tool

- Molecular dynamics / Monte Carlo
- Arbitrary mixtures of rigid molecules
- Several ensembles
- Grand Equilibrium method for VLE calculations

- Many static properties (thermal, caloric, entropic)
- Transport properties (Green-Kubo)

- Consistent FORTRAN90 code
- Reasonably object oriented
- Distributed memory parallelization by MPI
- All relevant loops vectorized
- Interface to 2,5D (OpenGL) and 3D Virtual Reality visualization
Monte Carlo embarrassing parallelization

Instead of performing one consecutive probabilistic simulation over $K$ loops

$M$ ensembles (on $M$ processors) can be performed over $K / M$ loops

- Efficient, as hardly any communication is necessary
Monte Carlo speed-up – without equilibration

- Number of processes: 20, 40, 60, 80, 100, 120
- Speed-up values for each number of processes:
  - 20: 1372 particles
  - 40: 640,000 loops
Summary

- Molecular force fields are comprehensive models for thermodynamic properties having strong predictive power.
- They allow for an efficient description of mixture properties.
- Molecular simulation is a versatile tool to investigate the behavior of fluids which is about to be transferred to industry.
- Using parallel simulation codes and appropriate computing equipment, acceptable response times may be achieved.
- Molecular modeling and simulation can be used to investigate a large variety of topics.
Vapor-liquid equilibrium of Phosgene + Toluene

\[ \xi = 0.99 \]

\[ 308.15 \text{ K} \]
\[ 423.15 \text{ K} \]
\[ 448.15 \text{ K} \]

\[ x_{\text{Phosgene}} \text{ / mol mol}^{-1} \]
\[ p \text{ / MPa} \]

Case:
- Molecular simulation and EOS agree well

+ Experiment
● Simulation
── Peng-Robinson EOS
Binary VLE of $\text{C}_2\text{H}_6 + \text{R22}$

- Experiment
- PR-EOS, $k_{ij}$ adjusted, $\xi$ adjusted
- Simulation, $\xi = 1$
- Simulation, $\xi = 0.95$ to 1.05
- Simulation, $\xi$ adjusted

$293.24 \text{ K}$

$p$ / MPa

$x_{\text{C}_2\text{H}_6}$ / mol mol$^{-1}$
Grand Equilibrium method

Specified: $T, x$

Liquid

NpT calculation of chemical potentials and partial molar volumes

$$\mu_i(p) \approx \mu_i(p_0) + v_i \cdot (p - p_0)$$

Vapor

Pseudo grand canonical simulation (at $\mu_i(p), V, T$)

$p, y$