Development of Molecular Models of Reals Fluids for Process Engineering Applications

Hans Hasse¹, Jadran Vrabec²

¹Lehrstuhl für Thermodynamik, TU Kaiserslautern
²Lehrstuhl für Thermodynamik und Energietechnik, Universität Paderborn
Molecular Modelling (Force Fields)

Geometry:
- Bond lengths and angles

Electrostatics:
- Position and strength of dipoles, quadrupoles, partial charges

Dispersion and Repulsion:
- Parameters of Lennard-Jones potentials

Many parameters
Model Parameters from Quantum Chemistry

Geometry
- HF with small basis set (z.B. 6-31G) or DFT methods

Electrostatics from electronic density distribution
- MP2 with small polarizable basis set (e.g., 6-311+G**)
- Molecule embedded in dielectric cavity for modeling dense fluid phase (COSMO)

Dispersion and Repulsion
- Requires simulation of arrangements of at least two molecules
- CCSD(T) or MP2 with large basis sets (TZV or QZV)
- Very high computational effort
- Unsatisfactory accuracy
  
  Fit to thermo-physical data preferred (VLE data)
Phase Equilibrium from Grand Equilibrium Method

Specs: $T, x$

Liquid

Simulation:
- Chemical potentials
- Partial molar volumes

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

Vapor

Pseudo grand canonical simulation
(Specification of $\mu_i^V(p), V, T$)

Result: $p, y$
Industrial Property Simulation Challenge 2007

Industrial Fluid Properties
Simulation Collective

Du Pont
3M
National Institute of Standards and Technology
Exxon
bp
Dow
Ohio Supercomputer Center
Ethylene Oxide

- Worldwide annual production about 18 Mio. tons
- Use: PET and anti-freeze
- Properties:
  - explosive
  - toxic
  - highly flammable
  - cancerogenic
  - mutagenic
- Explosion @ Sterigenics Intl., Ontario, CND (2004)
- 4 wounded, hall destroyed
IFPSC Challenge 2007 : Problem Description

- Development of a new molecular model for Ethylene Oxide
- Prediction of 17 properties in 3 categories
  - Vapor liquid equilibria / thermal properties
  - Saturated densities
  - Vapor pressure
  - Enthalpy of vaporization
  - Critical properties
  - Normal boiling temperature
  - Second virial coefficient
  - Second derivatives / surface tension
  - Heat capacity
  - Isothermal compressibility
  - Surface tension
  - Transport properties
  - Shear viscosity
  - Thermal conductivity

- Benchmarked to “reference data”
Molecular Model of Ethylene Oxide

- 3 LJ Sites (one for the oxygen atom, one for each methylene group)
- 1 static point dipole along symmetry axis
- Rigid, non-polarizable
- Adjustment of five parameters ($\sigma_O$, $\varepsilon_O$, $\sigma_{CH}$, $\varepsilon_{CH}$, $\mu$) to experimental VLE data
Deviations from Reference Data

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

sat. vap. thermal conductivity
sat. liq. thermal conductivity
sat. vapor shear viscosity
sat. liquid shear viscosity
surface tension
sat. liquid isob. heat capacity
sat. vapor isob. heat capacity
sat. liq. isoth. compressib.
sat. vap. isoth. compressib.

uncertainty
Round-Robin model
new model
score:
331/350

deviation from reference / %
IFPSC Party 2007
Transport Property Prediction: Strongly Polar H-bonding Fluids

- Pure Fluids / Models:
  - Methanol (own model)
  - Ethanol (own model)
  - Water (literature: SPC/E, TIP4P)

- Mixtures
  - Lorentz-Berthelot rules for unlike LJ parameters

\[ \sigma_{AB} = \left( \frac{\sigma_A + \sigma_B}{2} \right) \quad \varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} \]

Not fitted to transport properties
Equilibrium Molecular Dynamics: Green-Kubo Formalism

Fluctuation \[ F_i = \sum_j L_{ij} Y_j \] Microscopic Equilibrium

Microscopic flux

Transport coefficients \[ \text{Autocorrelation functions} \]

- Self diffusion
  \[ D_i = \frac{1}{3N_i} \int_0^\infty \! dt \left\langle \sum_{i=1}^{N_i} v_i(0) \cdot v_i(t) \right\rangle \]

- Binary Maxwell-Stefan transport diffusion
  \[ D_{12} = \frac{x_2}{3N_1} \left( \frac{M_1 x_1 + M_2 x_2}{M_2 x_2} \right)^2 \int_0^\infty \! dt \left\langle \sum_{i=1}^{N_i} v_i(0) \cdot \sum_{j=1}^{N_i} v_j(t) \right\rangle \]

- Shear viscosity
  \[ \eta_s = \frac{1}{V k_B T} \int_0^\infty \! dt \left\langle J_{xy}^x(t) \cdot J_{xy}^y(0) \right\rangle \]
  \[ J_{xy}^{xy} = \sum_{i=1}^N m_i \cdot v_i^x \cdot v_i^y - \sum_{i=1}^N \sum_{j>i} \int_{r_{ij}} \frac{\partial \phi(r_{ij})}{\partial r_{ij}^y} \]
Correlation Functions

- Velocity autocorrelation function (VACF)
- Self-diffusion coefficient ($D_i / 10^{-10} \text{ m}^2 \text{s}^{-1}$)
- Shear viscosity autocorrelation function (SACF)
- Shear viscosity ($\eta / 10^4 \text{ Pa s}$)
Non Equilibrium Molecular Dynamics

„Normal“ NEMD: $\Delta T \rightarrow$ heat flux

„Reverse“ NEMD: heat flux $\rightarrow \Delta T$

modified PEX method (Müller-Plathe)
Prediction of Transport Coefficients of Methanol

- Graph 1: Diffusivity $D / 10^9 \text{m}^2\text{s}^{-1}$ vs. Temperature $T / \text{K}$
- Graph 2: Viscosity $\eta / 10^3 \text{Pa s}$ vs. Temperature $T / \text{K}$
- Graph 3: Thermal conductivity $\lambda / \text{W m}^{-1} \text{K}^{-1}$ vs. Temperature $T / \text{K}$

- Symbols:
  - Black circles: Prediction / MD Simulation
  - Plus signs: Experiment (Literature)
Prediction of Transport Coefficients of Ethanol

![Graphs showing transport coefficients vs. temperature](image)

- **Diffusion Coefficient** $D$ vs. Temperature $T$
  - Units: $10^{-9} \text{m}^2 \text{s}^{-1}$
  - Data points:
    - Prediction / MD Simulation
    - Experiment (Literature)

- **Viscosity** $\eta$ vs. Temperature $T$
  - Units: $10^{-3} \text{Pa s}$

- **Thermal Conductivity** $\lambda$ vs. Temperature $T$
  - Units: $\text{W m}^{-1} \text{K}^{-1}$

The graphs illustrate the comparison between predicted and experimental values for transport coefficients of ethanol across different temperatures.
Prediction of Transport Properties of Water

- $D_i / 10^{-9} \text{m}^2\text{s}^{-1}$ vs. $T / K$
- $\eta / 10^{-9} \text{m}^2\text{s}^{-1}$ vs. $T / K$

- SPCE Model / MD Simulation
- TIP4P Model / MD Simulation
- Experiment (Literature)
Fickian Diffusion Coefficients

Methanol + Water (298 K)

Ethanol + Water (298 K)

- Prediction / MD simulation
- Experiment (literature)
Fickian Diffusions Coefficients in Methanol + Ethanol

\[ D / 10^{-9} \text{ m}^2 \text{s}^{-1} \]

\[ x_{\text{CH}_3\text{OH}} / \text{mol mol}^{-1} \]

- Black dots: Prediction / MD simulation
- Blue triangles: Exp.: Taylor Dispersion (this work)

298 K
Shear Viscosity of Mixtures

Methanol + Water

Ethanol + Water

Ethanol + Methanol

- $\eta / 10^{-4}$ Pa s
- $x_{\text{CH}_3\text{OH}} / \text{mol mol}^{-1}$
- $298 \text{ K}$

- $\eta / 10^{-4}$ Pa s
- $x_{\text{C}_2\text{H}_5\text{OH}} / \text{mol mol}^{-1}$
- $298 \text{ K}$

- $\eta / 10^{-4}$ Pa s
- $x_{\text{CH}_3\text{OH}} / \text{mol mol}^{-1}$
- $298 \text{ K}$

- Prediction / MD simulation
- Experiment (literature)
### Comprehensive study for mixtures of 78 fluids

<table>
<thead>
<tr>
<th>Non-polar, 1CLJ</th>
<th>Dipolar, 2CLJD</th>
<th>Quadrupolar, 2CLJQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>neon (Ne)</td>
<td>carbon monoxide (CO)</td>
<td>flourine (F₂)</td>
</tr>
<tr>
<td>argon (Ar)</td>
<td>R11 (CFCl₃)</td>
<td>chlorine (Cl₂)</td>
</tr>
<tr>
<td>krypton (Kr)</td>
<td>R12 (CF₂Cl₂)</td>
<td>bromine (Br₂)</td>
</tr>
<tr>
<td>xenon (Xe)</td>
<td>R13 (CF₃Cl)</td>
<td>iodine (I₂)</td>
</tr>
<tr>
<td>methane (CH₄)</td>
<td>R13B1 (CBrF₃)</td>
<td>nitrogen (N₂)</td>
</tr>
<tr>
<td></td>
<td>R22 (CHF₂Cl)</td>
<td>oxygen (O₂)</td>
</tr>
<tr>
<td></td>
<td>R23 (CHF₃)</td>
<td>carbon dioxide (CO₂)</td>
</tr>
<tr>
<td></td>
<td>R32 (CH₂F₂)</td>
<td>carbon disulfide (CS₂)</td>
</tr>
<tr>
<td></td>
<td>R41 (CH₃F)</td>
<td>ethane (C₂H₆)</td>
</tr>
<tr>
<td></td>
<td>R123 (CHCl₂-CF₃)</td>
<td>ethene (C₂H₄)</td>
</tr>
<tr>
<td></td>
<td>R124 (CHFCl-CF₃)</td>
<td>ethine (C₂H₂)</td>
</tr>
<tr>
<td></td>
<td>R125 (CHF₂-CF₃)</td>
<td>R116 (C₂F₆)</td>
</tr>
<tr>
<td></td>
<td>R134a (CH₂F-CF₃)</td>
<td>C₂F₄</td>
</tr>
<tr>
<td></td>
<td>R141b (CH₃-CFCl₂)</td>
<td>C₂Cl₄</td>
</tr>
<tr>
<td></td>
<td>R142b (CH₃-CF₂Cl)</td>
<td>propadiene (CH₂-C≡CH)</td>
</tr>
<tr>
<td></td>
<td>R143a (CH₃-CF₃)</td>
<td>propyne (CH₃-C≡CH)</td>
</tr>
<tr>
<td></td>
<td>R152a (CH₃-CHF₂)</td>
<td>propylene (CH₃-CH=CH₂)</td>
</tr>
<tr>
<td></td>
<td>CH₂Cl</td>
<td>SF₆</td>
</tr>
<tr>
<td></td>
<td>R40B1 (CH₃Br)</td>
<td>R14 (CF₄)</td>
</tr>
<tr>
<td></td>
<td>CH₃I</td>
<td>CCl₄</td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂</td>
<td>R113 (CFCl₂-CF₂Cl)</td>
</tr>
<tr>
<td></td>
<td>R30B2 (CH₂Br₂)</td>
<td>R114 (CF₂Cl-CF₂Cl)</td>
</tr>
<tr>
<td></td>
<td>CH₂I₂</td>
<td>R115 (CF₃-CF₂Cl)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R134 (CHF₂-CF₂Cl)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂Br-CH₂Br</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CBrF₂-CBrF₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHCl=CCl₂</td>
</tr>
</tbody>
</table>
## Available Experimental Data vs. Combinatorial Explosion

### Theroretical Numbers

<table>
<thead>
<tr>
<th>Type</th>
<th>Formula</th>
<th>Value</th>
<th>Exp. Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure fluids</td>
<td>$N$</td>
<td>78</td>
<td>78 (100%)</td>
</tr>
<tr>
<td>Binary mixtures</td>
<td>$N(N-1)/2$</td>
<td>3,003</td>
<td>266 (9%)</td>
</tr>
<tr>
<td>Ternary mixtures</td>
<td>$N(N-1)(N-2)/6$</td>
<td>76,076</td>
<td>33 (0.05%)</td>
</tr>
<tr>
<td>Quaternary mixtures</td>
<td>$N(N-1)(N-2)(N-3)/24$</td>
<td>1,426,425</td>
<td>0</td>
</tr>
</tbody>
</table>

* Systems for which experimental VLE data is available in Dortmund Data Bank
Molecular Modelling of Mixtures

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

Predictions $\xi = 1$
or
Fit to one experimental data point $p(T,x)$ oder $H(T)$

Modified Lorentz-Berthelot

$$\sigma_{AB} = \left(\sigma_A + \sigma_B\right)/2$$
$$\varepsilon_{AB} = \xi \cdot \sqrt{\varepsilon_A \varepsilon_B}$$
Example: CO$_2$ + R140a (CH$_3$CCl$_3$)

- Adjustment of $\xi$ to VLE at 323 K and 0.46 mol/mol CO$_2$
- Prediction of VLE at other conditions
- Prediction of Henry’s law constant
Vapor-Liquid Equilibria of Binary Mixtures

- Above: some examples (45/266 studied systems)
- Strategy always successful (259/266 studied systems)
Binary interaction parameter distribution

Number of mixtures

\[ \xi \]

[Graph showing a distribution of binary interaction parameters with peaks around \( \xi = 0.95 \) and \( \xi = 1.0 \).]
Vapor-Liquid Equilibria of R14 + R23 + R13

- No further adjustment
- Completely predictive
- Always successful
  (32/33 studied systems)

\[ T = 199.8 \text{K} \]
\[ p = 0.3447 \text{ MPa} \]

- + Experiment
- ● Simulation, $\xi$ adjusted
- — Peng-Robinson EOS
## Optimizing Molecular Models Using Reduced Quantities

- Molecular simulations internally use „reduced quantities“
- Reference to $\sigma_R$ and $\varepsilon_R$ (and $m_R$)

### Example: Optimizing a 2CLJQ – Model for CO$_2$ using VLE data

<table>
<thead>
<tr>
<th>Reduction</th>
<th>Simulation</th>
<th>Re-dimensioning</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T \cdot k/\varepsilon_R$ = $T^*$</td>
<td>$T^*$</td>
<td>$T^*$ / $\varepsilon_R/k$ = $T$</td>
<td>$T$</td>
</tr>
<tr>
<td>$\sigma_O /\sigma_R$ = $\sigma_O^*$</td>
<td>$\sigma_O^*$</td>
<td>$\sigma_R /\sigma_O^<em>$ = $\sigma_R^</em>$</td>
<td>$\sigma_R^*$</td>
</tr>
<tr>
<td>$\varepsilon_O /\varepsilon_R$ = $\varepsilon_O^*$</td>
<td>$\varepsilon_O^*$</td>
<td>$\varepsilon_R /\varepsilon_O^<em>$ = $\varepsilon_R^</em>$</td>
<td>$\varepsilon_R^*$</td>
</tr>
<tr>
<td>$\sigma_C /\sigma_R$ = $\sigma_C^*$</td>
<td>$\sigma_C^*$</td>
<td>$\sigma_R /\sigma_C^<em>$ = $\sigma_R^</em>$</td>
<td>$\sigma_R^*$</td>
</tr>
<tr>
<td>$\varepsilon_C /\varepsilon_R$ = $\varepsilon_C^*$</td>
<td>$\varepsilon_C^*$</td>
<td>$\varepsilon_R /\varepsilon_C^<em>$ = $\varepsilon_R^</em>$</td>
<td>$\varepsilon_R^*$</td>
</tr>
<tr>
<td>$Q /\left(\varepsilon_R\sigma_R^5\right)^{0.5}$ = $Q^*$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L /\sigma_R$ = $L^*$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results hold for all $\sigma_R$ and $\varepsilon_R$.

Analytical variation of $\sigma_R$ and $\varepsilon_R$ is possible without new simulations.

- Model optimization by varying $\sigma_R$ and $\varepsilon_R$ without new simulations
- Attractive for fine tuning

Comparison simulation vs. experiment
A Long Way Around to Larger Molecules

Pure component

Benzene

Point quadrupole

Mixture

Benzene + HCl

more realistic
The not very unexpected solution

6 Pointquadrupoles

✓ works well in pure componets and mixtures
✓ computationally much more expensive
Extension of Parallel Molecular Simulation Code 
*ms2* to Flexible Molecules

n-Hexane, 1 bar, 333 K
Summary
Later this year