Thermodynamic properties of ammonia by molecular simulation

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Overview on numerical methods

- **Time**: (s) $10^0$, (ms) $10^{-3}$, (µs) $10^{-6}$, (ns) $10^{-9}$, (ps) $10^{-12}$, (fs) $10^{-15}$

- **Length**: (nm) $10^{-10}$, (µm) $10^{-6}$, (m) $10^{-4}$

**Methods**:
- **Continuum methods**
- **Meso-scale methods**
- **Force field methods**
- **Semi-empirical QM**
- **Ab initio QM**
Molecular Simulation – Basic Idea

- Assumption of a force field $u$
- Explicit calculation of all interactions within $r_C$
- Corrections for $r > r_C$

$$U = \left\langle \sum_{i < j \atop r < r_C} u(r_{ij}) \right\rangle + \frac{N\rho}{2} \int_{r_C}^{\infty} dV \cdot u(r)$$

- Periodic boundary condition
- Minimum-image convention
- Cut-off radius $r_C$
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
Thermodynamics with molecular approach

- Models of intermolecular interactions
  - Parameters can physically be interpreted

- Contain all thermodynamic properties
  - Static: thermal, caloric, entropic
  - Dynamic: viscosity, diffusion, thermal conductivity, ...
  - Surface properties, e.g. surface tension

- Mixture properties well accessible
- Strong predictive and extrapolative capabilities
- Technical accuracies achievable

- Directly applicable to investigate fluid properties
  - in geometries, e.g. adsorption, zeolites, ...
  - in dynamic processes, e.g. condensation, flow, ...
Molecular models for intermolecular interactions

**Geometry**
- Bond lengths and angles

**Electrostatics**
- Magnitude of point charges
Molecular models for intermolecular interactions

Geometry
- Bond lengths and angles

Electrostatics
- Magnitude of point charges

Dispersion and repulsion
- Parameters e.g. of Lennard-Jones sites

Potentially, a large number of parameters
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) x
- Large computational effort due to large basis set and accurate electron correlation

Better to be optimized to VLE data
Adjustment to experimental VLE data

- 2 Lennard-Jones parameters optimized to saturated liquid density and vapor pressure
- Optimization result:
  - \( \delta p' = 0.7\% \)
  - \( \delta p = 1.6\% \)
### Parameters of the ammonia model

<table>
<thead>
<tr>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$\sigma$</th>
<th>$\varepsilon/k_B$</th>
<th>$q$</th>
</tr>
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<tr>
<td>N</td>
<td>0</td>
<td>0</td>
<td>0.0757</td>
<td>3.376</td>
<td>182.9</td>
<td>0.9993</td>
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<tr>
<td>H(1)</td>
<td>0.9347</td>
<td>0</td>
<td>0.3164</td>
<td>–</td>
<td>–</td>
<td>0.3331</td>
</tr>
<tr>
<td>H(2)</td>
<td>0.4673</td>
<td>0.8095</td>
<td>0.3164</td>
<td>–</td>
<td>–</td>
<td>0.3331</td>
</tr>
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<td>–</td>
<td>–</td>
<td>0.3331</td>
</tr>
</tbody>
</table>

**Five parameters**

- 1 angle, 1 length, 1 charge magnitude
- 2 Lennard-Jones parameters
Molecular dynamics simulation (I)

Gas @ 393 K and 0.1 MPa
Molecular dynamics simulation (II)

Liquid @

323 K and 3 MPa
Prediction of second virial coefficient and enthalpy of vaporization
Prediction of density and enthalpy
In the homogeneous region

Deviations with respect to the equation of state by Tillner-Roth, Harms-Watzenberg, Baehr: DKV-Tagungsbericht 20, 167 (1993).
Prediction of shear viscosity and thermal conductivity in the homogeneous region

Shear viscosity / $10^{-4}$ Pa s

Thermal conductivity / W/(m·K)

- Correlations of exp. data
- Simulation
Summary

- Molecular force fields are comprehensive models for thermodynamic properties with a strong predictive power
- Mixture properties are well accessible
- 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
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
Phase equilibrium from Grand Equilibrium method @ \( ms2 \)

**Specs:** \( T, x \)

- **Liquid**
- **Vapor**

Simulation:
- Chemical potentials
- Partial molar volumes

\[
\mu_i(p) \approx \mu_i(p_0) + v_i \cdot (p - p_0)
\]

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

Result: \( p, y \)
Transferability to mixtures

- Assumption: pairwise additivity
- Unlike electrostatics straightforward
- Unlike dispersion a priori not known

Unlike Lennard-Jones parameters

\[ \sigma_{AB} = \left( \sigma_A + \sigma_B \right)/2 \]
\[ \varepsilon_{AB} = \xi \cdot \sqrt{\varepsilon_A \varepsilon_B} \]
Binary VLE of C$_2$H$_6$ + R22

\[ p \text{ / MPa} \]

\[ x_{C2H6} / \text{mol mol}^{-1} \]

\[ \xi = 0.981 \]

293.24 K

- experiment
- PR-EOS, \( k_{ij} \) adjusted
- simulation, \( \xi = 1 \)
- simulation, \( \xi = 0.95 \) to 1.05
- simulation, \( \xi \) adjusted
Vapor-liquid equilibria of binary mixtures

- Strategy applied to >350 binary mixtures regarding different types