Molecular Modeling and Simulation of Phase Equilibria for Chemical Engineering

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Modeling and Simulation in Chemical Engineering

Bottom up ➢

Top down

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

- Length / m
  - 10^{-10}
  - 10^{-9}
  - 10^{-8}
  - 10^{-7}
  - 10^{-6}
  - 10^{-5}
  - 10^{-4}

- Molecular Force Fields
- Semiempirical QM
- Ab initio QM
- Mesoscale Methods
- Continuum Methods
Molecular Simulation with Force Fields

Molecular Dynamics (MD)
- Numerical solution of Newtonian equations of motion
- Deterministic
- Static and dynamic properties

Monte-Carlo (MC)
- Statistical method
- Energetic acceptance criteria
- Static properties only
- Reactive MC

MD/MC Code: www.ms-2.de

Molecular Model Type

Example: Ethylene Oxide

- Rigid, non-polarizable
- Multicenter Lennard-Jones (LJ) + electrostatic sites
- United atom approach
- All properties from one model

Molecular Model Development

Geometry:
- bond lengths
- bond angles
  - QM

Electrostatics:
- partial charges
- dipoles
- quadrupoles
  - QM / VLE

Dispersion, Repulsion:
- Lennard-Jones (LJ) potentials
  - VLE

Parameterizing of Molecular Models with VLE Data

Multi-Objective Optimization
- Vapor-pressure
- Saturated liquid density
- Enthalpy of vaporization
Molecular Models from Multi-Objective Optimization: Pareto-based Approach

Introduction by well known example

Pareto optimality
Improvement in any chosen objective leads inevitably to a decline in at least one other objective.

- Pareto frontier: best compromises
- Design by navigation on Pareto frontier
Lennard-Jones (LJ) Pair Potential

\[ \frac{U}{k_B \varepsilon} = 4 \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

- Radial symmetry
- Accounts for:
  - Repulsion
  - Dispersion
- Two parameters:
  - Size \( \sigma \)
  - Energy \( \varepsilon \)
Pareto-based Lennard-Jones Modeling of Argon

Parameter space

Objective space

\( \varepsilon / K \)

\( \sigma / \text{Å} \)

\( \delta \Delta h_v \)

\( \delta \rho \)

\( \delta \rho' \)
Pareto-based Lennard-Jones Modeling of Argon

Parameter space

Objective space

Pareto-based Lennard-Jones Modeling of Methane

Parameter space

Objective space

Molecular Models of Fluids: Examples

**Phosgene Group**

- CCl₂O
- HCl
- C₆H₆
- C₆H₅-CH₃
- C₆H₅-Cl
- o-C₆H₄-Cl₂

**Ethylene Oxide Group**

- C₂H₄O
- H₂O
- HO(CH₂)₂OH

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

- Excellent test cases for molecular modeling and simulation

Y. L. Huang et al. AIChE J. 57 (2011) 1043-1060
Vapor Pressures

Symbols: Simulation
Lines: Reference DIPPR

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Saturated Densities

Symbols: Simulation
Lines: Reference DIPPR

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Predictions: Transport Properties of Liquid HCl

- Prediction EMD Simulation
- Prediction NEMD Simulation
- Experiment (Literature)
- DIPPR Correlation

\[ \lambda / \text{W m}^{-1}\text{K}^{-1} \]

\[ \eta / \times 10^{-4} \text{ Pa s} \]

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

Molecular Modelling of Mixtures

Unlike interaction A-B:

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

\[
\begin{align*}
\sigma_{AB} &= \frac{(\sigma_A + \sigma_B)}{2} \\
\varepsilon_{AB} &= \xi \cdot \sqrt{\varepsilon_A \varepsilon_B}
\end{align*}
\]

Predictions \(\xi = 1\)

or

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

Vapor-Liquid Equilibrium HCl + Chlorobenzene

Symbols:
- simulation (full)
- experiment (cross)

Lines:
- Peng-Robinson EOS

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Application to Reaction Studies
Phosgeneation, Liquid Mixture (110 °C, 1 bar)

Phosgene + Cl-Benzene + HCl + 2,4-Diaminetoluene
50 mol% 40 mol% 7 mol% 3 mol%

Local concentration ≠ Overall concentration

Study of radial pair correlation functions

\[ g_{ij}(r) = \frac{\text{local concentration } c_{j,i}}{\text{overall concentration } c_j} \]
Radial Pair Correlation Functions: Amine Groups – HCl
Important for Formation of Undesired Hydrochlorides

- Deviations between overall and local concentration up to a factor of 8
- HCl strongly prefers amine group N2 over N4
- HCl docks preferentially with the proton at amine group N2
Proton Catalyzed Reaction Ethylene Oxide + Water
Proton Catalyzed Reaction Ethylene Oxide + Water
Radial Pair Correlation Functions

\[ g(r) \]

\[ H_2O + EOX \quad x_w = 0.995 \text{ mol/mol} \]

- 340 K, 56.6 mol/l
- 460 K, 51.9 mol/l

\[ CH_2-O (\text{with EOX}) \quad CH_2-O (\text{with HEOX}^+) \]
Transient Radial Pair Correlation Functions

oxygen + methyl 400 K

10 ps after protonation

2 ps after protonation

unprotonated protonated... in liquid water (TIP4P/2005)
Henry’s Law Constants of Ethylene Oxide

EO in Water

EO in (Water + Ethylene glycole)

- Physical solubility
- No chemical reactions

Spherical Vapor-Liquid Interfaces

- Droplet + metastable vapor

Spinodal limit: For the external phase, metastability breaks down.
Spherical Vapor-Liquid Interfaces

- Droplet + metastable vapor
- Bubble + metastable liquid

Spinodal limit: For the external phase, metastability breaks down.

Planar limit: The curvature changes its sign and the radius $R_\gamma$ diverges.

\[ \Delta p = \frac{2\gamma}{R_\gamma} \]

\[ T = 0.6 T_c \]

\[ \text{gas} \quad \text{liq} \quad \text{spinodal} \quad \text{planar} \]

RKS ($\omega = 0$)
Curvature Dependence of Surface Tension

Equimolar radius (from density profile)

\[ \int_0^{R_\rho} \left( \rho_0 - \rho_R \right) R^2 dR = \int_{R_\rho}^\infty \left( \rho_R - \rho_\infty \right) R^2 dR \]

Laplace radius

\[ R_\gamma = \frac{2\gamma}{\Delta p} \]

Capillarity radius

\[ R_\kappa = \frac{2\gamma_0}{\Delta p} \]

Curvature Dependence of Surface Tension

- No evidence for curvature dependence of surface tension of small droplets

Planar Vapor-Liquid Interfaces

Surface tension:
- Abundant studies on small droplets, i.e. simultaneous variation of curvature & size
- No previous studies on thin slabs with planar surfaces, i.e. variation of size only
Planar Vapor-Liquid Interfaces

Lennard-Jones fluid

- Evidence for finite size effects for very thin slabs

Wetting and Dispersive Fluid-Wall Interactions

Young's equation

$$\gamma_{SV} + \gamma_{SL} - \gamma_{LV} = \cos \theta$$

solid (S)
liquid (L)
vapor (V)
three phase contact
contact angle $\Theta$

Symbols:
Simulation (LJTS)

Lines:
correlations

Curve parameter:
reduced temperature
Reduced wall density $5.876 \sigma^{-3}$

M. Horsch et al., Langmuir 26 (2010) 10913-10917
Wetting and Dispersive Fluid-Wall Interactions

Density in droplet

ρ / σ⁻³

Density profile center

LJTS

Simulation
Correlation

θ
Wetting, Adsorption and Surface Diffusion

- Molecular dynamics
- LJTS Model
Summary

- Molecular modeling and simulation in chemical engineering
  - Atomistic force fields

- Molecular simulations of real systems are feasible

- Wide range of applications
  - Fluid properties (static, dynamic, …)
  - Surfaces (nucleation, wetting, adsorption, …)
  - Reactions
  - …

- Challenges
  - Complex molecules, electrolytes
  - Fluid-wall interactions
  - Bridging scales (long times, large systems, …)
  - Computational efficiency, massive parallelization

- High potential (to be exploited …)
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