Fully automatized determination of Fundamental Equations of State based on molecular simulations in the cloud

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Computational Molecular Engineering
For pure chemical substances...

accurate knowledge in entire fluid region: \( \sim 10 \) substances

satisfactory knowledge: \(< 100 \) substances

For mixtures...

the knowledge is much worse

Problem: scarce experimental data

**Fundamental equation of state (FEOS) correlation**

\[ E(N, V, S) \quad H(N, p, S) \quad F(N, V, T) \quad G(N, p, T) \]

\[ F / T(N, 1/T, V) \]

= “explicit function in terms of \( N \), \( 1/T \), and \( V \)”

\[ \frac{\partial^xyz F / T}{\partial^x (1/T) \partial^y V \partial^z N} \]

- \( E \): internal energy
- \( H \): enthalpy
- \( F \): Helmholtz energy
- \( G \): Gibbs energy
- \( S \): entropy
- \( V \): volume
- \( p \): pressure
- \( T \): temperature
- \( N \): particle number
Thermodynamic properties from FEOS

\[
\frac{\partial^{mn} F}{\partial^m (1/T) \partial^n \rho} (1/T)^m \rho^n = A_{mn}
\]

\( \rho = N / V \)

- Internal energy: \( \frac{E}{RT} = A_{10} \)
- Enthalpy: \( \frac{H}{RT} = A_{10} + A_{01} \)
- Pressure: \( \frac{p}{\rho RT} = A_{01} \)
- Isochoric heat capacity: \( \frac{c_v}{R} = -A_{20} \)
Thermodynamic properties from FEOS

isothermal comp. \[ \rho RT \cdot \beta_T = \frac{1}{A_{02} + 2A_{01}} \]

isobaric heat cap. \[ \frac{c_p}{R} = -A_{20} + \frac{(A_{01} - A_{11})^2}{2A_{01} + A_{02}} \]

speed of sound \[ \frac{Mw^2}{RT} = 2A_{01} + A_{02} - \frac{(A_{01} - A_{11})^2}{A_{20}} \]

Joule-Thomson coeff. \[ \rho R \cdot \eta = \frac{-\left(A_{01} + A_{02} + A_{11}\right)}{\left(A_{01} - A_{11}\right)^2 - A_{20} \left(2A_{01} + A_{02}\right)} \]
Molecular Simulation

Molecular dynamics (MD)  
Monte Carlo (MC)
Simulation framework

A single MD or MC simulation run per state point yields:

\[
\frac{\partial^{mn} (F / T)}{\partial^m (1 / T) \partial^n \rho} = A_{mn}
\]

\[
c_p, w \quad f(A_{01}, A_{20}, A_{11}, A_{02})
\]


www.ms-2.de
Molecular simulation as engineering mainstream tool* 
(for equilibrium thermodynamic property generation)

**Advantages:**
- much cheaper than experiment
- faster than experiment (once source code is available)
- several thermodynamic properties simultaneously
- applicable under all conditions

**Problems:**
- dependent on the quality of molecular models
- code development and usage require considerable expertise

Cloud-based automatized FEOS fitting

Goals: - target substances/fluid regions for which there are no data available
- perform the simulation and obtain a FEOS within 24 h
- little human interaction

How: - use simulation data only
- simple fitting approach (linear fit)

\[ A^{Res}(\tau, \delta) = \sum_{i=1}^{N} a_i \tau^i \delta^d_i + \sum_{j=k+1}^{M} a_i \tau^i \delta^d_i \exp(-\delta^c_i) + \ldots \]

(everything else is taken from generalized FEOS)
Cloud-based automatized FEOS fitting

**User's task:** - select state points and molecular model
Cloud-based automatized FEOS fitting

Automatized deployment:
- Distribution of simulations to available High Performance Computers (HPC) in the Cloud
Cloud-based automatized FEOS fitting

User’s task: - select fitting options and check results
Cloud-based automatized FEOS fitting

Example: Phosgene (extremely toxic, yet millions of tons produced annually)

~ 300 state points x 9 derivatives (= 2700 measurements)
Quality of the FEOS from Simulation (Phosgene)

RDEV(p)
RDEV(c_p)
RDEV(c_v)
RDEV(n)

Density / mol · dm^{-3}

Quality of the FEOS from Simulation (Phosgene)

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<th>( T/\text{K} )</th>
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Quality of the FEOS from Simulation (Ethylene Oxide)

Experiments

- Molecular simulation based FEOS (top plots)
- Experiment based FEOS, advanced fitting approach (bottom plots)

Summary

Molecular simulation data sets
• Useful for FEOS development (cost effective, fast)
• Applicable under all conditions

Cloud-based FEOS fitting
• Enables non-expert users to create FEOS in a matter of days
• Contribution to making molecular simulation more accessible

Outlook
• Creation of force fields may be automatized extending this workflow
Thank you for listening!

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