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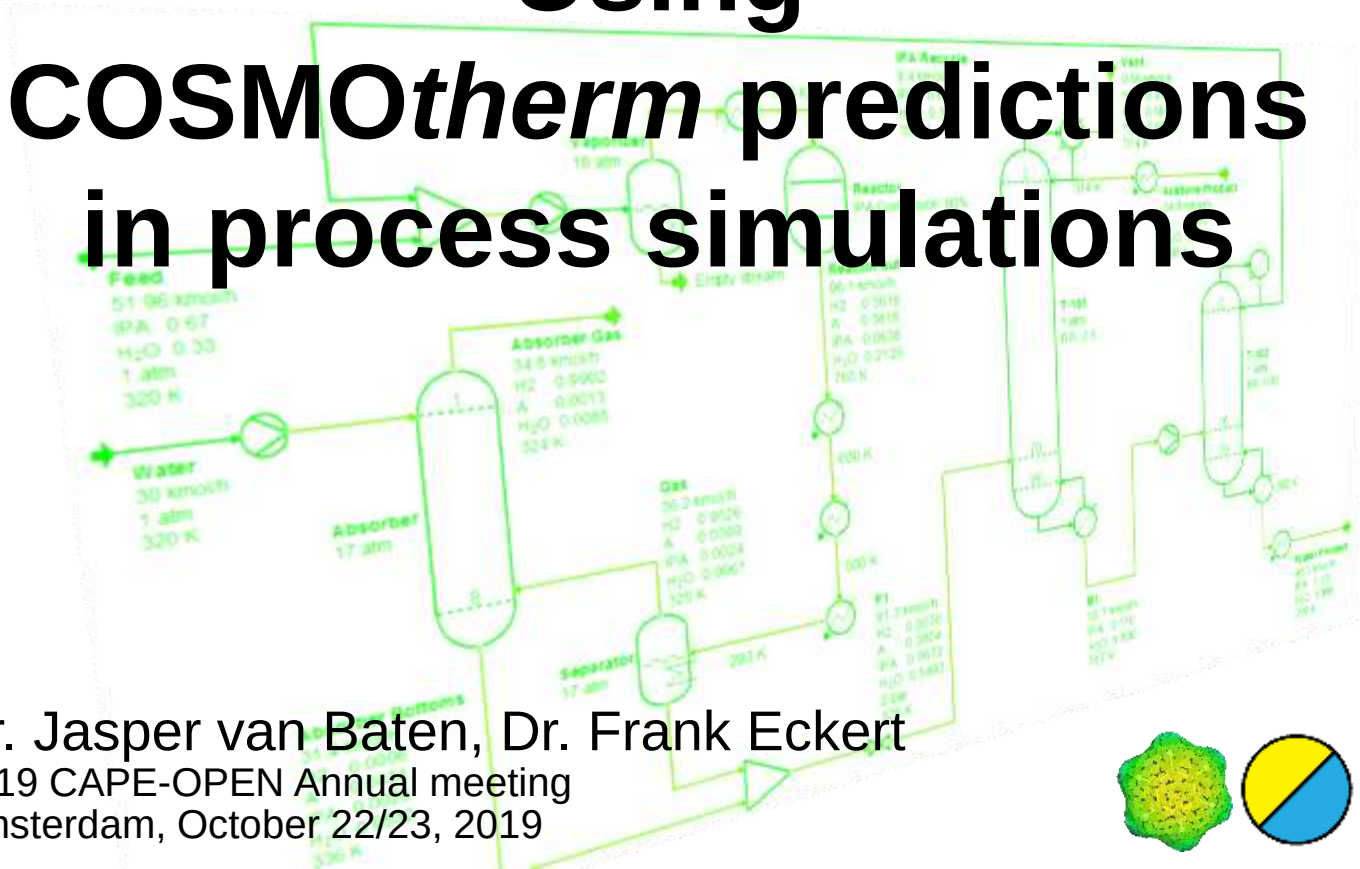
Using COSMO*therm* predictions in process simulations



Dr. Jasper van Baten, Dr. Frank Eckert

2019 CAPE-OPEN Annual meeting
Amsterdam, October 22/23, 2019

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COSMO*therm*

Property prediction for molecules in pure and mixed liquids

Prediction of thermodynamic properties

COSMO*therm* is a software to predict thermodynamic properties such as solubilities, activity coefficients or vapor pressures in liquid mixtures.

Works without experimental data

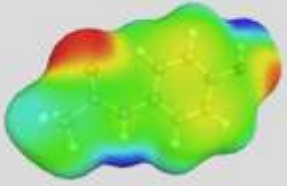
COSMO*therm* applies the fully predictive COSMO-RS model and requires no experimental data. All information is taken from COSMO files for each compound, which can be generated with quantum chemistry programs (e.g. TURBOMOLE) and stored for later use.

Your benefit

- Guide your experiments to save lab time and improve your results
- Find new or unexpected solutions by screening large databases of possible solvents, co-solvents, entrainers, and other additives
- Investigate new areas of chemistry without further adjustments

Application Areas

- Chemical engineering
- Drug design & development
- Chemistry
- Environmental science
- Formulation
- Quantum chemistry



COSMO surface of paracetamol

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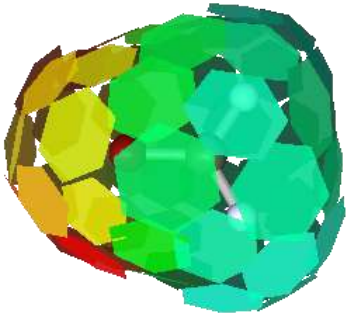
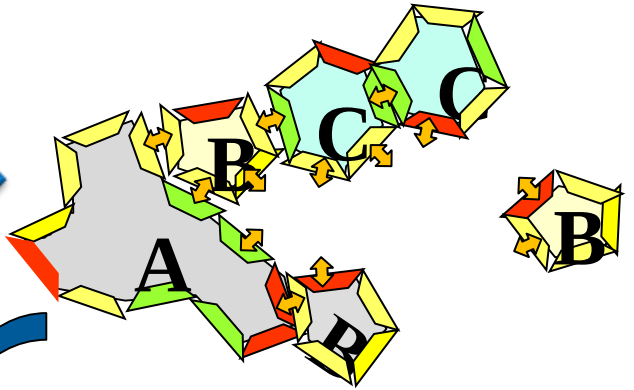
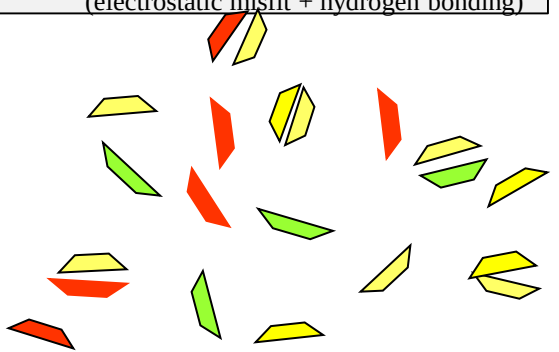


σ–profile
= histogram of
surface polarity



$\sigma \leftrightarrow \sigma'$ pairwise interactions of surface segments based on σ and σ'
(electrostatic misfit + hydrogen bonding)



A.Klamt, J. Phys. Chem. 1995, 99, 2224-2235
A.Klamt, G.J.P. Krooshof, and R. Taylor: AIChE Journal 2002, **48**, 2332-2349

- **History: lnGamma calculation routine**
  - Very early in CAPE-OPEN: 2006
  - *ICapeThermoCalculationRoutine* (v1.0)
  - ~~*ICapeThermoPropertyRoutine* (v1.1)~~
  - Direct access to COSMO*therm* calculations
  - Slow.... No composition derivatives.
  - Unexpectedly little support for calculation routines (although seemingly useful concept)
  - Only Property Package available to deal with COSMO*therm*: COCO/TEA
  - Using TEA, wide support. LITE with COCO.

Pure compound

- Constants
  - Critical properties
  - Molecular weight
  - Correlation inputs
- Correlations
  - T-dependent
  - C_P(IG)
  - P_{sat}
  - H_{vap}
  - Transport props

Pure compound

T, P, X
Phase

Mixture

- Constants
  - Critical properties
  - Molecular weight
  - Correlation inputs
- Correlations
  - T-dependent
  - C_P(IG)
  - P_{sat}
  - H_{vap}
  - Transport props

- Chemical potential
  - Fugacity
  - Activity
- Properties
  - *H, S, ...*
  - Mix props
  - Transport props

Pure compound

- Constants
  - Critical properties
  - Molecular weight
  - Correlation inputs
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Mixture

- Chemical potential
  - Fugacity
  - Activity
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Pure compound

- Constants
  - Critical properties
  - Molecular weight
  - Correlation inputs
- Correlations
  - T-dependent
  - C_P(IG)
  - P_{sat}
  - H_{vap}
  - Transport props

Mixture

- Chemical potential
  - Fugacity
  - Activity

excess

- Properties
  - *H, S, ...*
  - Mix props
  - Transport props

Pure compound

- Constants
  - Critical properties
  - Molecular weight
  - Correlation inputs
- Correlations
  - T-dependent
  - C_P(IG)
  - P_{sat}
  - H_{vap}
  - Transport props

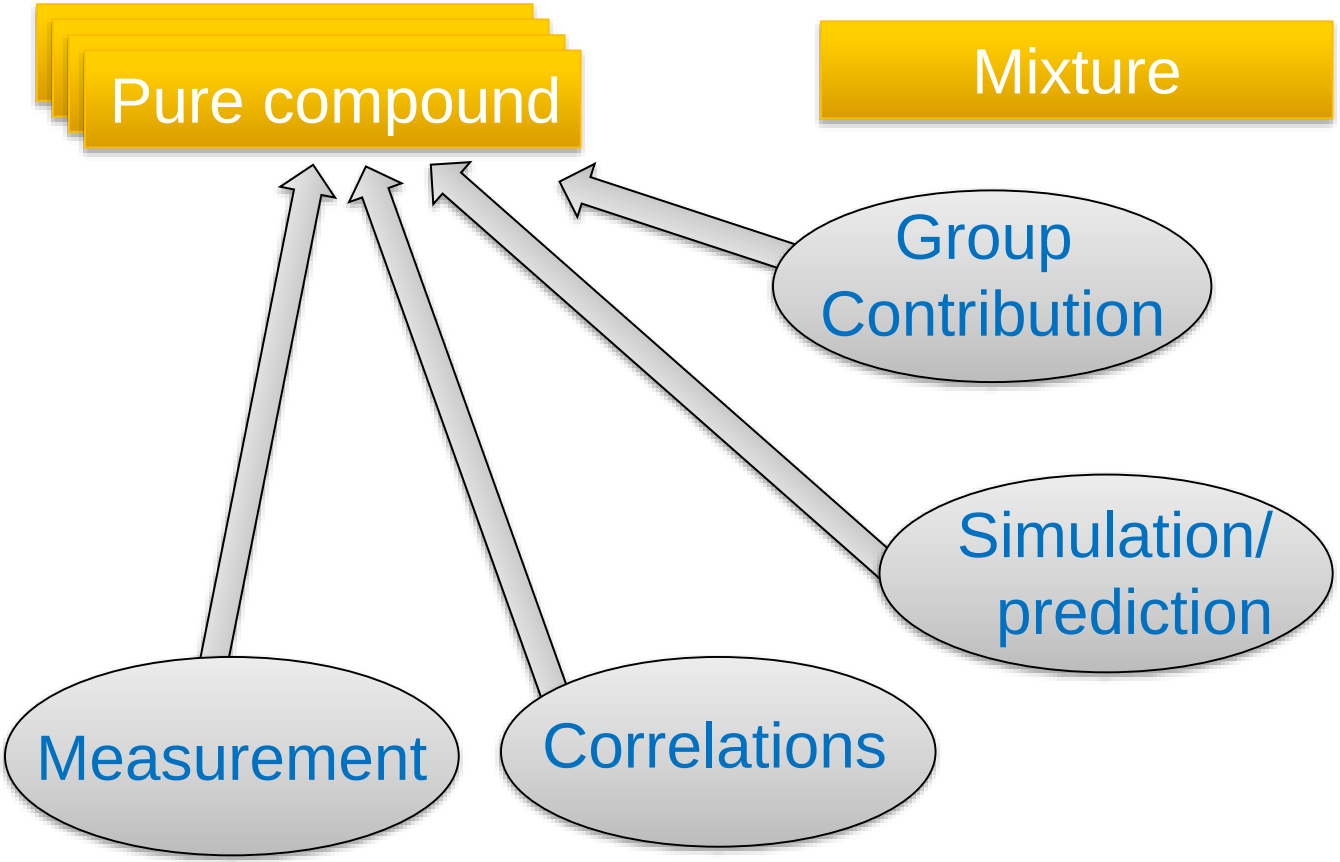
Mixture

- Chemical potential
  - Fugacity
  - Activity

corresponding states

- Properties
  - *H, S, ...*
  - Mix props
  - Transport props

mix rules


Pure compound
Mixture
Group Contribution
Simulation/ prediction
Measurement
Correlations

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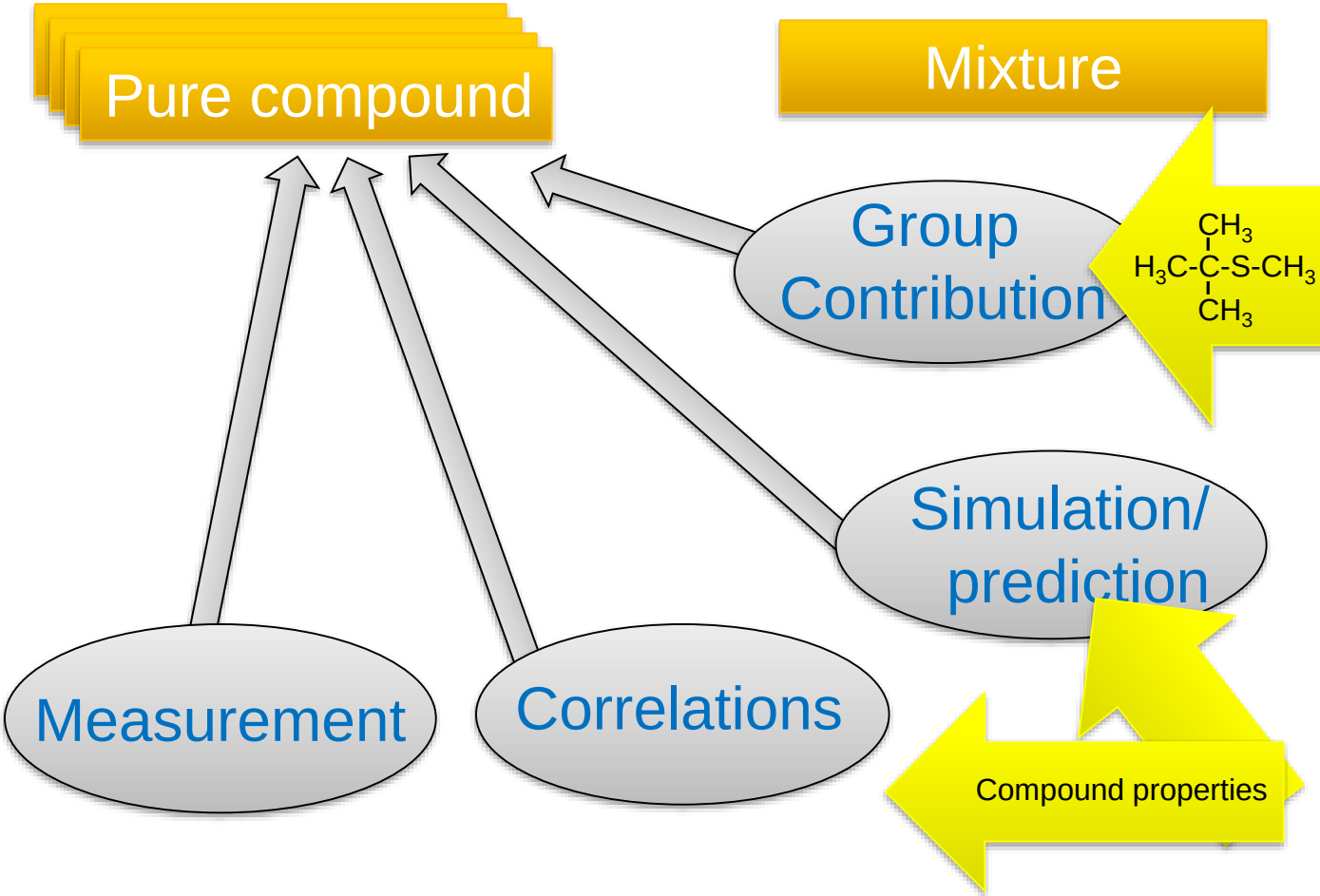

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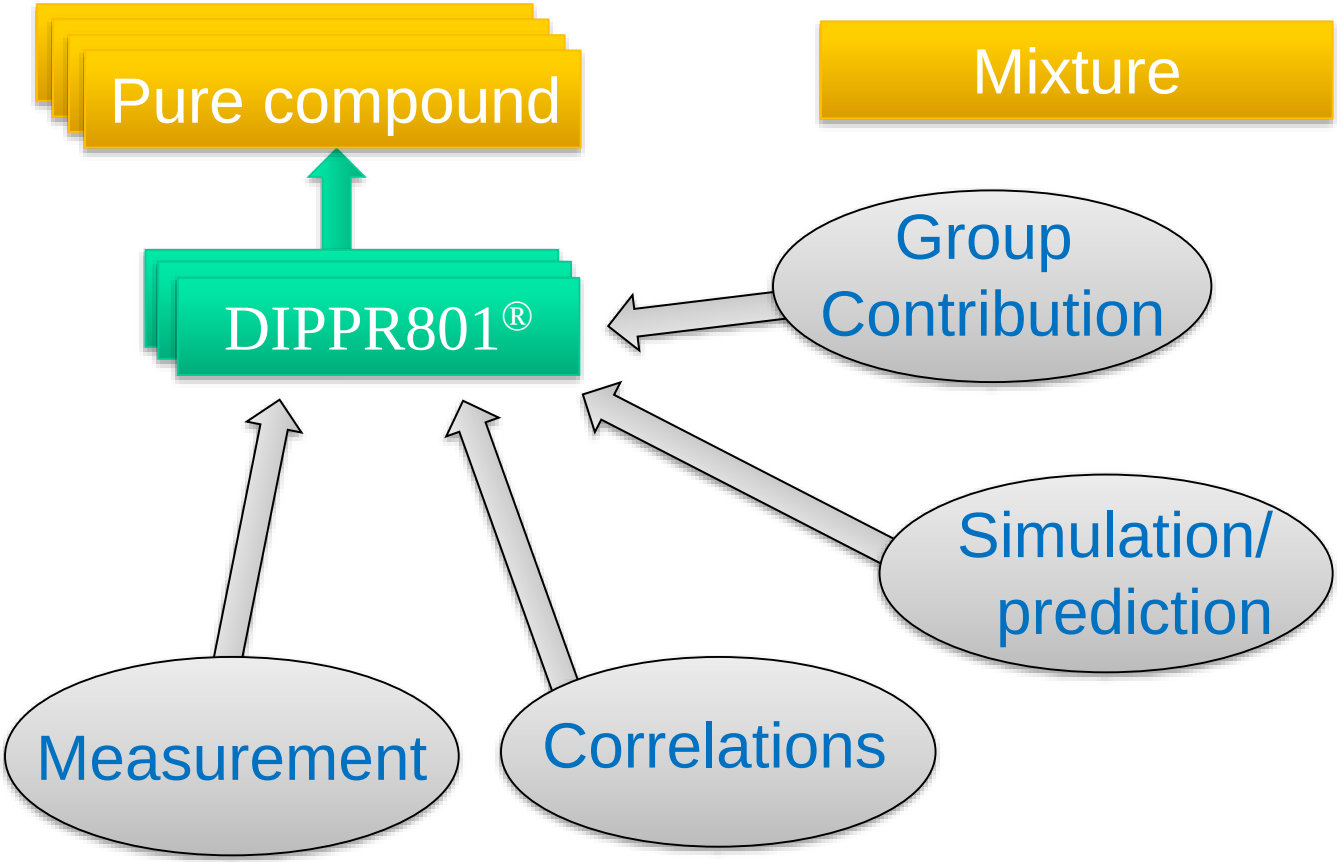

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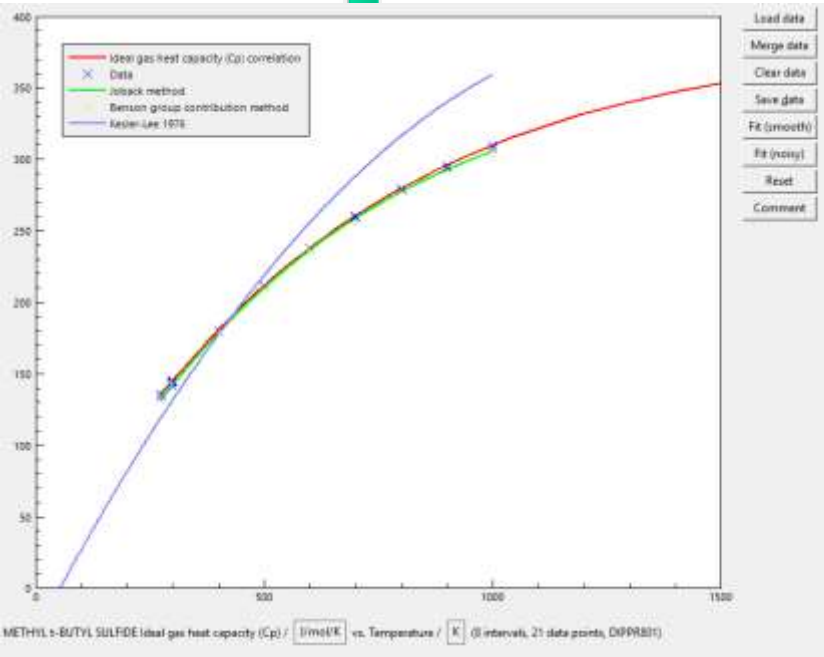
Pure compound

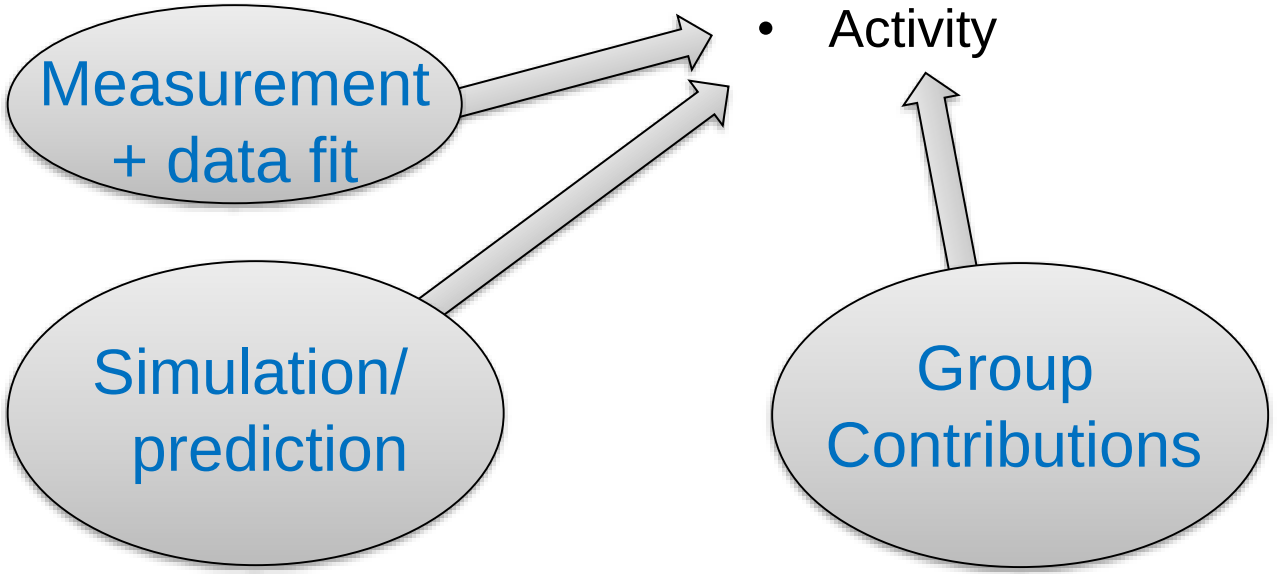
Mixture



Pure compound

Mixture

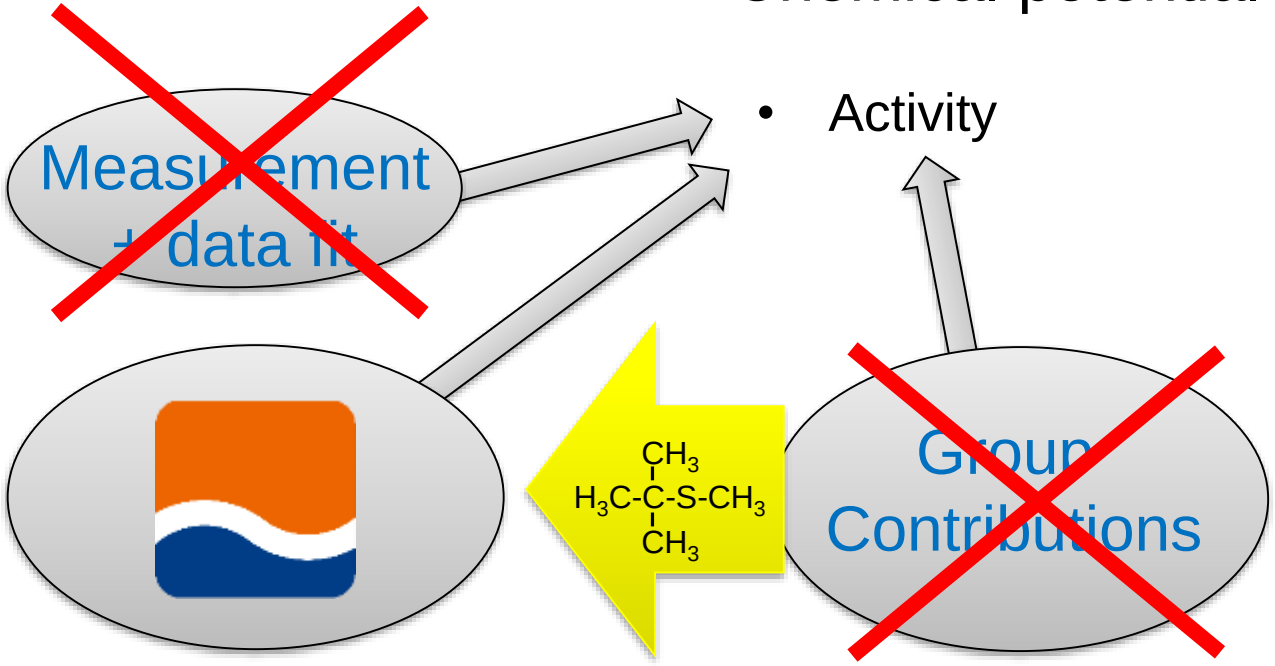
- Chemical potential
- Activity



Pure compound

Mixture

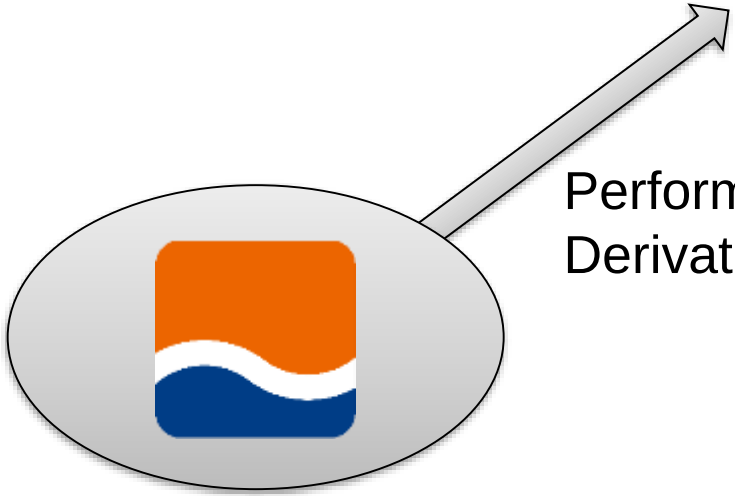
- Chemical potential
- Activity



Pure compound

Mixture

- Chemical potential
  - Activity

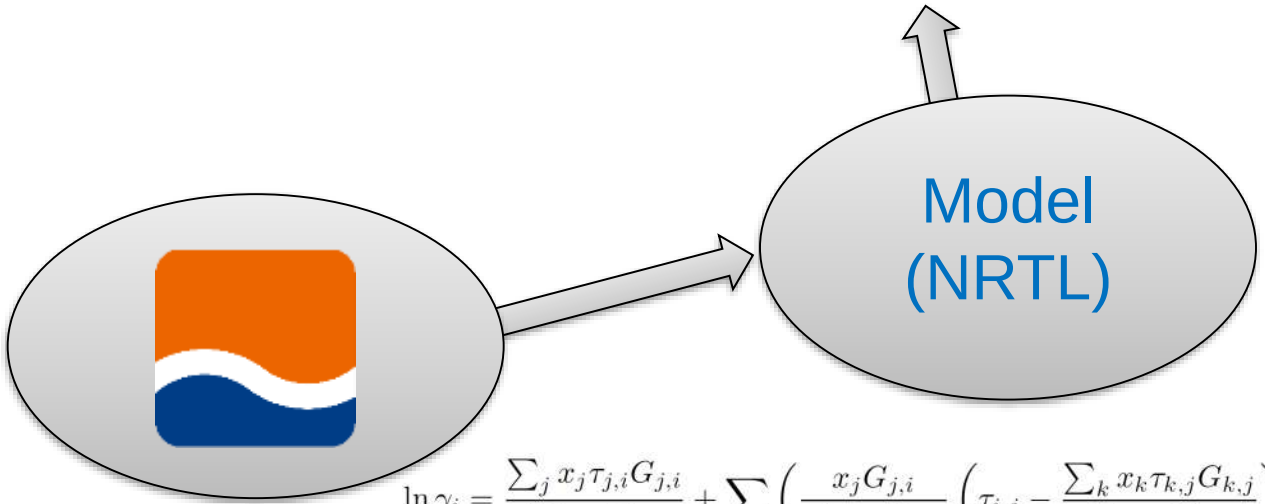


Performance?
Derivatives?

Pure compound

Mixture

- Chemical potential
  - Activity



$$\ln \gamma_i = \frac{\sum_j x_j \tau_{j,i} G_{j,i}}{\sum_j x_j G_{j,i}} + \sum_j \left(\frac{x_j G_{j,i}}{\sum_k x_k G_{k,j}} \left(\tau_{i,j} - \frac{\sum_k x_k \tau_{k,j} G_{k,j}}{\sum_k x_k G_{k,j}} \right) \right)$$

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{j,i} G_{j,i}}{\sum_j x_j G_{j,i}} + \sum_j \left(\frac{x_j G_{j,i}}{\sum_k x_k G_{k,j}} \left(\tau_{i,j} - \frac{\sum_k x_k \tau_{k,j} G_{k,j}}{\sum_k x_k G_{k,j}} \right) \right)$$

Each binary has 4 parameters, each of which can be a function of temperature

$$G_{i,j} = \exp\left(-\alpha_{i,j}\tau_{i,j}\right) = g_{i,j}(T)$$
$$G_{j,i} = \exp\left(-\alpha_{j,i}\tau_{j,i}\right) = g_{j,i}(T)$$
$$\tau_{j,i} = t_{j,i}(T)$$
$$\tau_{j,i} = t_{j,i}(T)$$

Common 3 parameter form

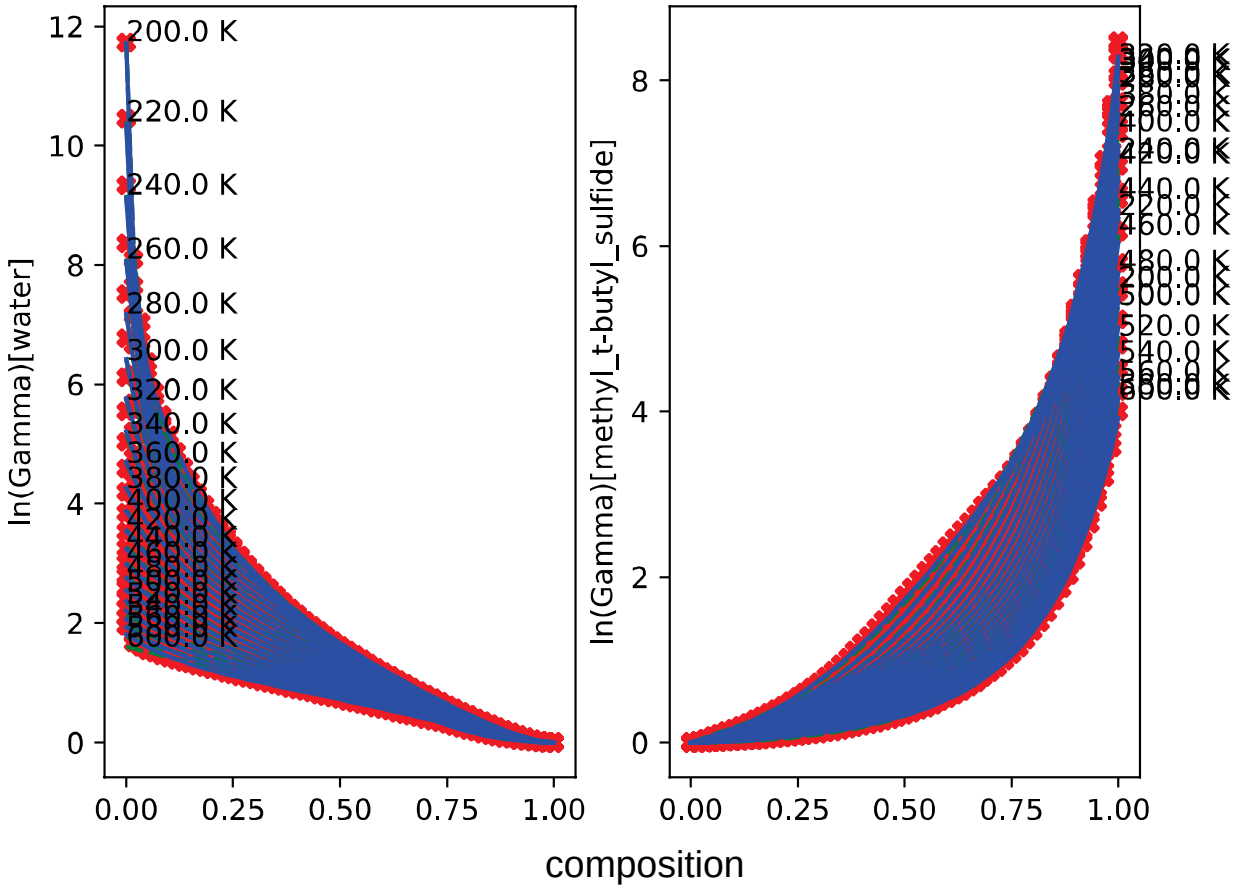
$$\tau_{i,j} = \frac{A_{i,j}}{T}$$
$$G_{i,j} = \exp\left(-\alpha\tau_{i,j}\right)$$

Fit Procedure:

Fit $G_{j,i}$, $G_{i,j}$, $\tau_{j,i}$, $\tau_{i,j}$ separately against $\gamma_{i,xj=1}$ and $\gamma_{j,xi=1}$

Fit all $G_{j,i}$, $G_{i,j}$, $\tau_{j,i}$, $\tau_{i,j}$ to all data.

Water / methyl t-butyl sulfide, 200 ≤ T/[K] ≤ 600



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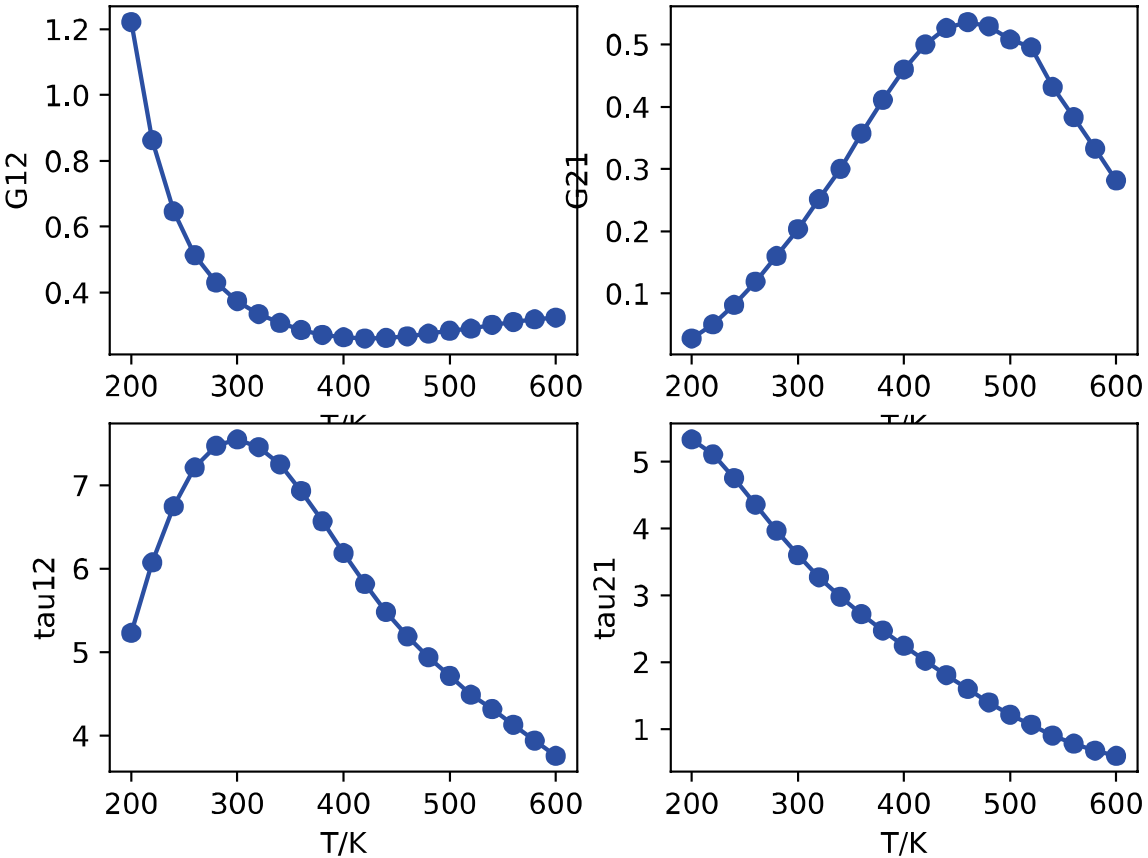

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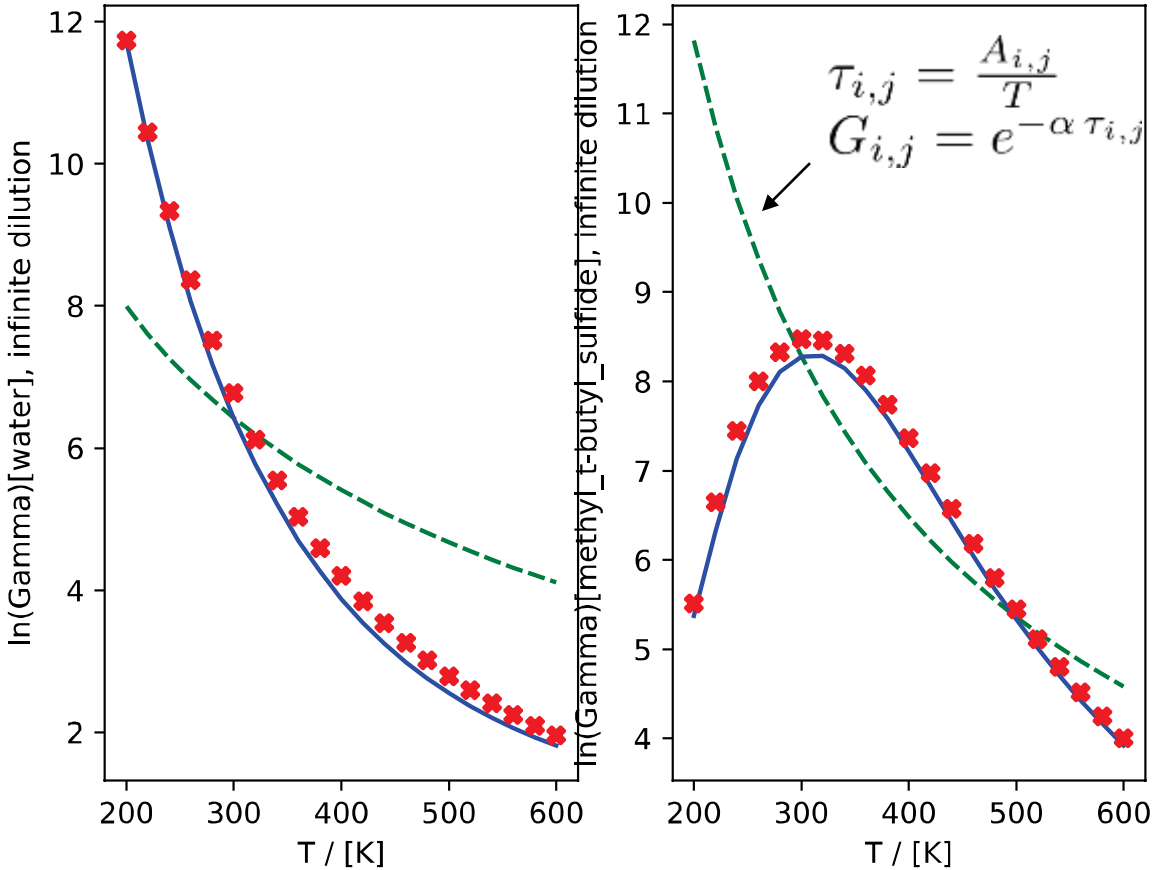
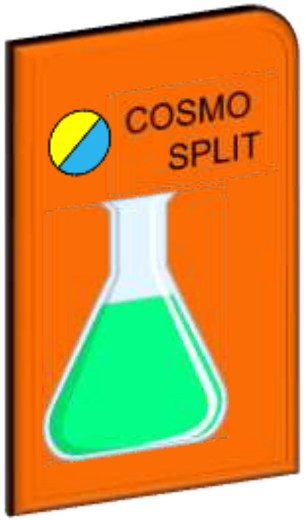


- Pure compound libraries (e.g. DIPPR801)
- Expt. Data import + fitting
- Group contribution data
- Correlations

- Mixture property routines
- Transport properties
- Analytic derivatives

- Multi-phase equilibrium calculator

- NRTL fitting



Software package

- Pure compound libraries (e.g. DIPPR801)
- Expt. Data import + fitting
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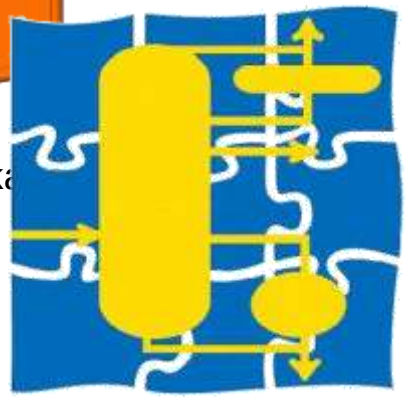
Software packa



Flowsheet Simulators consuming thermo PMCs

Other thermo PMC client software

(*) Plus a variety of in-house simulators
(**) This is not an exhaustive list

Summary

- Design requirements summarized for application framework for Using COSMO*therm* predictions in process simulations
- Technology validated
- Exposed via CAPE-OPEN
- Ready for use

Thank you

- **Questions?**