ADVANCED PROCESS MODELLING FORUM **2014**

gSAFT

Advances in thermodynamic modelling in gPROMS

Thomas Lafitte – Senior Scientist

gPROMS product family

General mathematical modelling

Model Builder

Advanced process modelling environment

Sector-focused modelling tools

Chemicals & Petrochemicals

Process Builder

Process flowsheeting

AML: GLC, AML: FBCR, AML: FT, AML: BCR, AML: TBR

Advanced model libraries for reaction & separation

Life Sciences, Consumer, Food, Spec & Agrochem

gSOLIDS

Solids process optimisation

gCRYSTAL

Crystallization process optimisation

gCOAS

Oral absorption

Power & CCS

gCCS

CCS system modelling

Fuel Cells & Batteries

gFUELCELL

Fuel cell stack & system design

Oil & Gas

gFLARE

Flare networks & depressurisation

Wastewater Treatment

gWATER

Wastewater systems optimisation

gPROMS

The gPROMS platform

Equation-oriented modelling & solution engine

Materials modelling

gSAFT

INFOCHEM Multiflash

OLI

Model deployment tools

Enterprise

gE:Web

Objects

gO:Run, gO:MATLAB, gO:CAPE-OPEN, gO:CFD

Deploy models in common engineering software

Physical properties in gPROMS

- **Multiflash®**
  - coupled with DIPPR® databank
  - used within most gPROMS-family products
- **OLI®**
  - aqueous and mixed solvent electrolytic systems
- **CAPE-OPEN thermo physical property interface**
  - allows access to Aspen Properties® and other CAPE-OPEN compliant physical property systems

- **Next-generation physical properties technology**
- **Based on SAFT equation of state**
  - theory developed by the Molecular Systems Engineering group at Imperial College London

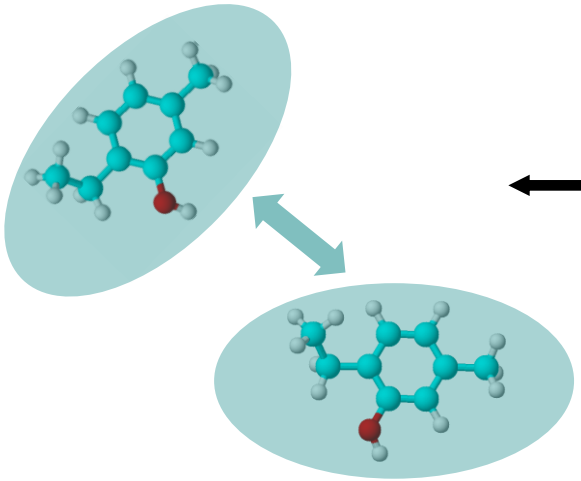
Equations of State

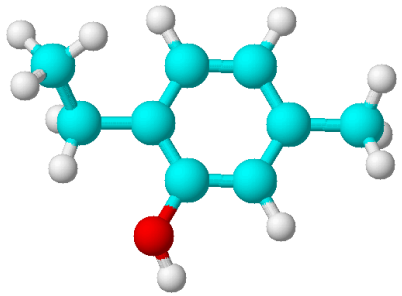
Molecular representation

Functional group representation

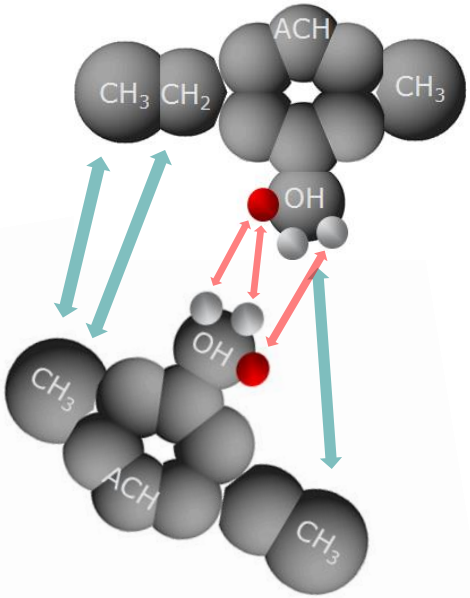
SAFT-VR SW

SAFT-γ Mie





2-ethyl-5-methylphenol



SAFT-γ Mie Equation of State

SAFT: Chapman, Gubbins, Jackson, Radosz, *Ind. Eng. Chem. Res*., 29, 1709 (1990)

SAFT-VR SW: Gil-Villegas, Galindo, Whitehead, Mills, Jackson, Burgess, *J. Chem. Phys*., 106, 4168 (1997)

SAFT-γ SW: Lymperiadis, Adjiman, Jackson, Galindo, *Fluid Phase Equilib.*, 274, 85 (2008)

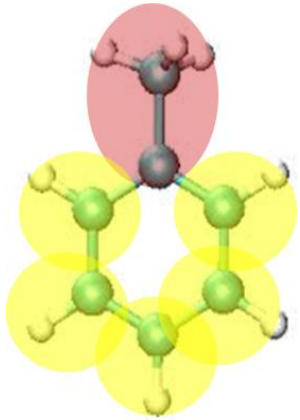
SAFT-VR Mie : Lafitte, Apostolakou, Avendaño, Galindo, Adjiman, Muller, Jackson, *J. Chem. Phys*., 139, 154504 (2013)

SAFT-γ Mie: Papaioannou, Lafitte, Avendaño, Adjiman, Jackson, Muller, Galindo, *J. Chem. Phys.,* 140*,* 054107 (2014)

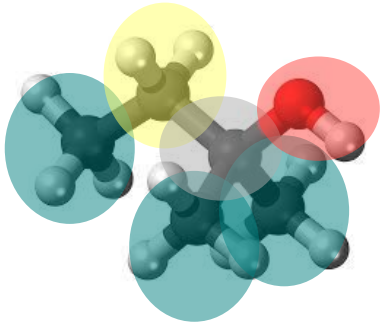
SAFT-γ Mie molecular model – I

- Each molecule comprises one or more (generally non-identical) functional groups

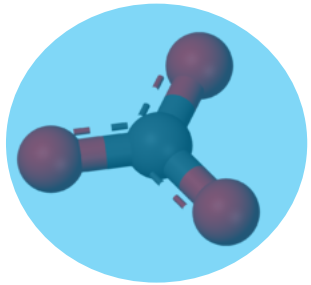
toluene



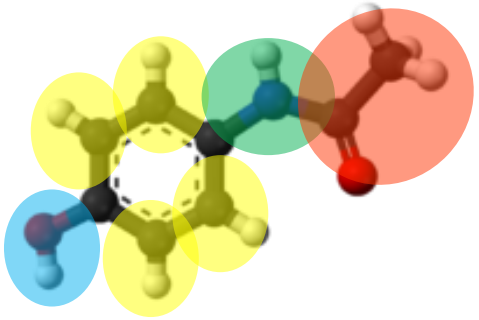
alcohols



carbonate ion

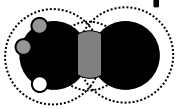


paracetamol

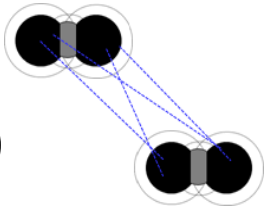


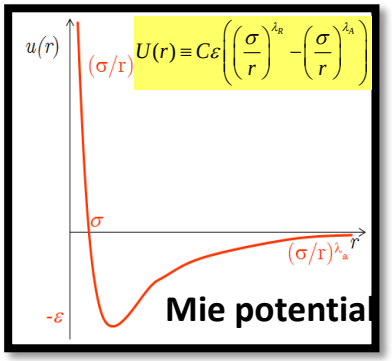
SAFT-γ Mie molecular model – II

- Each functional group comprises one or more identical segments

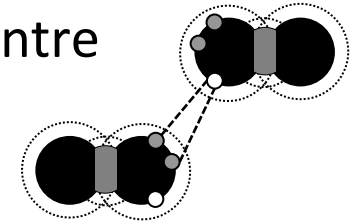


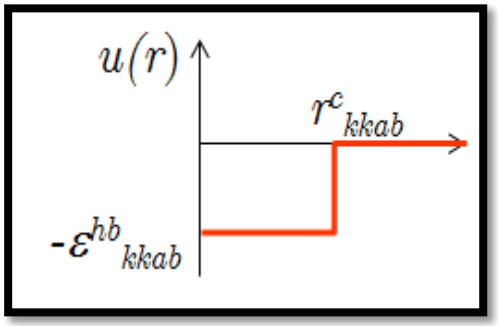
- Interactions between segments
  - dispersion/repulsion (van der Waals) forces



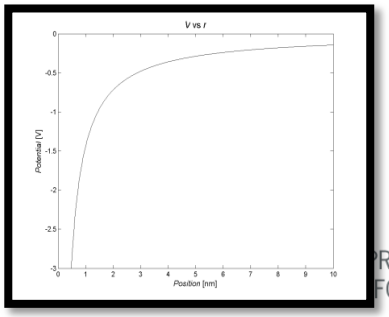


  - hydrogen bonding via off-centre electron donor/acceptor ("association") sites





  - ionic (coulombic) forces

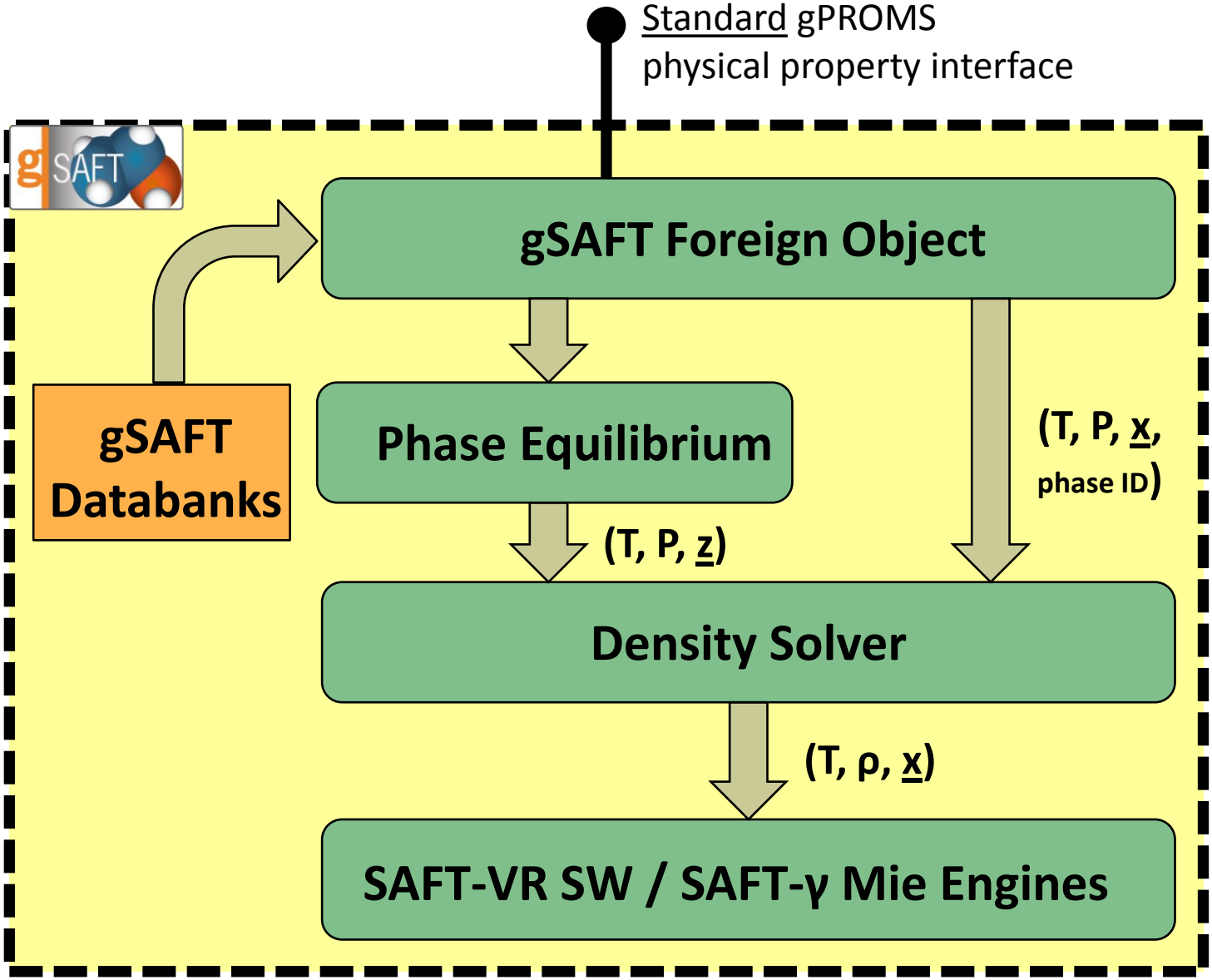


Increasing strength

Apply Statistical Thermodynamics ➔ SAFT γ Mie Equation of State

Using gSAFT in gPROMS models

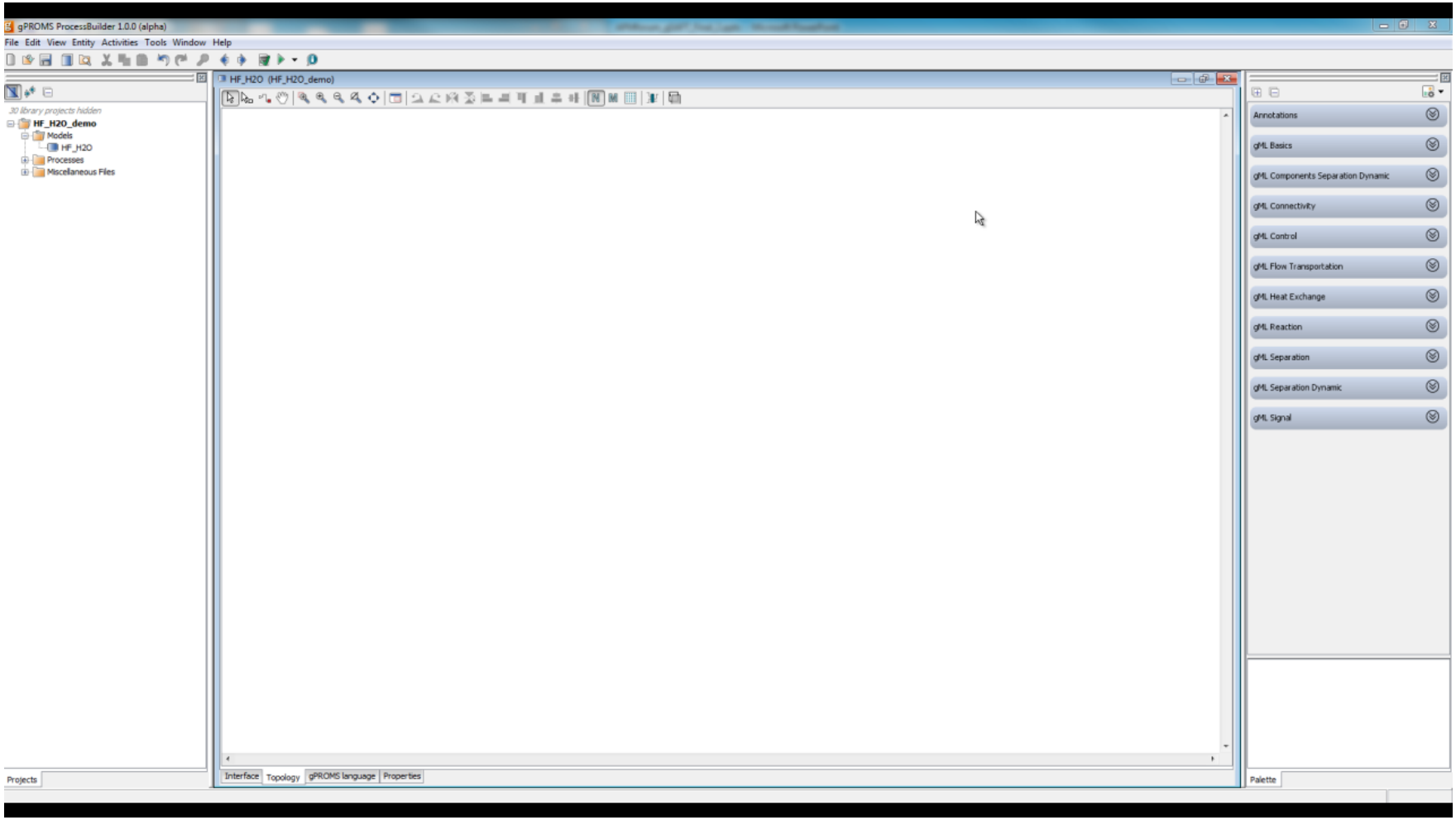
gSAFT code architecture



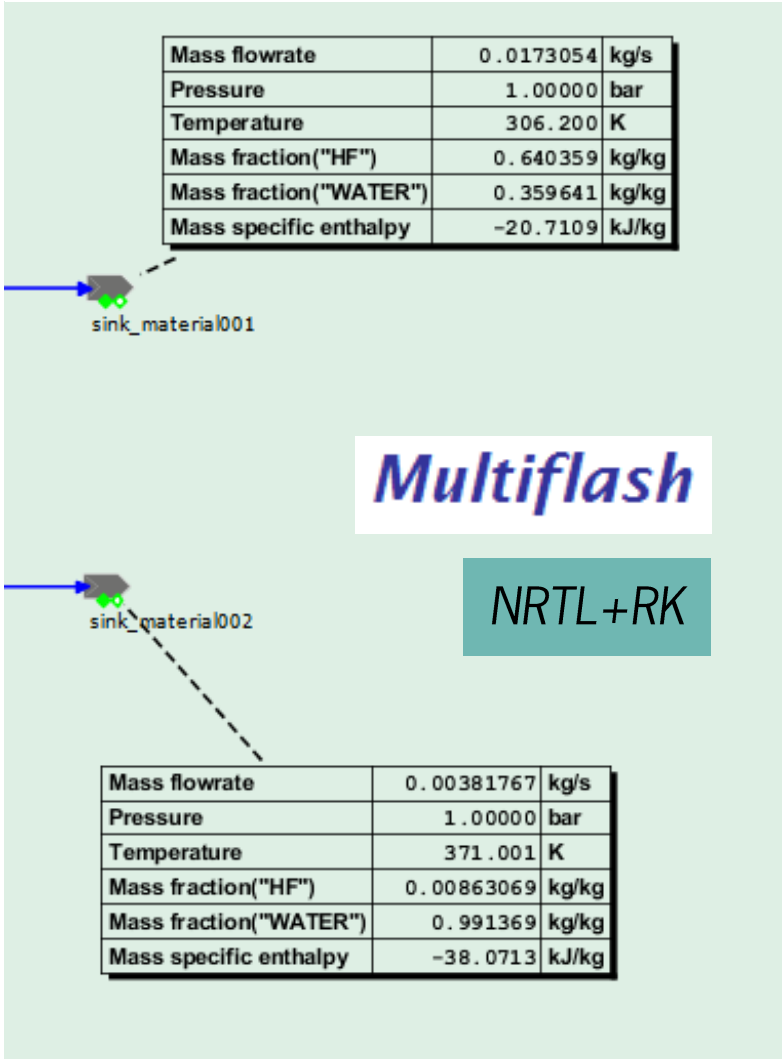
Example 1: HF + H_2O separation process

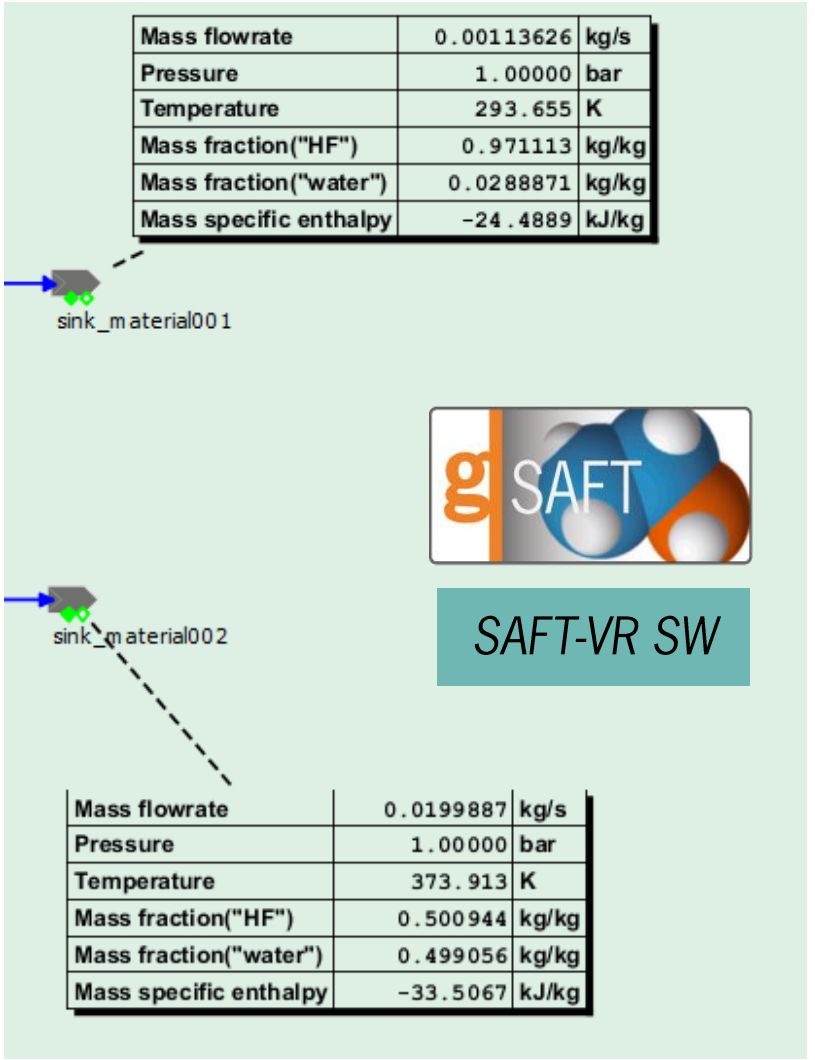
$HF-H_2O$ separation

modelling with gPROMS ProcessBuilder



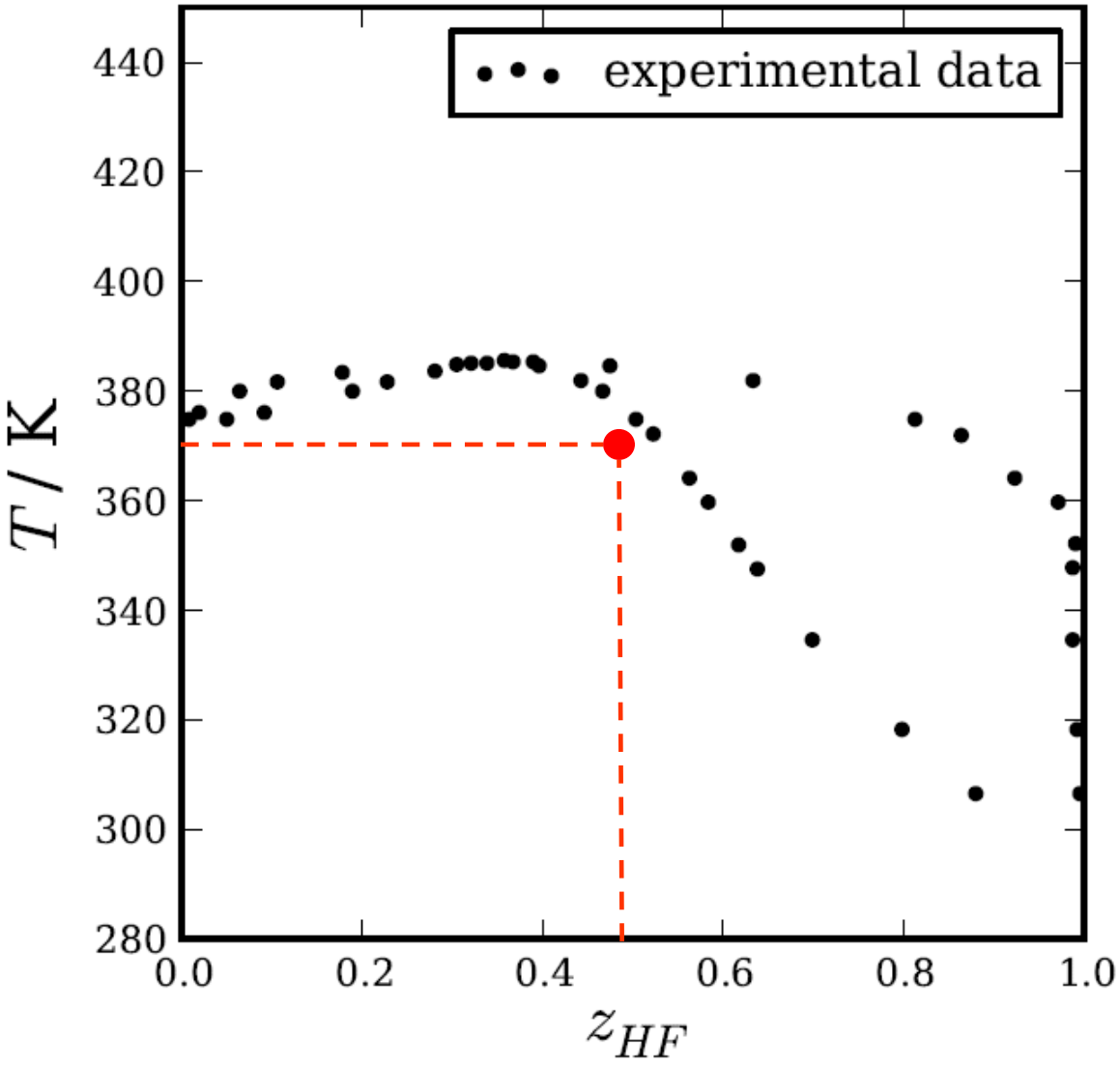
HF-H_2O separation
modelling with ProcessBuilder





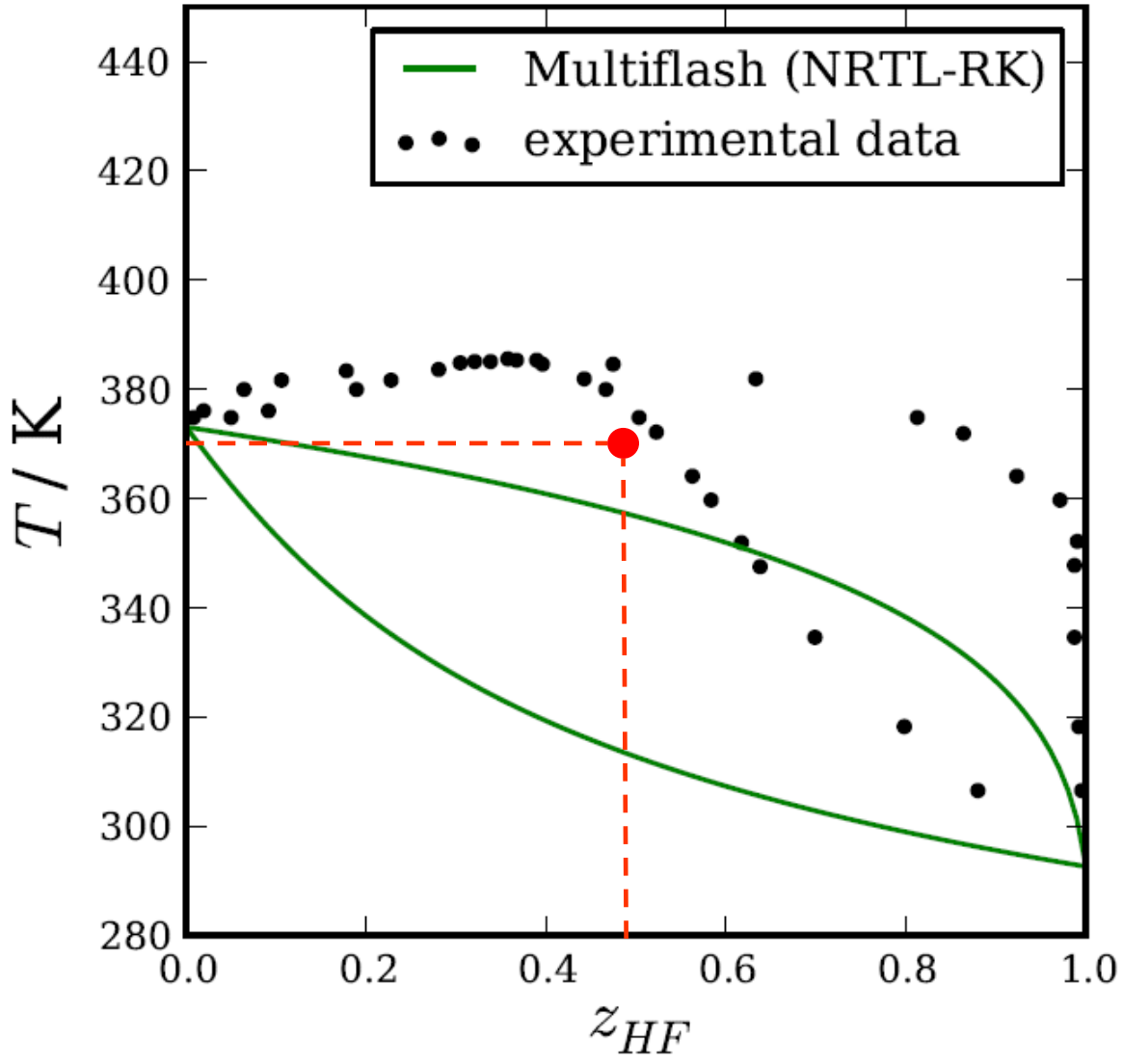
HF-H_2O separation

phase equilibrium prediction



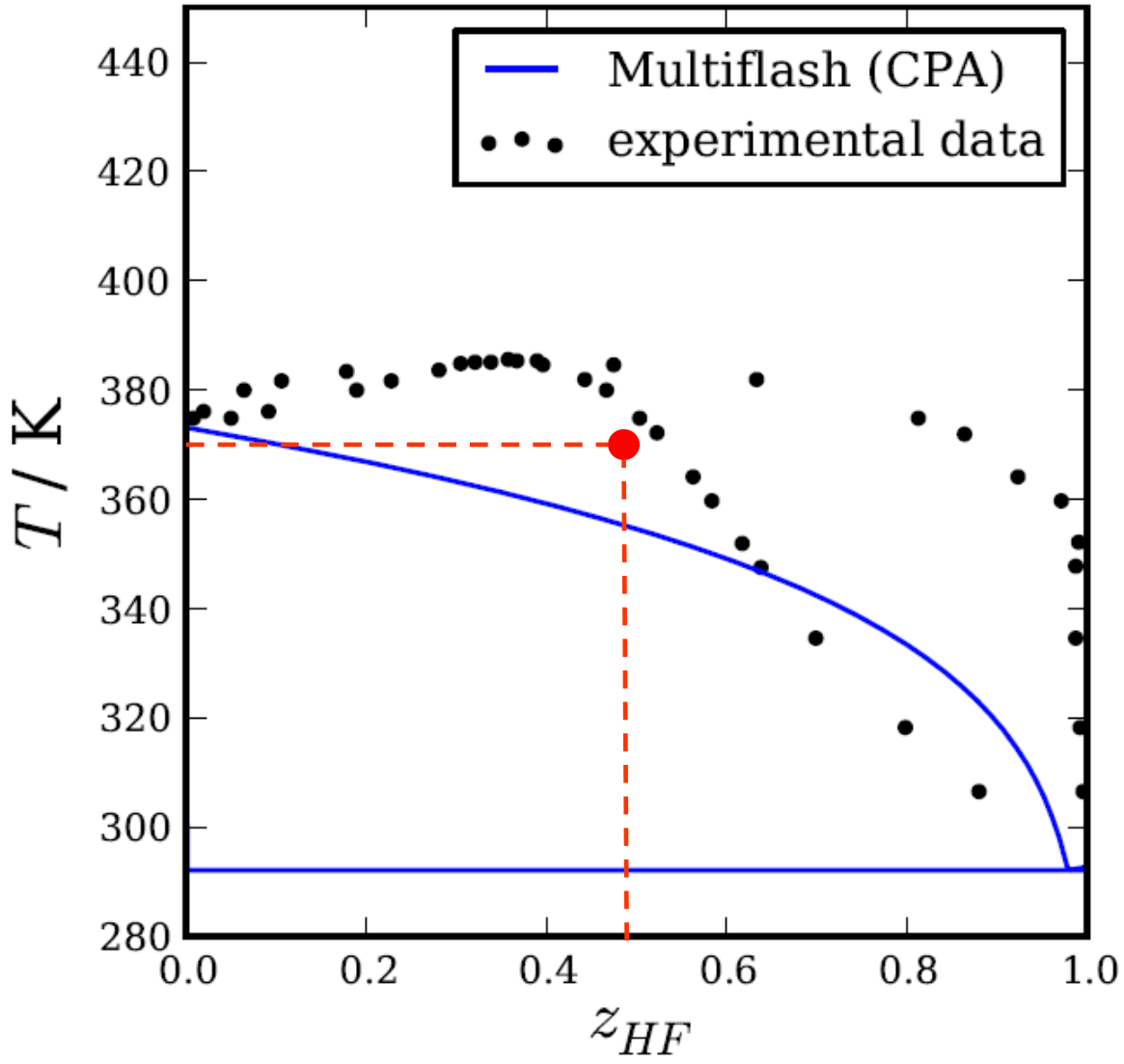
HF-H_2O separation

phase equilibrium prediction



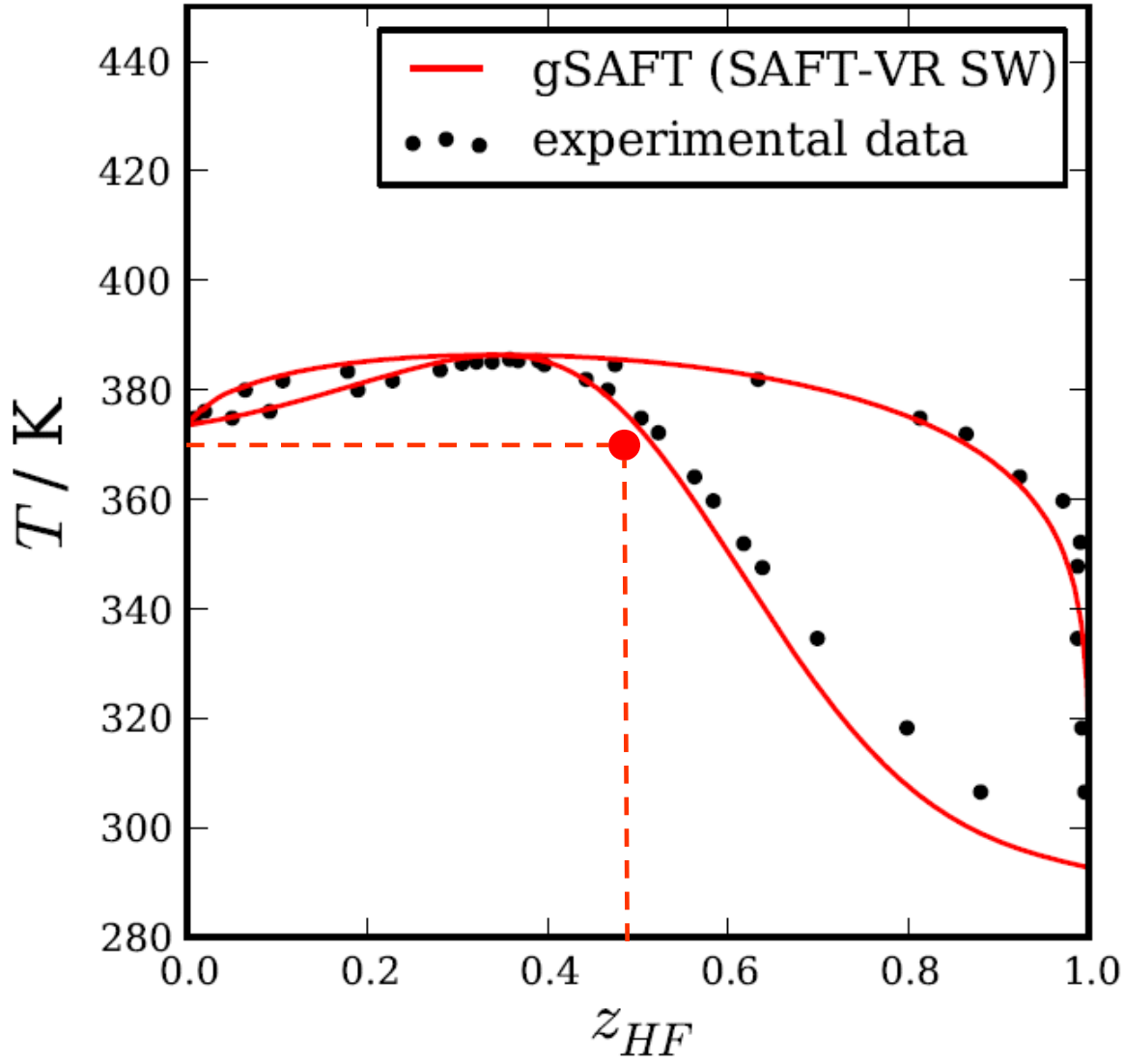
HF-H_2O separation

phase equilibrium prediction



HF-H_2O separation

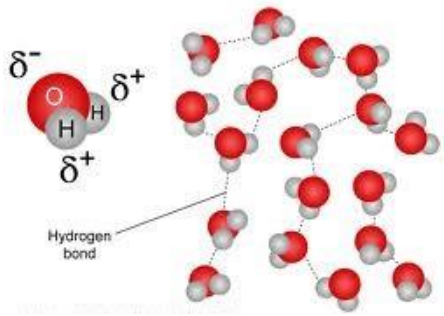
phase equilibrium prediction



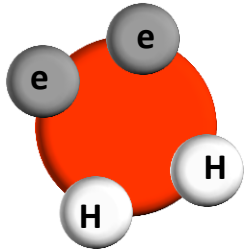
HF-H_2O separation

Importance of **molecular level** description

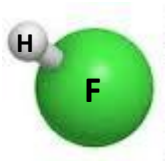
- Complex self interactions
  - Water

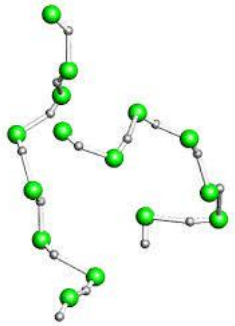


SAFT representation →

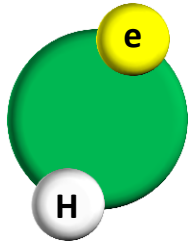


  - Hydrogen fluoride





SAFT representation →

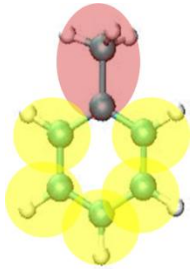


- Highly non-ideal mixture
  - Need to account for cluster formation between HF and H_2O
  - Leads to extreme negative azeotrope

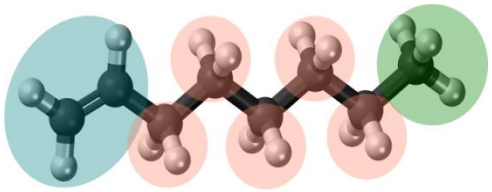
Example 2: LAO separation process

Molecules of interest to LAO process
and their functional group decomposition

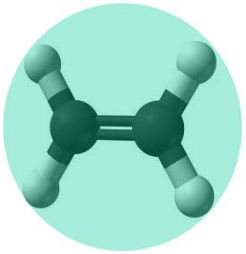
- Molecular structure



toluene



Linear α-olefin



ethylene

- SAFT-γ Mie databank

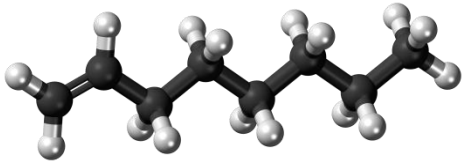
group	CH_3	CH_2	$H_2C{=}CH$	aCH	aCCH3	$H_2C{=}CH2$
CH_3						
CH_2						
$H_2C{=}CH$						
aCH						
aCCH3						
$H_2C{=}CH2$						

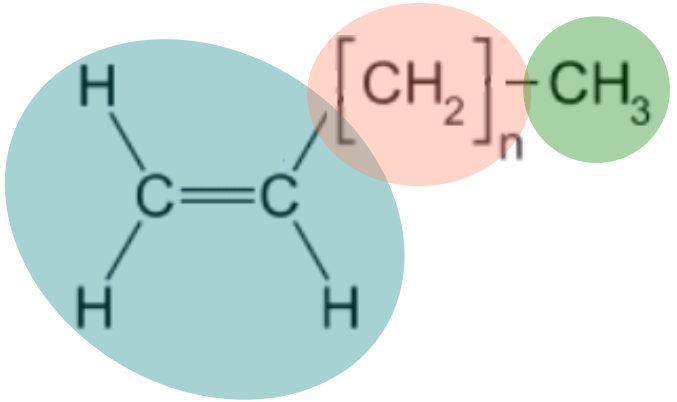
available

combining rules

gSAFT group parameters: Linear α-Olefins

- Molecular structure:





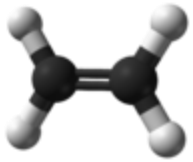
- SAFT-γ Mie parameters estimated from pure component vapour pressure & saturated liquid densities
  - CH_3- and -CH_2- parameters from pure alkanes
  - H_2C=CH- parameters from pure 1-butene, 1-hexene and 1-octene

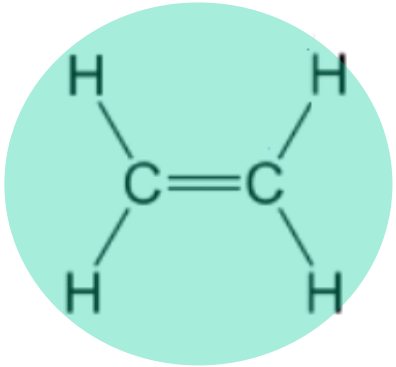
groups	σ [Å]	λ_{rep} [-]	λ_{att} [-]	S
CH_3	xxx	xxx	xxx	xxx
CH_2	xxx	xxx	xxx	xxx
H_2C=CH	xxx	xxx	xxx	xxx

ε/k_B [K]	CH_3	CH_2	H_2C=CH
CH_3	xxx	---	---
CH_2	xxx	xxx	---
H_2C=CH	xxx	xxx	xxx

gSAFT group parameters: Ethylene

- Molecular structure:





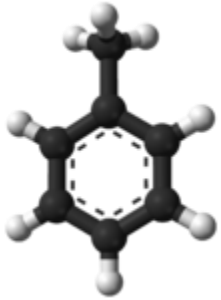
- SAFT-γ Mie parameters estimated using vapour pressure & saturated liquid densities of pure ethylene

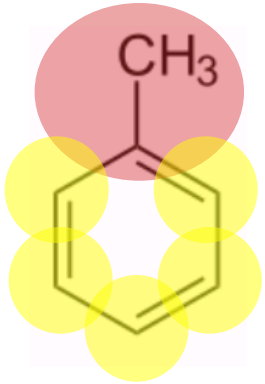
groups	σ [Å]	λ_{rep} [-]	λ_{att} [-]	S
$H_2C=CH_2$	xxx	xxx	xxx	xxx

ε/k_B [K]	$H_2C=CH_2$
$H_2C=CH_2$	xxx

gSAFT group parameters: Toluene

- Molecular structure:





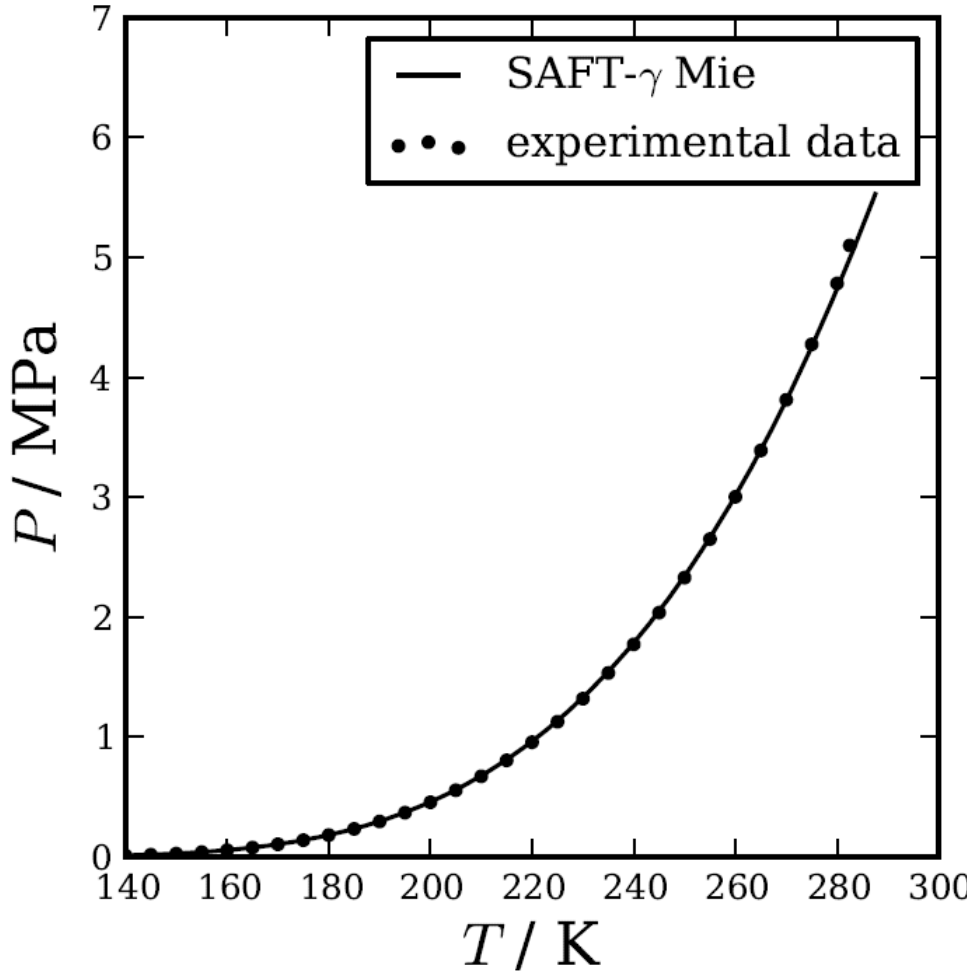
- SAFT-γ Mie parameters estimated from pure component vapour pressure & saturated liquid densities
  - aCH parameters from pure benzene
  - $aCCH_3$ parameters from pure toluene

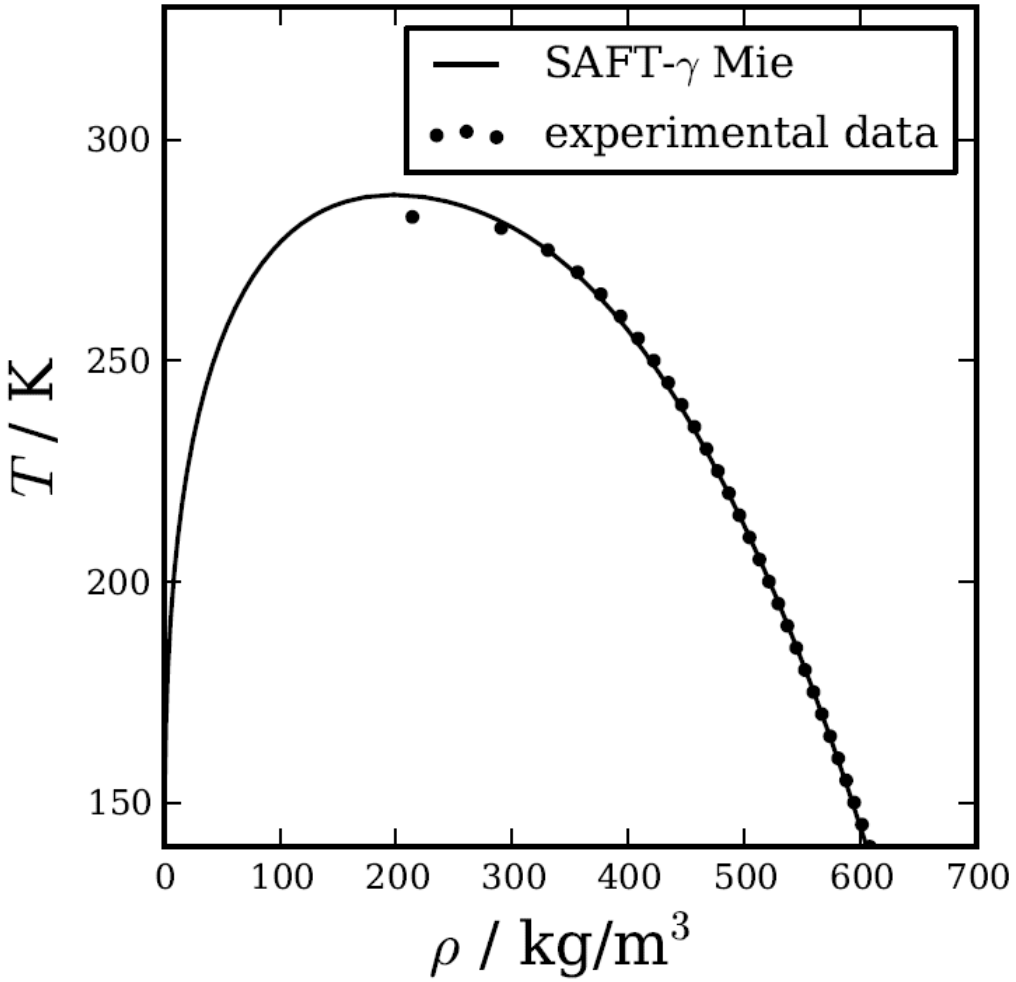
groups	σ [Å]	λ_{rep} [-]	λ_{att} [-]	S
aCH	xxx	xxx	xxx	xxx
$aCCH_3$	xxx	xxx	xxx	xxx

ε/k_B [K]	aCH	$aCCH_3$
aCH	xxx	-----
$aCCH_3$	xxx	xxx

Ethylene

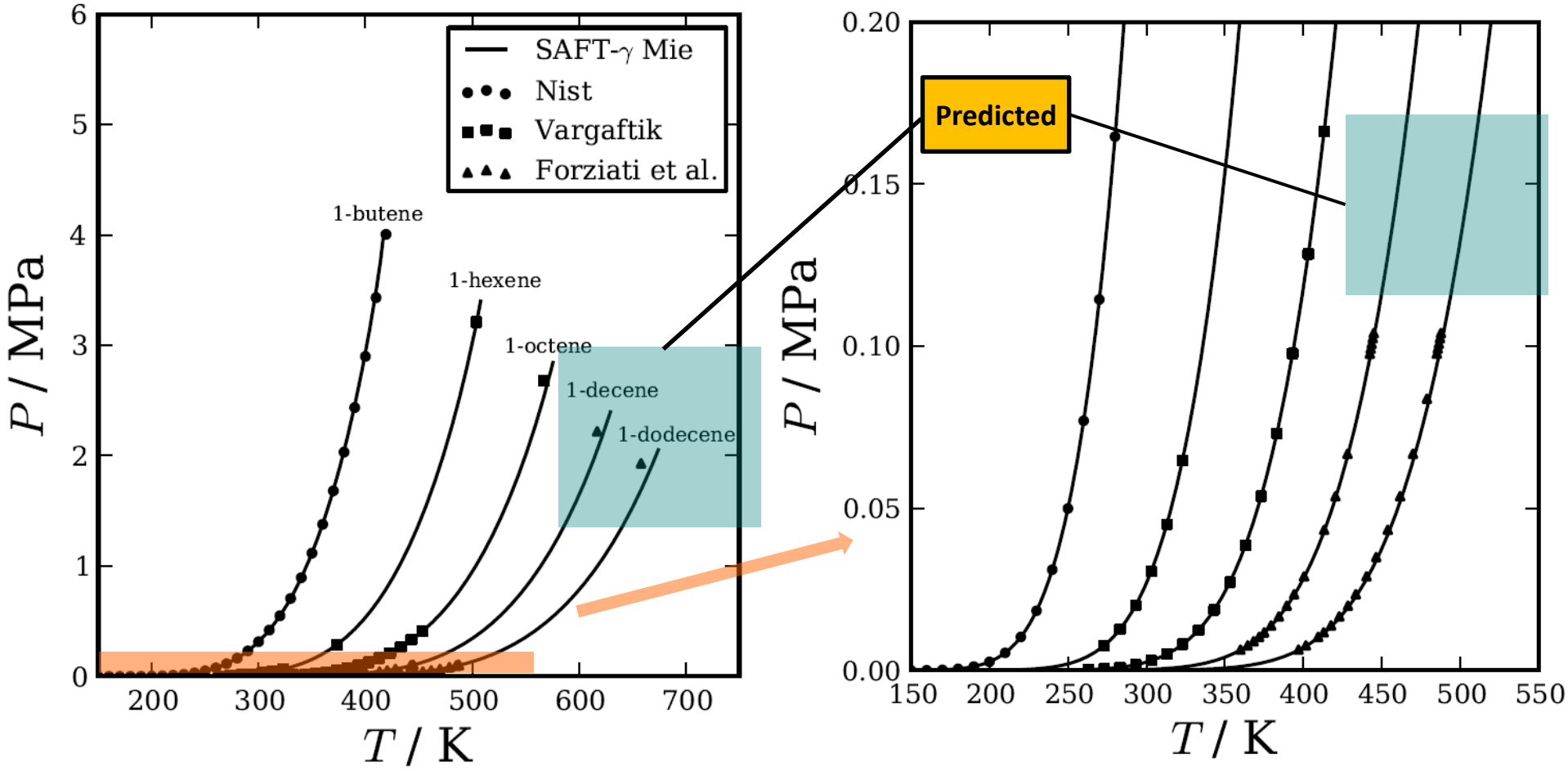
vapour pressure – saturated densities





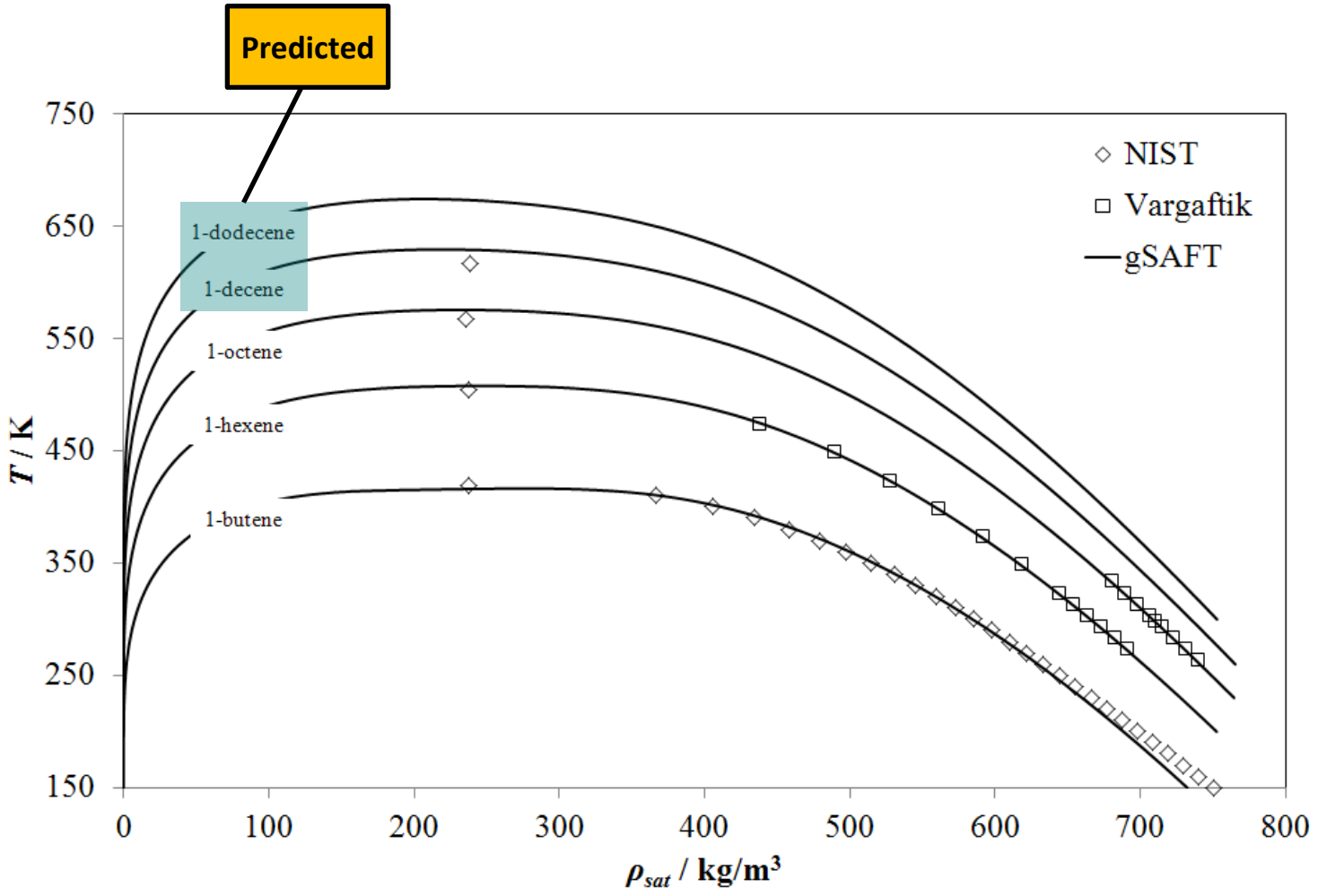
- NIST WebBook (http://webbook.nist.gov/chemistry/)

α-Olefins – vapour pressure



- NIST WebBook (http://webbook.nist.gov/chemistry/)
- Forziati *et al*., *J. Res. Nat. Bur. Stand*., 45 , 5 (1950)
- Vargaftik, N.B., Tables on the Thermophysical properties of Liquids and Gases, Hemisphere Publishing (1975)

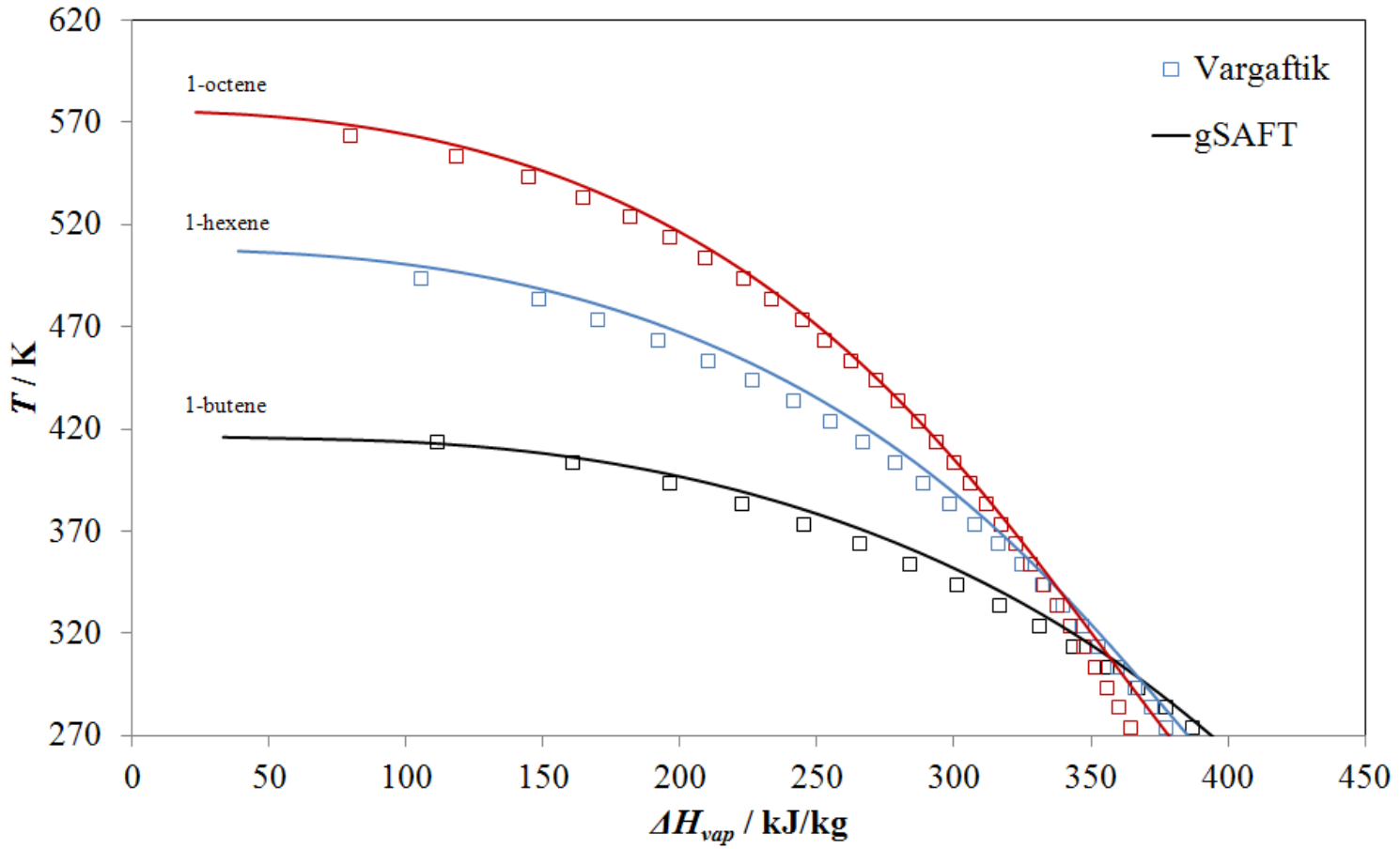
α-Olefins – Saturated densities



- NIST WebBook (http://webbook.nist.gov/chemistry/)
- Vargaftik, N.B., Tables on the Thermophysical properties of Liquids and Gases, Hemisphere Publishing (1975)

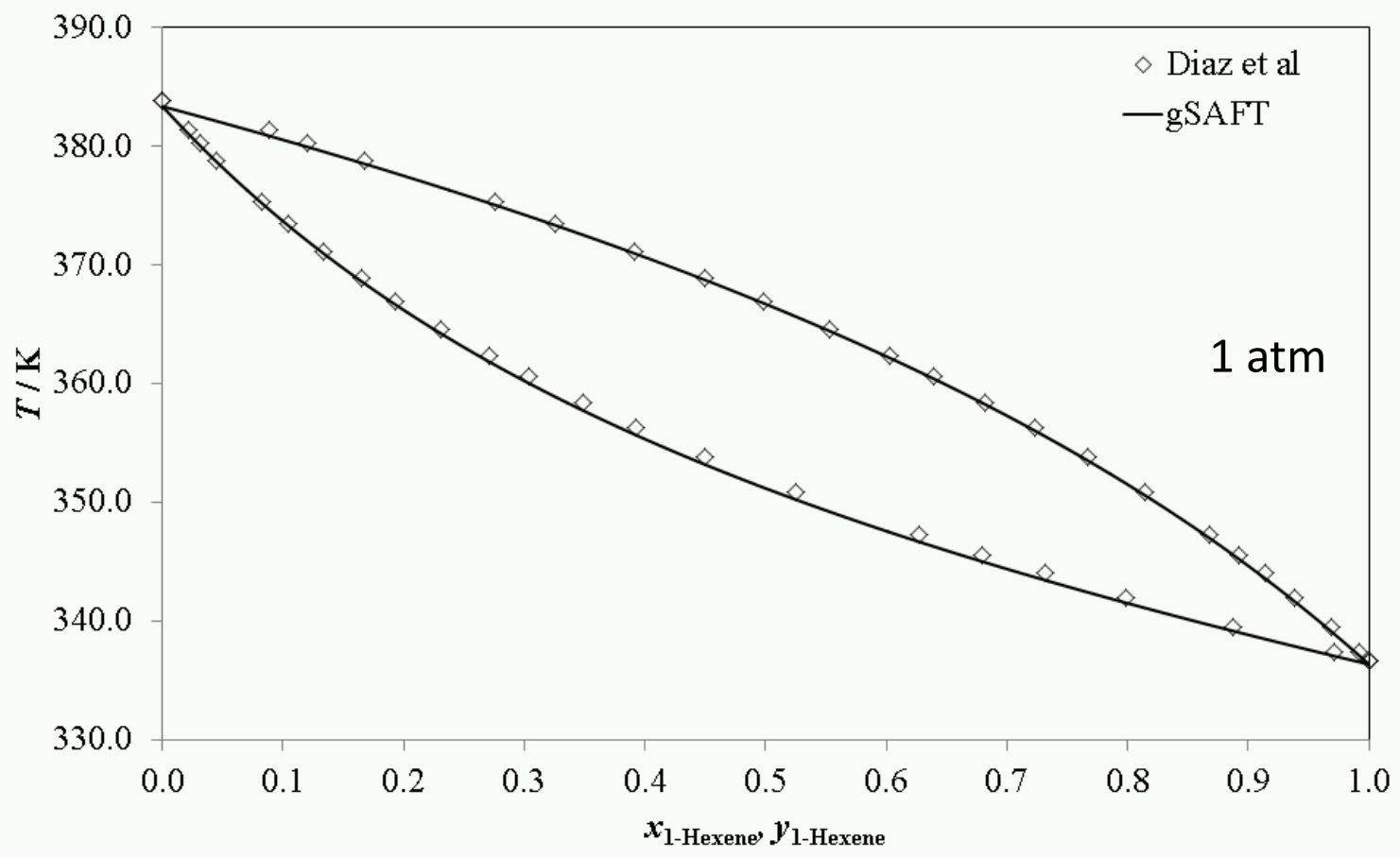
α-Olefins – heat of vaporisation

NB. Pure predictions – none of these data used for parameter estimation



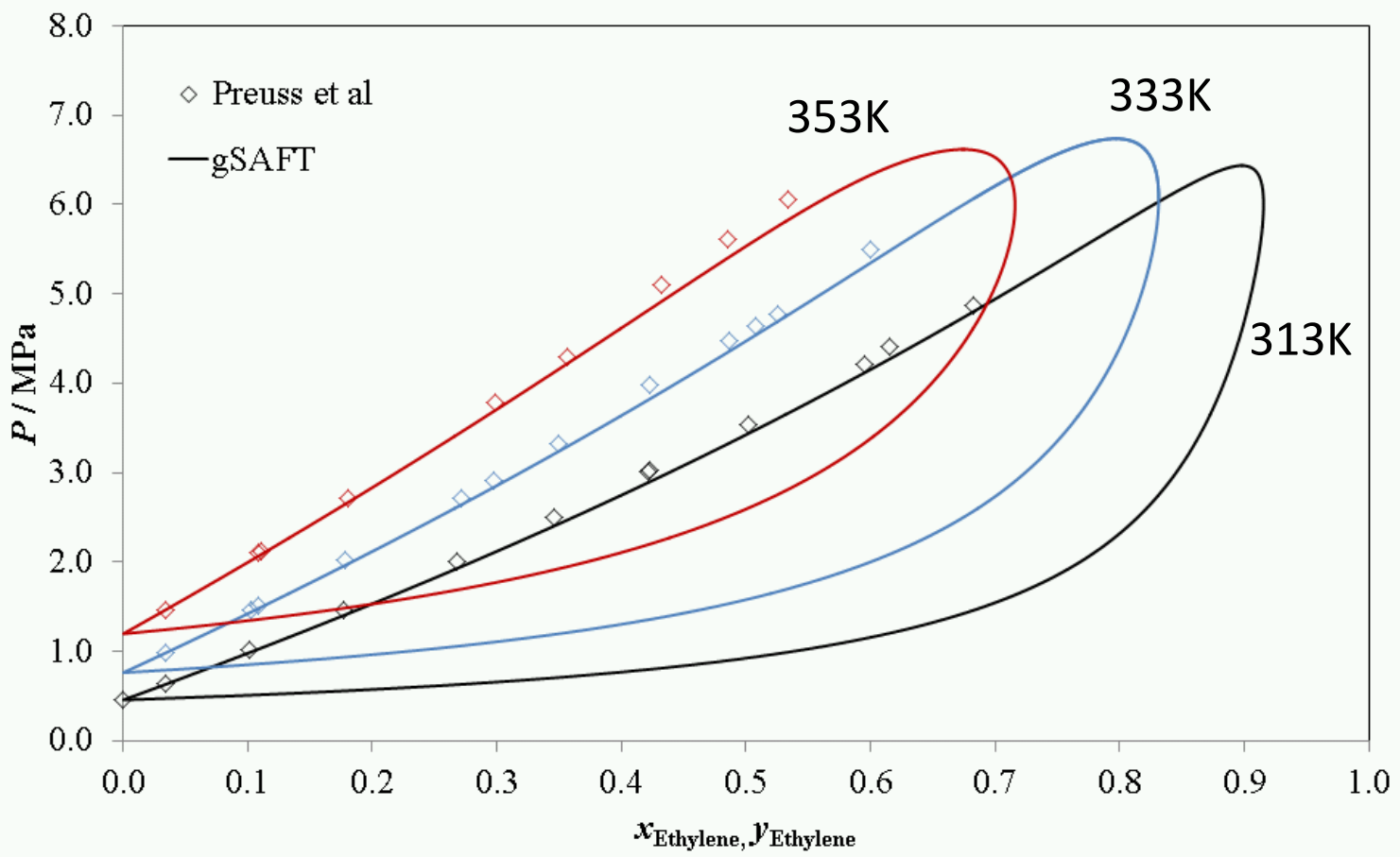
- Vargaftik, N.B., *Tables on the Thermophysical properties of Liquids and Gases*, Hemisphere Publishing (1975)

Vapour-Liquid Equilibrium: 1-Hexene + Toluene



- Diaz *et al.*, *J. Chem. Eng. Data*, 47, 4 (2002)

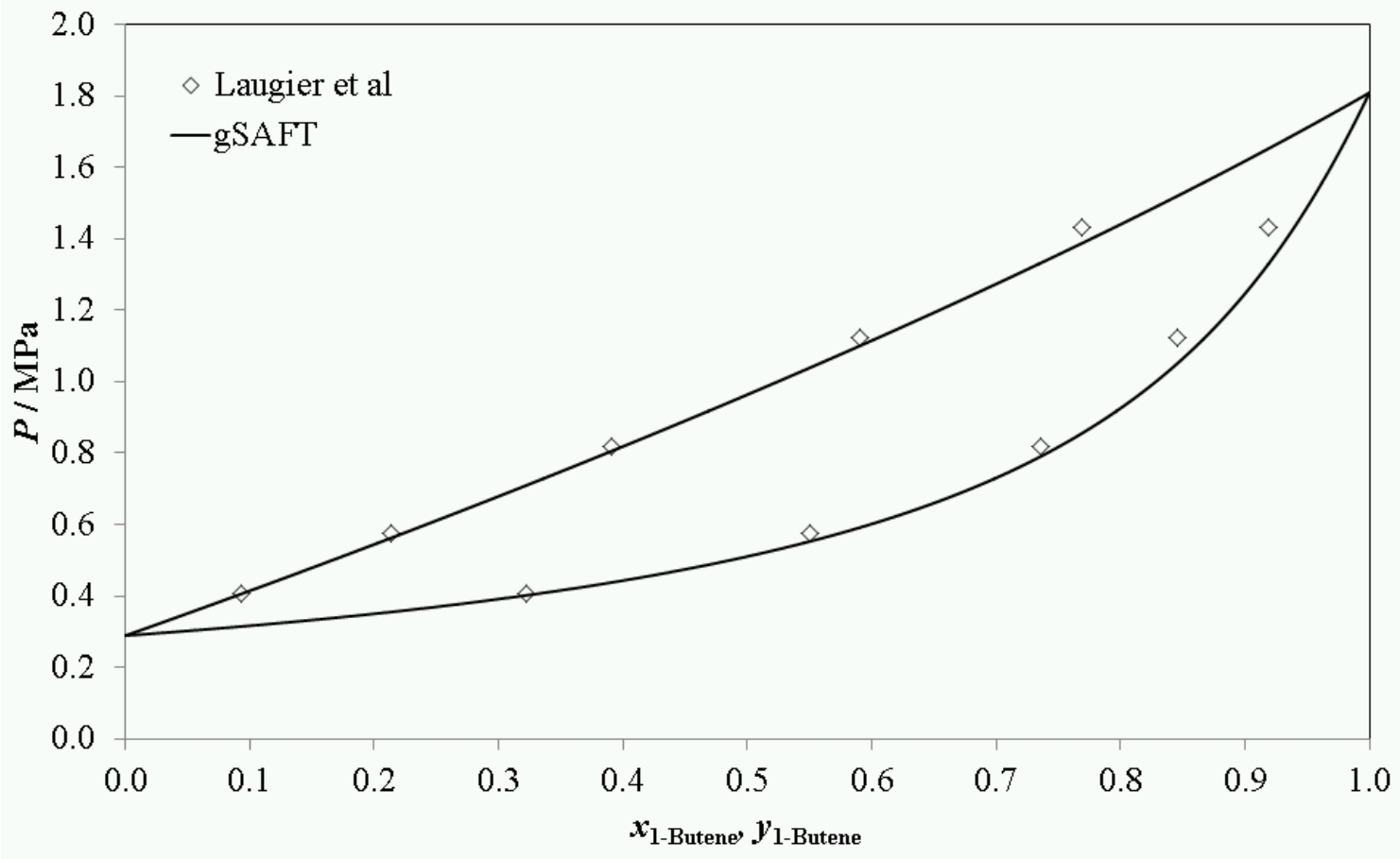
Vapour-Liquid Equilibrium: Ethylene + 1-Butene



- Preuss *et al.*, FIZ Report, 9261 (1984)

Vapour-Liquid Equilibrium: 1-Butene + 1-Hexene

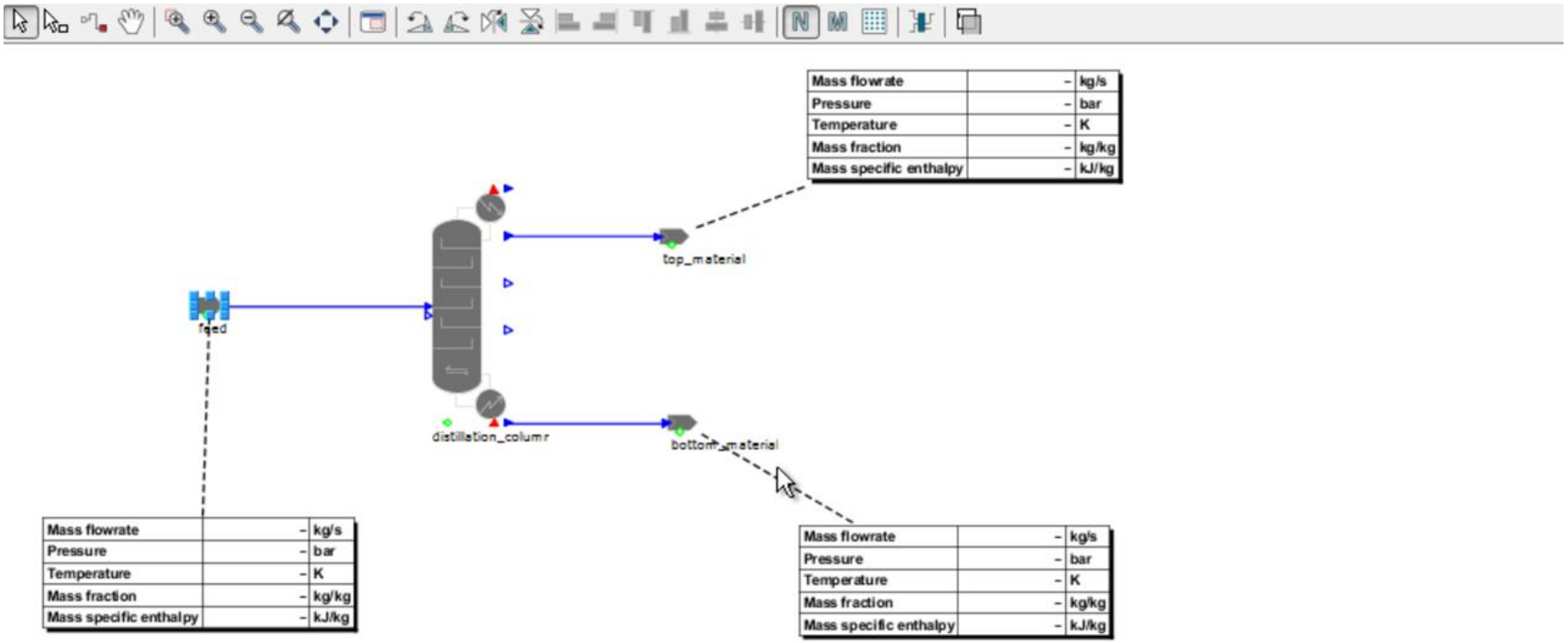
NB. Pure predictions – none of these data used for parameter estimation



- Laugier *et al.*, *J. Chem. Eng. Data*, 41 , 2 (1996)

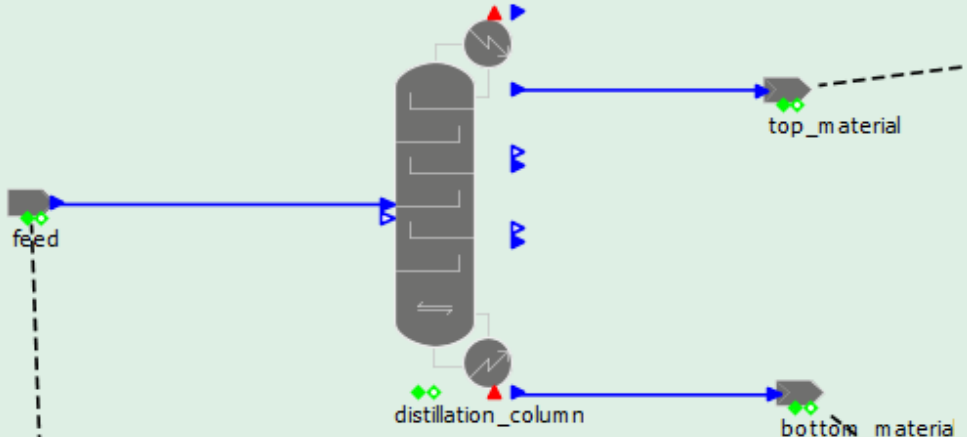
LAO separation process

modelling with ProcessBuilder/**SAFT-γ Mie (gSAFT)**



LAO separation process

modelling with ProcessBuilder/**SAFT-γ Mie (gSAFT)**



Mass flowrate	0.00136748	kg/s
Pressure	30.0000	bar
Temperature	260.325	K
Mass fraction("toluene")	9.82219E-08	kg/kg
Mass fraction("ethylene")	0.984576	kg/kg
Mass fraction("1-butene")	0.0154095	kg/kg
Mass fraction("1-hexene")	1.43070E-05	kg/kg
Mass fraction("1-octene")	1.21734E-08	kg/kg
Mass fraction("1-decene")	1.02050E-11	kg/kg
Mass fraction("1-dodecene")	8.45976E-15	kg/kg
Mass specific enthalpy	-10.4764	kJ/kg

Mass flowrate	0.0170274	kg/s
Pressure	30.0000	bar
Temperature	300.000	K
Mass fraction("toluene")	0.300633	kg/kg
Mass fraction("ethylene")	0.0915453	kg/kg
Mass fraction("1-butene")	0.450516	kg/kg
Mass fraction("1-hexene")	0.124174	kg/kg
Mass fraction("1-octene")	0.0270423	kg/kg
Mass fraction("1-decene")	0.00517607	kg/kg
Mass fraction("1-dodecene")	0.000913058	kg/kg
Mass specific enthalpy	-24.9218	kJ/kg

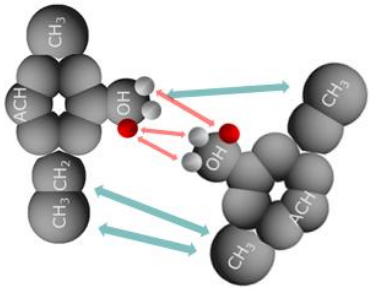
gSAFT

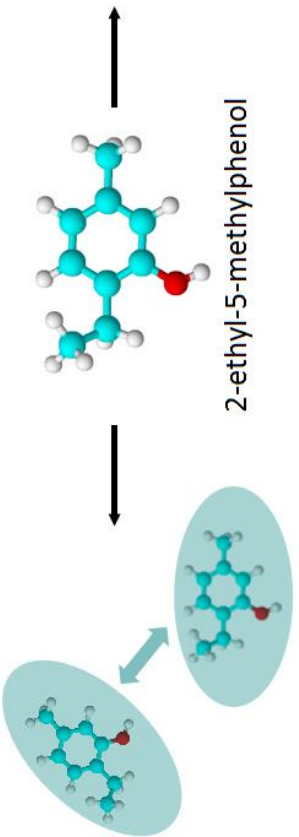
SAFT-γ Mie

Mass flowrate	0.0156599	kg/s
Pressure	30.0000	bar
Temperature	419.081	K
Mass fraction("toluene")	0.326885	kg/kg
Mass fraction("ethylene")	0.0135626	kg/kg
Mass fraction("1-butene")	0.488512	kg/kg
Mass fraction("1-hexene")	0.135016	kg/kg
Mass fraction("1-octene")	0.0294037	kg/kg
Mass fraction("1-decene")	0.00562806	kg/kg
Mass fraction("1-dodecene")	0.000992789	kg/kg
Mass specific enthalpy	-9.09223	kJ/kg

Summary

- gSAFT: industrial-strength implementation of
  - two state-of-the-art thermodynamic models
  - advanced phase equilibrium algorithms
- Parameter databases being continually augmented
- SAFT-γ Mie group contribution method:
  step change in capability to predict material behaviour with little/no experimental data
- Straightforward usage in gPROMS models
  - no changes required to existing models
- Release as part of gPROMS Platform v4.0 (April 2014)
  - immediate use within
    gPROMS ProcessBuilder & gCCS





ADVANCED PROCESS
MODELLING FORUM **2014**

Thank you