



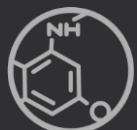
# ADVANCED PROCESS MODELLING FORUM

## 22-23 APRIL 2015

### gSAFT

Advanced thermodynamic modelling in gPROMS

Dr Thomas Lafitte – Senior Scientist



# gPROMS product family



General  
mathematical  
modelling



gPROMS ModelBuilder  
Advanced process  
modelling environment

## Sector-focused modelling tools

Chemicals &  
Petrochemicals



gPROMS ProcessBuilder  
Advanced process  
simulation

Life Sciences,  
Consumer, Food,  
Spec & Agrochem



Solids process  
optimisation



Crystallization  
process optimisation



Oral absorption

Power & CCS



CCS system modelling

Oil & Gas



Flare networks &  
depressurisation

Wastewater  
Treatment



Wastewater systems  
optimisation

Fuel Cells &  
Batteries



Fuel cell stack &  
system design



## The gPROMS platform

Equation-oriented modelling & solution engine

Materials  
modelling



INFOCHEM  
*Multiflash*

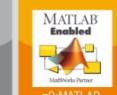


Model  
deployment  
tools

Enterprise Objects



Deploy models in common engineering software





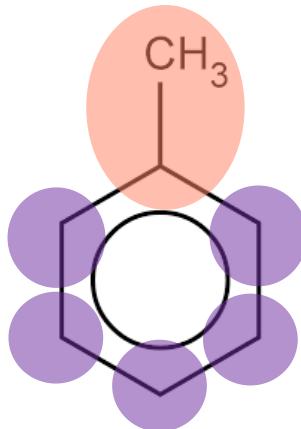
gSAFT

# The SAFT- $\gamma$ Mie Equation of State

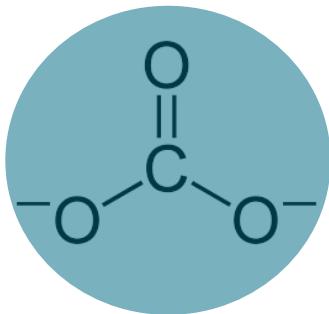
Papaioannou, Lafitte, Avendaño, Adjiman, Jackson, Müller, Galindo, *J. Chem. Phys.*, 140, 054107 (2014)

- Each molecule comprises one or more functional groups

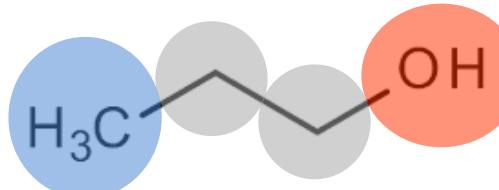
toluene



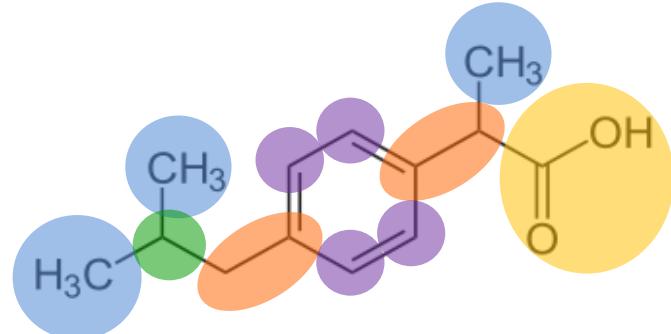
carbonate ion



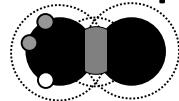
alcohols



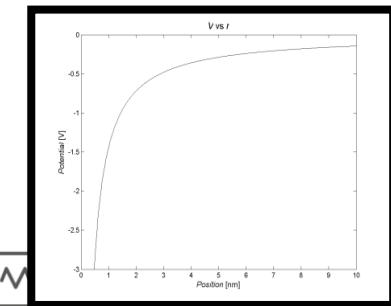
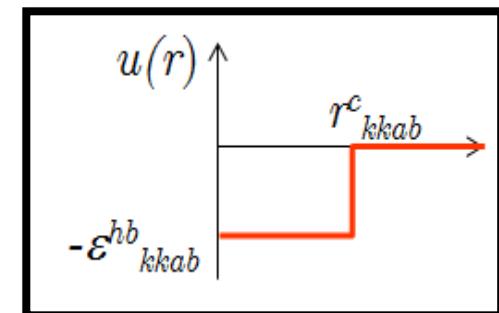
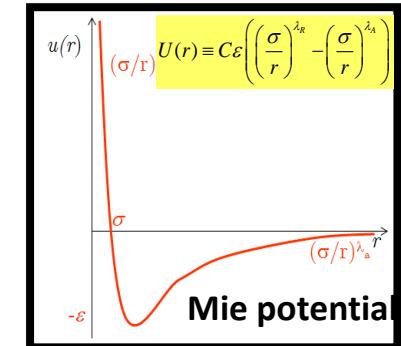
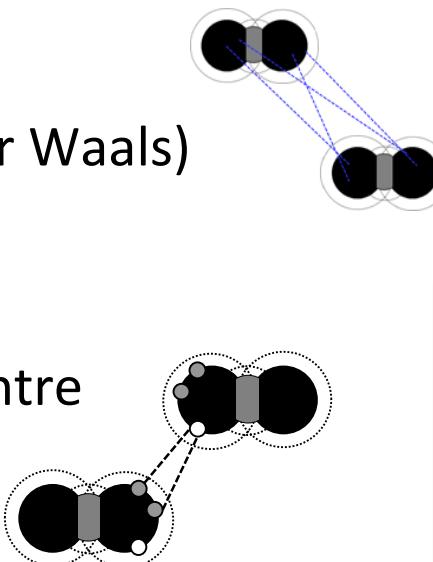
Ibuprofen



- Each functional group comprises one or more identical segments...



- ...which interact via...
  - dispersion/repulsion (van der Waals) forces
  - hydrogen bonding via off-centre electron donor/acceptor (“association”) sites
  - ionic (coulombic) forces



Increasing strength

# SAFT- $\gamma$ Mie Databank

Current status (April 2015)



groups	CH <sub>3</sub>	CH <sub>2</sub>	CH	C	COOH	CH <sub>3</sub> COCH <sub>3</sub>	H <sub>2</sub> O	aCH	aCCH <sub>3</sub>	aCCH <sub>2</sub>	aCCH	COO	OH	O (ether)	CH <sub>2</sub>	CH	CO <sub>2</sub>	CH <sub>3</sub> OH	CH <sub>4</sub>	cCH <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>4</sub>	Ar	O <sub>2</sub>	SO <sub>2</sub>	N <sub>2</sub>	CO	H <sub>2</sub>	H <sub>2</sub> S
CH <sub>3</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH <sub>2</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
COOH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH <sub>3</sub> COCH <sub>3</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H <sub>2</sub> O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
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aCCH <sub>3</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
aCCH <sub>2</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
aCCH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
COO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
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O (ether)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
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CH <sub>3</sub> OH	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH <sub>4</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
cCCH <sub>2</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C <sub>2</sub> H <sub>4</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C <sub>3</sub> H <sub>4</sub>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
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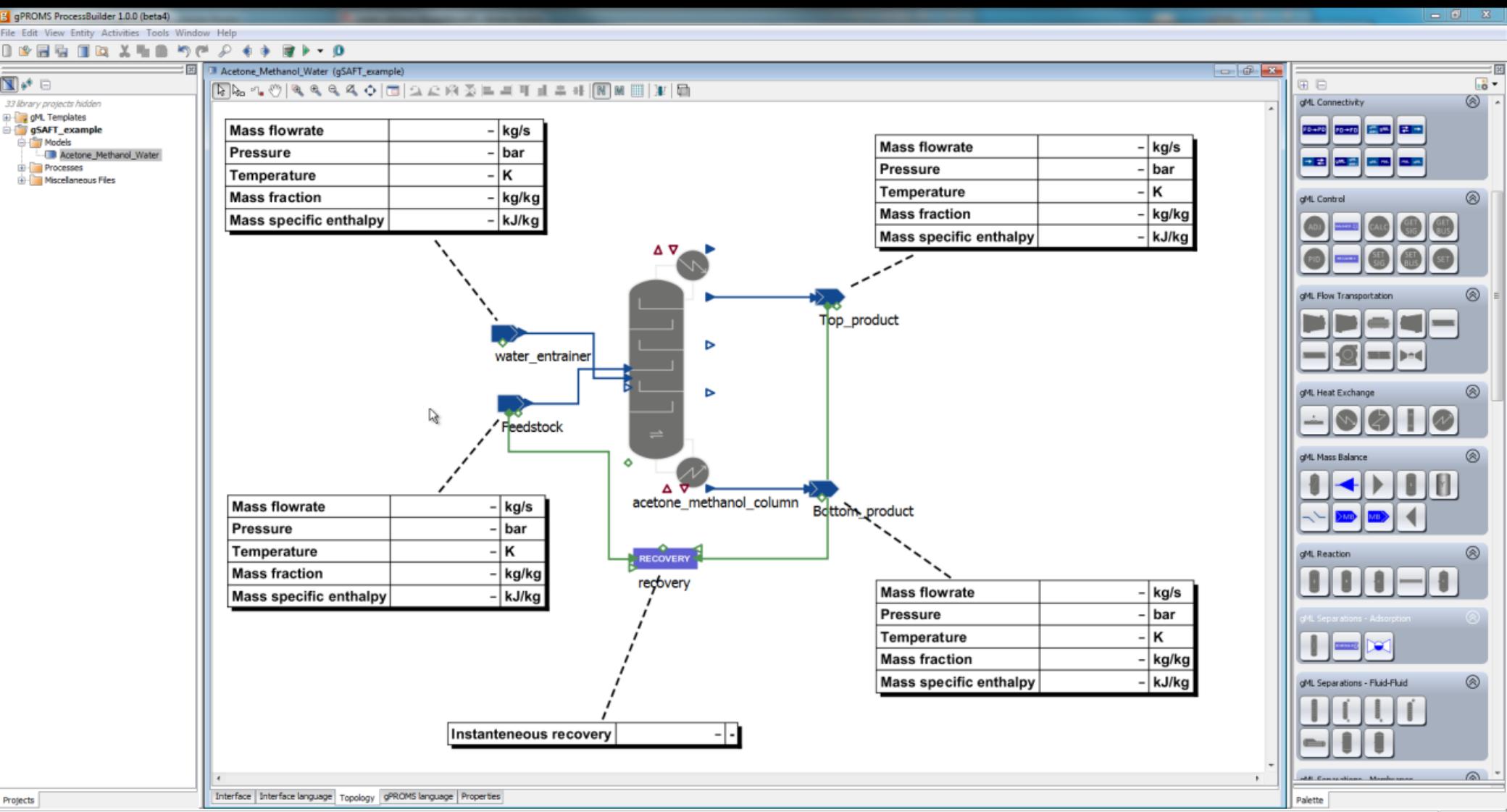
One databank  
for all systems

## gSAFT deployment within gPROMS

- Fully implemented
  - ...from single-phase properties to multi-phase equilibria
  - emphasis on robustness & efficiency
- Accessible from all gPROMS models
  - standard gPROMS physical property interface

# gSAFT in ProcessBuilder

## example : acetone + water + methanol distillation



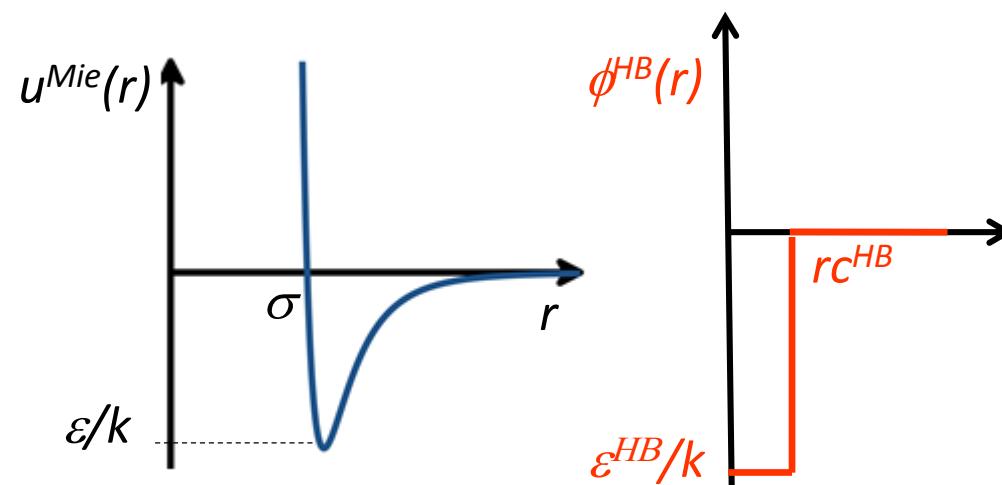
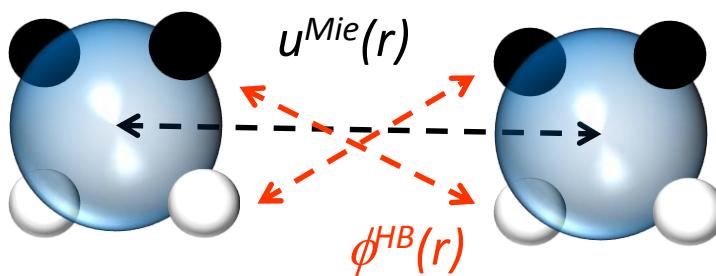


# Application #1 gSAFT for polar/strongly associating fluids



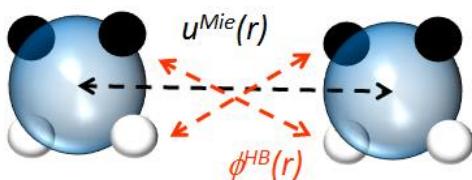
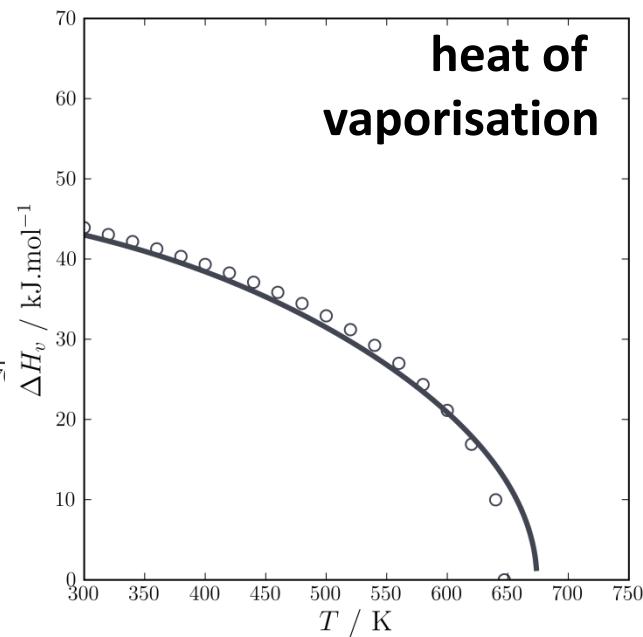
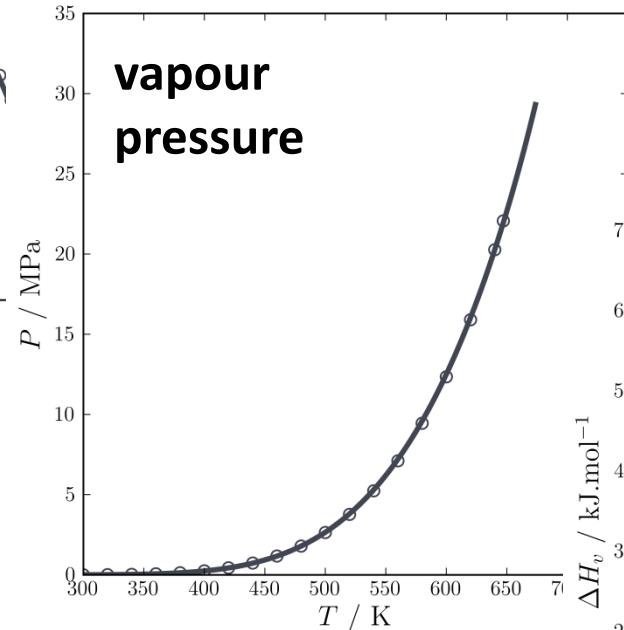
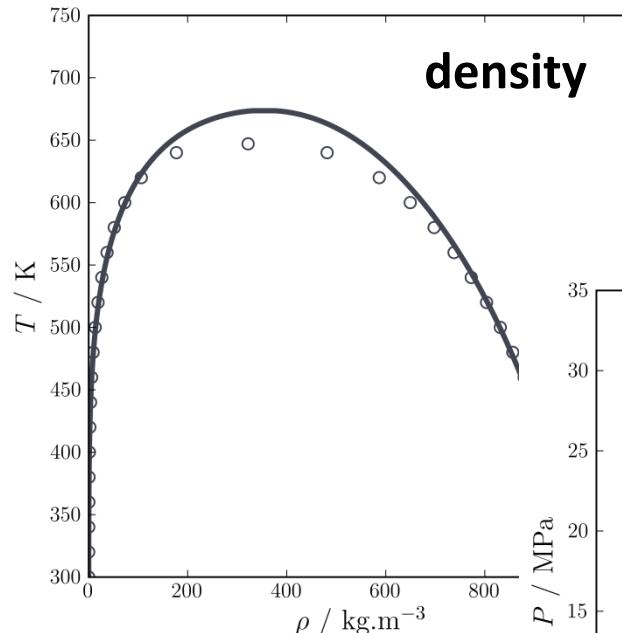
- Arguably the most complex molecule to model
- ...present in large proportion of process models
- Crucial need for an equation that can
  - capture all its thermodynamic properties
  - be used over a wide range of conditions
  - be used for other molecules in mixture  
(non-polar, polymers, ions etc..)

SAFT- $\gamma$  Mie model



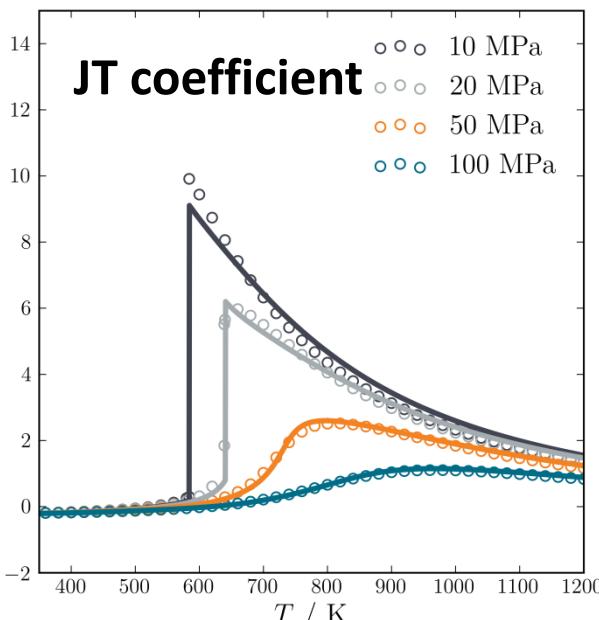
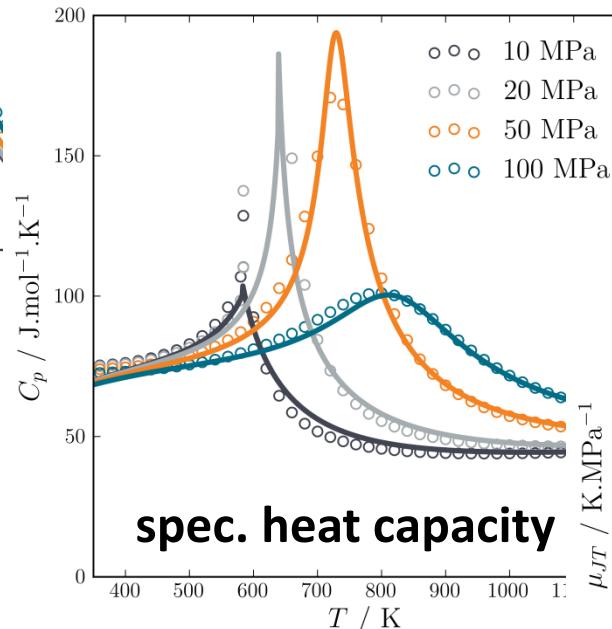
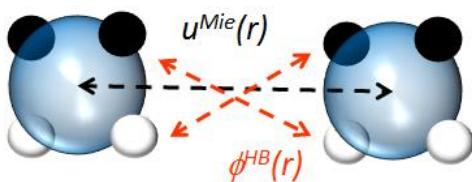
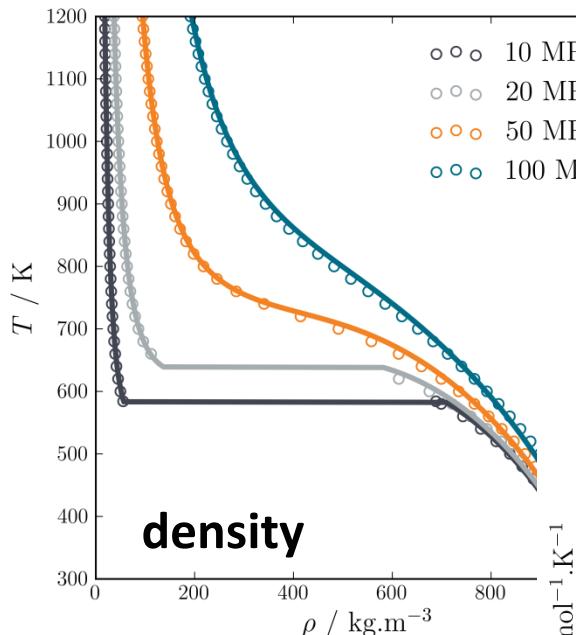
# gSAFT for polar/strongly associating fluids

## Water - VLE



# gSAFT for polar/strongly associating fluids

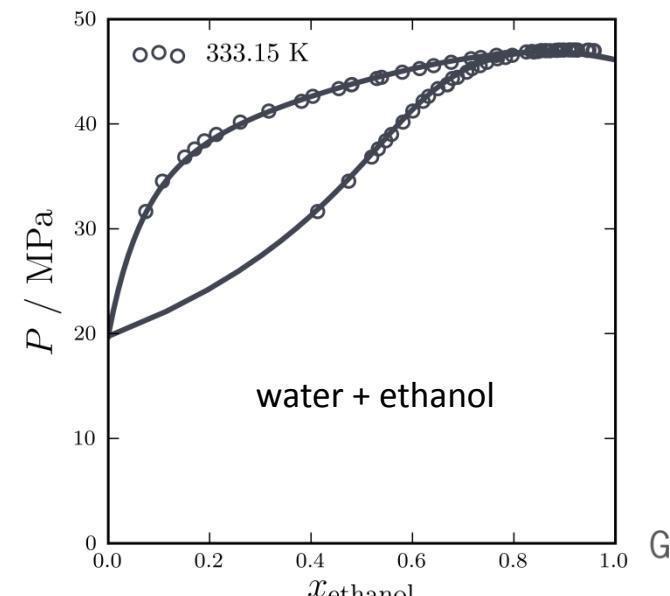
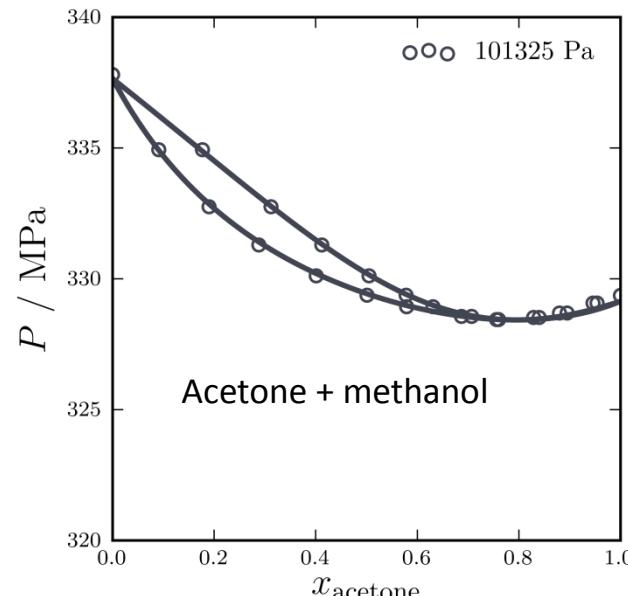
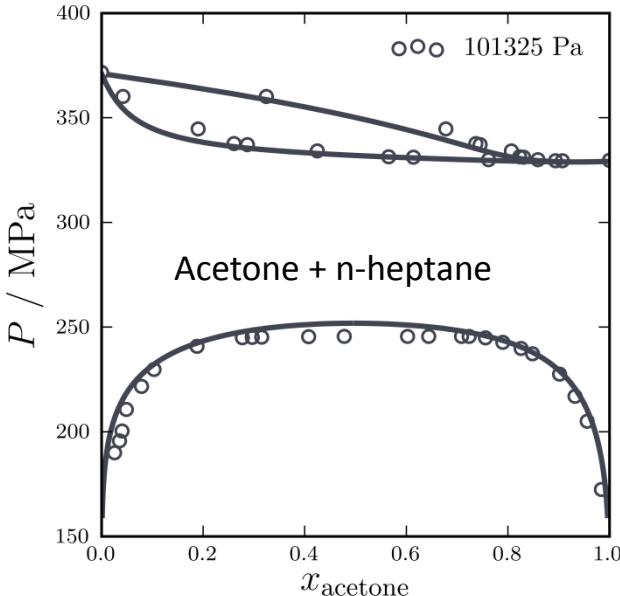
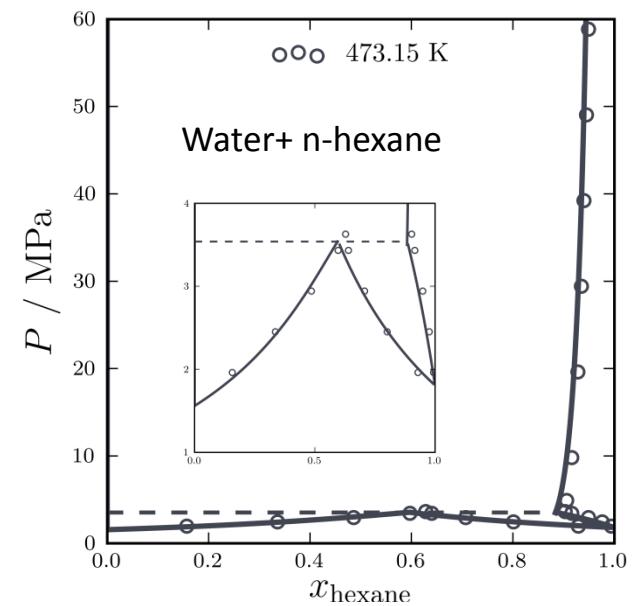
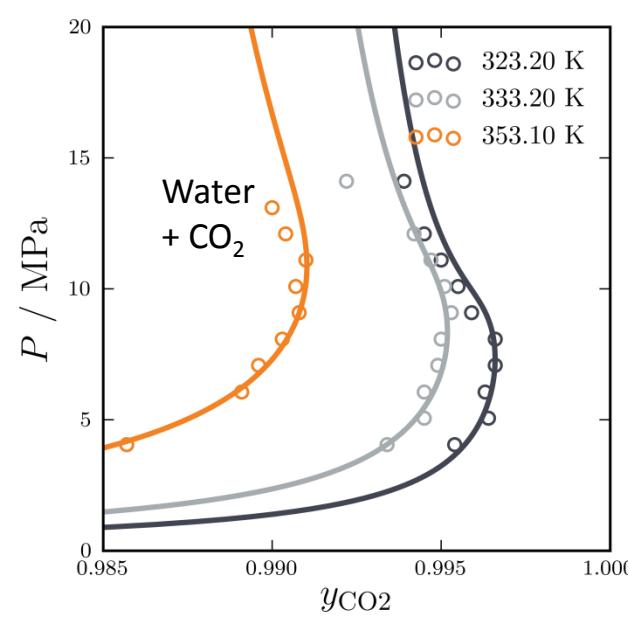
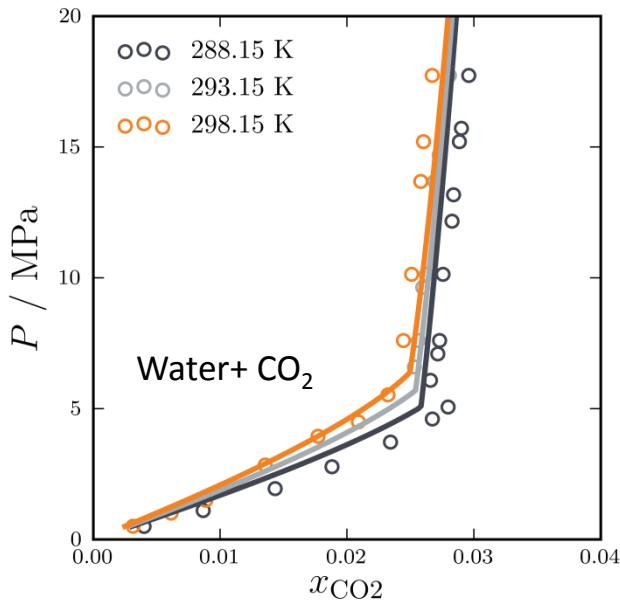
## Water – single phase properties



Accurate derivative properties  
with a single set of parameters

Experimental data : NIST Chemistry webbook

# gSAFT for polar /strongly associating fluids mixtures

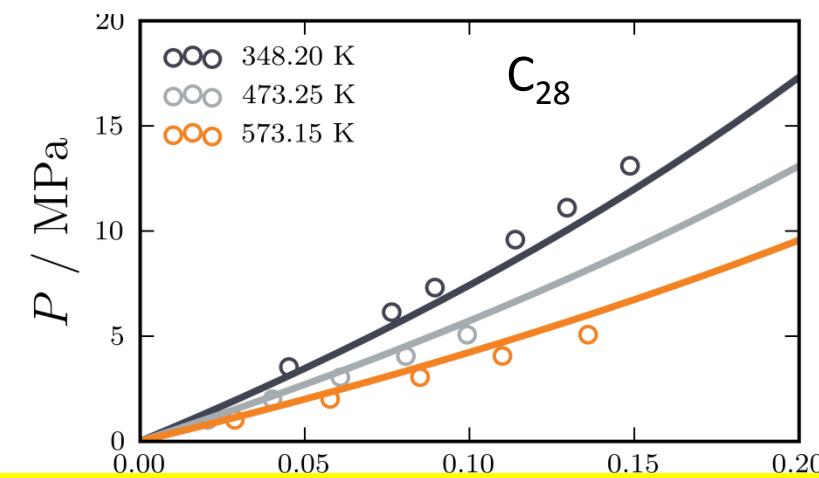
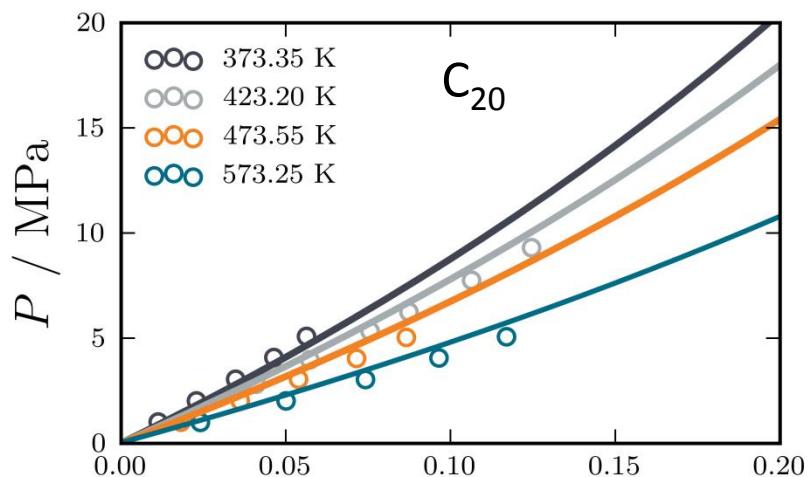
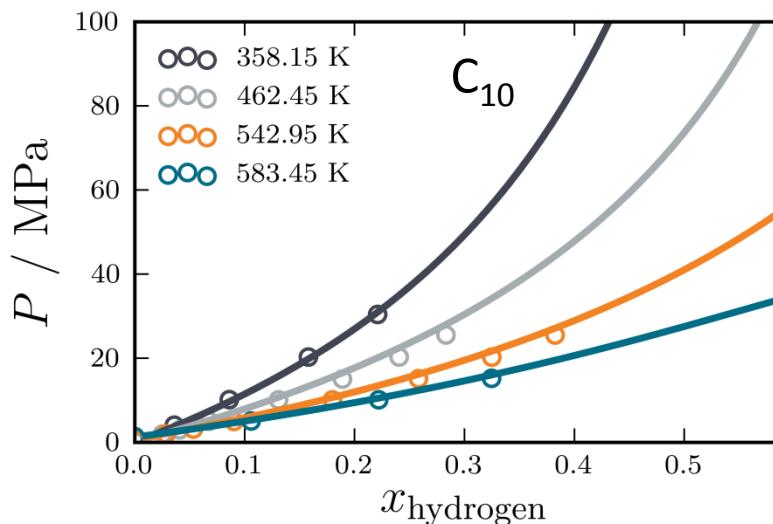
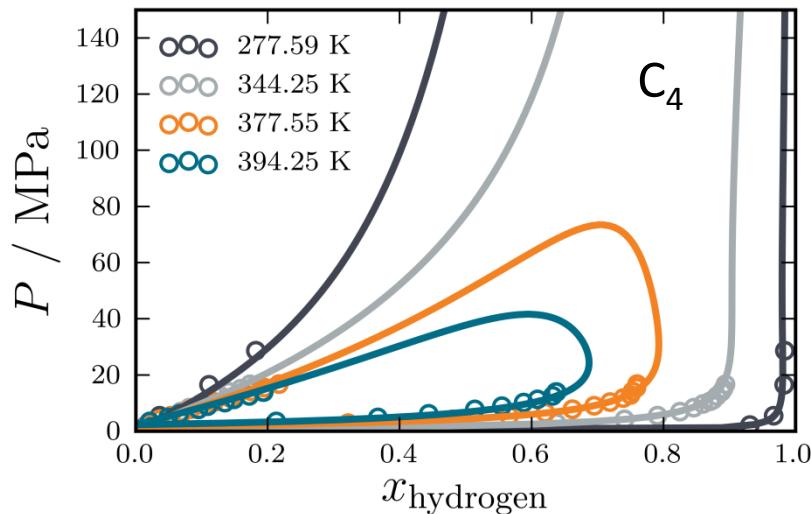




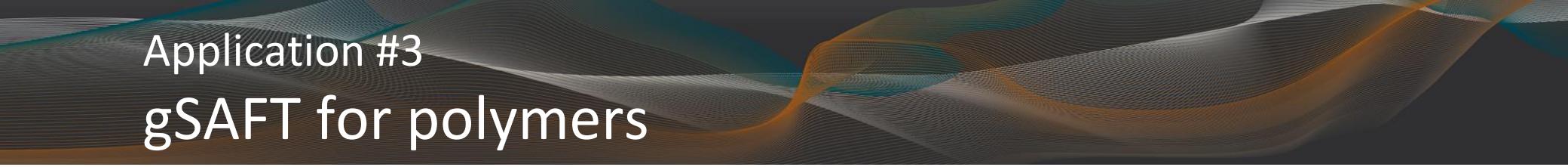
## Application #2 gSAFT for complex, non-polar systems

# gSAFT for complex, non-polar systems

example: hydrogen + n-alkanes

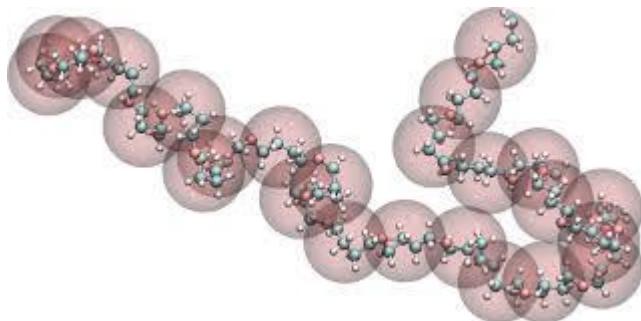


- Reliable predictions with increasing chain length
- Key thermodynamic behaviour for Gas-to-Liquid/Fischer Tropsch processes



## Application #3 gSAFT for polymers

- Challenges in modelling polymer behaviour
  - highly non-ideal system
  - experimental data are extremely scarce
  - phase equilibrium can be numerically challenging
- SAFT- $\gamma$  Mie is ideal for modelling polymeric species

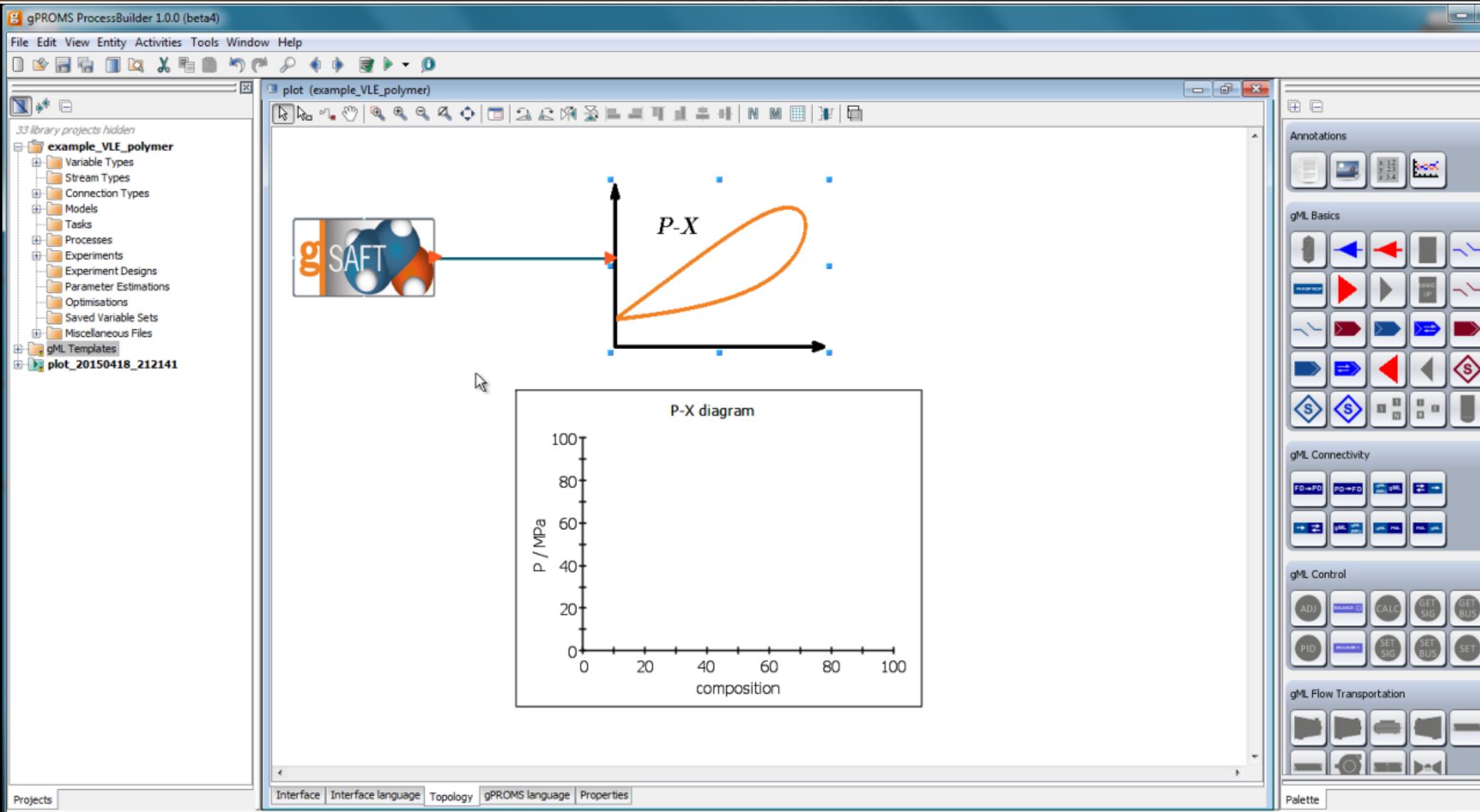


Molecule is divided into functional groups

- Group parameters do not need to be fitted to polymer data

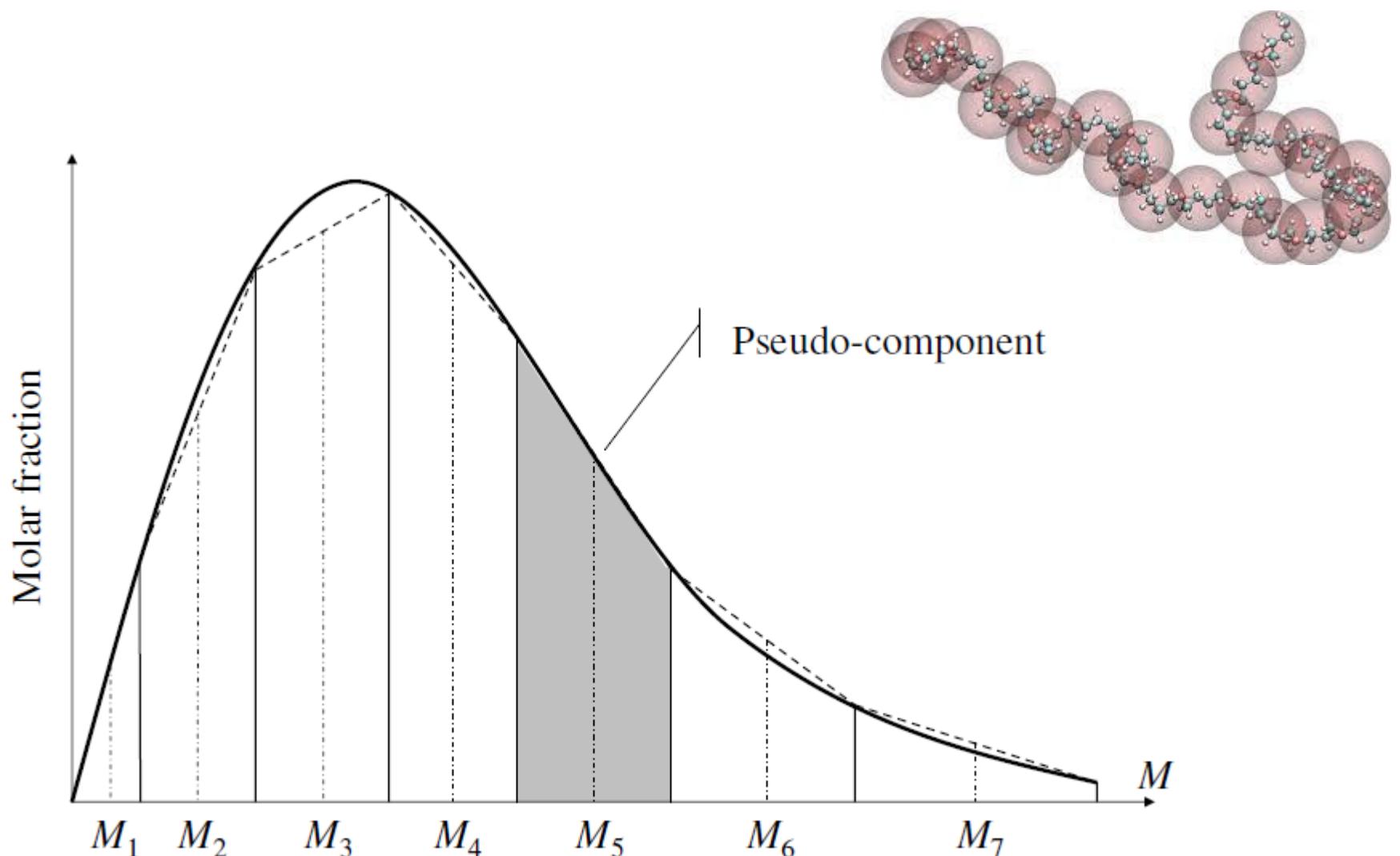
# gSAFT for polymers

## example VLE calculation



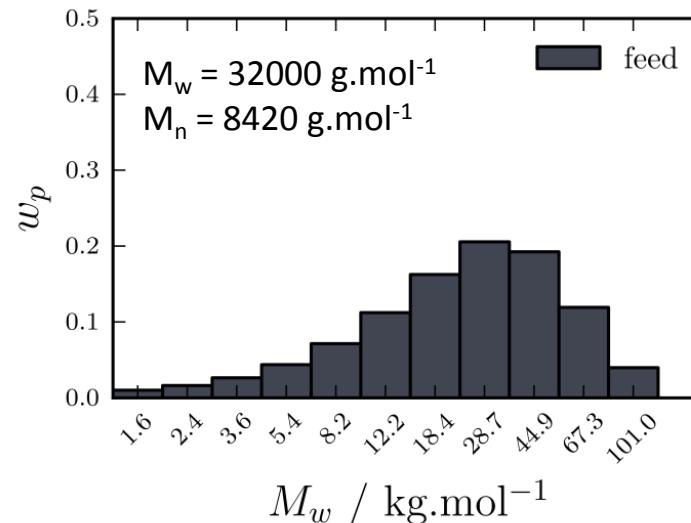
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FORUM 22–23 APRIL 2015

# gSAFT for polymers handling polydispersity

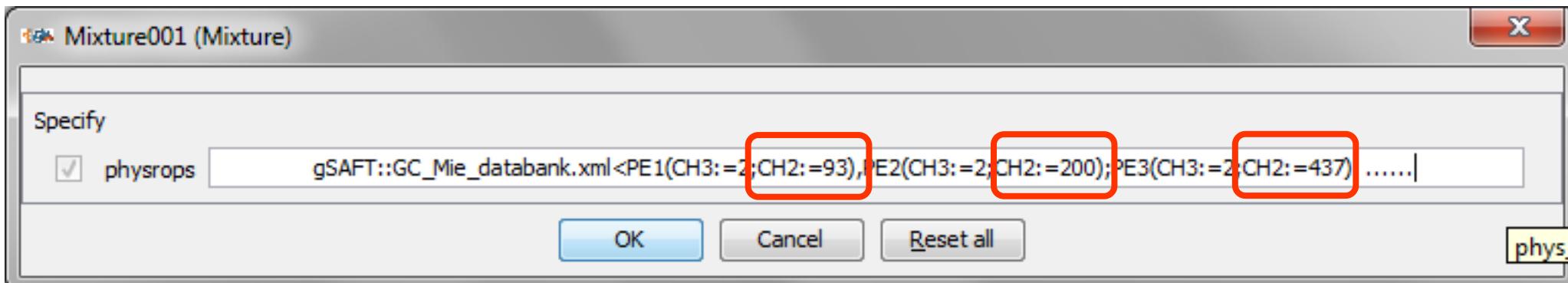


# gSAFT for polymers handling polydispersity

gPROMS  
polymerisation  
reactor model



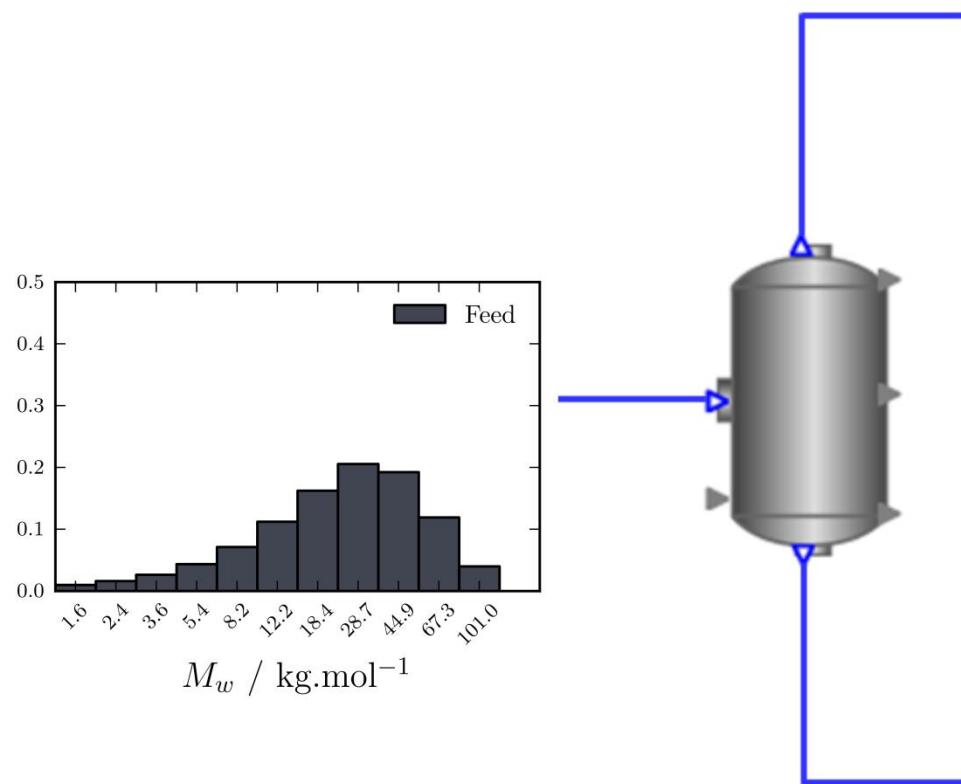
Definition of polymeric mixture in gSAFT



gPROMS model can define one or more compounds directly in terms of functional groups  
→ create new compounds “on-the-fly” without changes to compound databank

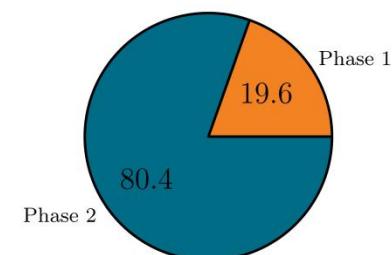
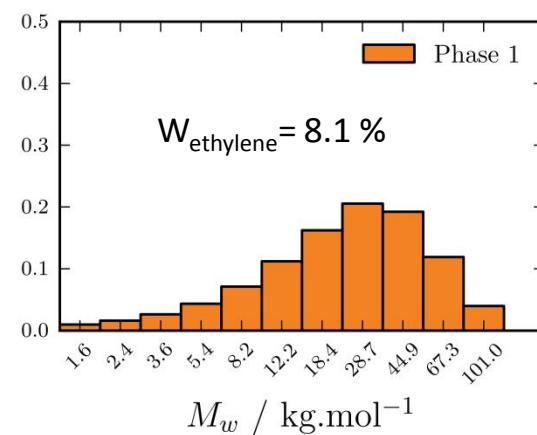
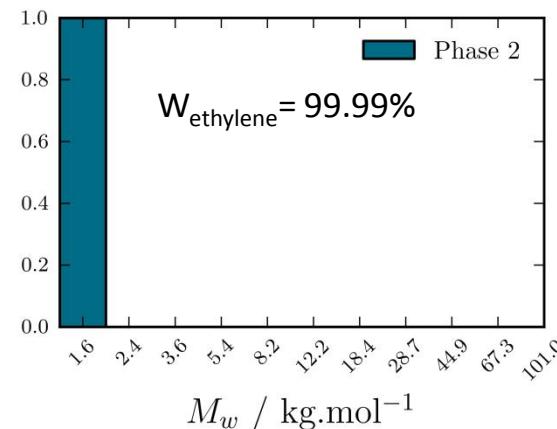
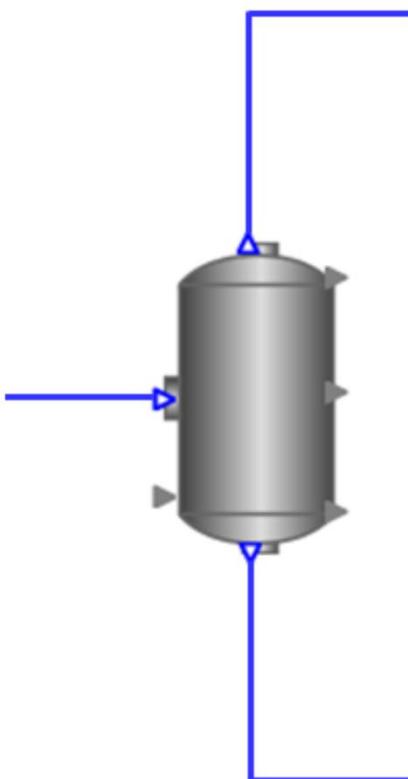
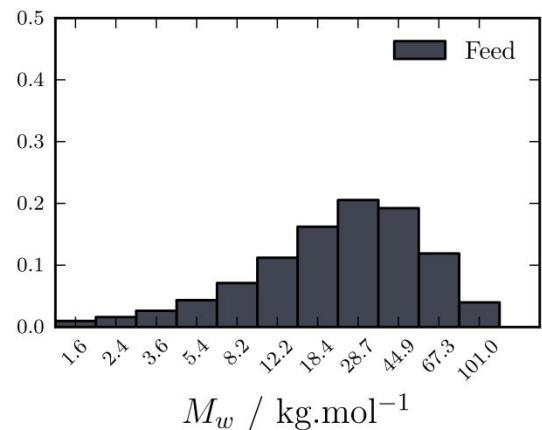
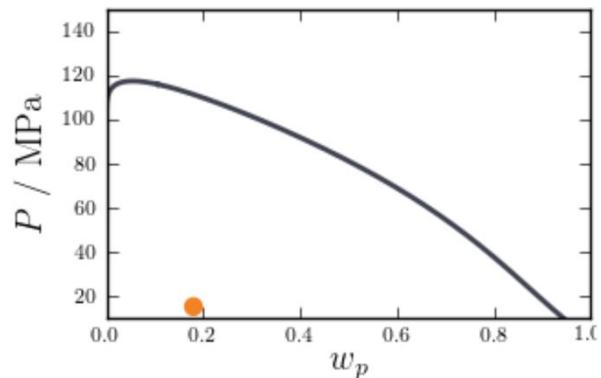
# gSAFT for polymers

TP-flash calculations: ethylene + LDPE



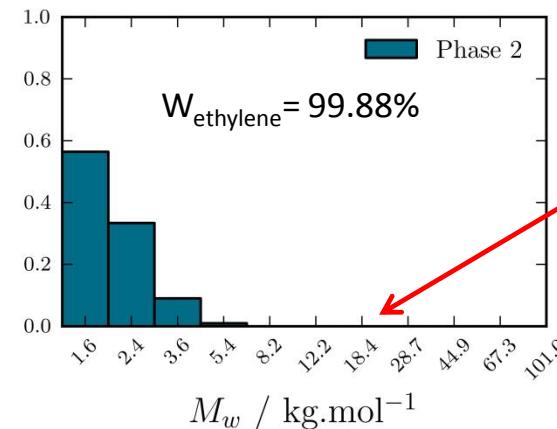
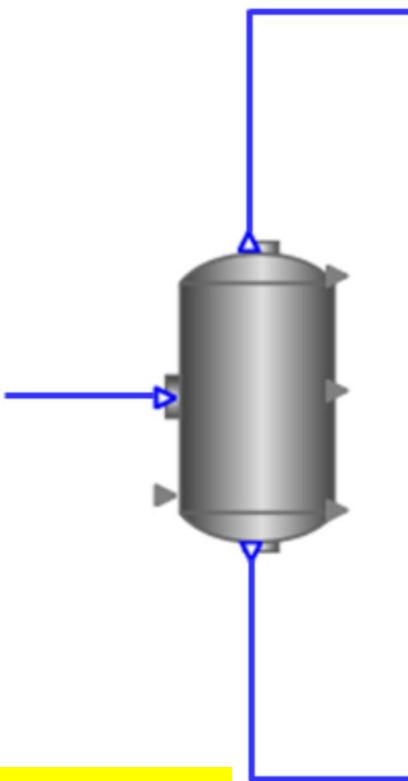
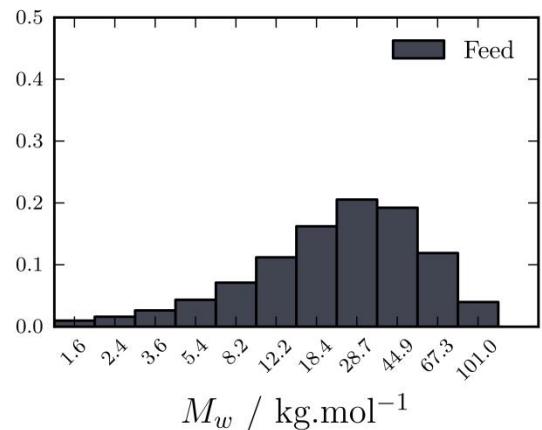
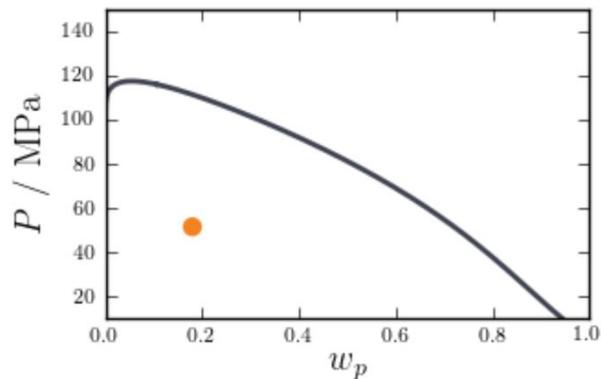
# gSAFT for polymers

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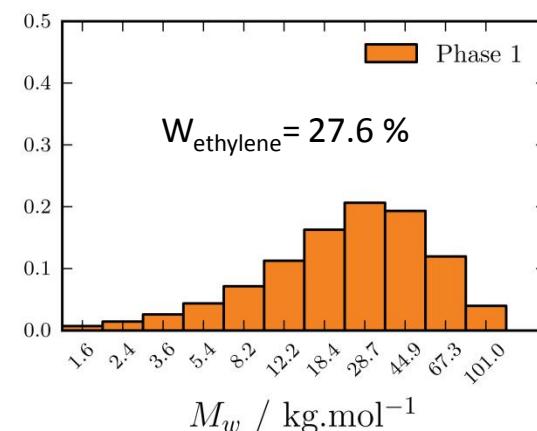
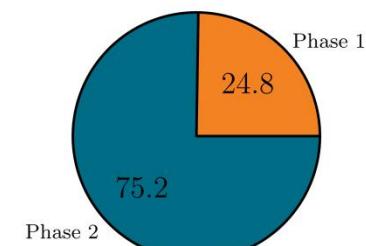


# gSAFT for polymers

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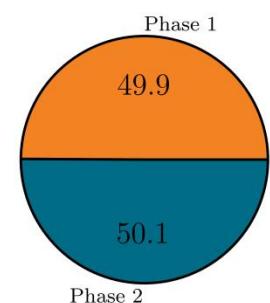
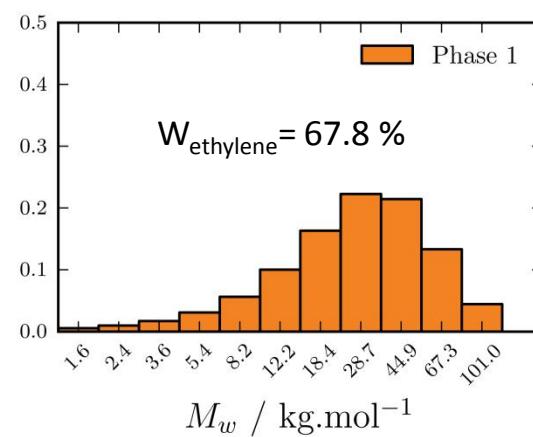
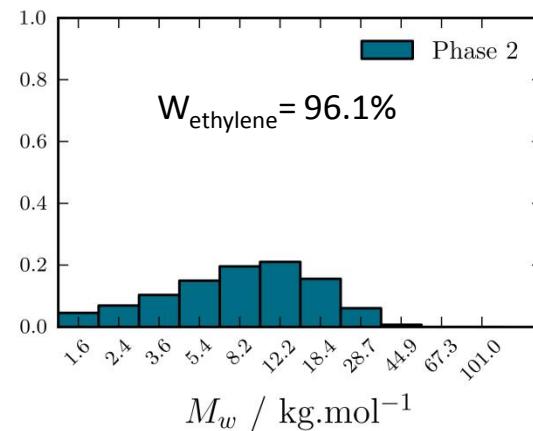
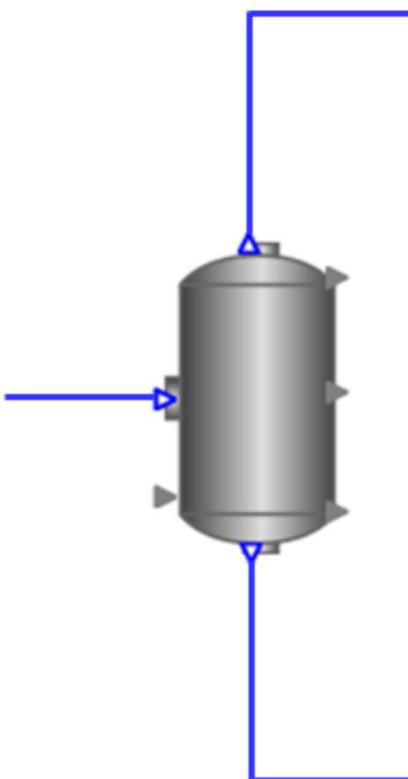
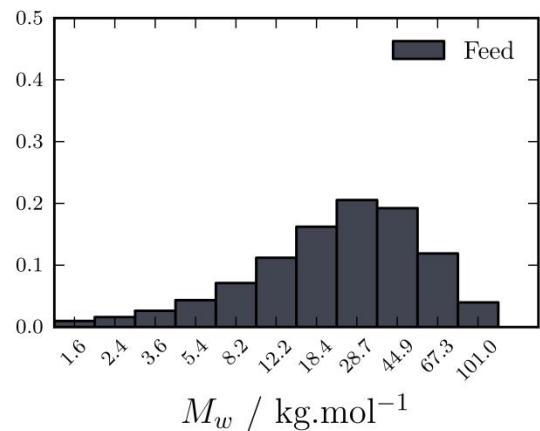
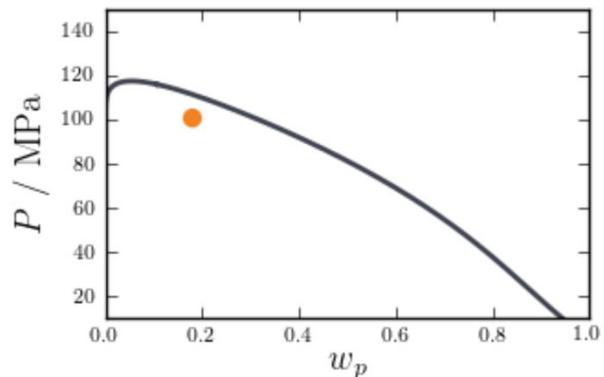
**Compositions extremely small but not zero!**



- Robust numerics in gSAFT phase equilibrium calculations
- Account for presence of polymer/oligomer in the gas phase

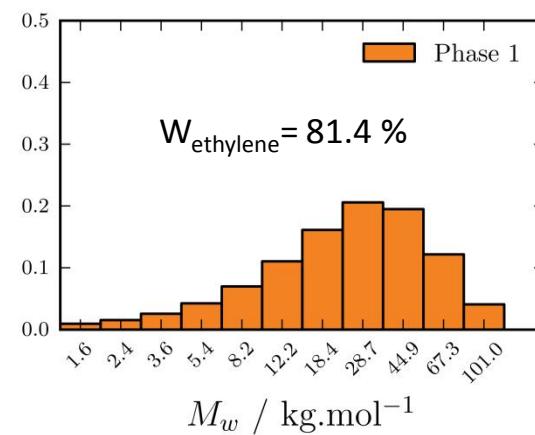
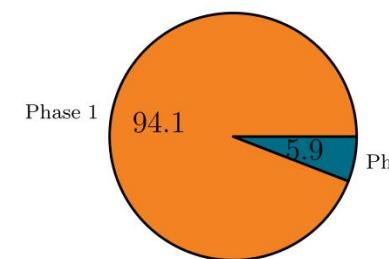
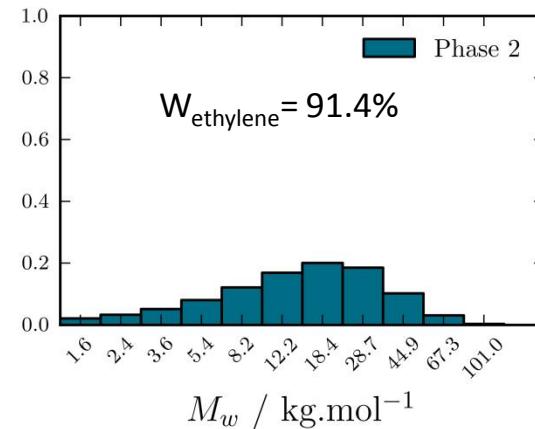
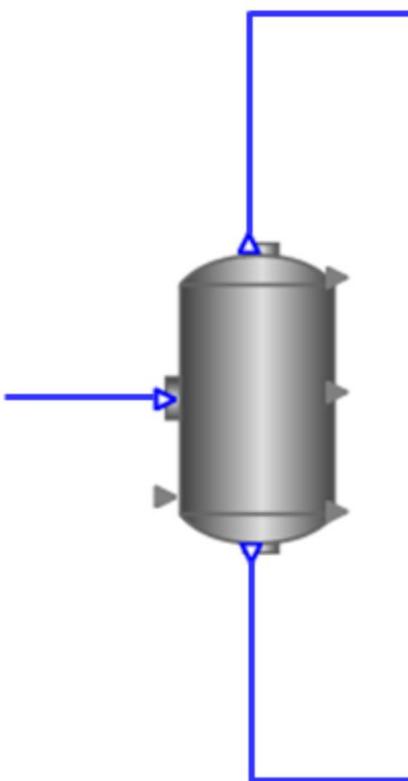
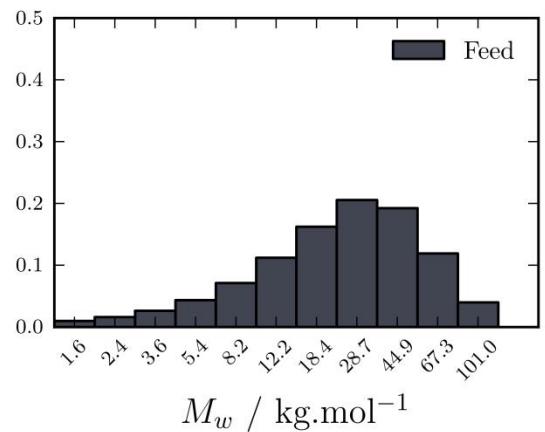
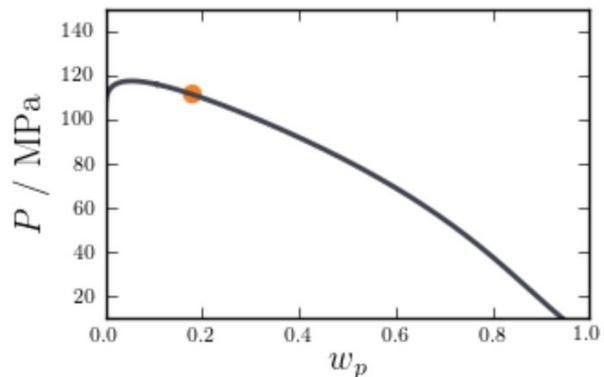
# gSAFT for polymers

TP-flash calculations: ethylene + LDPE



# gSAFT for polymers

TP-flash calculations: ethylene + LDPE



# gSAFT for polymers

## water soluble polymers



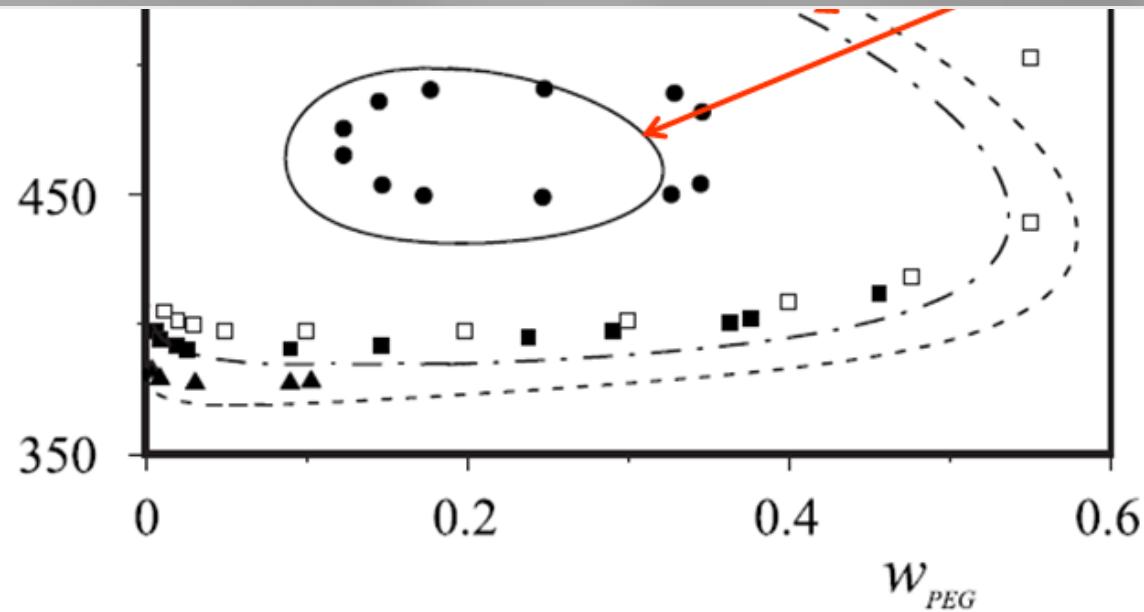
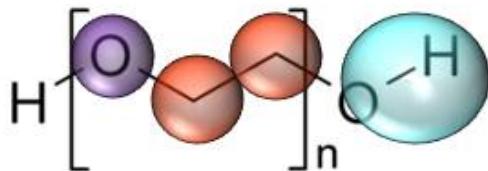
Mixture001 (Mixture)

Specify

physrops    `gSAFT:::GC_Mie_databank.xml<water,PEG2180(CH2:=99;cO:=50;OH:=2)>`

OK Cancel Reset all

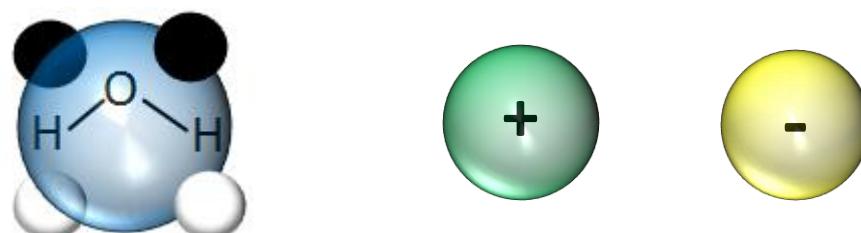
PEG



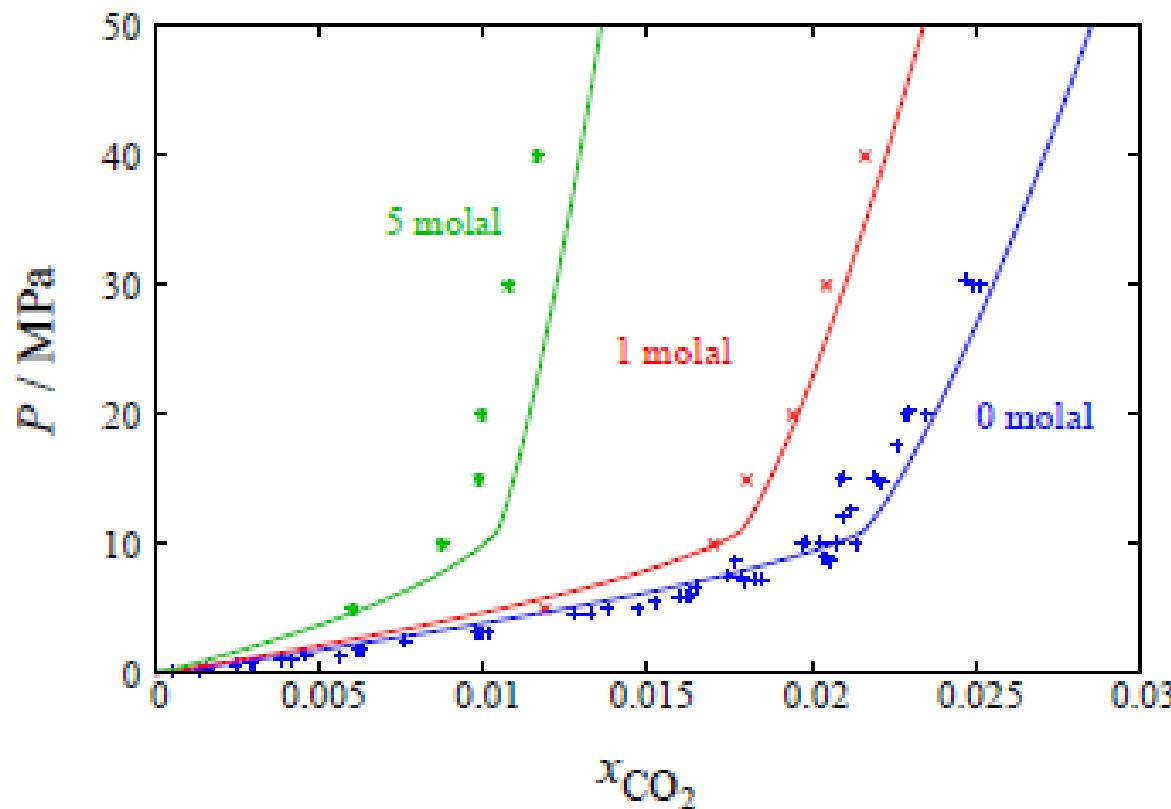
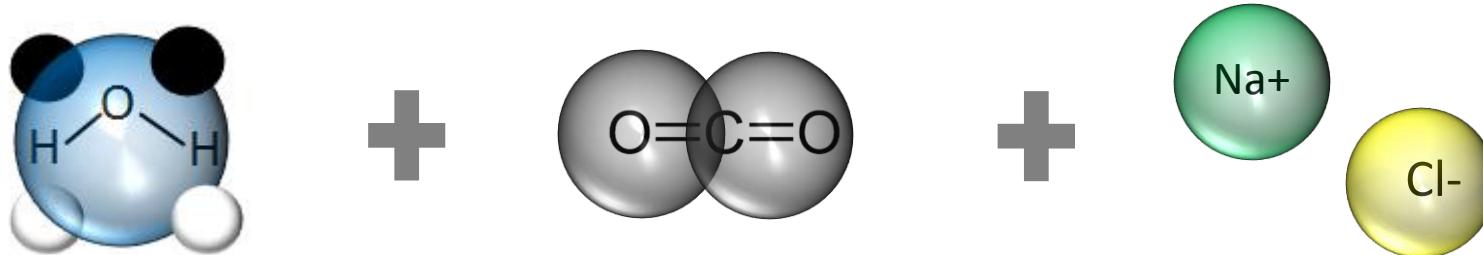


## Application #4 gSAFT for electrolytes

- Usually described with activity coefficients models
- Often an unsatisfactory solution
  - thermodynamic consistency between different phases (vapour, liquid) is lost
  - ionic and non-ionic compounds have different activity coefficient models
  - many parameters (sometimes empirical) need to be determined
  - lack of predictive capability at high pressure
  - some thermodynamic quantities (e.g. volume) cannot be computed
- **gSAFT modelling framework for electrolytic systems**
  - same model for all compounds and all phases in the system
  - rigorous physical models
  - predictive accuracy

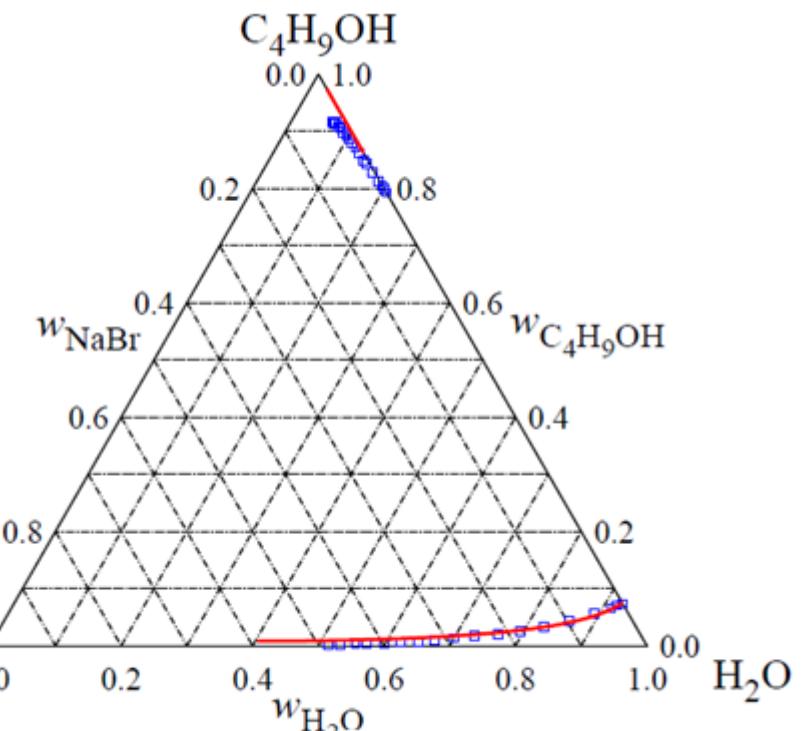
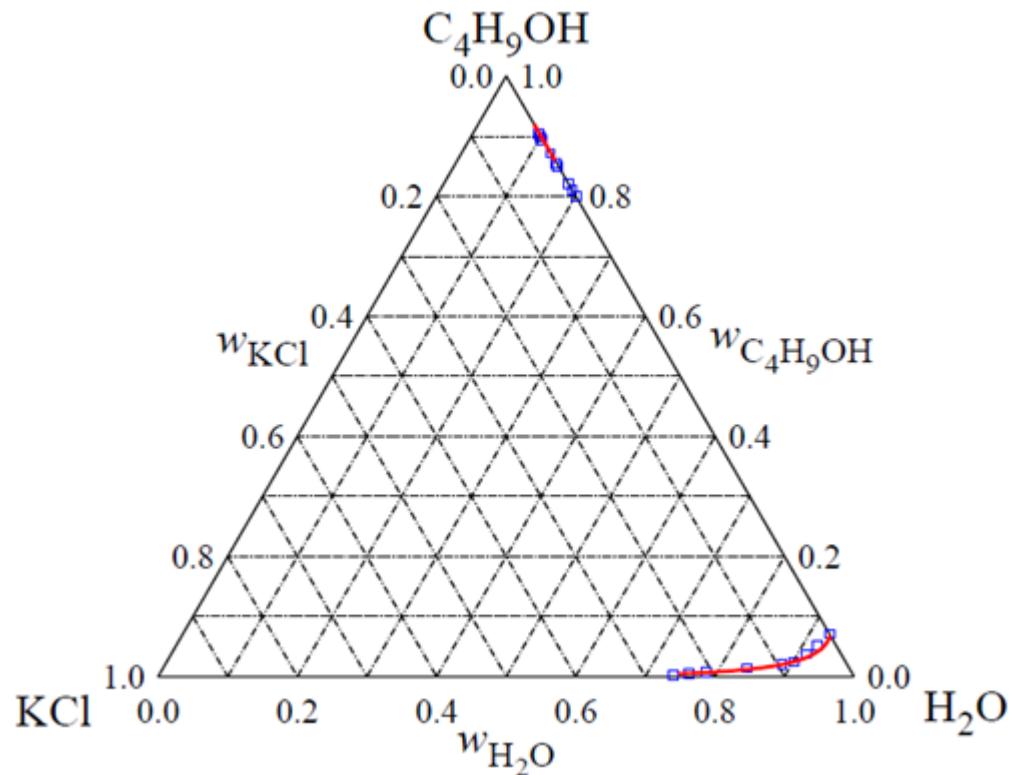
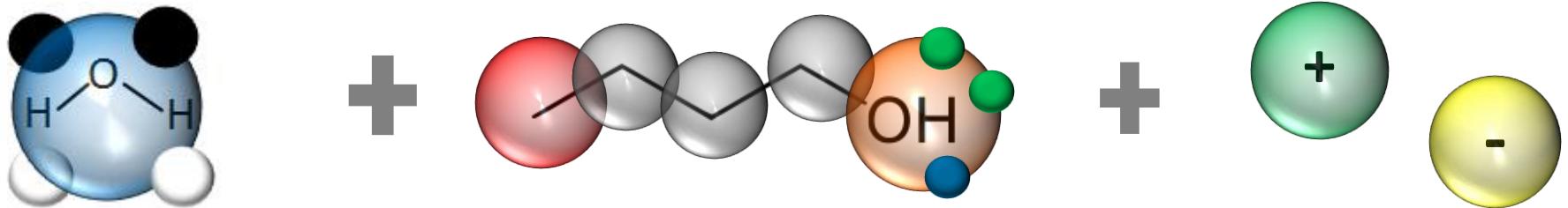


# gSAFT for electrolytes mixed solvent calculations



# gSAFT for electrolytes

## mixed solvent calculations



# Application #5 gSAFT for pharmaceutical compounds

**NOTE**  
**No experimental solubility data  
used for estimating gSAFT parameters**

# gSAFT for pharmaceutical compounds solid/liquid equilibria



gPROMS ProcessBuilder 1.0.0 (beta4)

File Edit View Entity Activities Tools Window Help

API\_solid\_liquid\_demo

SolubilityCalculator (API\_solid\_liquid\_demo)

Annotations

Projects

Interface | Interface language | Topology | gPROMS language | Properties

Palette

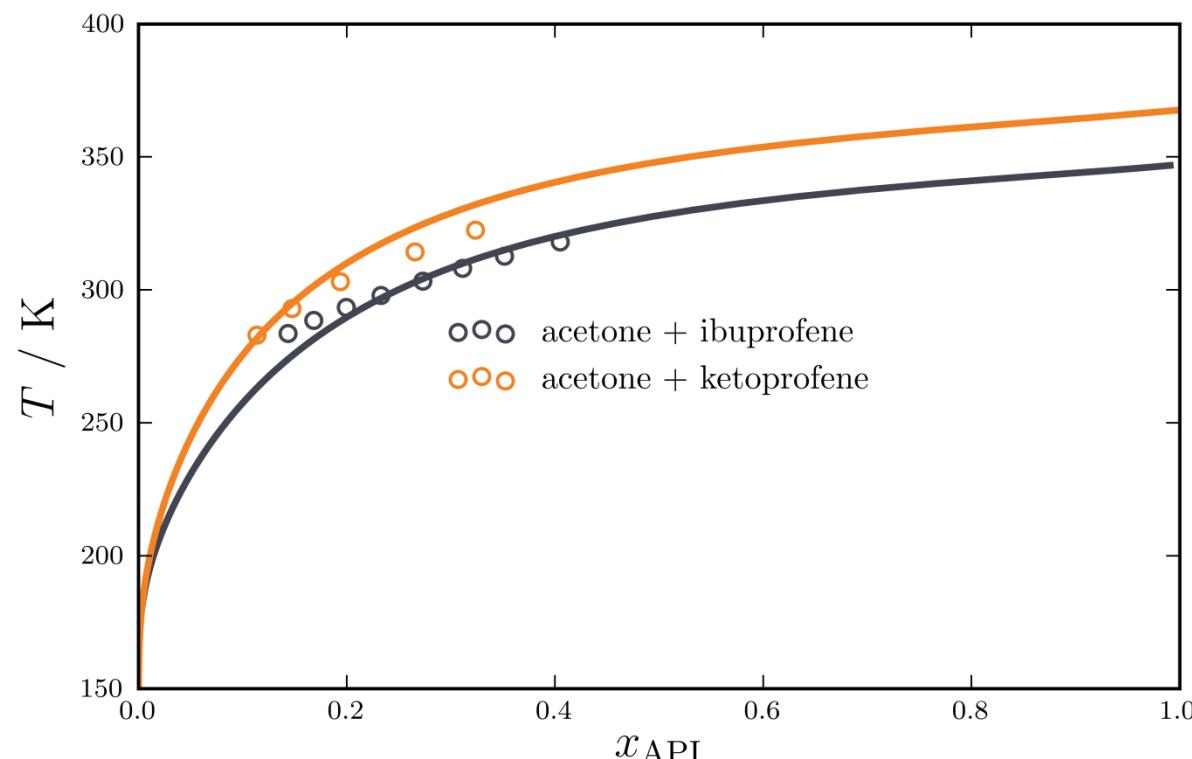
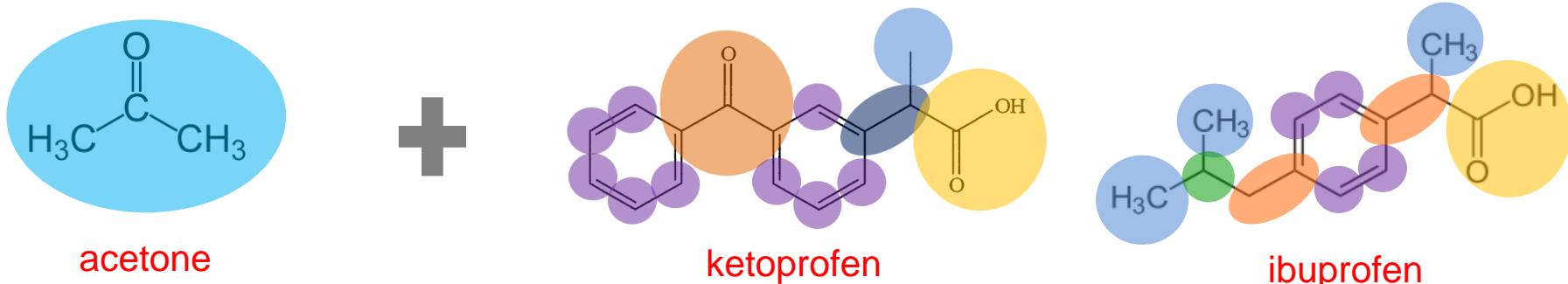
The screenshot shows the gPROMS ProcessBuilder software interface. On the left, there's a project tree titled 'API\_solid\_liquid\_demo' containing various categories like Variable Types, Stream Types, Connection Types, Models, Tasks, Processes, Experiments, etc. The main workspace displays a diagram of a tablet dissolving in a glass of water, with a red arrow indicating the flow from the tablet to the glass. To the right of the diagram is a 'Solubility diagram' plot titled 'Solubility diagram'. The y-axis is labeled 'Temperature / K' and ranges from 0 to 100. The x-axis is labeled 'Solubility' and ranges from 0 to 100. The plot area is currently empty.



ADVANCED PROCESS MODELLING  
FORUM 22–23 APRIL 2015

# gSAFT for pharmaceutical compounds

## solubilities of APIs in acetone



S. Gracin and A. C. Rasmussen, *J. Chem. Eng. Data*, **47**, 1379 (2002)

# gSAFT for pharmaceutical compounds

## Effect of changing the solvent

gPROMS ProcessBuilder 1.0.0 (beta4)

File Edit View Entity Activities Tools Window Help

SolubilityCalculator (API\_solid\_liquid\_demo)

API\_solid\_liquid\_demo

- Variable Types
- Stream Types
- Connection Types
- Models
- Tasks
- Processes
- Experiments
- Experiment Designs
- Parameter Estimations
- Optimisations
- Saved Variable Sets
- Miscellaneous Files

SolubilityCalculator\_20150420\_135428

SolubilityCalculator\_20150420\_135523

Annotations

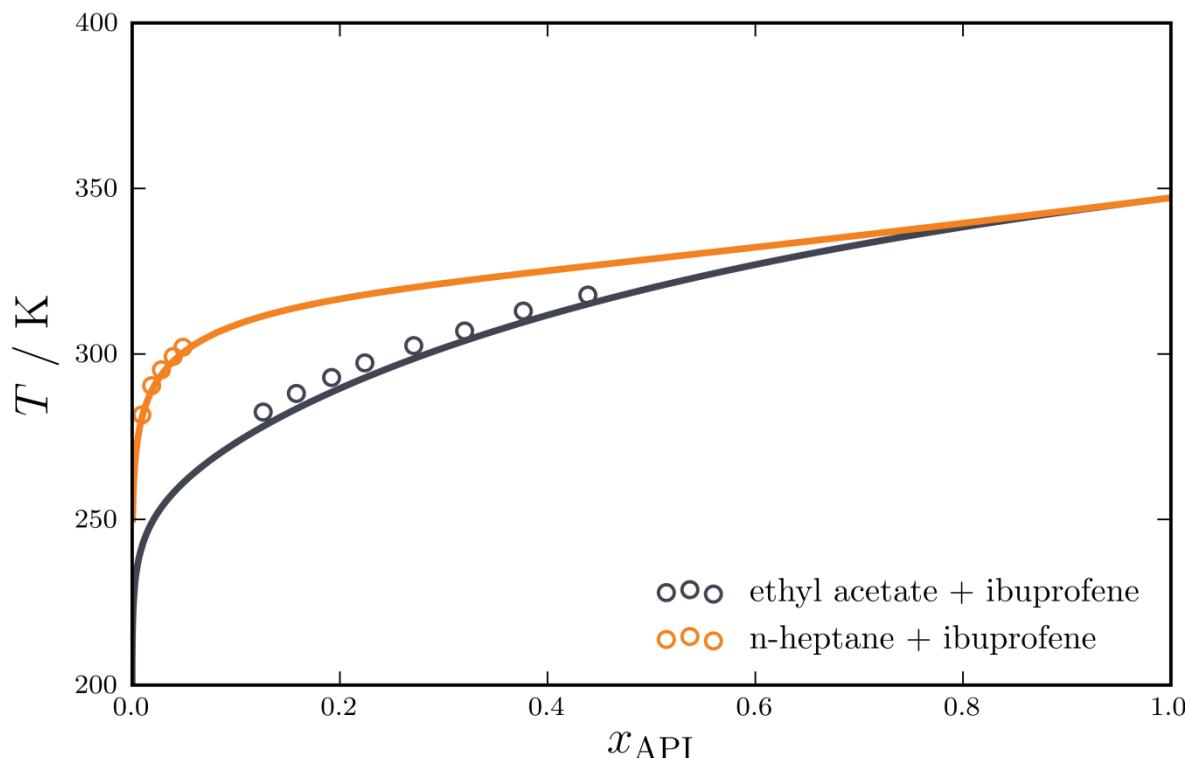
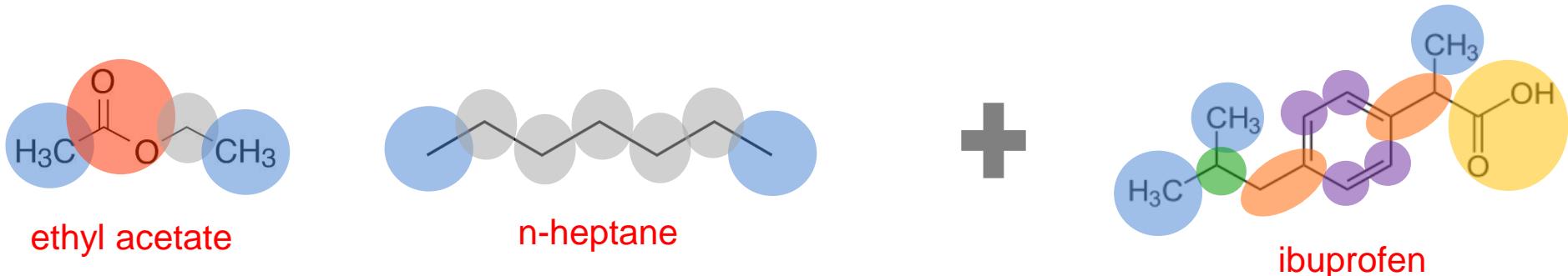
Projects

Interface | Interface language | Topology | gPROMS language | Properties

Palette

# gSAFT for pharmaceutical compounds

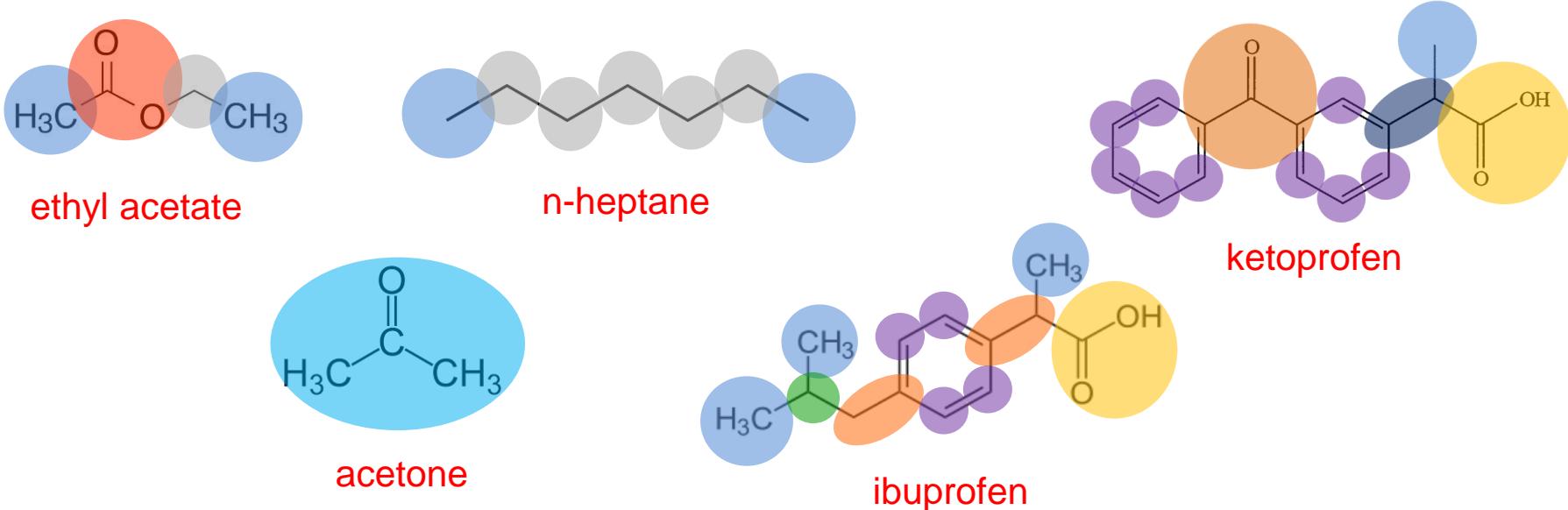
## Effect of changing the solvent



S. Gracian and A. C. Rasmussen, *J. Chem. Eng. Data*, **47**, 1379 (2002)

# gSAFT for pharmaceutical compounds

## pure predictions

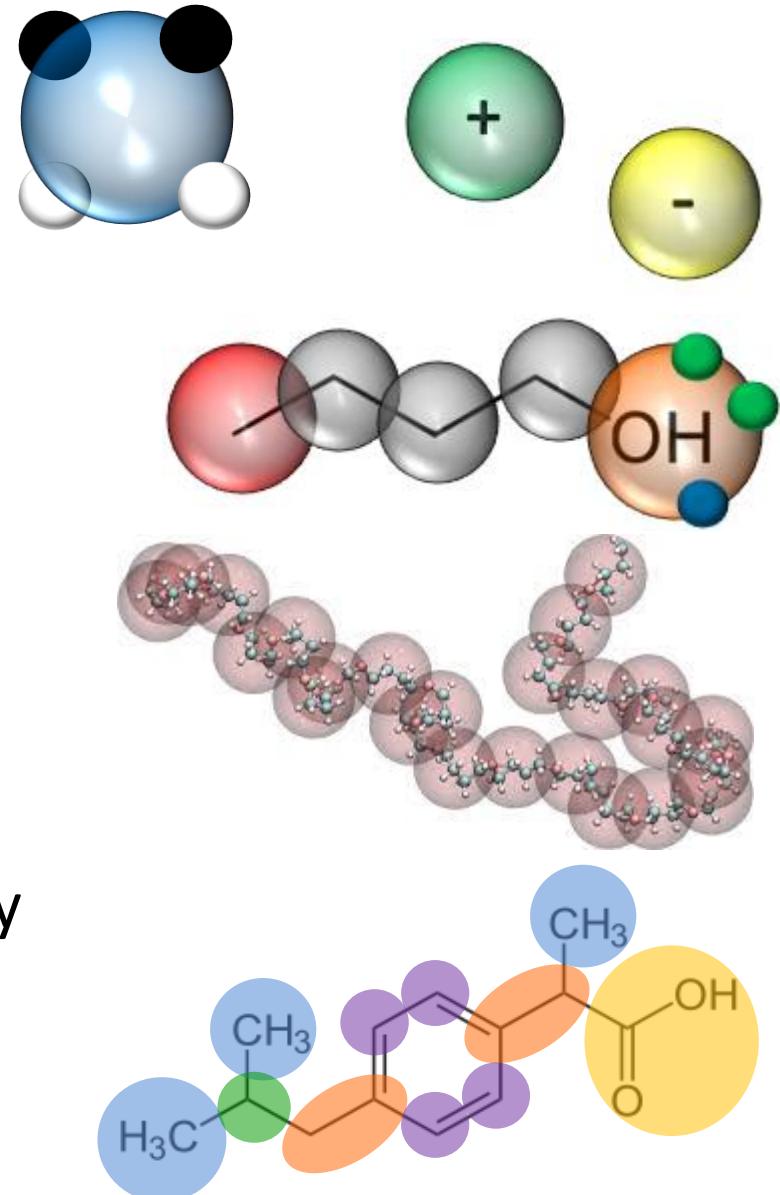


group	CH <sub>3</sub>	CH <sub>2</sub>	CH	aCH	aCCH	aCCH <sub>2</sub>	COOH	CH <sub>3</sub> COCH <sub>3</sub>	COO	aCCoAaC
CH <sub>3</sub>	green	-	-	-	-	-	-	-	-	-
CH <sub>2</sub>		green	-	-	-	-	-	-	-	-
CH			green	-	-	-	-	-	-	-
aCH			yellow	green	-	-	-	-	-	-
aCCH				green	-	-	-	-	-	-
aCCH <sub>2</sub>				yellow	green	-	-	-	-	-
COOH			yellow	green	green	-	-	-	-	-
CH <sub>3</sub> COCH <sub>3</sub>			yellow	green	green	yellow	green	-	-	-
COO	green	green	yellow	yellow	yellow	yellow	yellow	green	-	-
aCCoAaC	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	green	-

- **Satisfactory prediction of SLE**
- **Correct ranking of solvents**
- **No fitting on SLE data**

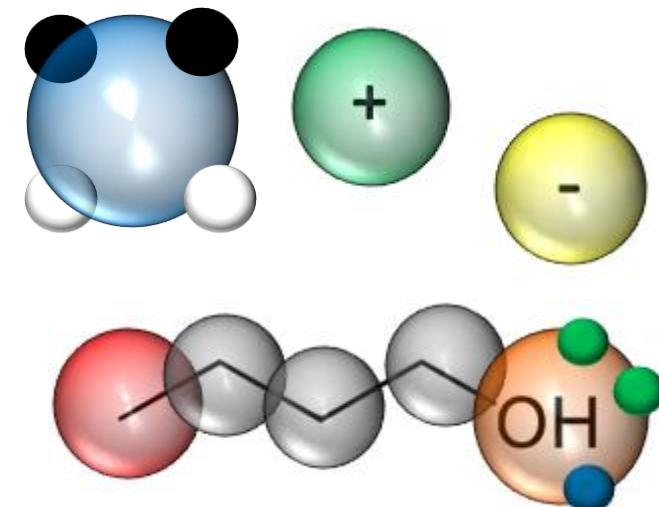
# Conclusions

- A rigorous, general framework for prediction of fluid behaviour
  - applicable to wide range of systems
  - ...with single set of parameters
- Robust & efficient implementation
  - advanced numerics
  - sophisticated software engineering
- Accessible throughout gPROMS-family products
  - fully integrated within gPROMS Platform



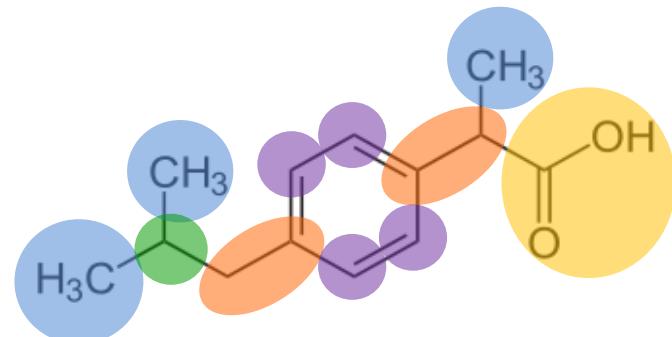
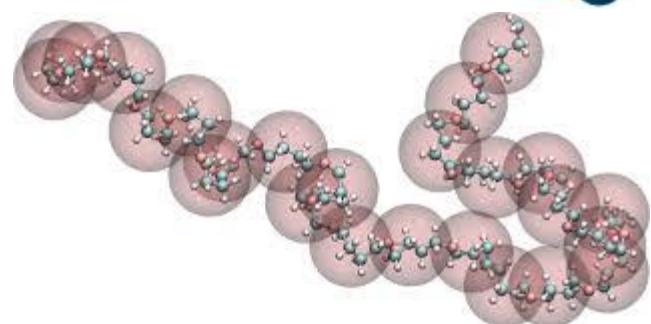
## 1. Combined phase & reaction equilibria

- including ionic systems
- thermodynamically consistent modelling of non-equilibrium reactions



## 2. Solid/liquid equilibrium

- accurate computation of solid-phase potentials

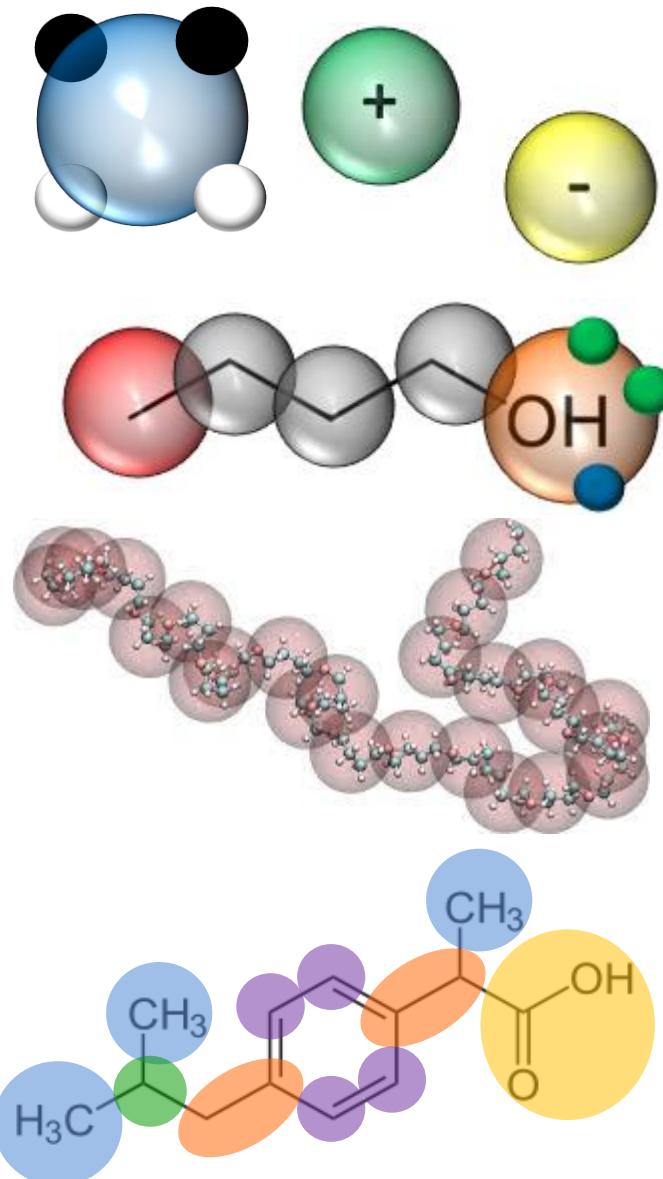


### 3. Wider range of systems

- extended database of group parameters
- particular focus on polymers & ions

### 4. Variable Molecular Structures

- allow gPROMS models to manipulate the molecular structure of individual compounds in system of interest
- molecular structure **not** pre-defined
- **already implemented & used in gSAFT v4.1**

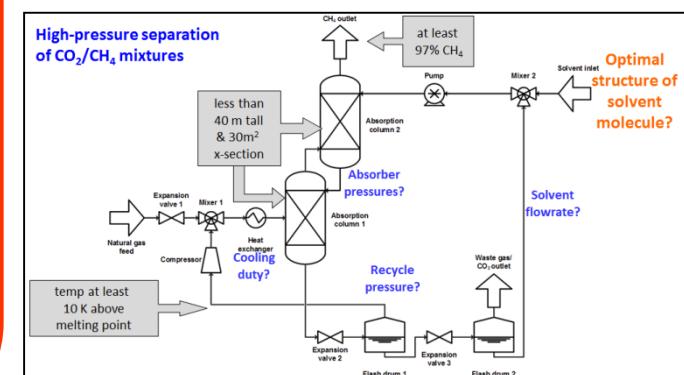
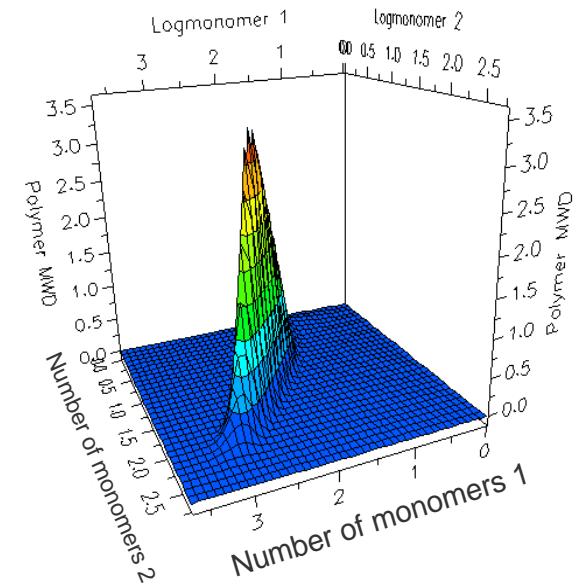


## ■ Application I: polymerisation modelling

- gPROMS polymerisation reactor models determine molecular weight distribution

## Application II: simultaneous design of process & molecules

- design “auxiliary” process materials
    - solvents
    - entrainers
    - working fluids for thermodynamic power cycles
  - use standard gPROMS mixed integer-continuous optimisation **2015 focus**



F.E. Pereira, E.Keskes,A.Galindo,G.Jackson,C.S.Aджиман,  
Integrated solvent and process design using a SAFT-VR thermodynamic  
description: High-pressure separation of carbon dioxide and methane,  
*Comput. Chem. Engng.*, **35**, 474-491 (2011)

■ **Vasileios Papaioannou**

■ **Javier Fuentes**

■ **Alex Mackay**

■ **Javier Rodriguez**

■ **Costas Pantelides**

Thank you

