Dissemination of University Research through CAPE-OPEN

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CAPE-OPEN Annual Meeting
September 19, 2013, Lyon, France

About Bjørn Maribo-Mogensen

- Academic Background
  - 2005-2010: BSc, MSc Chemical Engineering, DTU
  - 2010-now: PhD Student, CERE, DTU
- Professional Experience
  - 2006-2008: Student programmer, Haldor Topsøe
  - 2009-2010: Student programmer, CERE, DTU
  - 2011-now: Software Manager, CERE, DTU
- 12+ years of experience with software development
  - C, C++, C#, FORTRAN, Databases, Web, …

Outline of Presentation

The Center for Energy Resources Engineering

Overview of CAPE-OPEN Activities at CERE

Chemicals in Gas Processing (CHIGP)

- The Cubic Plus Association Equation of State (CPA)

ThermoSystem 4.0

- Software engineering with research code…

New Challenges

- Electrolytes with VLE / VLLE… in CAPE-OPEN?

The Center for Energy Resources Engineering

Interdisciplinary center

- Chemistry, Civil Engineering, Chemical Engineering, Compute, Space
- Chairman: Erling H. Stenby

Facts

- Formed in 2009 from IVC-SEP
- 11 faculty members, 15+ postdocs+senior researchers, 25+ PhD students

Expertise

- Chemical engineering thermodynamics
- Geology & petrophysics
- Mathematical modeling & Geostatistics

Industrial Consortium 2013

The History of CAPE-OPEN in CERE

- CERE develops models for prediction and correlation of physical properties as well as models for processing equipment
- CAPE-OPEN effort was initiated by Prof. Erling H. Stenby at IVC-SEP in 2003 in collaboration with BP
- CAPE-OPEN plays a key role in the joint industry projects (JIPs) at DTU CERE
  - Allows our thermodynamic models to be used on a daily basis by process engineers for e.g. designing novel processes with more accurate physical properties
  - Allows international collaboration without code sharing

Overview of CERE Thermodynamics Software

Stand-Alone

- SPECS
- DLLs
- MATLAB add-in

CAPE-OPEN

ThermoSystem

- CPA (CHIGP)
- sPC-SAFT
- Soave Redlich-Kwong
- Peng-Robinson

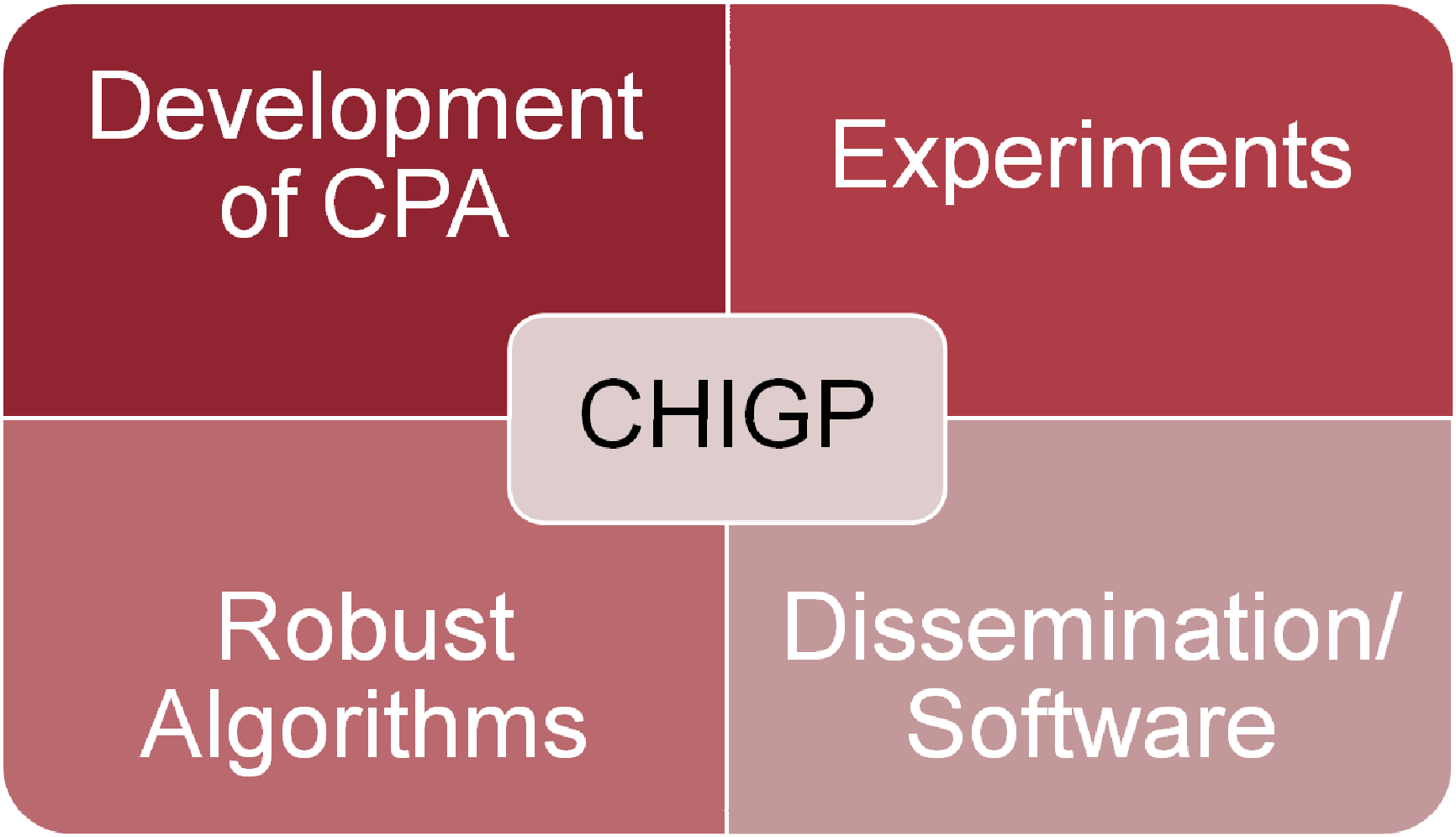
.NET C# CAPE-OPEN Library

- Thermodynamic models
- Unit Operations

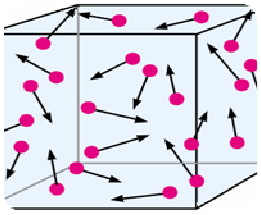
Aspen Plus User Models

- Extended UNIQUAC
- CPA

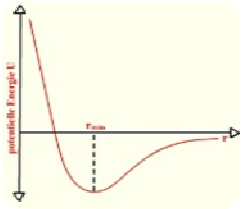
Chemicals **i**n **G**as **P**rocessing



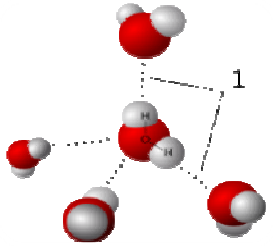
The Cubic Plus Association (CPA) EoS



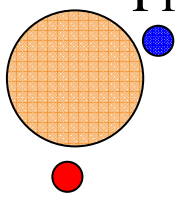
Ideal gas

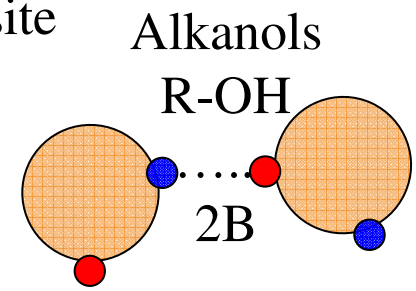


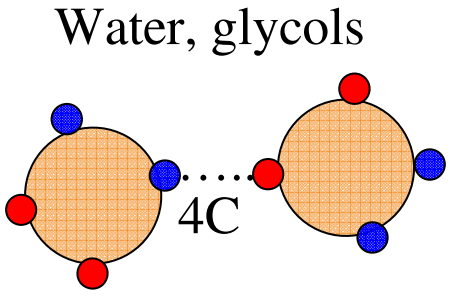
Short-Range Forces (SRK)

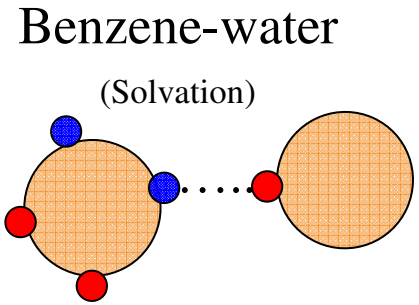


Hydrogen bonding (SAFT)









Kontogeorgis et al. Ind. Eng. Chem. Res. (1996), 35 (11), 4310-4318

The Cubic Plus Association (CPA) EoS

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2}\frac{RT}{V_m}\left(1 + \frac{1}{V_m}\frac{\partial \ln g}{\partial(1/V_m)}\right)\sum_i x_i \sum_{A_i}\left(1 - X_{A_i}\right)$$

Pure component parameters (3 or 5) are fitted to vapor pressure/liquid density

Associating components are given an association scheme

Binary interaction parameters kij fitted to binary data

Three physical parameters

b_i Co-volume parameter

Γ_i Attractive energy at T_c

c_1 Soave α-function T-dependency

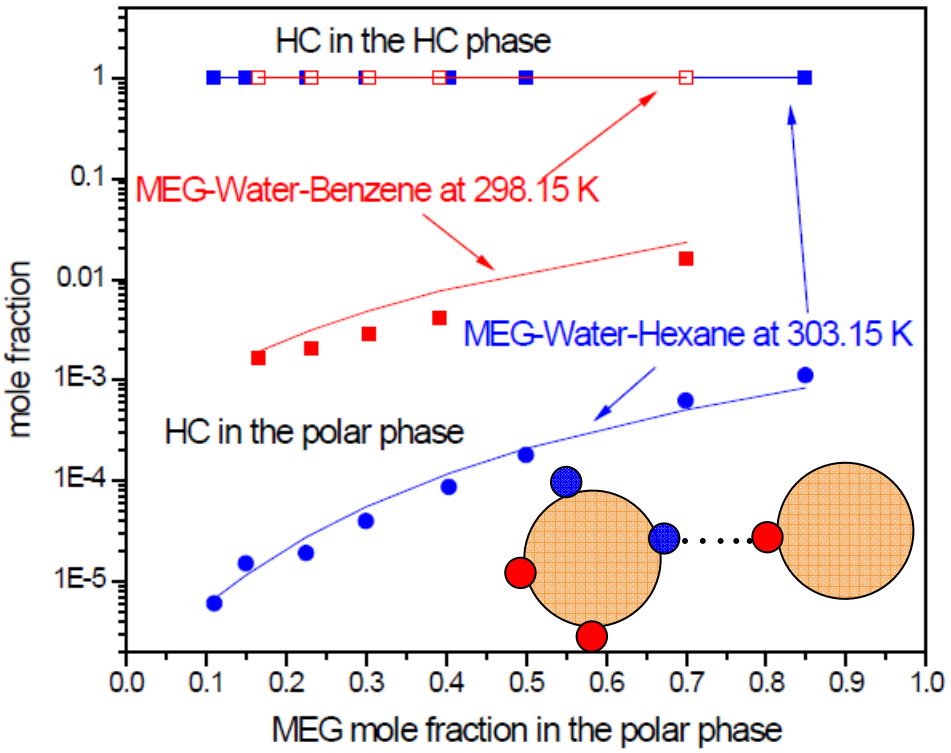
Two association parameters

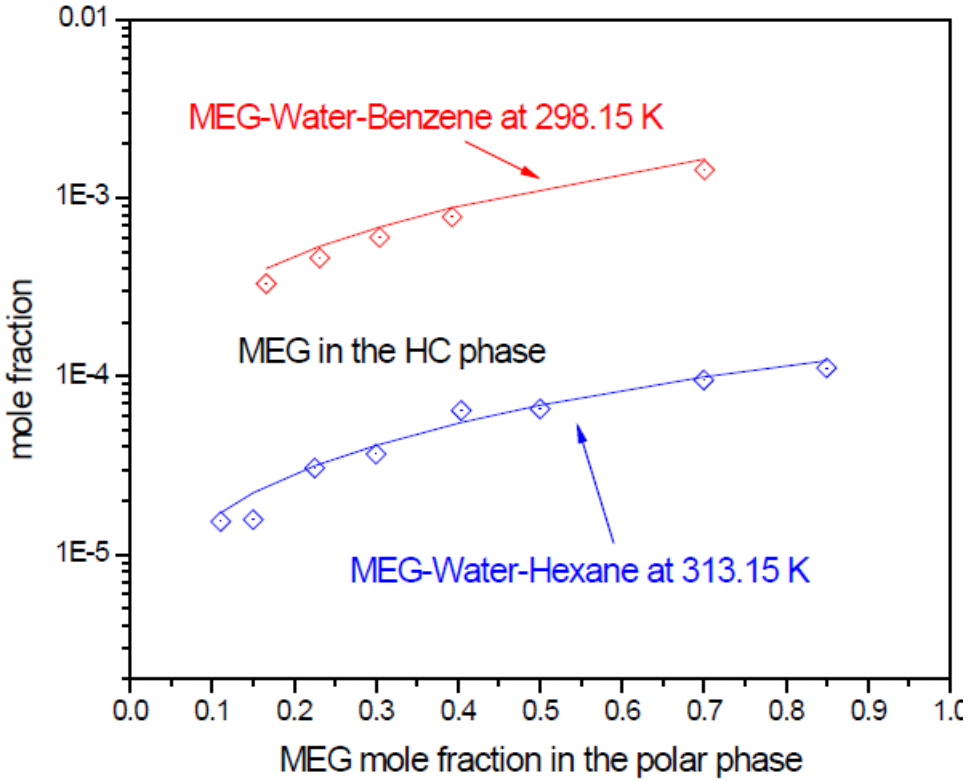
β Association strength

ε Association energy

MEG-Water-Hexane vs. MEG-water-benzene

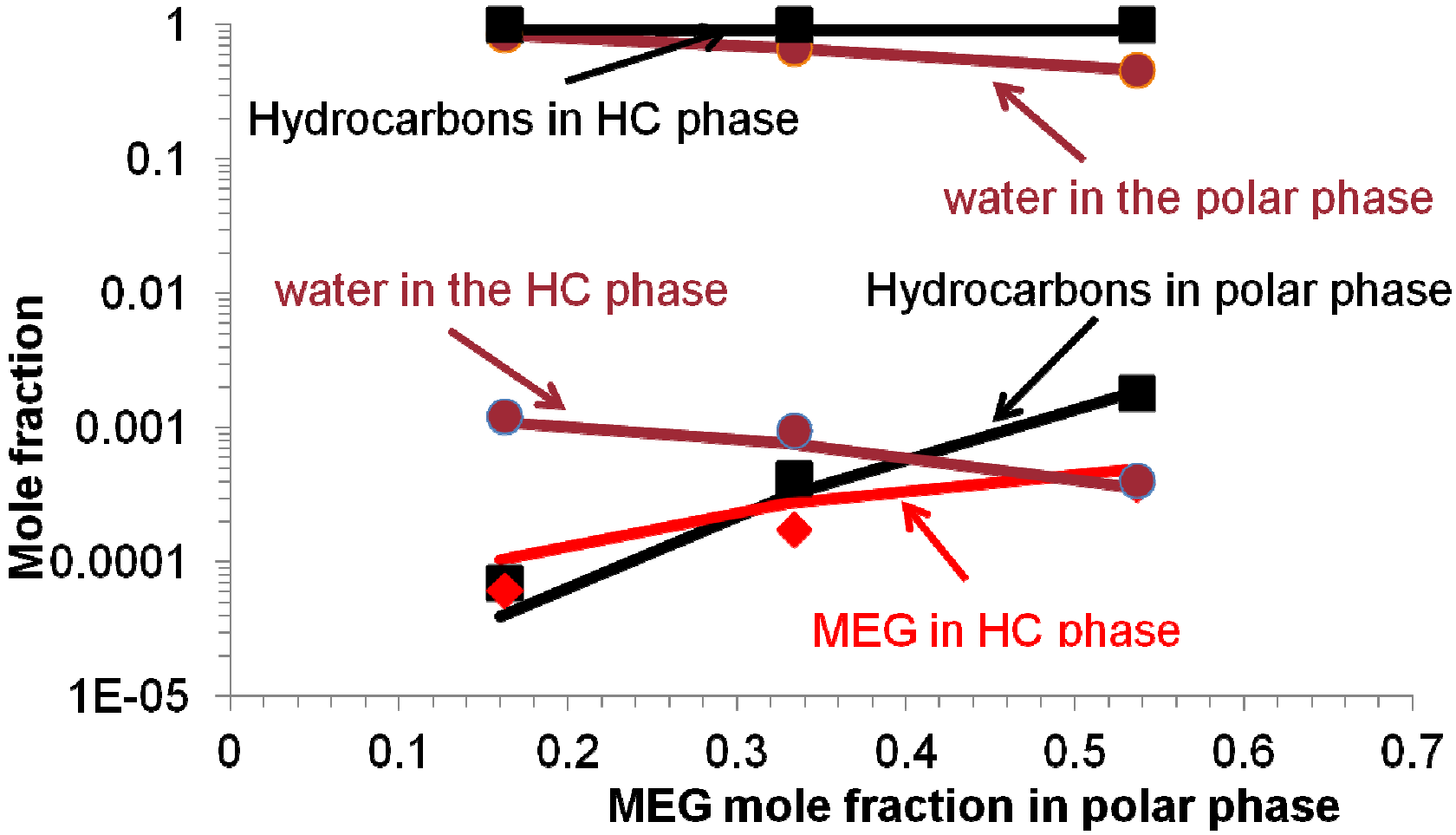
Kontogeorgis, Tsivintzelis et al. 2011, Fluid Phase Equilibria, 301: 244





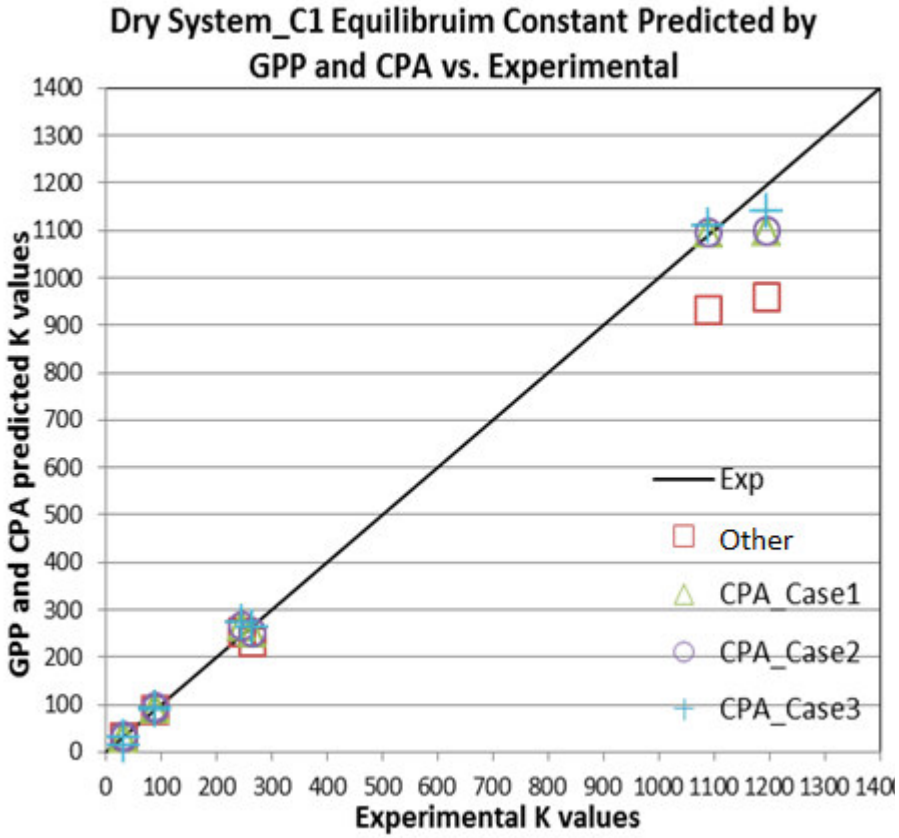
Exp. Data: Razzouk et al., **2010**, J.Chem.Eng.Data, 55: 1468
Modeling: Folas et al., **2006**, J. Chem. Eng. Data, 51 : 977

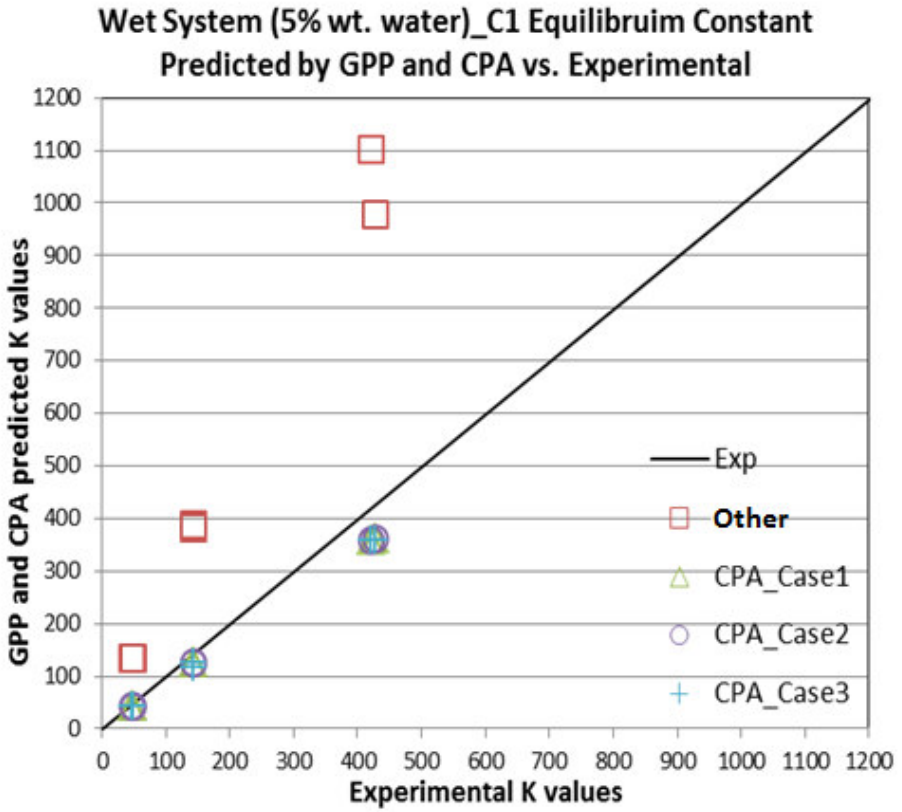
Condensate-1 + MEG + Water, T = 313.15K



BTEX emissions in TEG-Water-Methane-BTEX

- Unpublished results, Alay Arya (2013)
- BTEX: Benzene, Toluene, Ethylbenzene, O-Xylene. Solvation parameters from 1 aromatic





Current research highlights

Contact: Prof. Georgios M. Kontogeorgis: gk@kt.dtu.dk

- Oil mixtures (the role of aromaticity)
- Acid Gases (H_2S, CO_2)
- Prediction of dew point and gas hydrate formation in natural gas and condensates
- Electrolytes (brines and beyond)
- Sulfur-containing compounds (mercaptans)
- Biodiesel mixtures
- Phase behavior during catalyzed oxidation in supercritical CO_2
- Ionic liquids-water systems

Dissemination of results with ThermoSystem

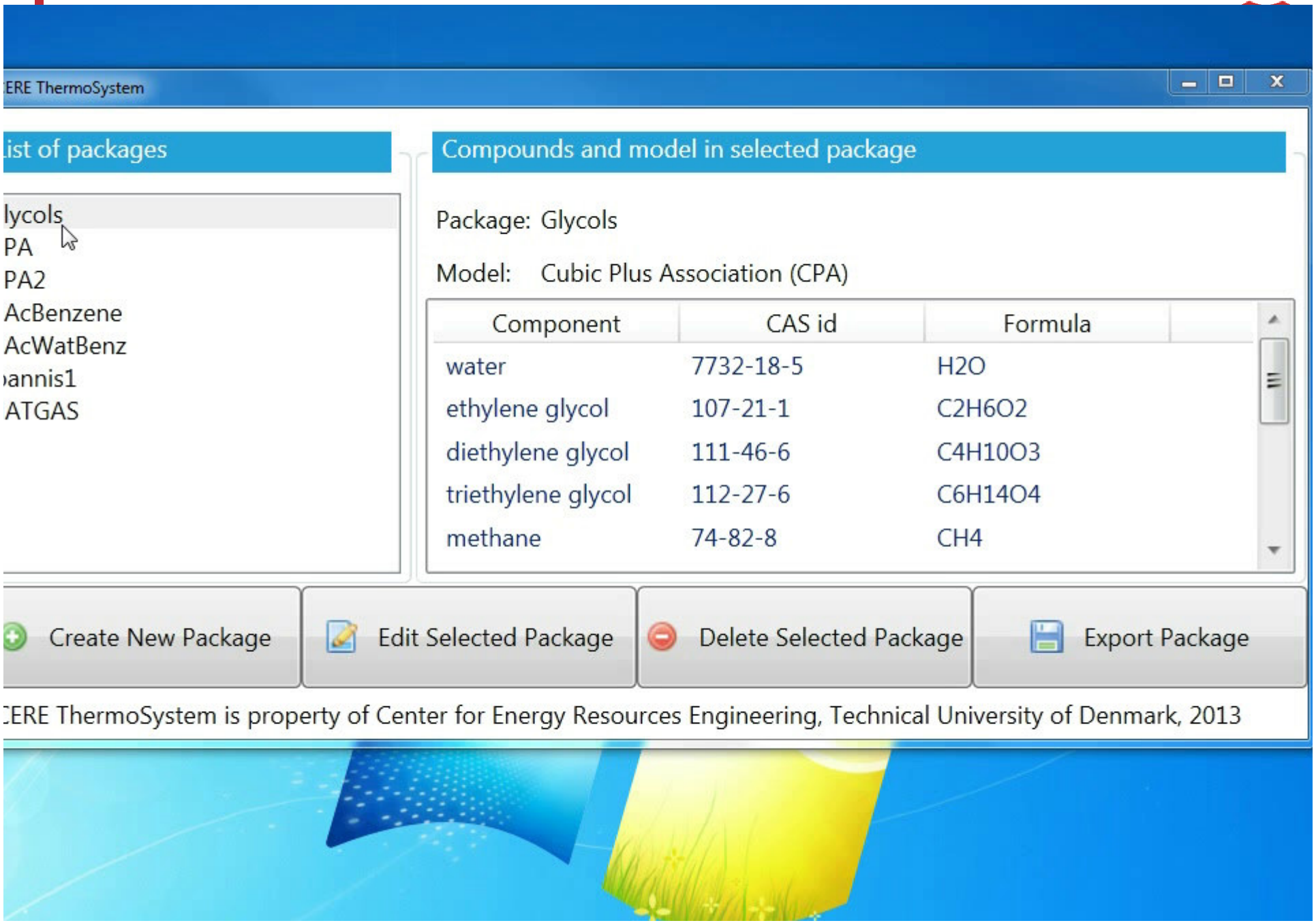
- ThermoSystem consists of:
  - A user interface for the parameter database
  - A CAPE-OPEN Property Package for CPA, PC-SAFT, PR, SRK
  - An Aspen Plus User Model for CPA
  - A stand-alone DLL for CPA
- Parameter database with user interface for exporting to CAPE-OPEN and Aspen Plus Input Files
  - 150+ pure components
  - 250+ binary interaction parameters

Towards ThermoSystem 4.0

- CERE has 10 years of experience with CAPE-OPEN
  - ..and PME-specific Aspen Plus User Models
  - Proof of concept: models are now being used actively in industry
  - Has increased the degree of direct collaboration with industry
- More users = greater responsibility
- We need to worry about new aspects (which universities are not always too familiar with)
  - Quality assurance and automated testing
  - Code maintainability
  - Code extensibility
  - Improving user interfaces
  - Support

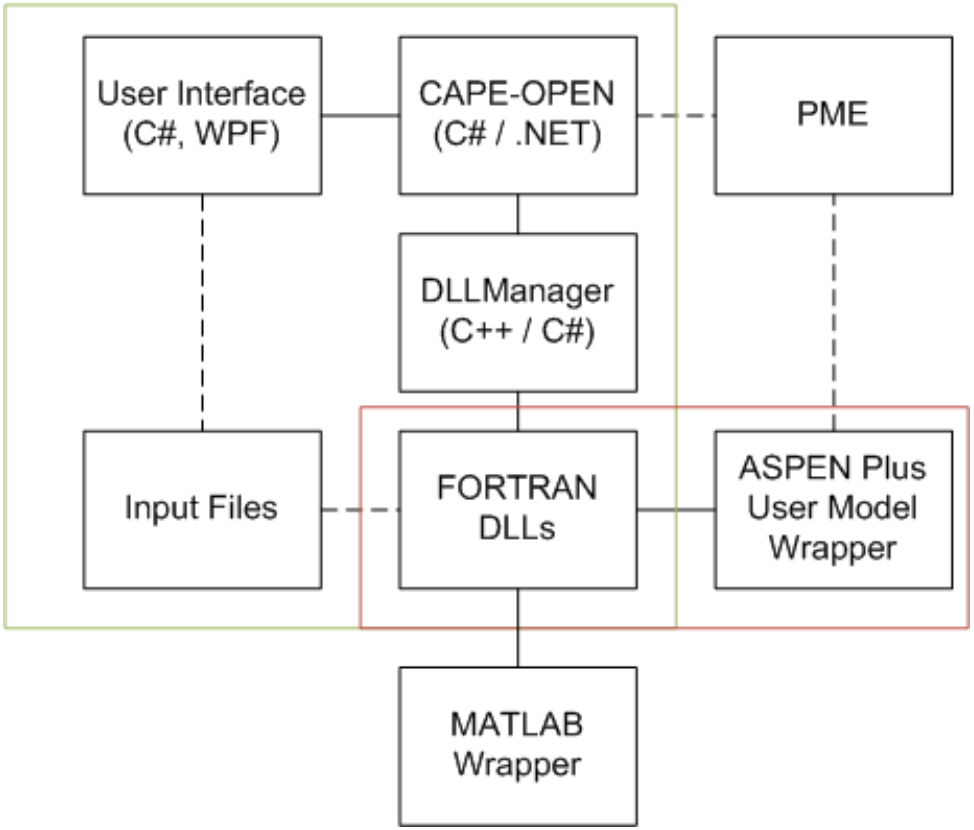
From Research Code to PMC

- PMC code must be robust
  - Or at least inform the user that something is wrong
  - Problems may or may not be caught by automated testing
- PMCs should allow multiple property package instances
  - But many researchers use FORTRAN with global variables…
- The CAPE-OPEN interfaces can be tricky
- And what about the end user?
  - GUI's are helpful in translating from experts to users
- And finally – a support structure is needed to handle requests and questions from users


ERE ThermoSystem
ist of packages
lycols
PA
PA2
AcBenzene
AcWatBenz
annis1
ATGAS
Compounds and model in selected package
Package: Glycols
Model: Cubic Plus Association (CPA)
Component
CAS id
Formula
water
7732-18-5
H2O
ethylene glycol
107-21-1
C2H6O2
diethylene glycol
111-46-6
C4H10O3
triethylene glycol
112-27-6
C6H14O4
methane
74-82-8
CH4
Create New Package
Edit Selected Package
Delete Selected Package
Export Package
ERE ThermoSystem is property of Center for Energy Resources Engineering, Technical University of Denmark, 2013

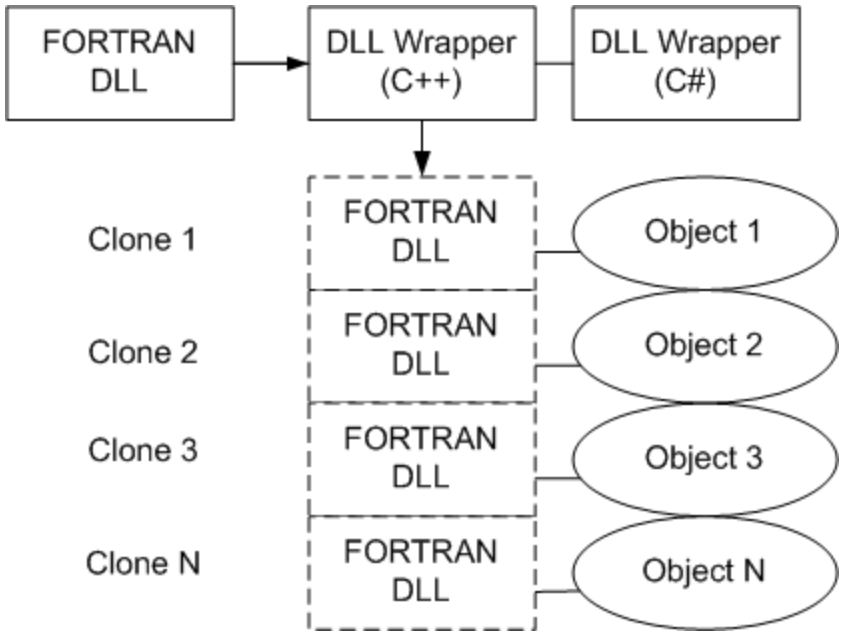
ThermoSystem 4.0

- New robust engine for thermodynamic models
- CAPE-OPEN .NET library for v/1.0 and 1.1
  - No persistence interfaces
- MATLAB / Aspen Plus User Model wrappers
- New user interface
- Quality assurance
  - Automated testing
  - Code documentation
  - Extensibility



DLL Wrapper for Support of Multiple Instances

- FORTRAN DLLs use global variables
- Time does not permit rewriting the modules as object-oriented
- A simple DLL wrapper was written that clones the original DLL, allowing us to form unique objects



CAPE-OPEN .NET Library

- ThermoSystem 3.x was based on a proof-of-concept C++ code. Focus was **not** on maintainability.
- ThermoSystem 4.0 is uses a CAPE-OPEN .NET library (1.0/1.1). *CO AM 2011 at ECCE-8 in Berlin*
- Conversion to/from CAPE-OPEN types is done by the library. Module needs just interfacing with FORTRAN.

Original CAPE-OPEN ICapeThermoPropertyPackage:

```
public void CalcSinglePhaseProp(object props, string phaseLabel)
{
     Parse properties
     Calculate requested properties and set all values in the material object
}
```

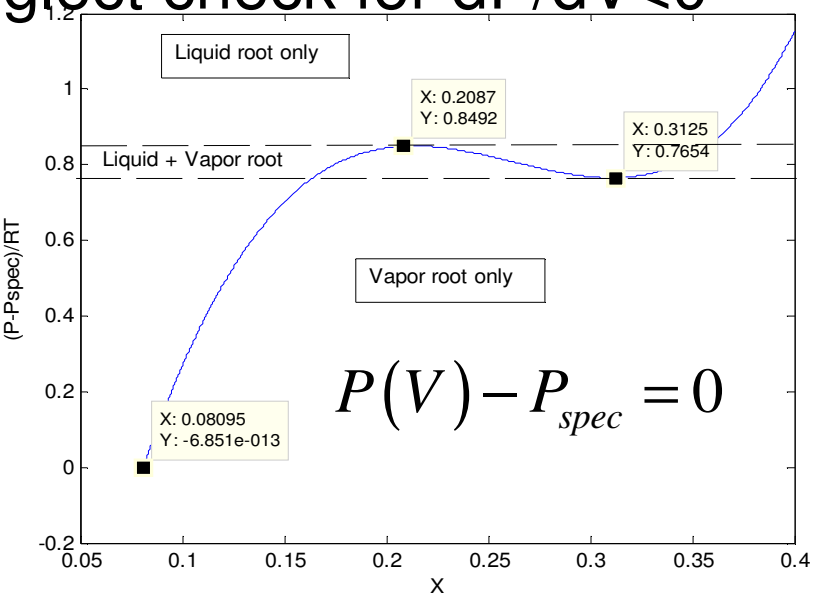
Object deriving from CapeThermoPropertyPackage in library

```
public override bool CalcSinglePhaseProp(SinglePhaseProperty Property, Derivative[] Derivatives,
                                         Phase PhaseType, double Temperature, double Pressure,
                                         double[] Composition, out Basis[] basis, out object[] values)
{
    Call thermodynamic routine and return requested property and optionally derivatives in values
}
```

The importance of robust routines

- The engineers must receive reliable results – PME is not responsible for errors in PMC
- PME-PMC communication may involve unphysical questions; e.g. calc. liquid fugacity of methane at 25ºC..
- Example at 10ºC, 5 bar if we neglect check for dP/dV<0 and return wrong volume
- False result from P-T flash

Comp.	Feed	Phase 1	Phase 2
Ethane	0.50003	.772 (.998)	3e-3 (2.5e-4)
MEG	0.03383	.009 (3e-6)	0.08 (.068)
Water	0.46617	.219 (2e-3)	0.92 (.932)

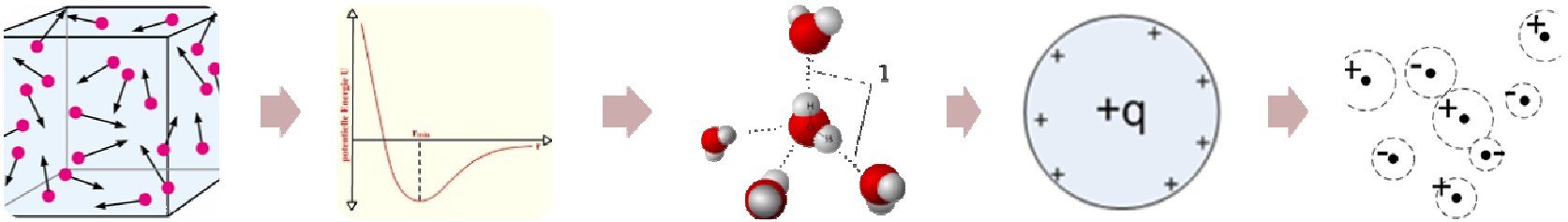


Missing on the TODO

- We miss a few usability interfaces
  - Persistence interfaces for our Thermo Packages for PME's that support this
  - User interface must open on Edit()
- Include DTU Flash routines
  - Currently we ship with a simple 2-phase PT flash
  - Currently, we recommend the use of the built-in flashes
    - Recent analysis has revealed problems with this approach – not only in relation to performance, but also robustness
- Include the electrolyte-CPA EoS

Property Models with Electrolytes

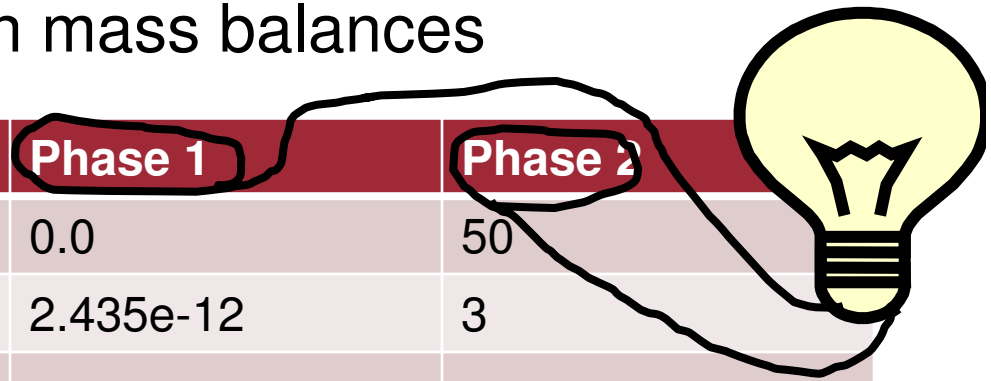
- e-CPA: electrolyte extension for CPA
- Handles electrolytes in mixed solvent systems
- Must handle VLLSE in mixtures with oil/gas/brine and gas hydrate inhibitors (methanol, ethanol, glycols)
- Solids: Gas hydrates and scaling
- Future: also chemicals (e.g. for gas sweetening)



Ideal gas | Short-Range Forces | Hydrogen bonding | Ion Charging | Coulombic Interactions

Electrolyte VLLE using standard PT-flash

- VLLE with electrolytes
- Electrolytes always come in pairs – anions and cations
- Charge balance must be obeyed – but normal PT flash routines are only based on mass balances



	Feed [mol]	Phase 1	Phase 2
Water	50	0.0	50
Isopropanol	3	2.435e-12	3
Na_2SO_4	1	-	-
Na^+	-	1.6595	0.3404
SO_4^{--}	-	0.0247	0.9753
Charge	0	+1.61	-1.61

Including Chemical Equilibrium

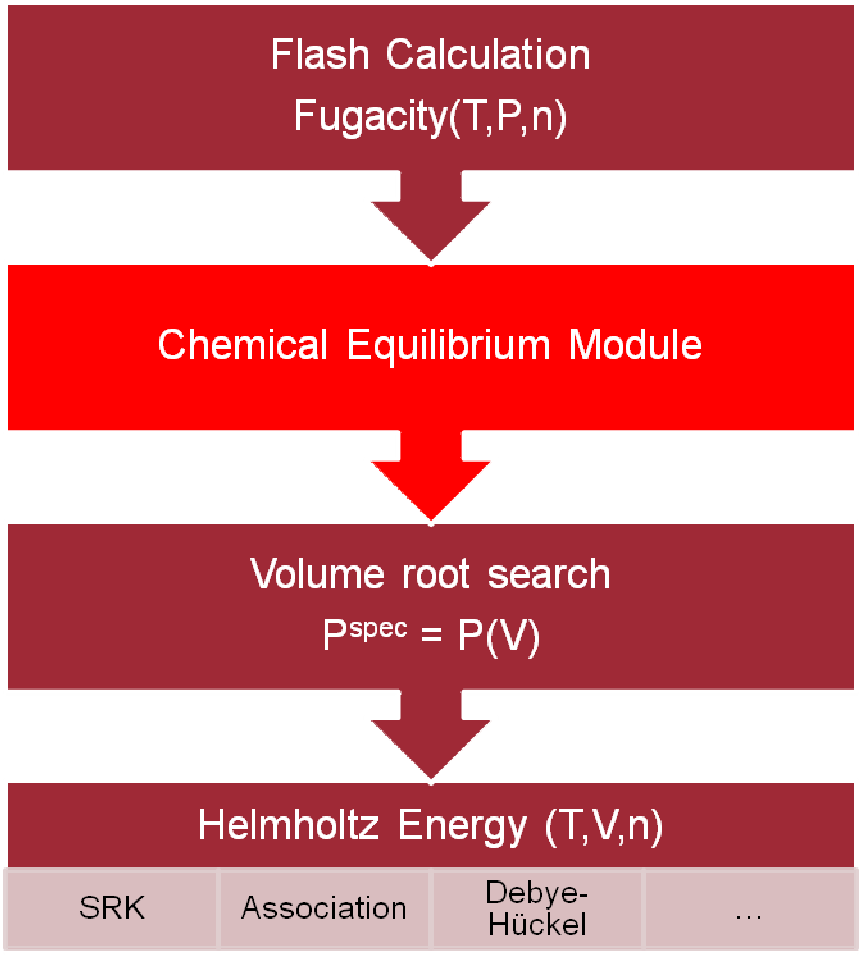
Hides complexity from flash routine

- Flash uses apparent composition
- Charge balance always satisfied
- Physical properties are calculated with true composition

$$\ln x_i^{\text{app}} \hat{\varphi}_i^{\text{app}} = \ln x_i^{true} \hat{\varphi}_i^{true}$$

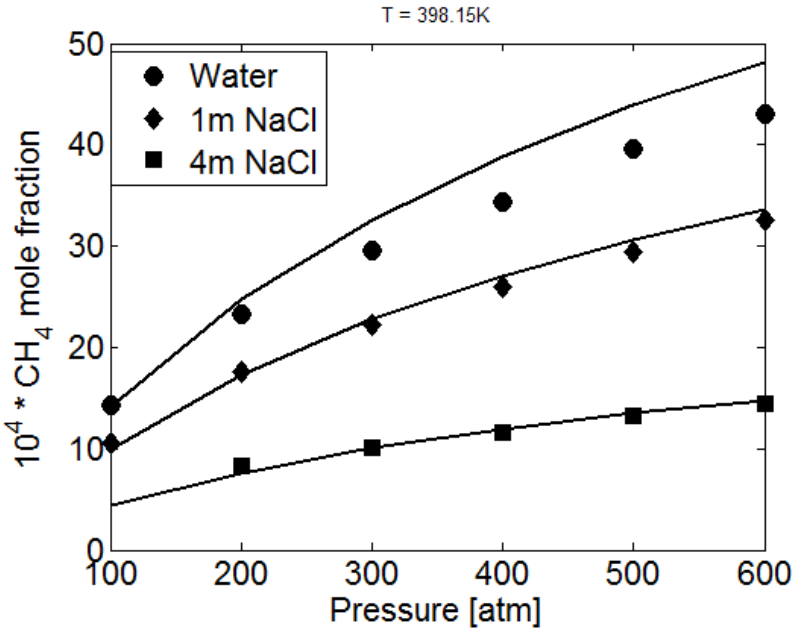
Impossible for external routines to calculate SLE

- Apparent components provides insufficient speciation for SLE
- Ion activity coefficients are only available inside the module



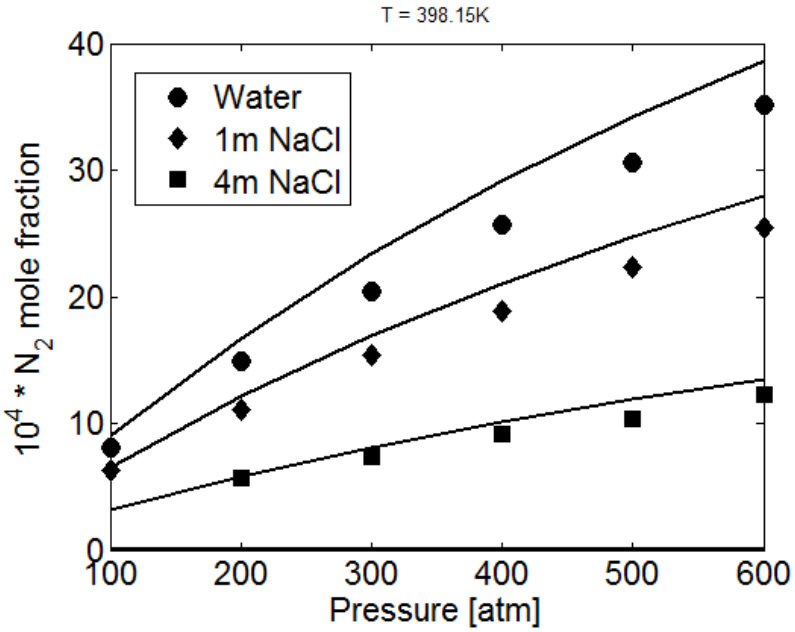
Light Gas Solubility Predictions

Methane in Water @ 125°C



k_{ij}=0.7988-236.5/T (H_2O-CH_4)

Nitrogen in Water @ 125°C



k_{ij}=1.0741-368.3/T (H_2O-N_2)

Data from: T. D. O'Sullivan, N. O. Smith, J. Phys. Chem. 74 (7), 1970, 1460-1466

It's not a perfect world…

- PME support for CAPE-OPEN is not always complete
  - Solid-liquid equilibria is not widely supported
  - Not all PME's support the persistence interfaces…
    - Distribution of property package file together with process simulation is prone to errors
- PME specific implementations may in some cases overcome the limitations
  - Aspen Plus User models for CPA and Extended UNIQUAC…
    - Varies from company to company (depending on the preferrred choice of process simulator)
    - APUM is more widely used for CO_2-capture and chemicals
  - But this results in more interfaces to maintain…

What we look forward to seeing

- Improved integration of PMC model parameters in PME
  - Guidelines for defining pure component + binary interaction parameters that integrate into the PME property system
- Process flowsheet monitoring
  - Solid formation potential (wax, scaling, gas hydrates)
  - Identification of regions operating near critical conditions – this may cause the property model to be less accurate…
  - Recommendation of physical property models for different areas
  - Material selection (corrosion potential)
  - Heat integration
  - Environmental impact assessment

Thank You for Your Attention

- Questions?