Centre for Process Systems Engineering

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Advanced thermodynamic and processing modelling integration for amine scrubbing in post-combustion CO_2 capture

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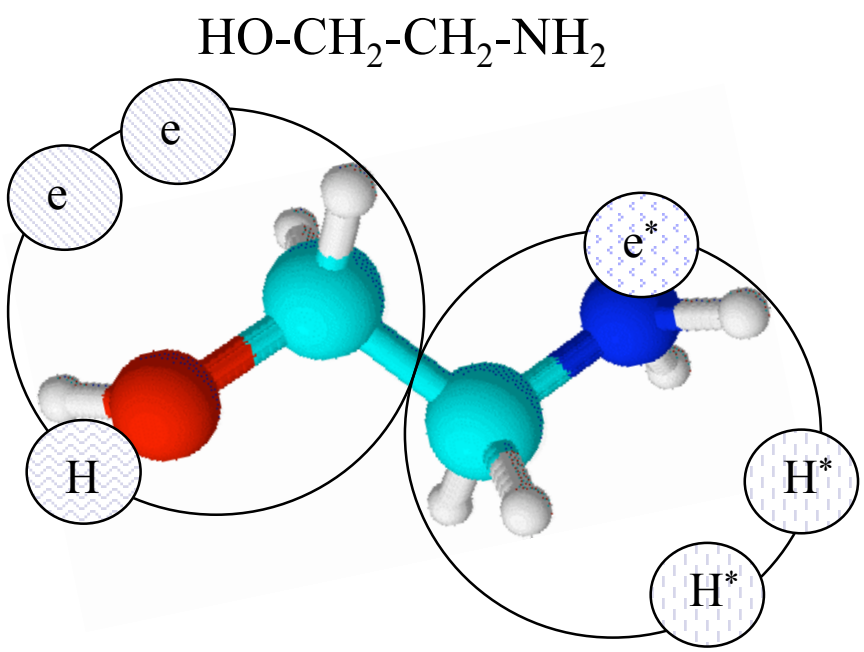
Outline

- Industrial relevance of complex fluids
- SAFT-VR : The molecular model
- Case study - MEA
- CO_2 capture process
- Conclusions

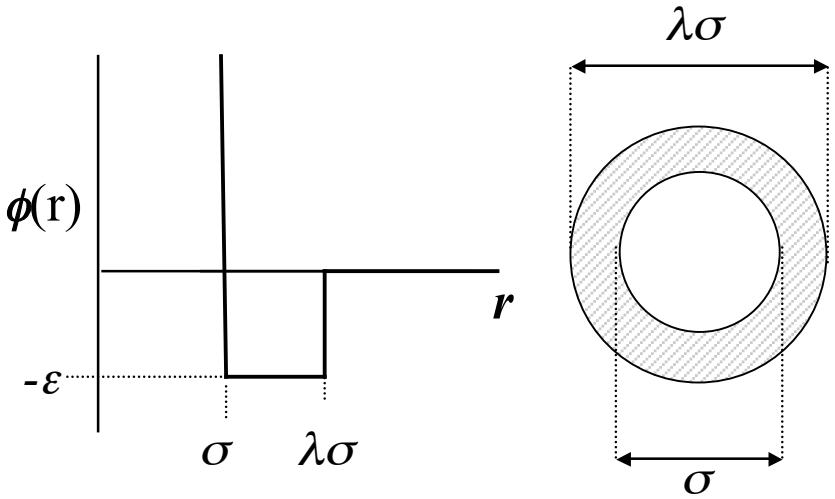
Industrial relevance of complex fluids

- Post-combustion capture (PCC) with **amine scrubbing is** seen as a useful route to reducing carbon emissions
- PCC is energy intensive – **solvent regeneration accounts for the vast majority of costs associated with CCS**, thus there is great interest in **solvent design** and **solvent blends**
- Detailed **understanding** of **solvent fluid phase behaviour is vital** in this endeavour
- Amines are **complex fluids** – need to be able to **predict non-ideal behaviour**
  - Azeotropy
  - Multiple vapour or liquid phases – liquid-liquid equilibrium (LLE)
- **Sophisticated thermodynamic treatment** required – **cubic EoS not applicable**, **quuasichemical-based theories not ideal**
- The **Statistical Associating Fluid Theory** for potentials of **Variable Range** is a suitable theory; **explicitly treats non-sphericity and association contributions to the free energy**, successful at **predicting azeotropy** and **LLE**
- **SAFT-VR** is a **free-energy EOS**: fluid is characterised once all the parameters are known

SAFT-VR: The molecular model



- Molecule as chain of ***m*** tangentially bonded homologous spherical segments of diameter σ
- Segments interact via a square well potential of depth ε and range λ



- Association;
  - ➢ Off-centre association sites of strength ε^{HB} and range K_{AB}

Other Wertheim-like treatments:

- Button and Gubbins (SAFT) 1999
- Avlund et al. (CPA) 2008

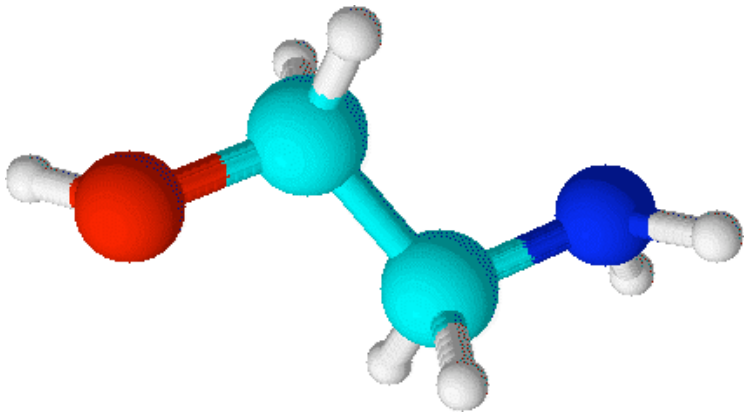
Gil-Villegas et al., J. Chem. Phys., 1997

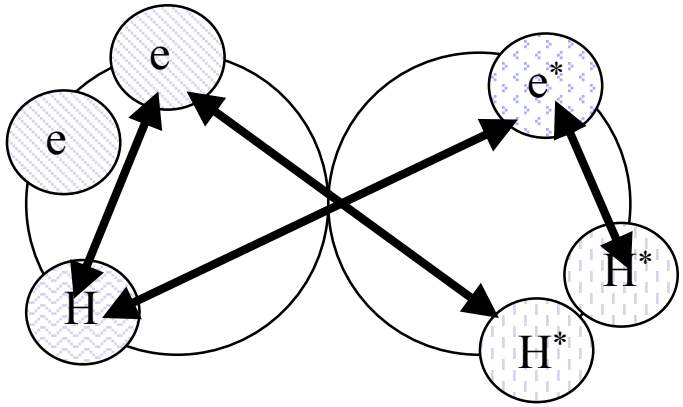
Alkanolamines HO-$(CH_2)_i$-NH_2

- Detailed molecular model developed taking into account all interactions
- Asymmetric interactions taken into account

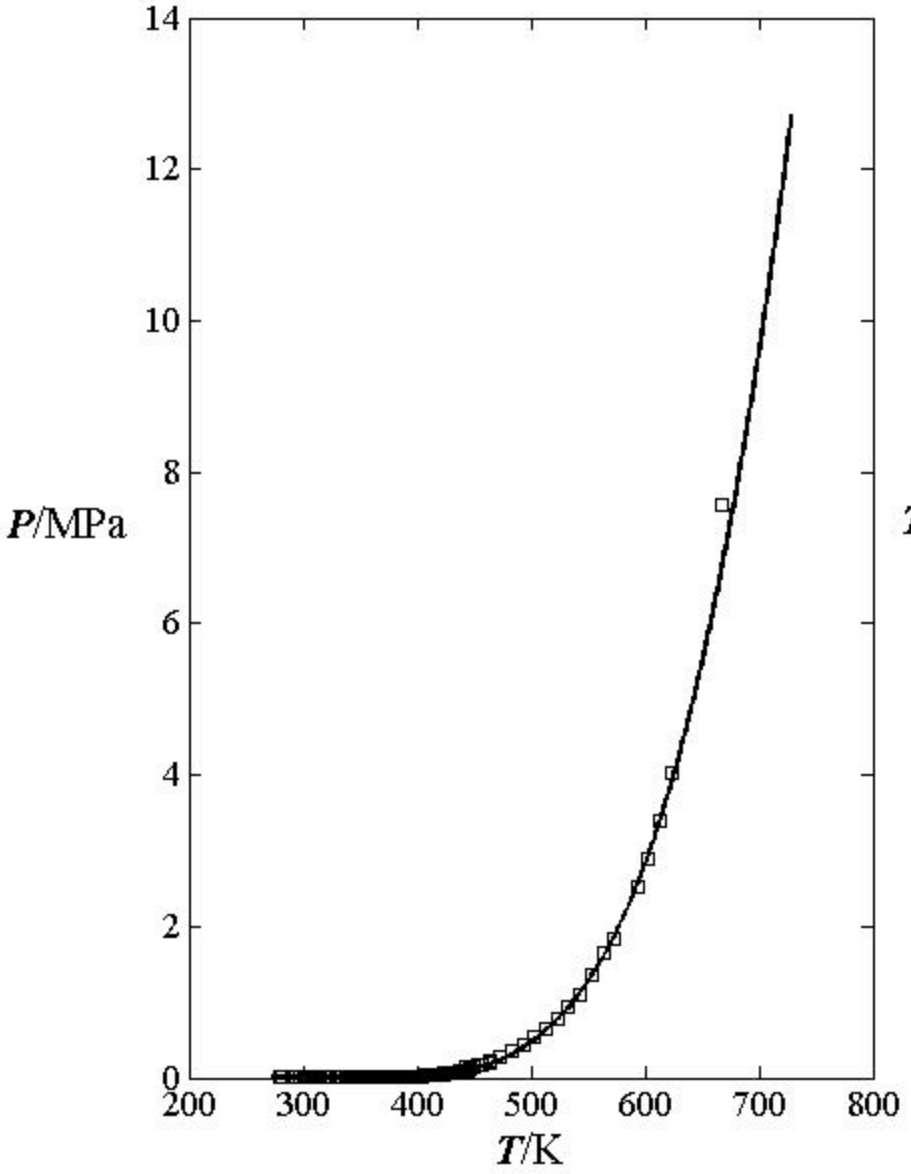
$$\varepsilon^{HB}_{eH} \neq \varepsilon^{HB}_{e^*H^*} \neq \varepsilon^{HB}_{eH^*} \neq \varepsilon^{HB}_{e^*H}$$

- Hypothesis: MEA behaves like C_2H_5OH interacting with $C_2H_5NH_2$
- Transfer self-association parameters from C_2H_5OH and $C_2H_5NH_2$ models
- Problem dimensionality reduced by over 50% by parameter transfer
- Parameter space descritised in terms of ε^{Disp}, ε^{HB}_{eH} and $\varepsilon^{HB}_{e^*H^*}$
- Excellent models for MEA have been developed
  - % Average Absolute Deviation = 2.4%

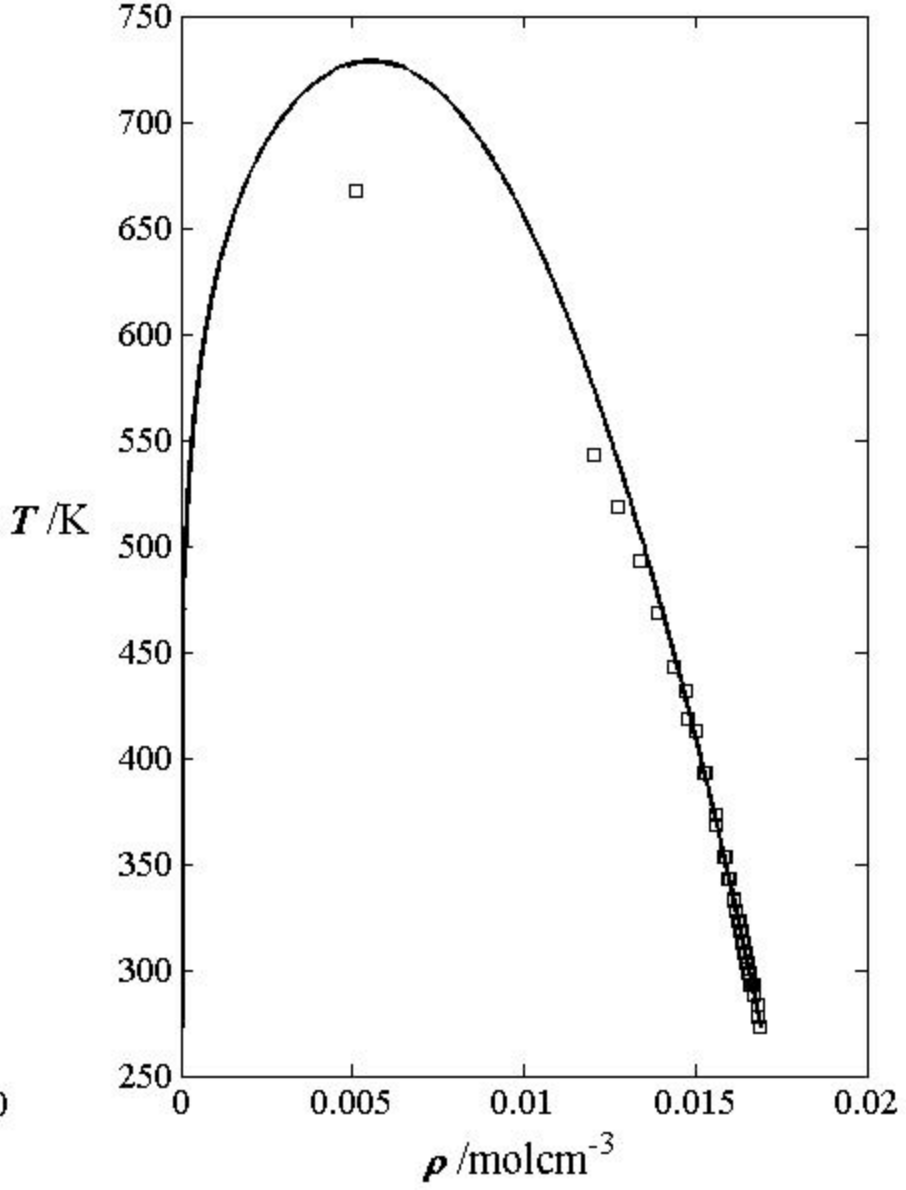




MEA Saturated Vapour Pressure



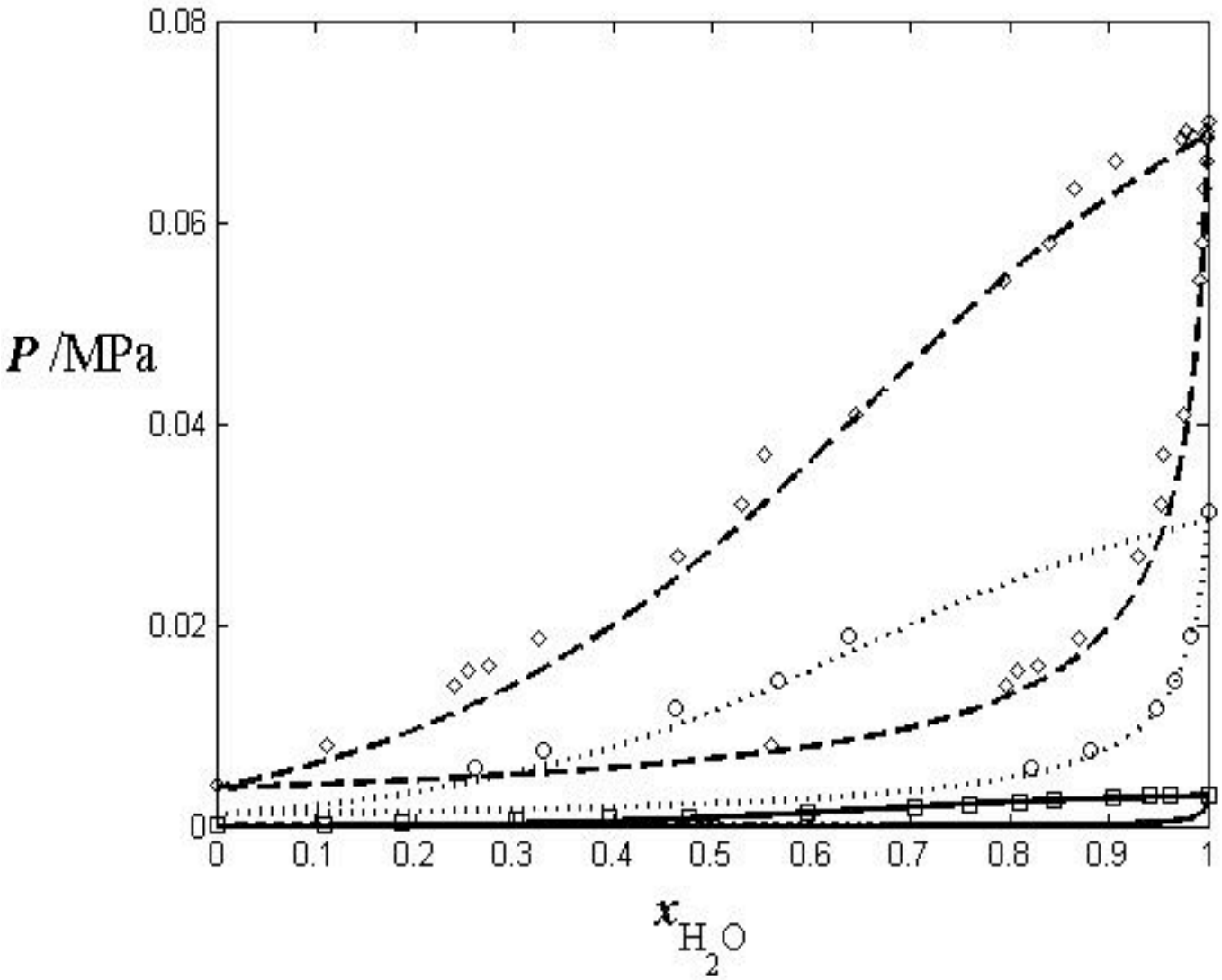
MEA Coexistence Density



MEA + H_2O binary mixture

- Complex cross-associating mixture
- Asymmetric MEA model leads to many unlike-interaction parameters
  - $-NH_2 - H_2O$ interaction: $\varepsilon_1^{HB}{}_{ij}$
  - $-OH - H_2O$ interaction: $\varepsilon_2^{HB}{}_{ij}$
  - MEA – H_2O dispersion interaction: ε_{ij}
- Many adjustable parameters: reduce dimensionality of problem by building on physical knowledge of system
- Distinct types of association interaction
  - $-NH_2 - H_2O$
  - $-OH - H_2O$
- Hypothesis: MEA behaves like EtOH interacting with $EtNH_2$
  - **Transfer unlike-association parameters** from
    - EtOH + H2O
    - $EtNH_2$ + H2O
- **Reduces number of adjustable parameters** to <u>one</u>: ε_{ij}
  - Unlike dispersion energy

MEA + H_2O Isothermal calculations



- ◊: 363.15K
- ○: 343.15K
- □: 298.15K
- %AAD P = 2.03%
- AAD y_{H2O} = 0.027

H_2O+CO_2 binary mixture

- SAFT-VR parameters transferred from the work of Clark *et al.* (2006) and Galindo *et al.* (2002) for H_2O and CO_2 respectively
- H_2O
  - Associating fluid, spherical, 6 parameters required
- CO_2
  - Non-associating fluid, non-spherical, 4 parameters required
- H_2O+CO_2
  - Extensive liquid-liquid immiscibility
  - Type III phase behaviour (Scott and van Konynenburg)

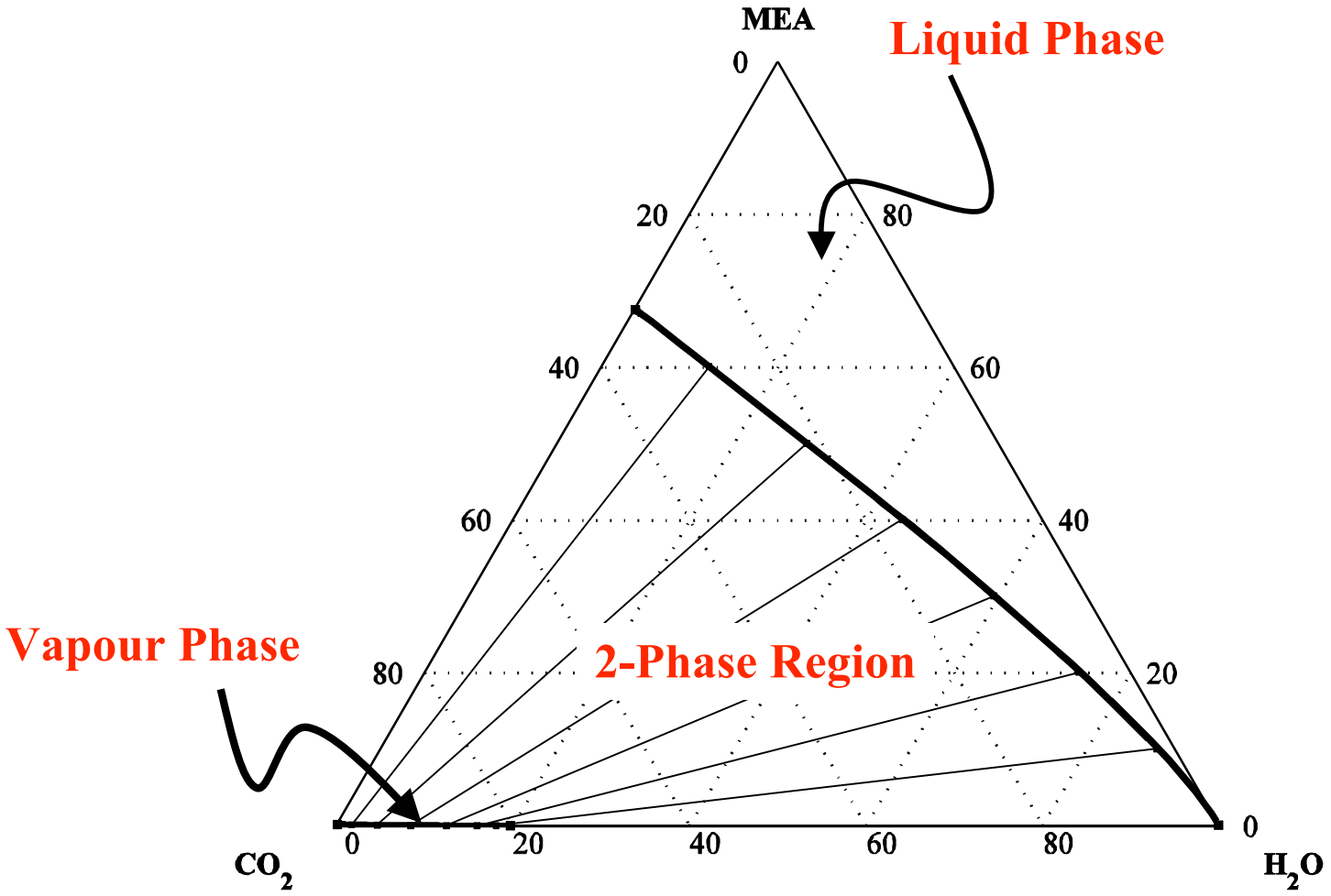
$MEA+CO_2$ binary mixture

- Reactive system-chemical interactions as opposed to polar interaction

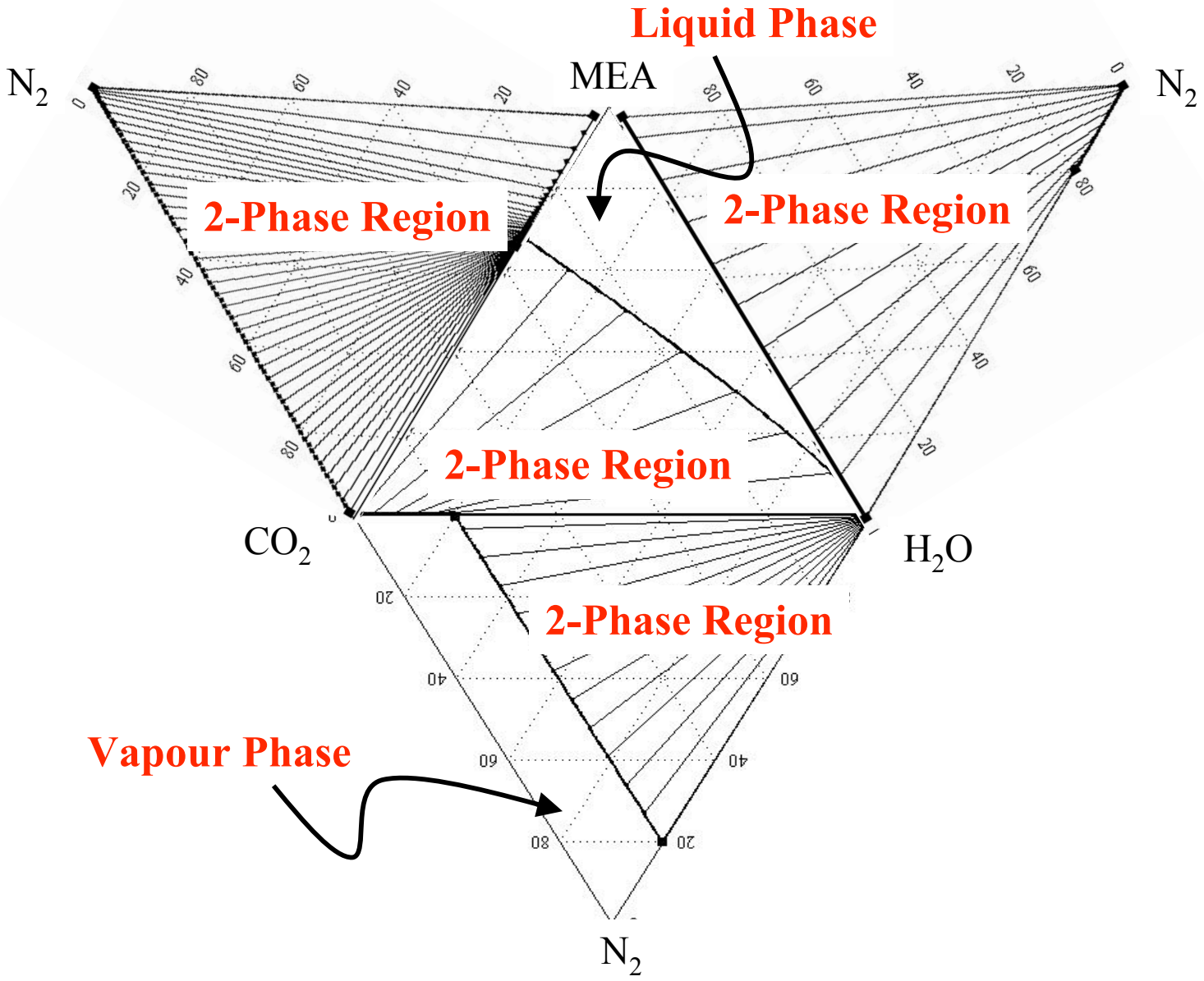
$$CO_2 + 2R_2HN \leftrightharpoons R_2HNH^+ + R_2NCOO^-$$

- Model CO_2 with 2 effective sites to mediate this reaction (effectively assuming tight ion-pair species)
- No data available for this system
  - Transfer parameters from previous work on NH_3+CO_2
- Novel application of the SAFT-VR formalism

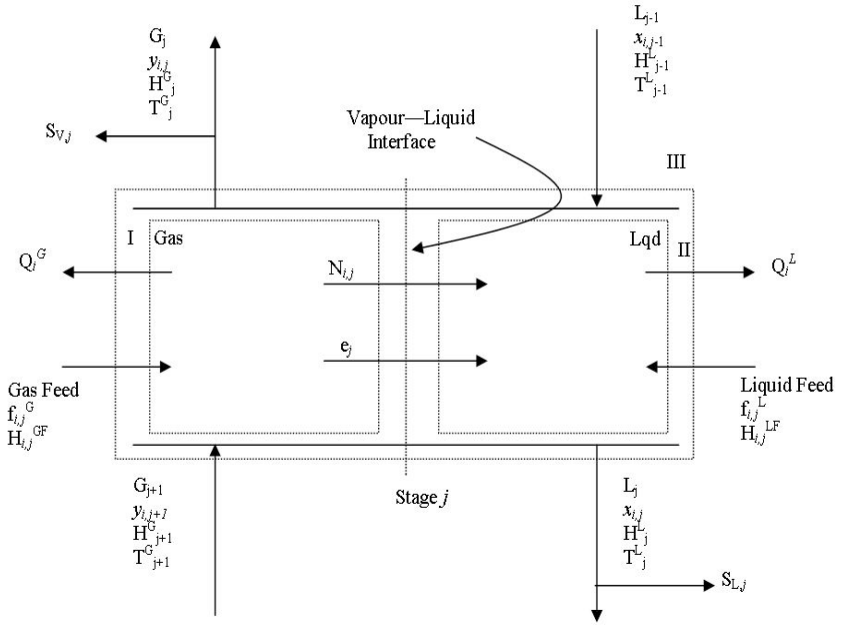
MEA+ H_2O + CO_2 T = 333.15K, P = 0.1 MPa



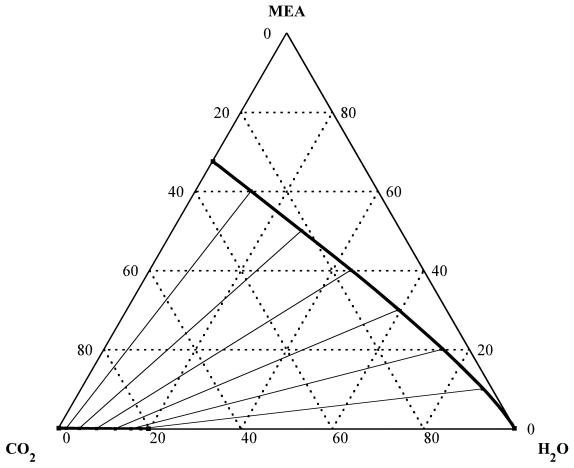
MEA + H_2O + CO_2 + N_2 T = 333.15K, P = 0.1 MPa



Process simulation



- Development of generic simulation tools for process and solvent optimisation
  - Rate-based non-equilibrium models
  - Sophisticated thermodynamics
  - gPROMS
  - ➢ Study transient behaviour scenarios
  - ➢ Understand the contribution of advanced thermodynamics to process simulation



Conclusions

- An **advanced molecular equation-of-state** approach is necessary for dealing with complex fluid systems
- **Molecular models** with **transferable parameters** have been developed
- Mediate **chemical reactions** via **effective sites**
- Allows **accurate description** of **VLE** and **LLE**
- **Phase behaviour** calculated for both **3** and **4 component systems –** realistic flue gas model
- The **predictive** abilities of SAFT-VR provide an excellent tool for investigating the phase behaviour of complex systems with confidence
- **VLE** is a fundamental assumption in **all** mass transfer models
- **Accurate** calculation of phase behaviour is vital in mass-transfer controlled processes
  - Chemisorption with rapid chemical reaction (Ha $\geq$ 3)

Thank you