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Evaluation of the SPUNG Equation of State for use in Carbon Capture and Storage Modelling

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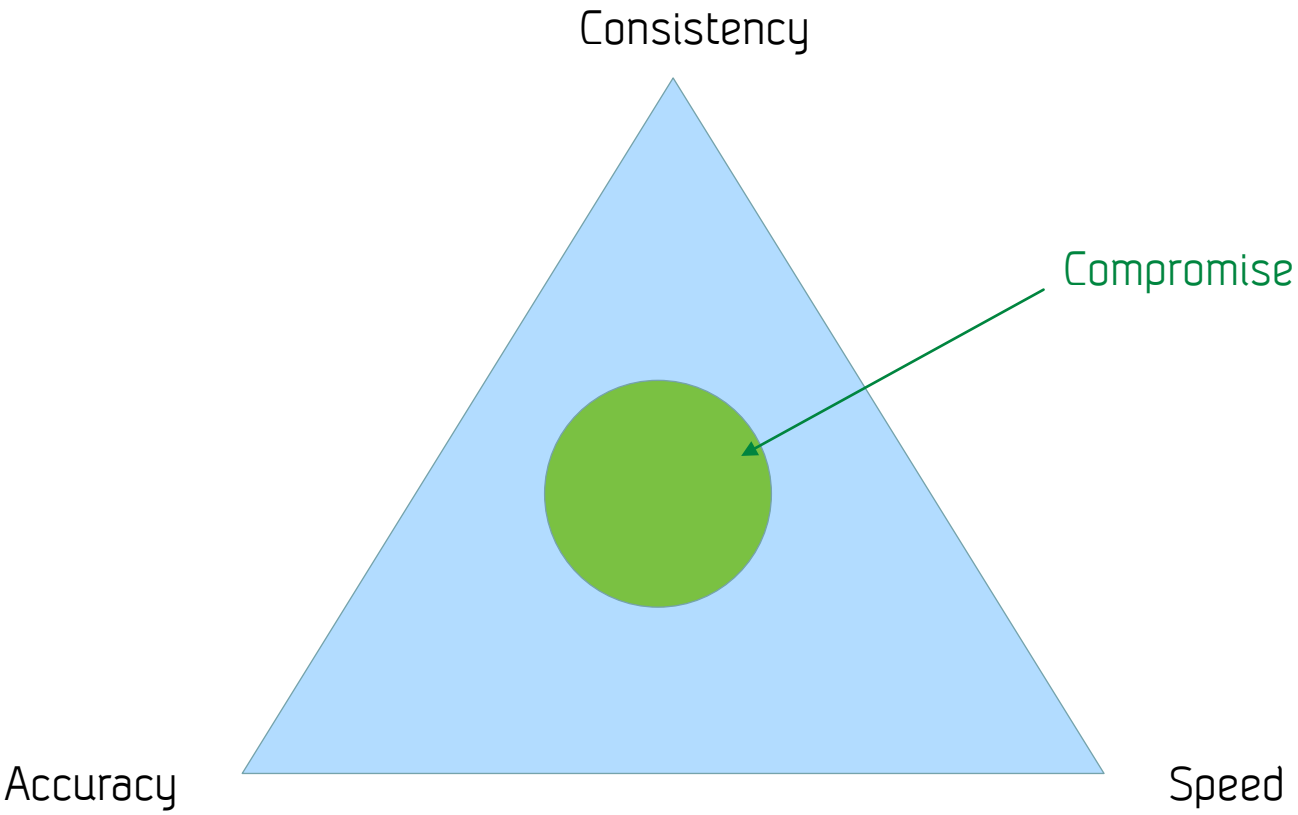
Outline of presentation

- Intro – thermodynamic modeling
- Introduction and some theory on the Corresponding State Principle
- The use and performance of the SPUNG equation of state for CO_2 and CO_2-mixtures
- Summary

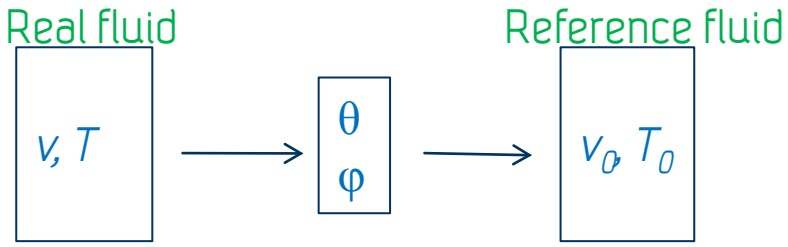
Thermodynamic modeling



Corresponding state principle

- Two fluids are in a corresponding state when the residual reduced Helmholtz Free Energy is equal for both fluids:
  - Reference fluid
  - Reference equation for state (T_0, v_0)
  - Scaling functions θ and φ - (shape factors)

Important that the reference equation covers a wide range – and that the triple point is above the triple point of any mixtures



  - Mixing rules

Corresponding state principle – Scaling functions

Scaling function $\varphi(v,T)$ and $\theta(v,T)$ used to calculated scaling factors f_{ii} and h_{ii}

$$f_{ii} = T/T_0 = f_{ii}^{c}\ \theta(v,T)$$
$$h_{ii} = v/v_0 = h_{ii}^{c}\ \varphi(v,T)$$

- Constant scaling functions

  Equal reduced specific volume and temperature $v_{ri} = v_{r0}$ and $T_{ri} = T_{r0}$

- Temperature dependent scaling functions

  $P(v,T) = f_{ii}/h_{ii}\ P_0(v_0,T_0) \quad => \quad Z(p,T) = Z_0(p_0,T_0)$ *<= SPUNG approach*

- Temperature and density dependent

$$Z = Z_0 - \frac{U_0}{RT_0}\left(\frac{\partial \ln f_{ii}}{\partial \ln v}\right)_T - (Z_0 - 1)\left(\frac{\partial \ln h_{ii}}{\partial \ln v}\right)_T$$

Scaling factors from 2 parameter equation of state for mixtures

- Based of equal reduced Helmholtz Free Energy

- Temperature dependent mixture scaling factors (a_{ij} and b_i from EoS)

$$h = \frac{b_{\text{mix}}}{b_0}$$

$$fh = \frac{a_{\text{mix}}(T)}{a_0(T_0)}$$

$$a_{\text{mix}} = \sum_i \sum_j n_i \cdot n_j \cdot a_{ij}$$

$$a_{ij} = a_{ji} = \sqrt{a_i \cdot a_j}\,(1 - k_{ij})$$

$$b_{\text{mix}} = \sum_i n_i b_i$$

One adjustable parameter

- SPUNG approach:
  - Uses Cubic Equation of state for mixture and for the reference fluid to calculate the *h* and *f* factors . "Classic" mixing rules are used for the mixture.
  - Uses a 32-term MBWR EoS for calculation of properties for the reference fluid
  - Default reference fluid is Propane

Performance of the SPUNG EoS for CO_2 mixtures in terms of accuracy and calculation speed

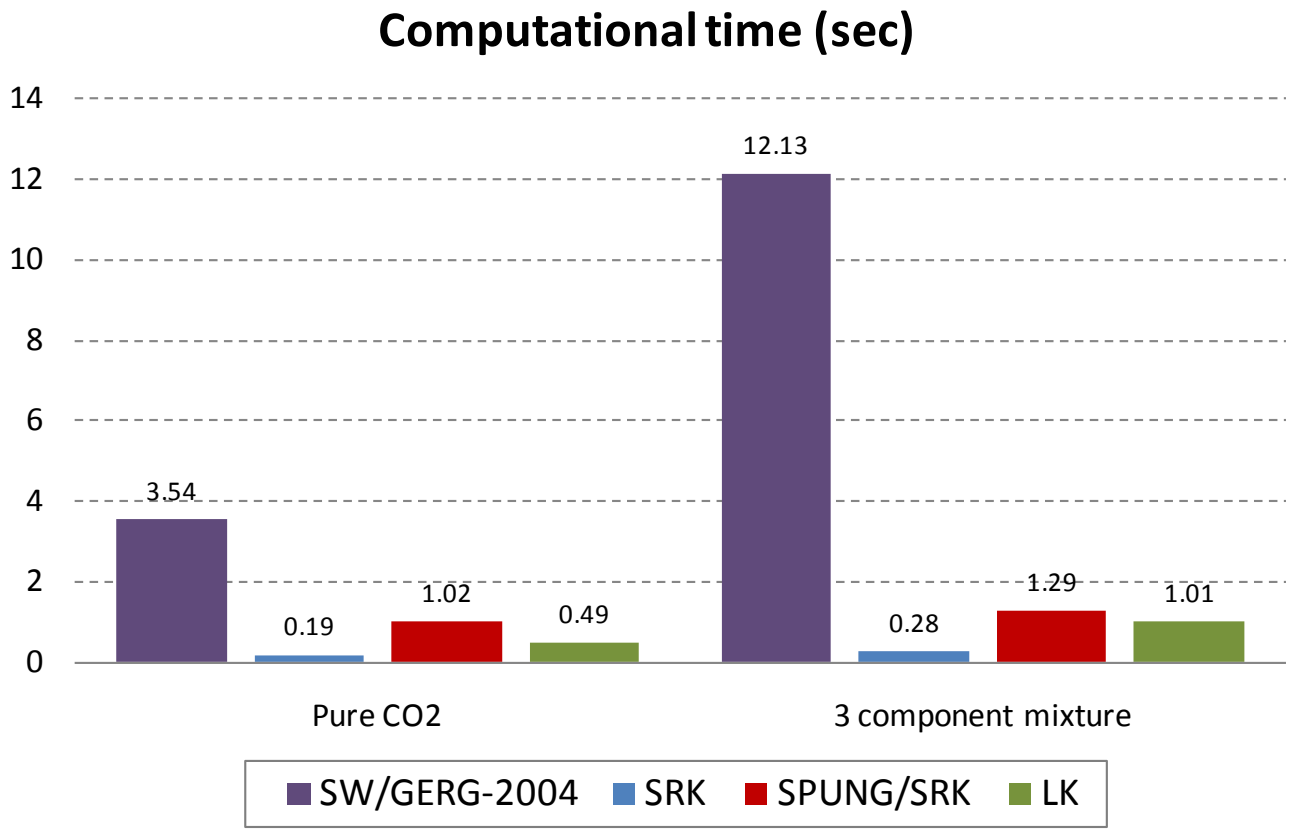
- For pure CO_2
  - Comparison with the Span-Wagner equation of state
  - Density, specific heat capacity and speed of sound compared
  - SRK, Lee-Kesler (LK), GERG-2004 and SPUNG corresponding state methods

- CO_2 mixtures
  - Densities and liquid (x) / vapor (y) equilibrium from literature data
  - Comparison between
    - SRK,
    - SPUNG (Propane, 32-term MBWR)
    - Lee-Kesler (Densities)
    - GERG-2004/08 (NIST implementation)

Results

- The full results shown as graphs and tables in the TCCS oral presentation will be published in full in Energy Procedia

Time comparisons - 10000 random T,P in supercritical-, vapour- and liquid region



Summary and conclusions

- An initial evaluation of the SPUNG extended corresponding state methodology for CO_2 and CO_2 -mixtures shows:
  - Increased accuracy possible for density compared to cubic and LK EOS – especially in the liquid and critical region
  - Fully consistent thermodynamic relations
  - Calculation time acceptable
  - Only one parameter to fit when new experimental VLE data is available
- Further work … evaluate:
  - Choice of reference equation
  - Choice of reference fluid
  - Choice of mixing rules

Thank you for your attention

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