Modeling solid – fluid equilibria with application to CO_2 mixtures

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Objectives

- Objectives
  - Pure CO_2 and multicomponent CO_2 mixtures thermodynamic modeling.
  - Multiphase equilibrium calculations with explicit account of solid phases.
  - Coupling of different solid models with various fluid EoS.
  - Development of efficient algorithms capable of handling multiple phases.

Equations of State for Fluids

- Soave – Redlich – Kwong (SRK) EoS:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)}$$

- Peng – Robinson (PR) EoS:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)}$$

- PC-SAFT EoS:

$$\frac{A^{res}(T,\rho)}{NRT} = \frac{a^{hs}(T,\rho)}{RT} + \frac{a^{disp}(T,\rho)}{RT} + \frac{a^{chain}(T,\rho)}{RT} + \frac{a^{assoc}(T,\rho)}{RT}$$

Extension to mixtures

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij}$$

$$b = \sum_{i=1}^{n} x_i b_i$$

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

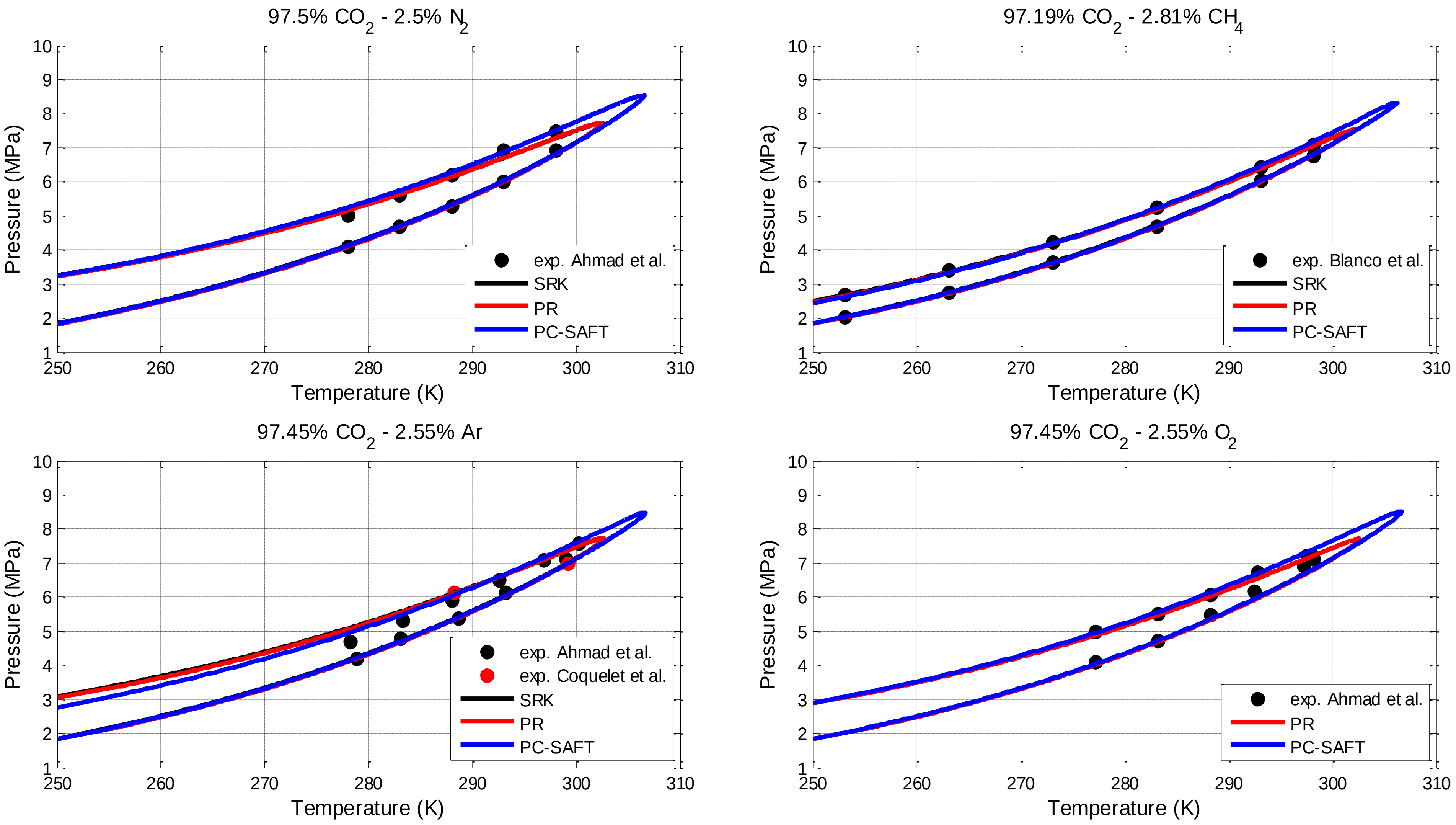
$$\bar{m} = \sum_i x_i m_i$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}(1 - k_{ij})$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

$$\overline{m^2 \varepsilon \sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \left[\frac{\varepsilon_{ij}}{kT}\right] \sigma_{ij}^3$$

Vapor – liquid phase equilibria (kij ≠ 0)



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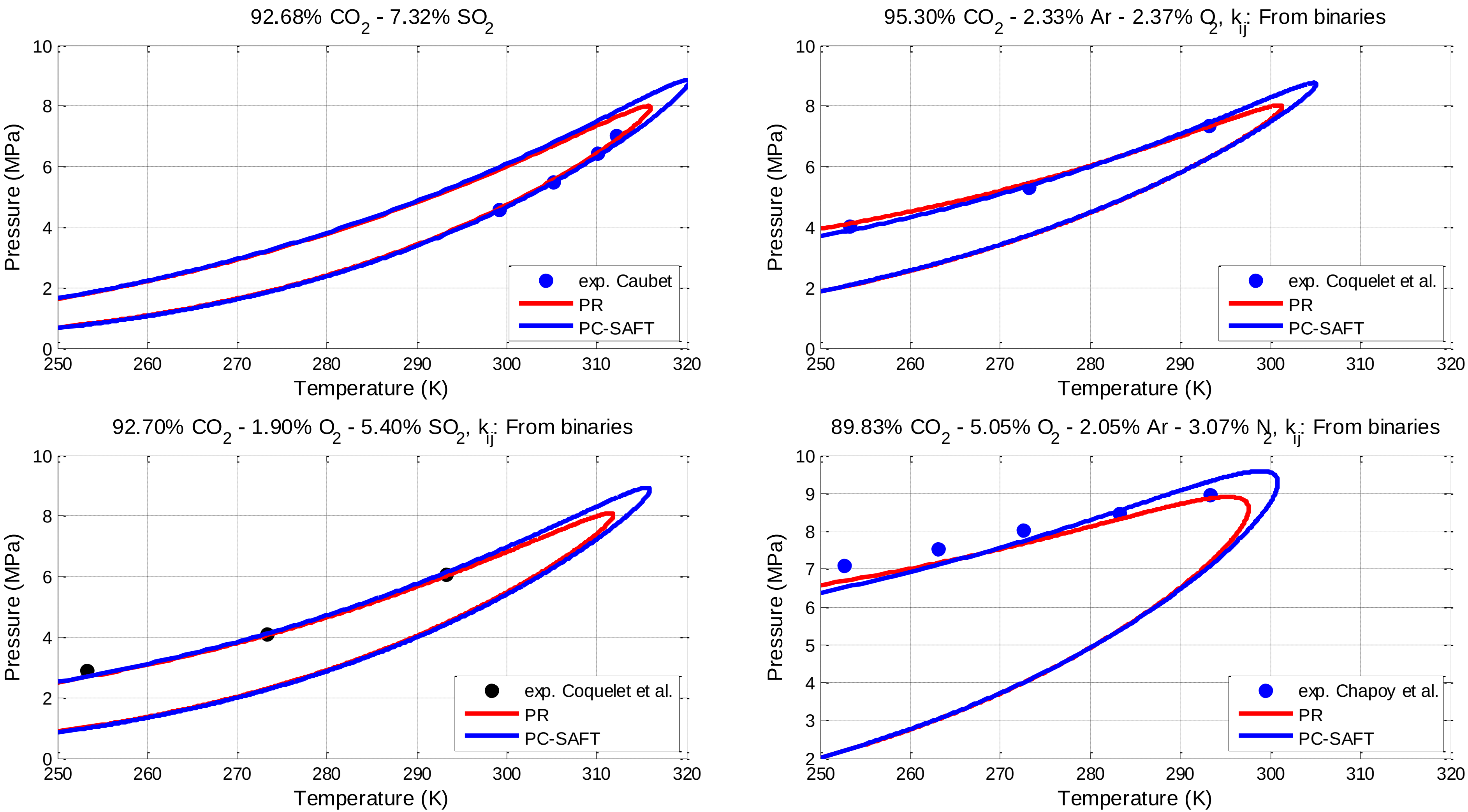


Motivation for developing solid models

- Hazard assessment studies associated with CO_2 transport include scenarios of accidental release through pipeline ruptures.
- Pipeline depressurization results in rapid cooling and subsequent solid – gas discharge.
- CFD modeling of the rapid expansion process and near field dispersion needs to take into account the solidification phenomena.

Woolley et al., *Int. J. Greenhouse Gas Control*, 2014;27:221-238.

Correlation model for mixtures

- Solid – fluid equilibrium → Equation of chemical potentials at the same temperature and pressure.
- The ideal gas reference state is used for both phases:

$$\mu_i^S(T,P) = \mu_i^F\left(T,P,\mathbf{x}^F\right)$$

$$\hat{f}_i^S(T,P) = \hat{f}_i^F\left(T,P,\mathbf{x}^F\right)$$

$$P_{0i}^{sat}(T)\hat{\varphi}_{0i}^{sat}\left(T,P_{0i}^{sat}\right)\exp\left[\frac{v_{0i}^S}{RT}\left(P - P_{0i}^{sat}(T)\right)\right] = x_i^F\hat{\varphi}_i^F\left(T,P,\mathbf{x}^F\right)P$$

- Solution at constant temperature and pressure:

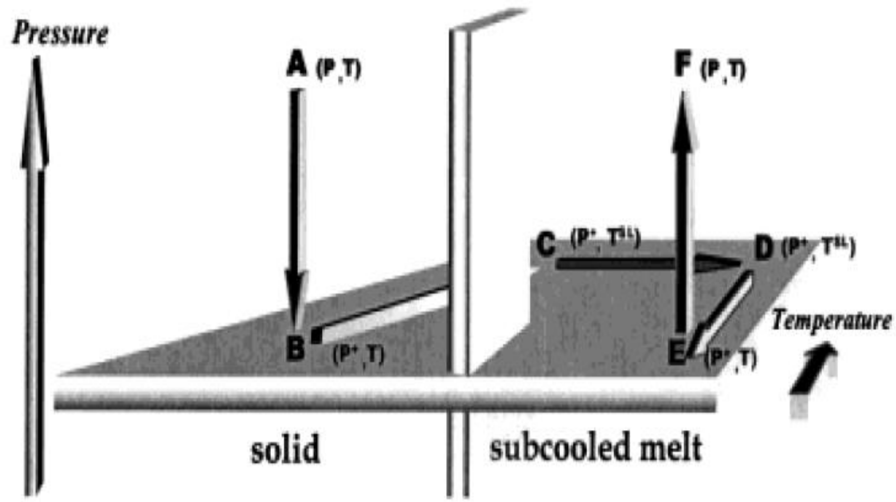
$$x_i^{F(k+1)} = \frac{\hat{\varphi}_{i0}^{sat}\left(T,P_{0i}^{sat}\right)P_{0i}^{sat}(T)}{P\hat{\varphi}_i^F\left(T,P,\mathbf{x}^{F(k)}\right)}\exp\left[\frac{v_{0i}^S}{RT}\left(P - P_{0i}^{sat}(T)\right)\right]$$

Thermodynamic Integration model for mixtures

$$\mu_i^S(T,P) = \mu_i^F(T,P,\mathbf{x}^F)$$

$$\mu_i^S(T,P) = \mu_{0i}^S(T,P) + RT\ln\frac{x_i^S\varphi_i^S(T,P,\mathbf{x}^S)P}{\varphi_{0i}^S(T,P)P}$$

$$\mu_i^F(T,P,\mathbf{x}^F) = \mu_{0i}^{F^*}(T,P) + RT\ln\frac{x_i^F\varphi_i^F(T,P,\mathbf{x}^F)P}{\varphi_{0i}^{F^*}(T,P)P}$$



$$x_i^F = \frac{x_i^S\varphi_i^S}{\varphi_{0i}^S}\cdot\frac{\varphi_{0i}^{F^*}}{\varphi_i^F}\cdot\exp\left[-\frac{1}{RT}\left(\mu_{0i}^{F^*}(T,P) - \mu_{0i}^S(T,P)\right)\right]$$

$$x_i^L = \frac{\varphi_{0i}^{L^*}}{\varphi_i^L}\cdot\exp\left[-\frac{(v_{0i}^S - v_{0i}^{L^*})(P^+ - P)}{RT} - \frac{\Delta h_{0i}^{SL}}{RT}\left(1 - \frac{T}{T_{0i}^{SL}}\right) + \frac{\Delta c_{P,0i}^{SL^*}}{RT}(T_{0i}^{SL} - T) - \frac{\Delta c_{P,0i}^{SL^*}}{R}\ln\frac{T_{0i}^{SL}}{T}\right]$$

Seiler et al., *Chemical Engineering & Technology*. 2001;24:607-612.

Jager and Span solid EoS for pure CO_2

- Empirical Gibbs free energy equation:

$$\frac{g}{RT_0} = g_0 + g_1\Delta\vartheta + g_2\Delta\vartheta^2 + g_3\left\{\ln\left(\frac{\vartheta^2 + g_4^2}{1 + g_4^2}\right) - \frac{2\vartheta}{g_4}\left[\arctan\left(\frac{\vartheta}{g_4}\right) - \arctan\left(\frac{1}{g_4}\right)\right]\right\}$$
$$+ g_5\left\{\ln\left(\frac{\vartheta^2 + g_6^2}{1 + g_6^2}\right) - \frac{2\vartheta}{g_6}\left[\arctan\left(\frac{\vartheta}{g_6}\right) - \arctan\left(\frac{1}{g_6}\right)\right]\right\}$$
$$+ g_7\Delta\pi\left[e^{f_\alpha(\vartheta)} + K(\vartheta)g_8\right] + g_9K(\vartheta)\left[(\pi + g_{10})^{(n-1)/n} - (1 + g_{10})^{(n-1)/n}\right]$$

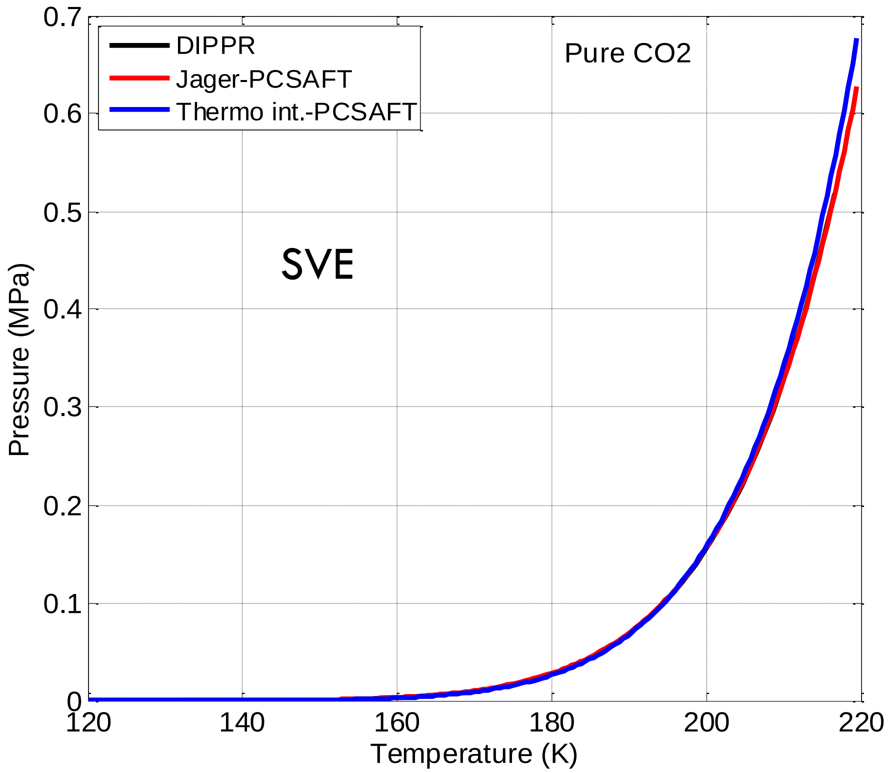
- Parameters g_0 and g_1 are adjusted for every fluid EoS used:

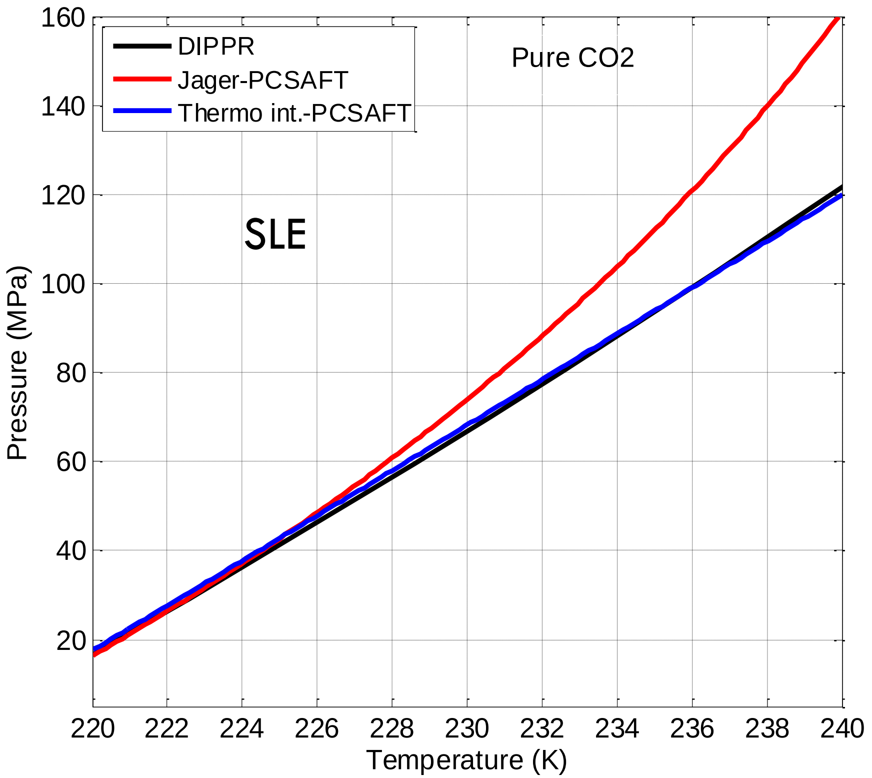
$$\Delta h^{melt} = h^{sol}(T_{tr}, P_{tr}) - h^{liq}(T_{tr}, P_{tr}) \quad s^{sol}(T_{tr}, P_{tr}) = s^{liq}(T_{tr}, P_{tr}) - \frac{\Delta h^{melt}}{T_{tr}}$$

- Calculation of saturation pressure is done with the Clausius – Clapeyron equation: $\left.\frac{dP}{dT}\right|_{equil} = \frac{\Delta H}{T\Delta V}$

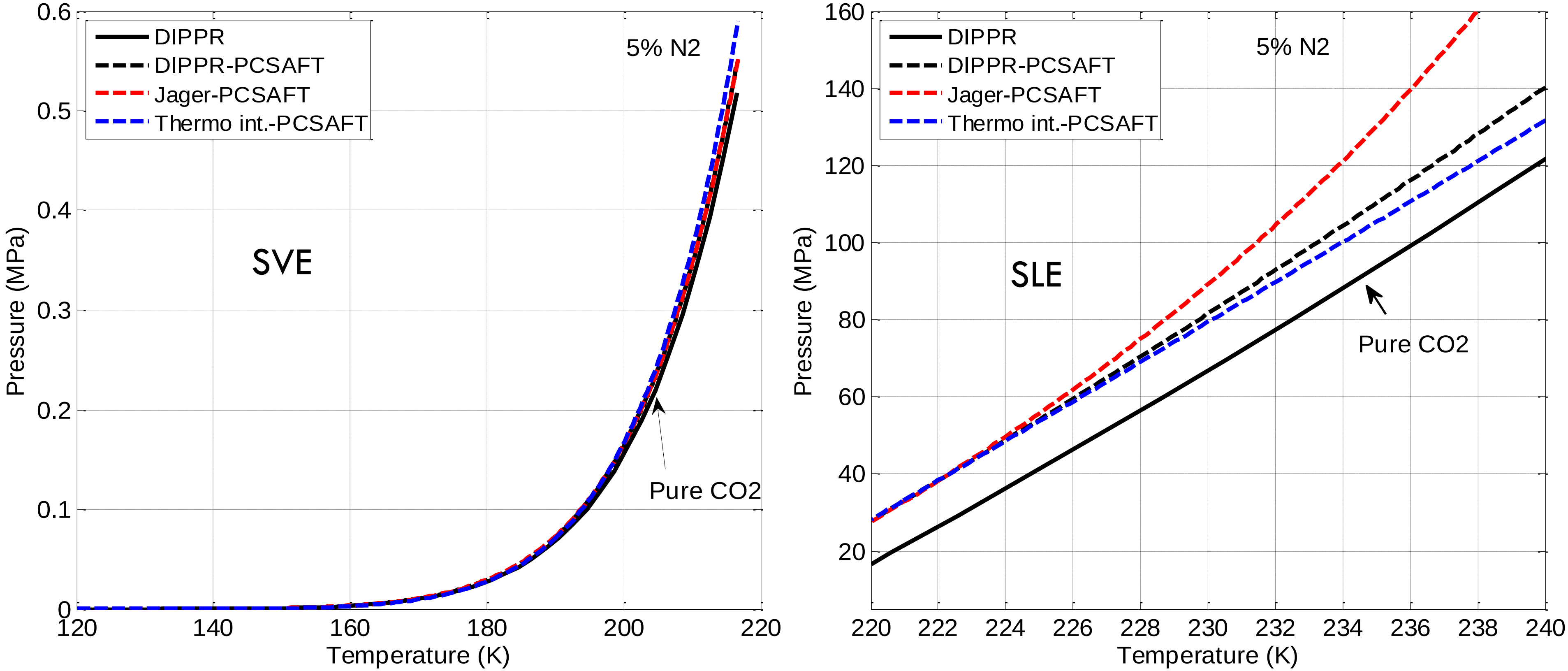
Jäger and Span, *J. Chem. Eng. Data*, 2012;57:590-597.

Pure solid CO_2 SVE and SLE

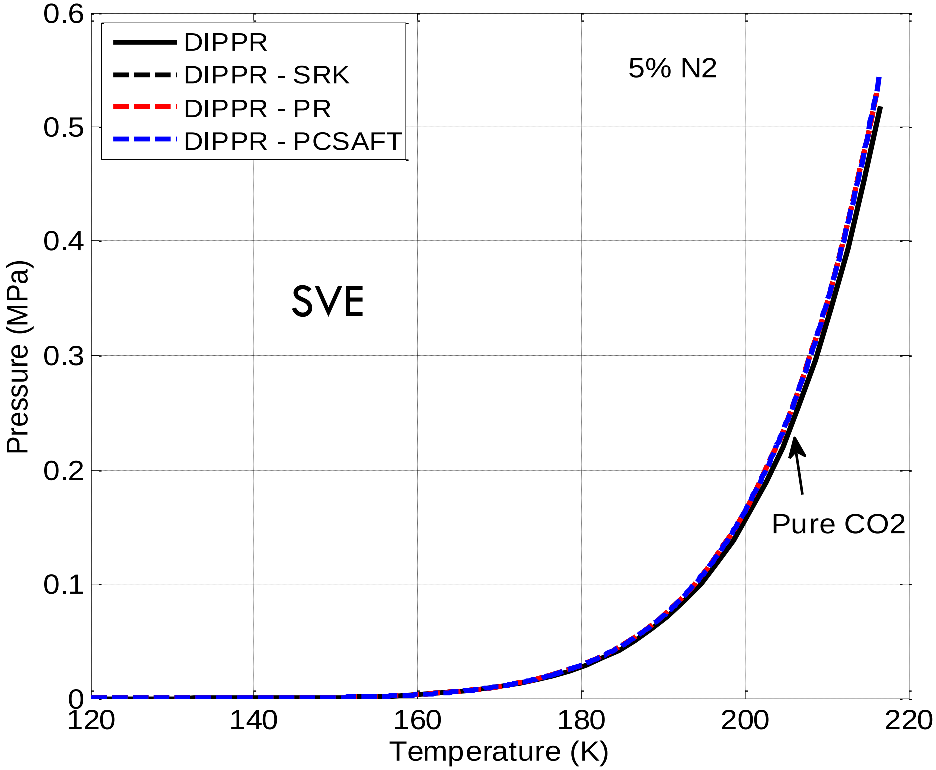


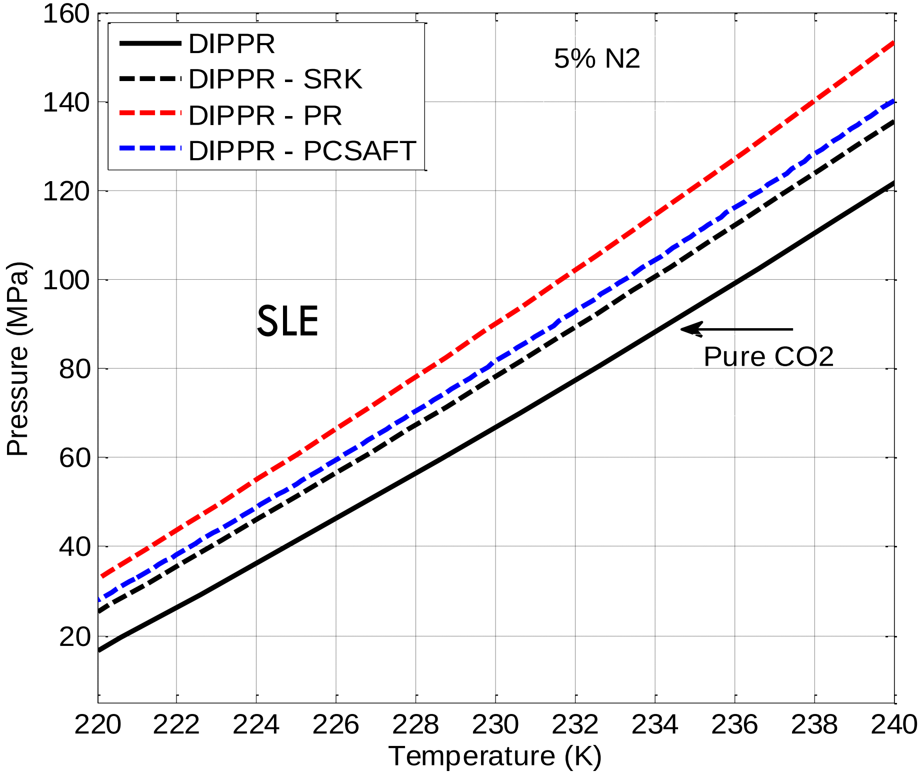


$CO_2 - N_2$ SVE and SLE
Solid model comparison



$CO_2 – N_2$ SVE and SLE Fluid EoS comparison





Solid – Liquid - Gas equilibrium

- Any solid model can be used.
- Basic equation that holds:

$$\mu_i^S(T,P) = \mu_i^l(T,P,\mathbf{x}^l) = \mu_i^v(T,P,\mathbf{y}^v)$$

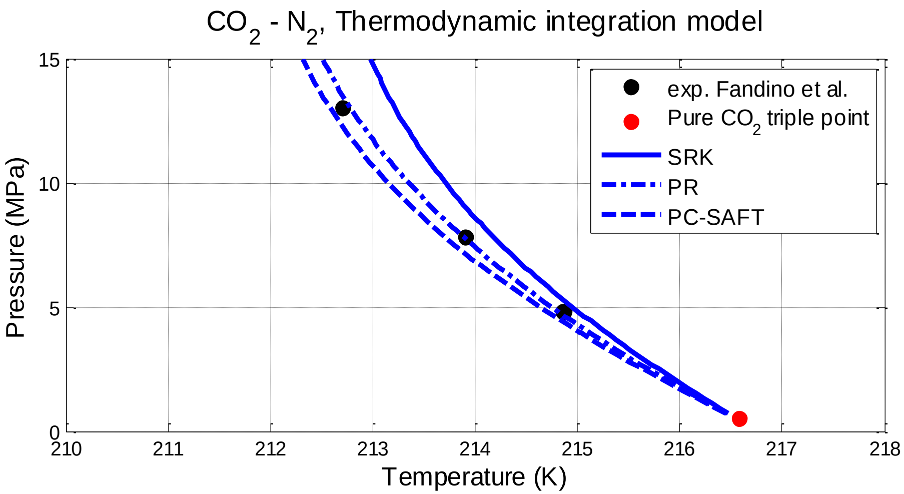
- This leads to satisfaction of two independent equations:

$$\mu_i^l(T,P,\mathbf{x}^l) = \mu_i^v(T,P,\mathbf{y}^v) \quad \text{and} \quad \mu_i^S(T,P) = \mu_i^l(T,P,\mathbf{x}^l)$$

or

$$\mu_i^l(T,P,\mathbf{x}^l) = \mu_i^v(T,P,\mathbf{y}^v) \quad \text{and} \quad \mu_i^S(T,P) = \mu_i^v(T,P,\mathbf{y}^v)$$

$CO_2 - N_2$ SLGE


CO2 - N2, Thermodynamic integration model
Pressure (MPa)
Temperature (K)
0
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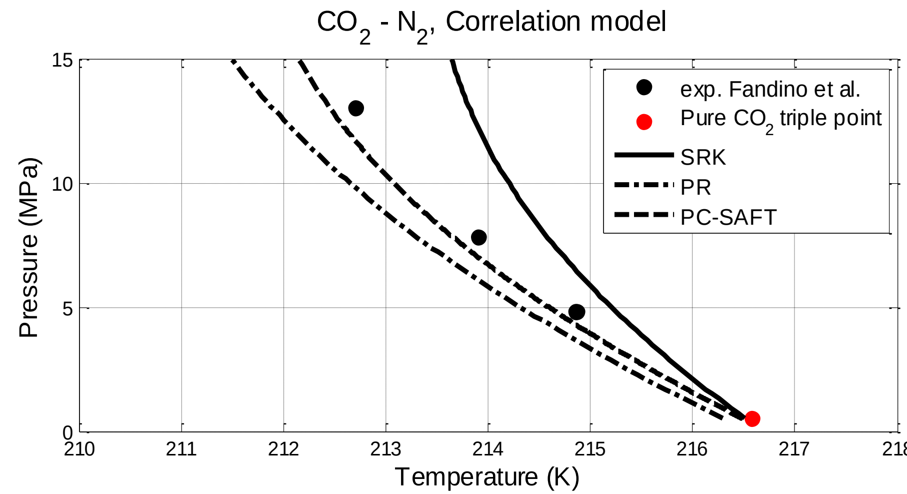
exp. Fandino et al.
Pure CO2 triple point
SRK
PR
PC-SAFT


CO2 - N2, Correlation model
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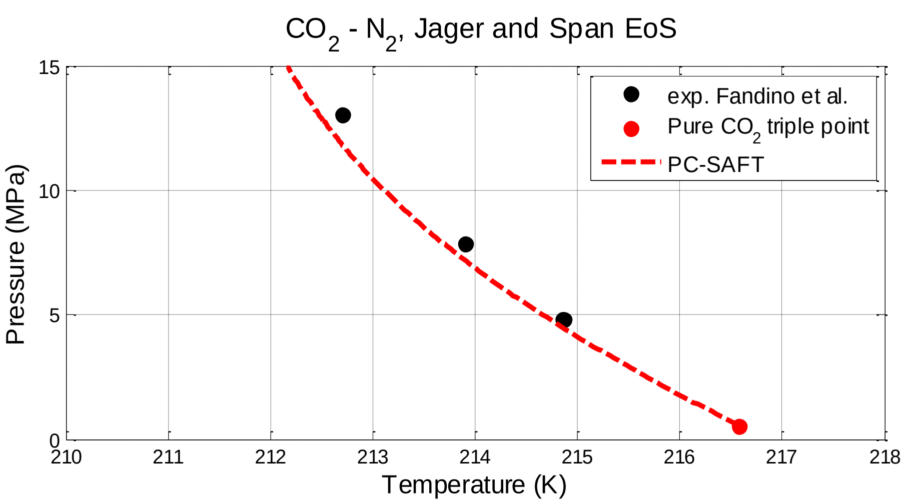
CO2 - N2, Jager and Span EoS
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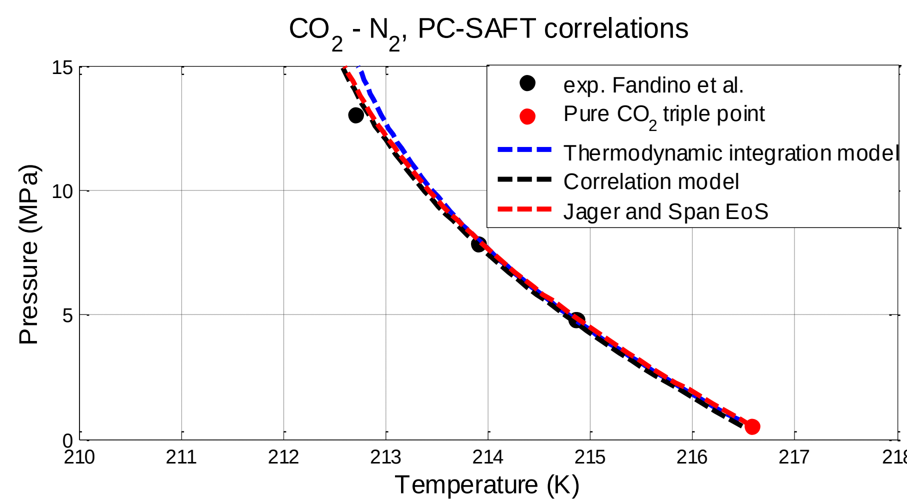
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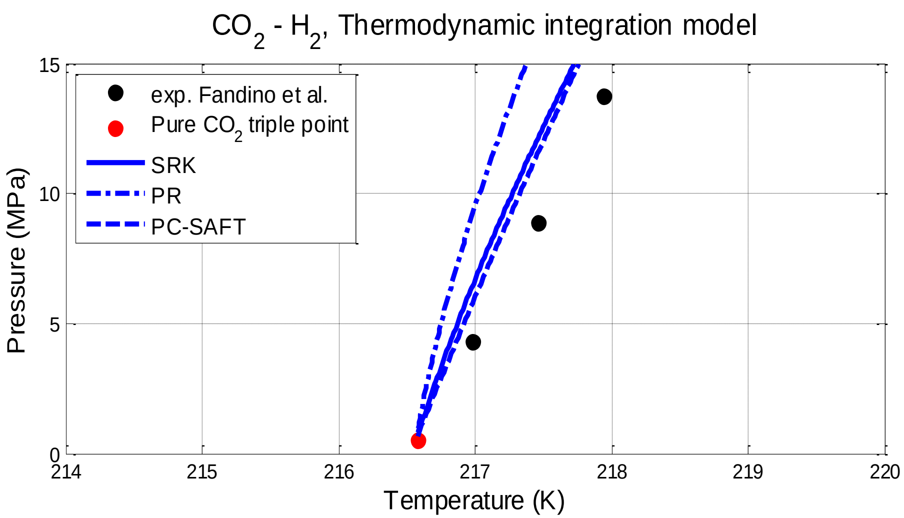
Thermodynamic integration model
Correlation model
Jager and Span EoS

CO_2 – H_2 SLGE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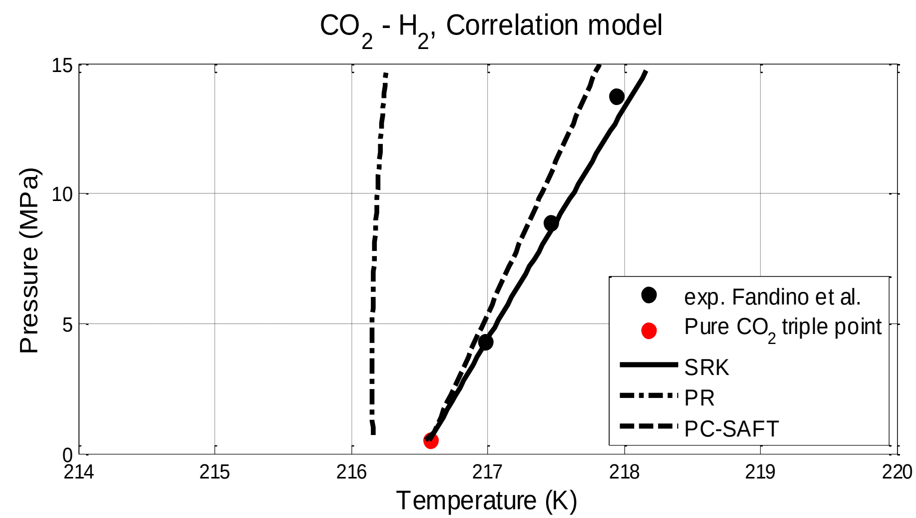
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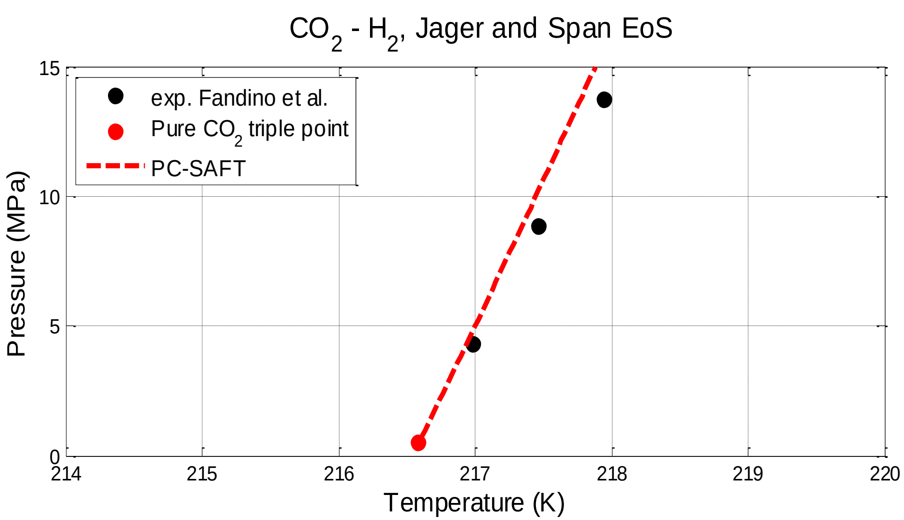
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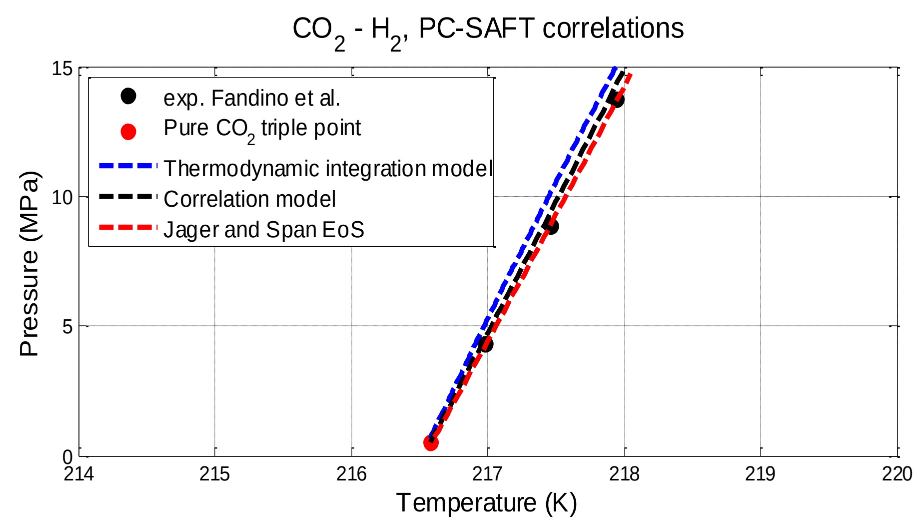
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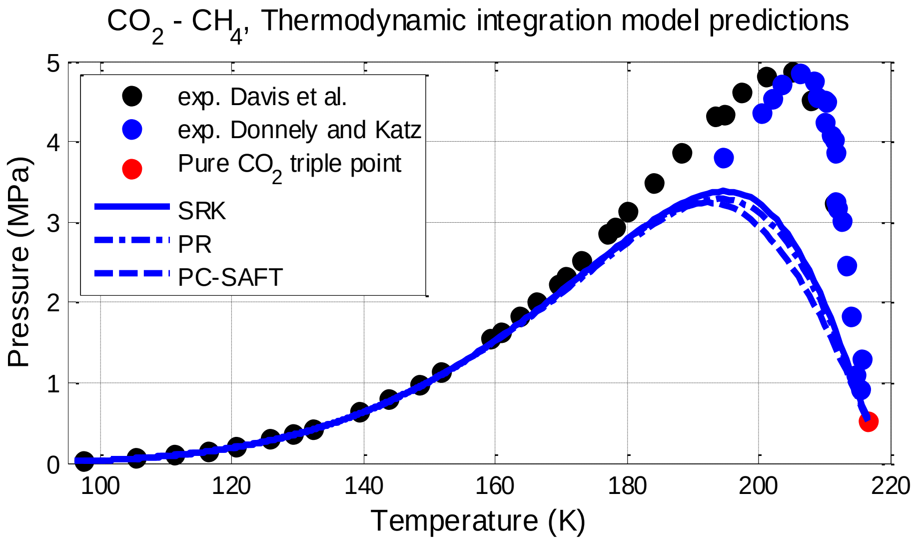
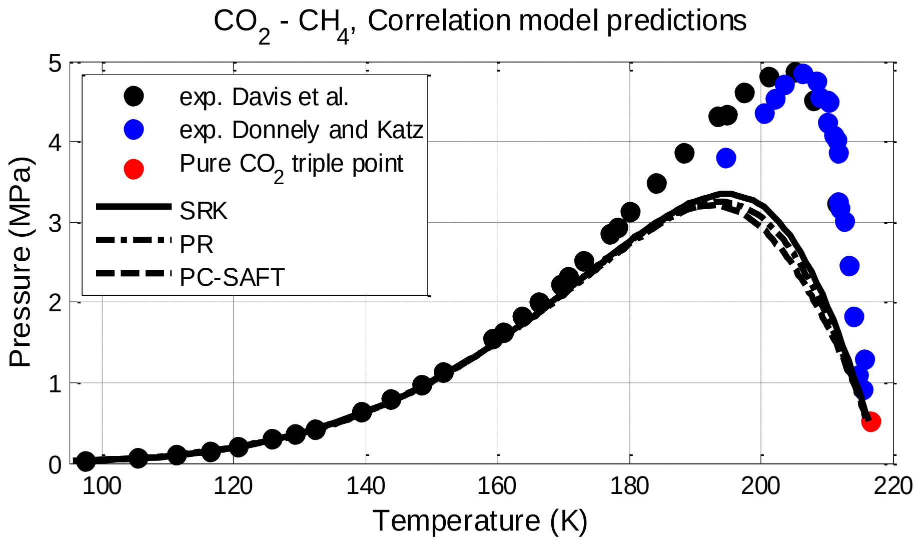
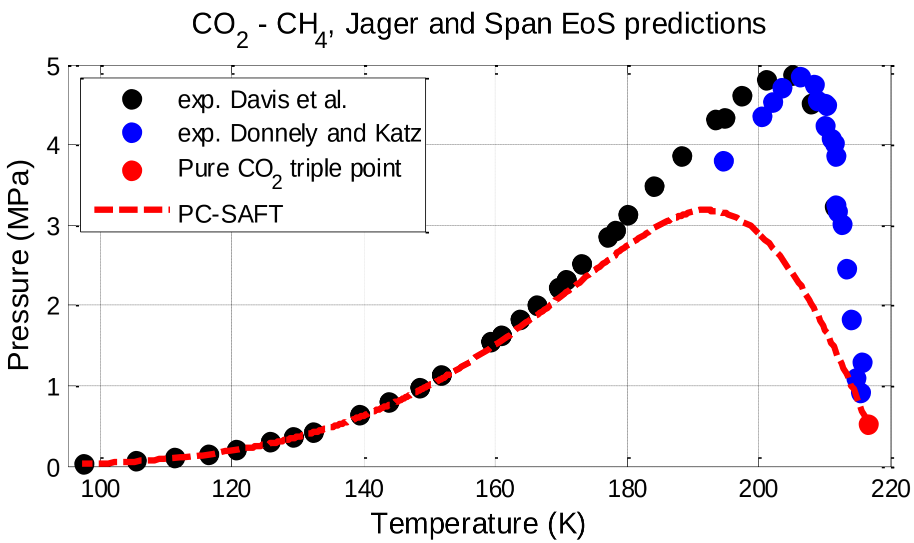
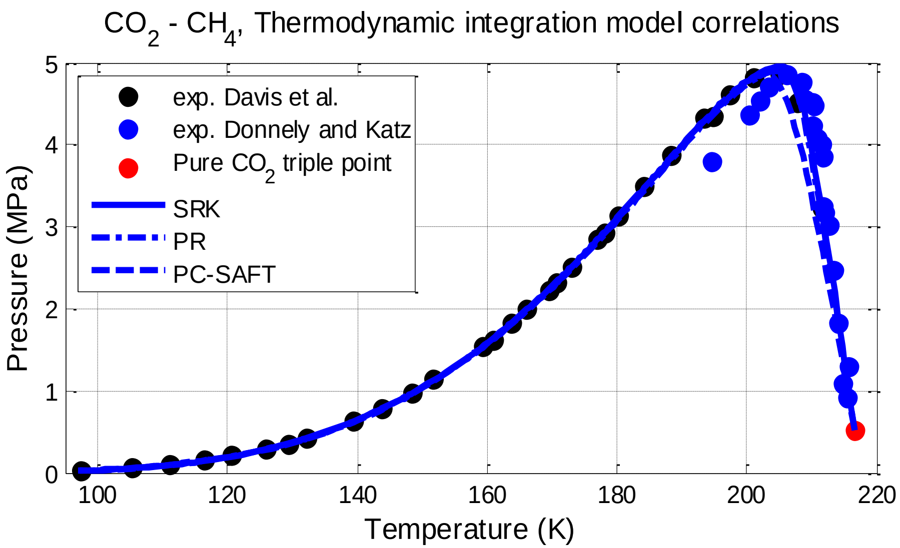
$CO_2 - CH_4$ SLGE (1)

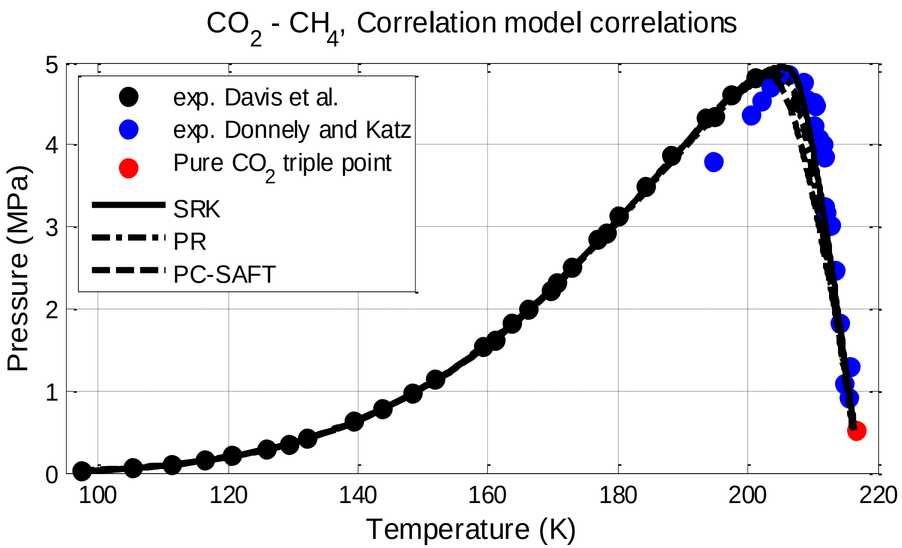


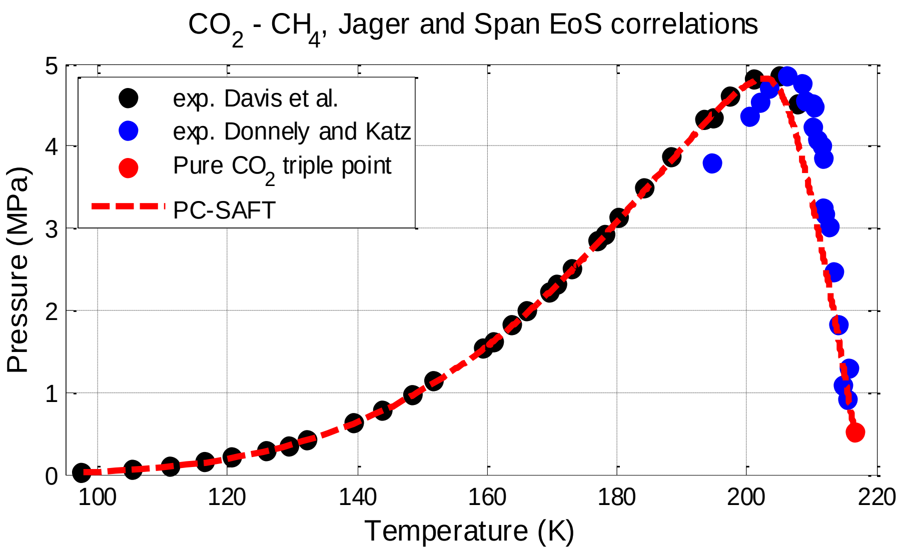




CO_2 – CH_4 SLGE (2)







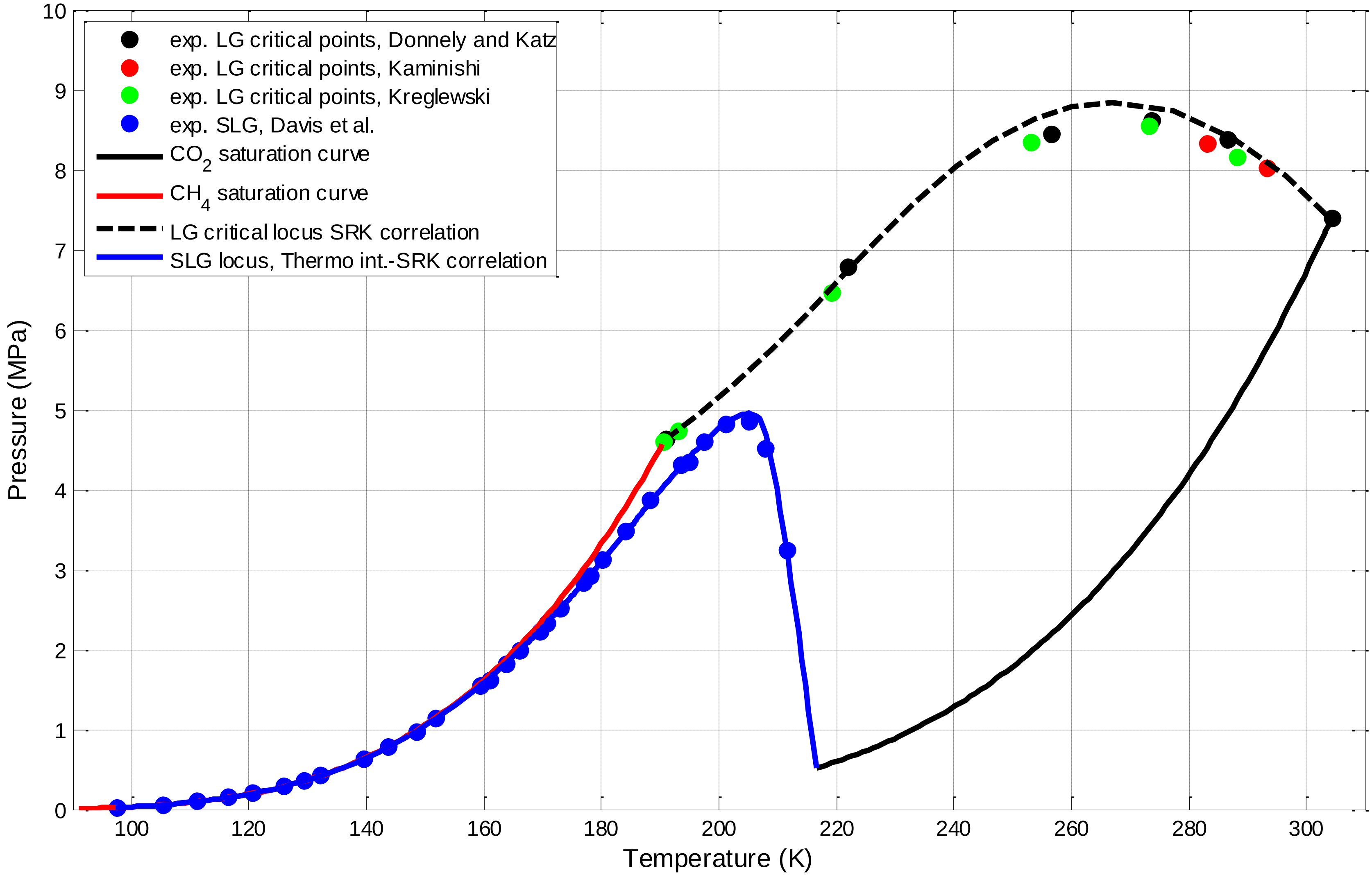
kij values taken from: Diamantonis et al. *Industrial & Engineering Chemistry Research*. 2013;52:3933-3942.

SRK: 0.103
PR: 0.100
PC-SAFT: 0.061

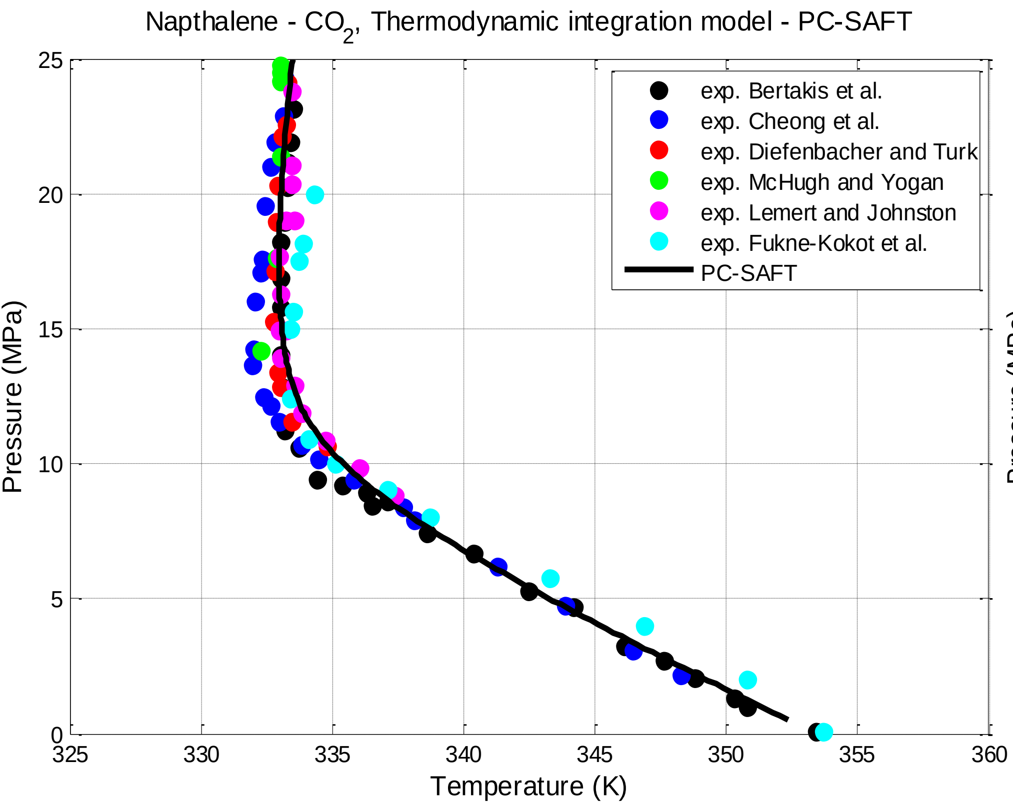
SLGE modeling results

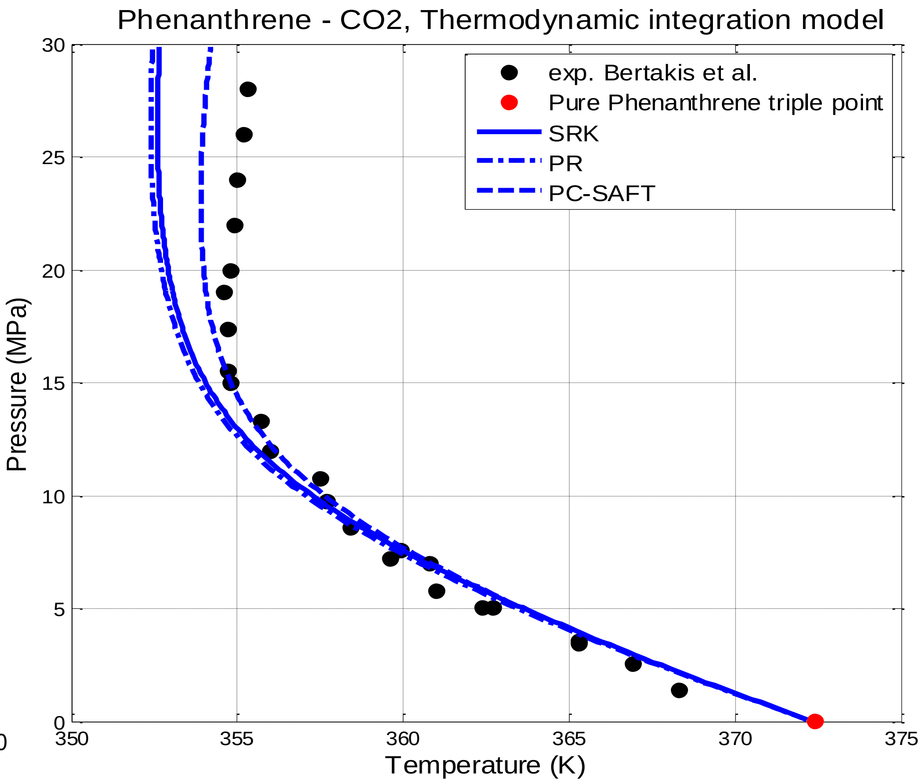
- Excellent agreement between experimental data and modeling results with all models.
- $CO_2 - N_2$ mixture
  - Most accurate predictions: Thermodynamic integration – PR.
  - Most accurate correlations: Jager and Span – PC-SAFT.
- $CO_2 - H_2$ mixture
  - Most accurate predictions: Correlation (DIPPR) – SRK.
  - Most accurate correlations: Jager and Span – PC-SAFT.
- $CO_2 - CH_4$ mixture
  - Most accurate predictions: Thermodynamic integration – SRK.
  - Most accurate correlations: Thermodynamic integration – PR.

CO_2 – CH_4, LG and SLG projections



SLGE of other mixtures





Conclusions

- Solid models of variable complexity have been coupled with different fluid EoS ; Efficient algorithms for multiphase equilibria calculations have been developed.
- Differences between the models are more pronounced in solid – liquid calculations, especially at high pressures.
- The models' accuracy has been validated against SLG experimental data available in the literature for many different mixtures.
- Excellent agreement between experimental data and modeling results for all mixtures.

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Consistency of solid – fluid models