

Introduction

Recent equations of state (EoS) based on statistical thermodynamics, like the SAFT models (Statistical Associating Fluid Theory) [1] are promising for determining thermodynamic properties of associating and polar fluids and for the simulation of processes involving complex fluid mixtures. Some physical properties of fluids change drastically in the vicinity of the mixtures' critical point. For many processes it is therefore important to accurately determine thermodynamic properties close to the critical point. Unfortunately, classical equations of state including the PC-SAFT EoS [2] fail to represent the critical region. The reason is that mean field theory is not adequate at the critical point – rather, a renormalisation theory must be used that accounts for the diverging fluctuations in some parameters at the critical point. White proposed a renormalization procedure based on a perturbation approach using well defined intermolecular potentials [3]. In this poster, we present results obtained for pure compounds and mixtures involving hydrocarbons and alcohols.

Renormalization Approach [4]

RENORMALIZATION SCHEME :

$$f_0 = f^{PCSAFT} = f^{id} + f^{hs} + f^{chain} + f^{disp} + f^{assoc}$$

$$f_n = f_{n-1} + \delta f_n$$

$$f^{total} = f_0 + \sum_{n=1}^{\infty} \delta f_n \simeq f_0 + \sum_{n=1}^5 \delta f_n$$

$$K_n = \frac{k_b T}{(2^n L)^3} \quad \text{WITH: } L^3 = \sum_{i=1}^2 x_i \hat{m}_i L_i^3$$

$$\text{and: } \hat{m}_i = \frac{m_i}{\sum_i x_i m_i}$$

PHASE-SPACE CELL APPROXIMATION :

$$\delta f_n(\rho_1, \rho_2) = -K_n \ln \left(\frac{\int_0^{\min(\rho_2, \rho_2^{\max} - \rho_2)} \int_0^{\min(\rho_1, \rho_1^{\max} - \rho_1)} \exp\left(-\frac{G_n^D}{K_n}\right) d\tau_1 d\tau_2}{\int_0^{\min(\rho_2, \rho_2^{\max} - \rho_2)} \int_0^{\min(\rho_1, \rho_1^{\max} - \rho_1)} \exp\left(-\frac{G_n^0}{K_n}\right) d\tau_1 d\tau_2} \right)$$

$$G_n^0 = \frac{f_{n-1}(\rho_1 + \tau_1, \rho_2 + \tau_2) + f_{n-1}(\rho_1 - \tau_1, \rho_2 - \tau_2) - f_{n-1}(\rho_1, \rho_2)}{2} + \frac{16}{9} \pi \tau^2 \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j m_i m_j \sigma_{ij}^3 \xi_{ij} \frac{\epsilon_{ij}}{kT}$$

$$G_n^D = \frac{f_{n-1}(\rho_1 + \tau_1, \rho_2 + \tau_2) + f_{n-1}(\rho_1 - \tau_1, \rho_2 - \tau_2) - f_{n-1}(\rho_1, \rho_2)}{2} + \frac{16}{7} \pi \tau^2 \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j m_i m_j \sigma_{ij}^5 \xi_{ij} \frac{\epsilon_{ij}}{kT} \frac{\phi_{ij}}{2^{2n+1} L_{ij}^2}$$

ISOMORPHIC APPROXIMATION :

$$\delta f_n(\rho) = -K_n \ln \left(\frac{\int_0^{\min(\rho, \rho^{\max} - \rho)} \exp\left(-\frac{G_n^D}{K_n}\right) d\tau}{\int_0^{\min(\rho, \rho^{\max} - \rho)} \exp\left(-\frac{G_n^0}{K_n}\right) d\tau} \right)$$

$$G_n^0 = \frac{f_{n-1}(\rho + \tau) + f_{n-1}(\rho - \tau) - f_{n-1}(\rho)}{2} + \frac{16}{9} \pi \tau^2 \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j m_i m_j \sigma_{ij}^3 \xi_{ij} \frac{\epsilon_{ij}}{kT}$$

$$G_n^D = \frac{f_{n-1}(\rho + \tau) + f_{n-1}(\rho - \tau) - f_{n-1}(\rho)}{2} + \frac{16}{7} \pi \tau^2 \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j m_i m_j \sigma_{ij}^3 \xi_{ij} \frac{\epsilon_{ij}}{kT} \frac{\bar{w}^2 \bar{\phi}}{2^{2n+1} L^2}$$

WITH: $\rho_i^{\max} = \frac{\sqrt{2}}{m_i d_i^3}$

$\tau = \tau_1 + \tau_2$

$L_{ij} = \sqrt{L_i L_j}$

$\xi_{ij} = \sqrt{\xi_i \xi_j}$

$\phi_{ij} = \frac{1}{2} (\hat{m}_i \phi_i + \hat{m}_j \phi_j)$

WITH: $\bar{\phi} = \sum_{i=1}^2 x_i \hat{m}_i \phi_i$

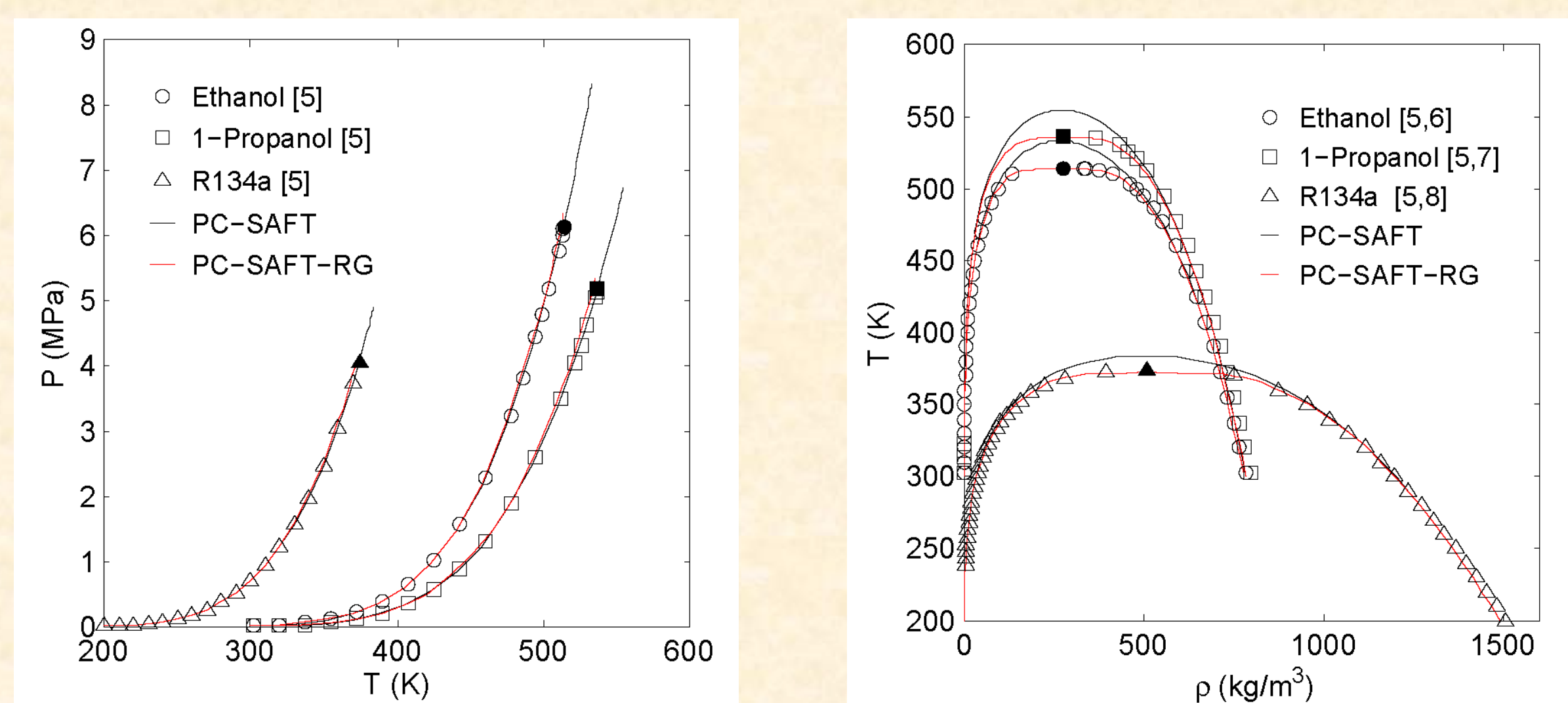
$\bar{w}^2 = \frac{9}{7} \sum_{i=1}^2 x_i \hat{m}_i \sigma_i^2$

$\xi_{ij} = \sqrt{\xi_i \xi_j}$

Results

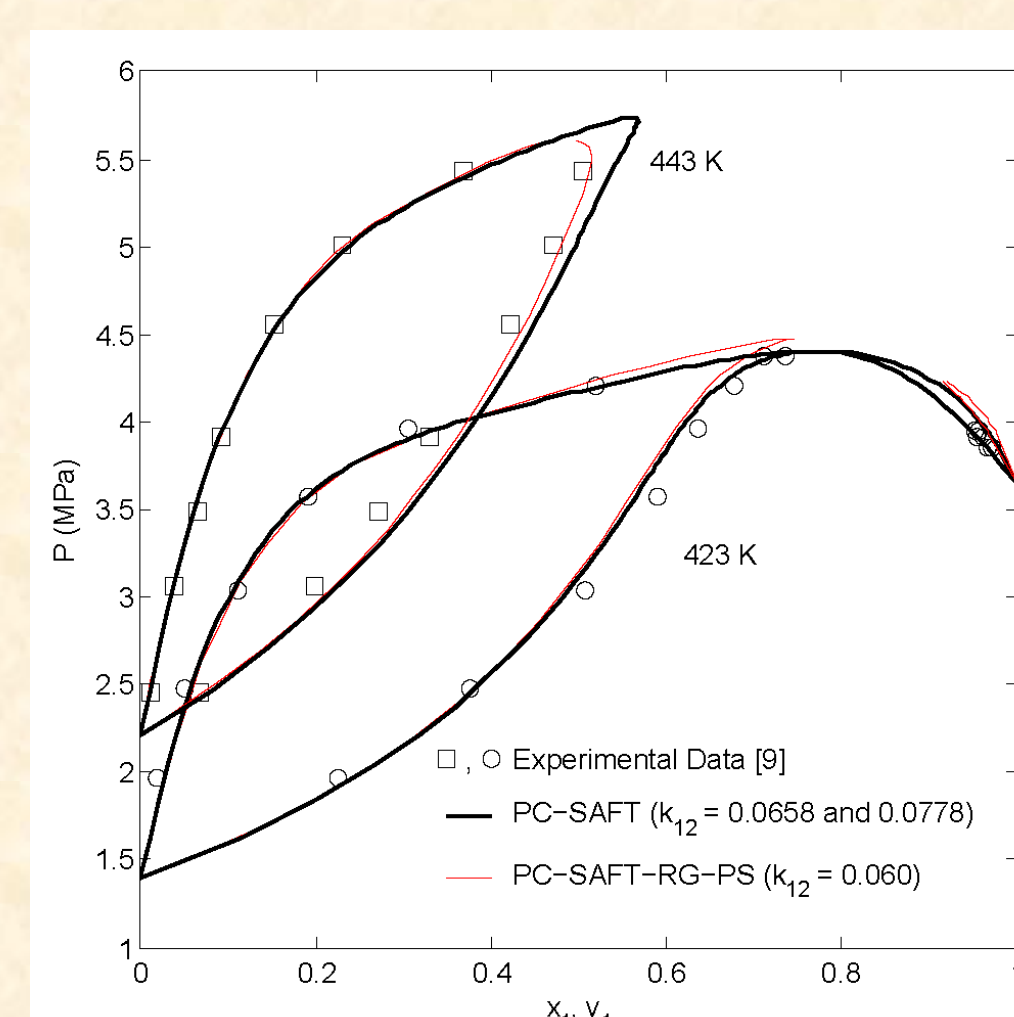
Pure compounds

ETHANOL ; 1-PROPANOL ; R134a

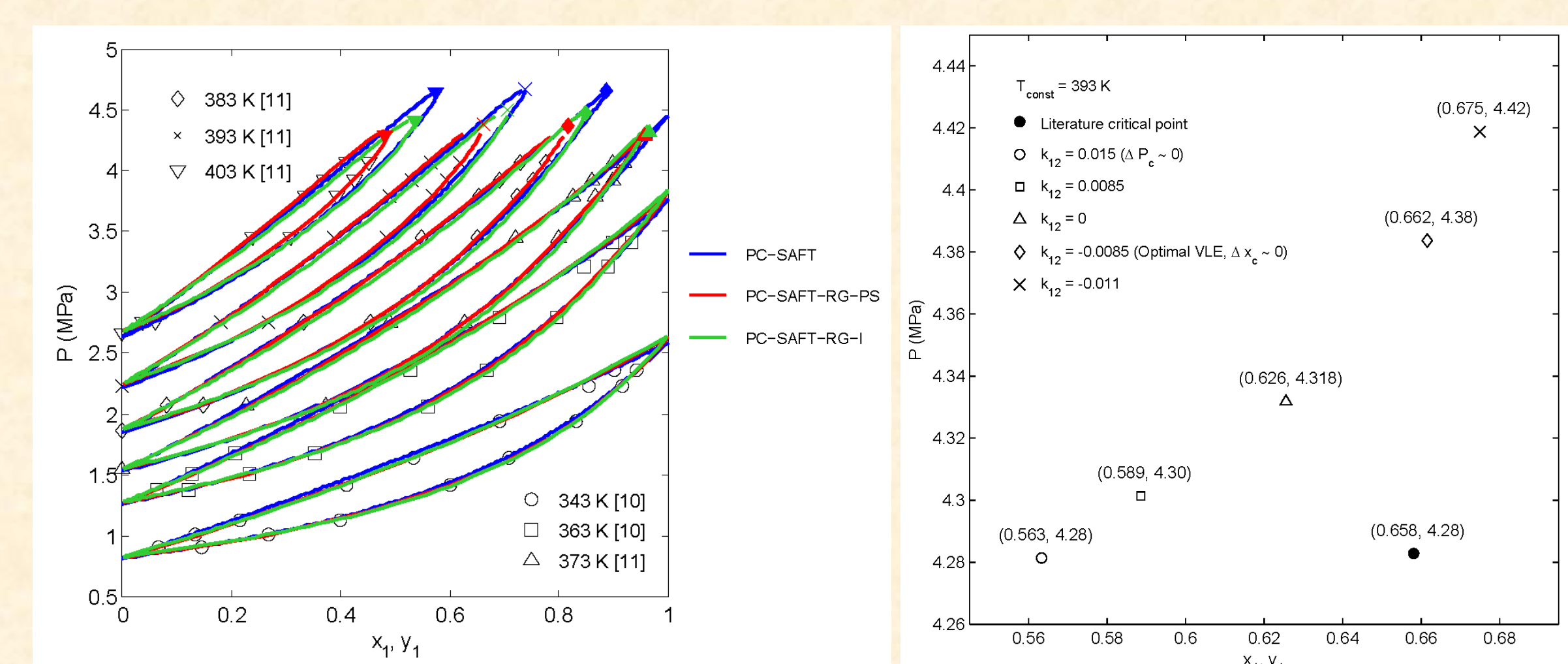


Binaries Phase Equilibria

n-BUTANE (1) + METHANOL (2)

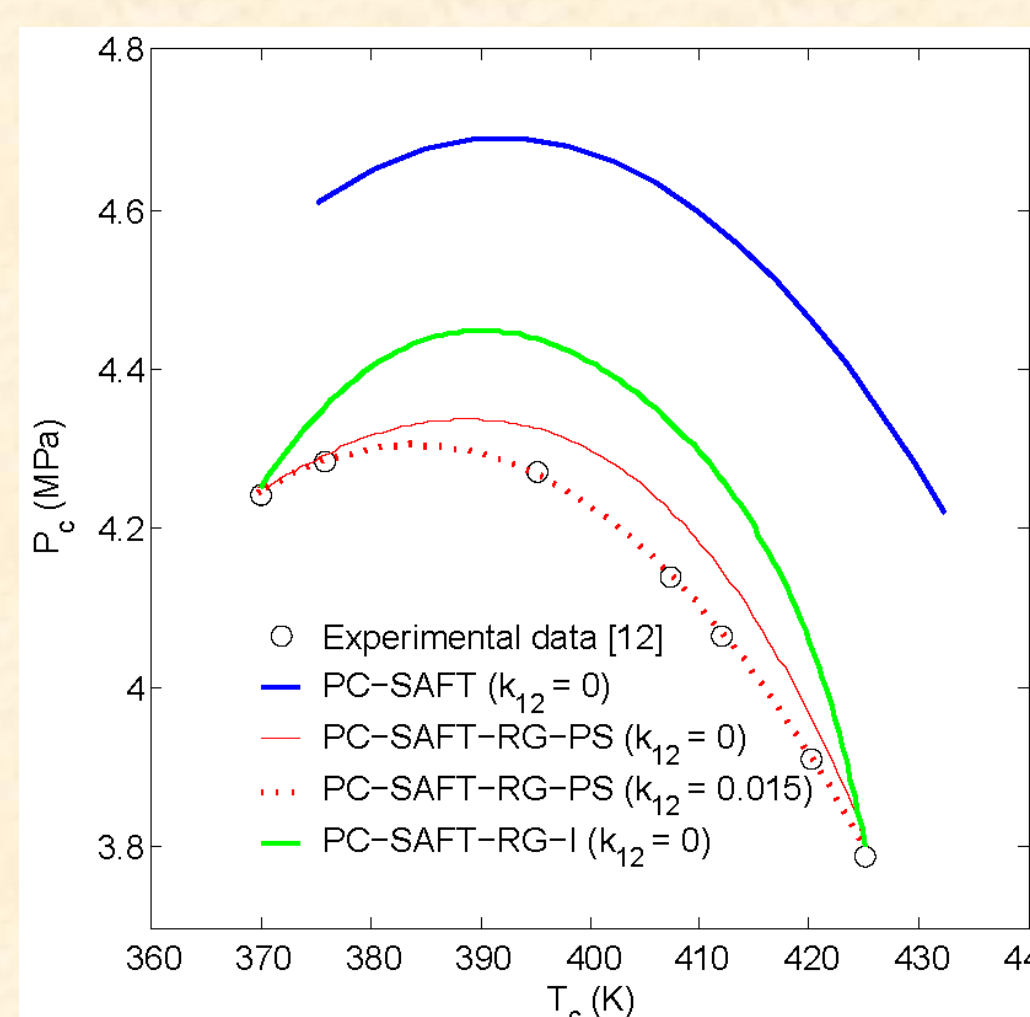


PROPANE (1) + n-BUTANE (2)

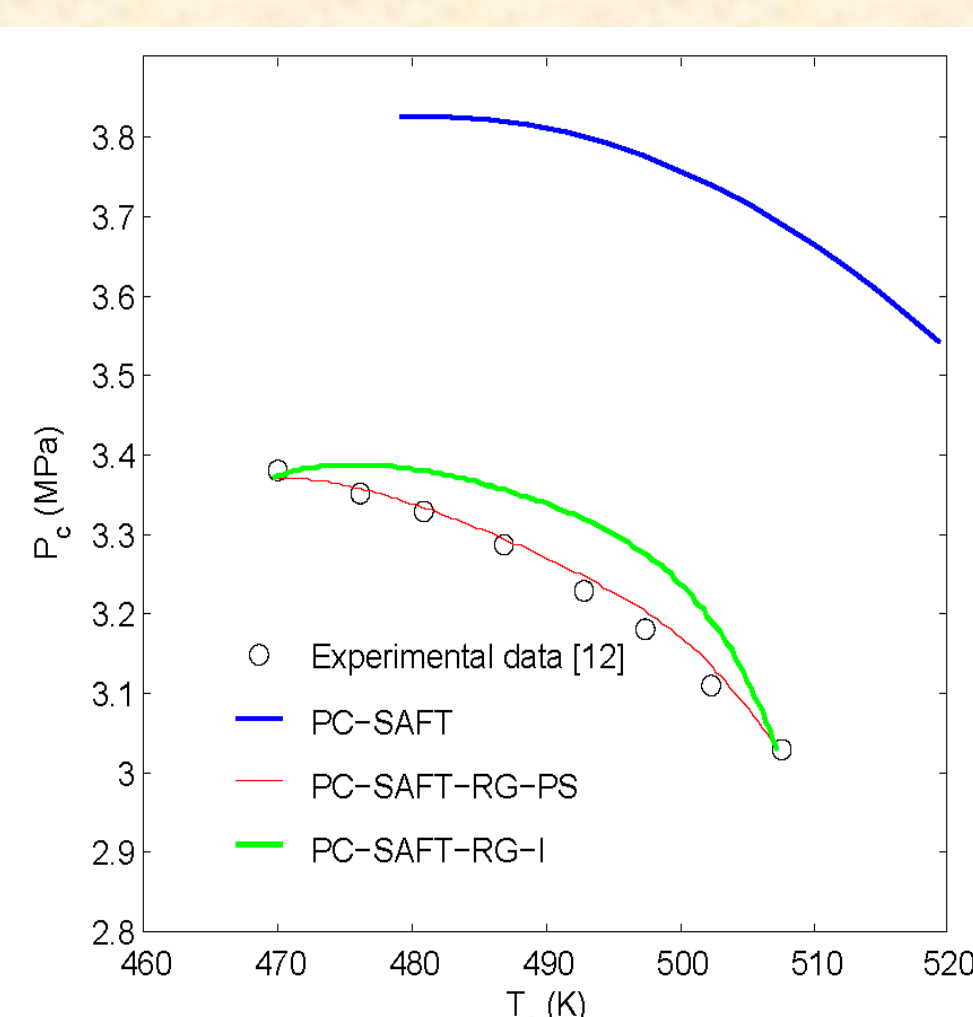


Critical Lines

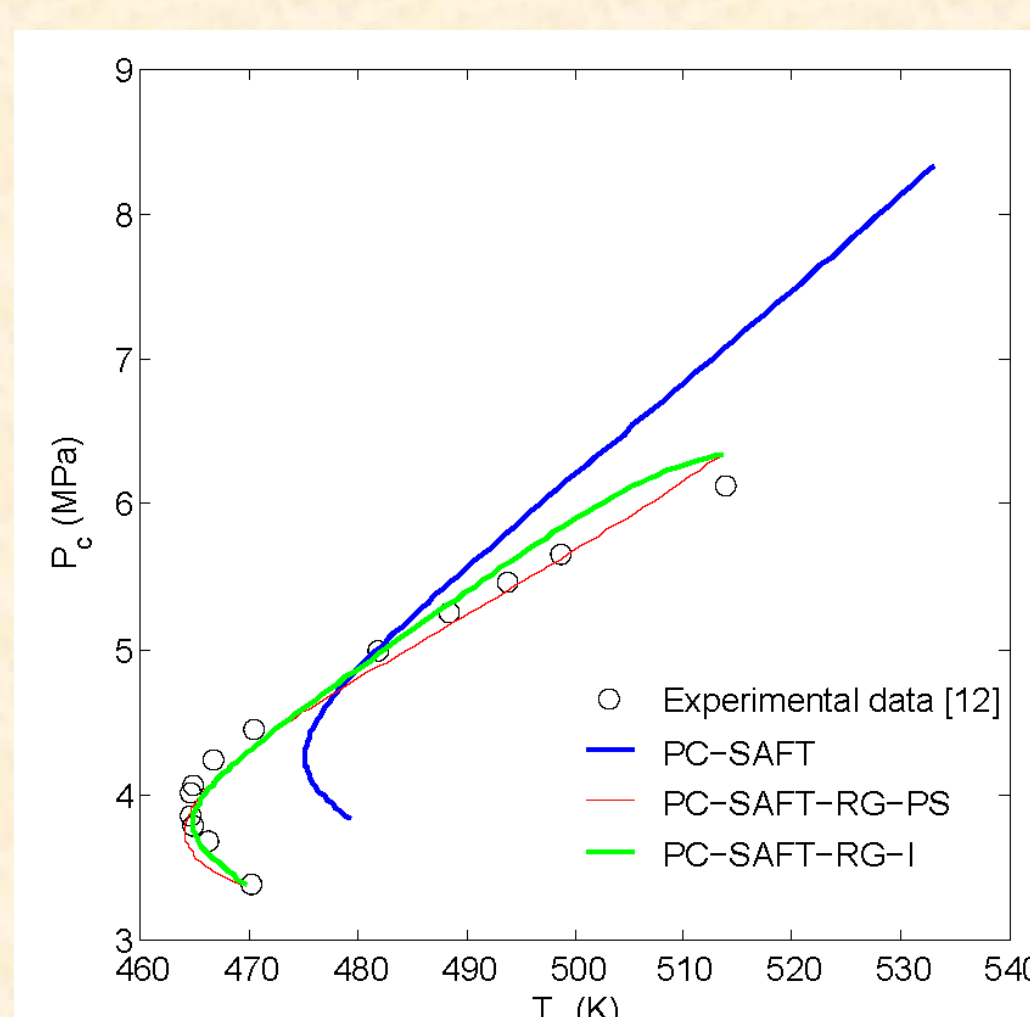
PROPANE + n-BUTANE



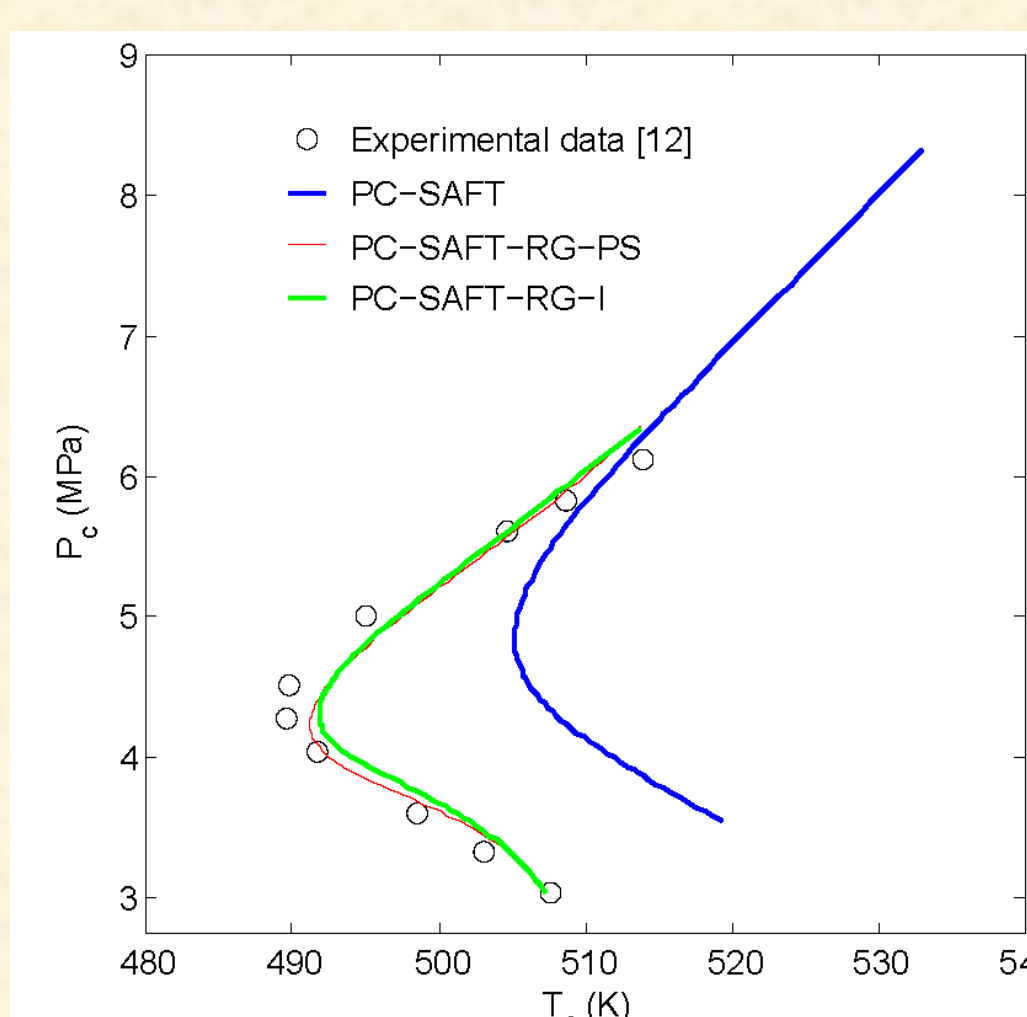
n-PENTANE + n-HEXANE



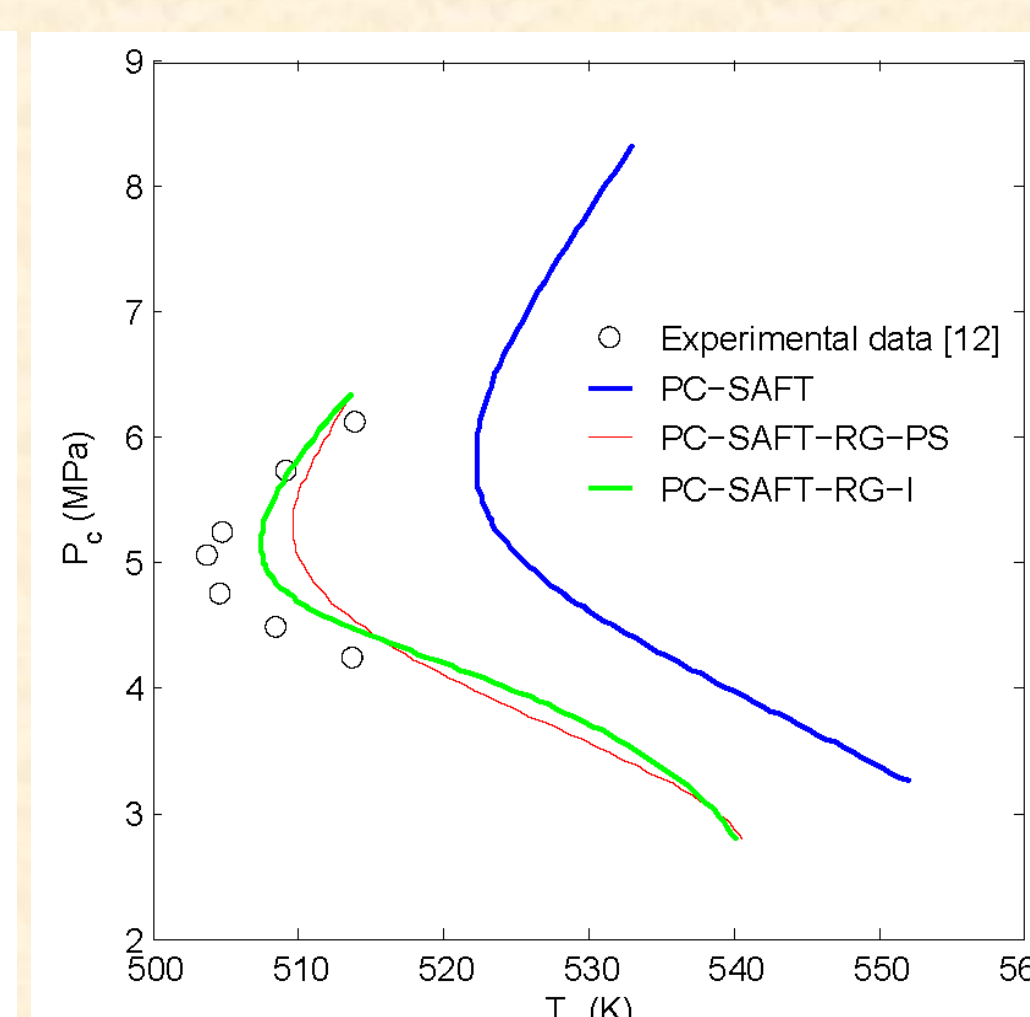
n-PENTANE + ETHANOL



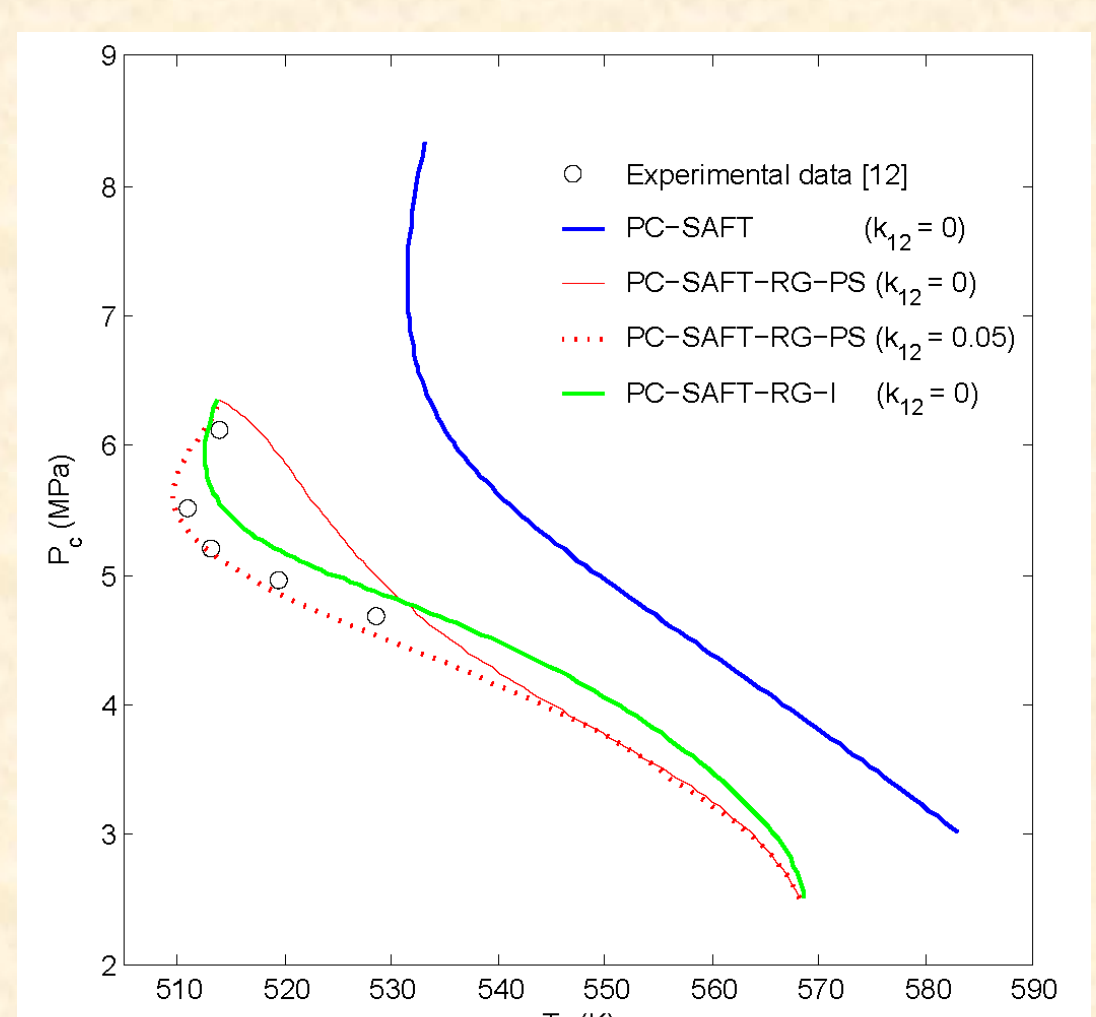
ETHANOL + n-HEXANE



ETHANOL + n-HEPTANE



ETHANOL + n-OCTANE



Conclusions

The renormalization theory of White applied with the PC-SAFT EoS leads to a significantly improved representation of the critical region in comparison with classical PC-SAFT EoS.

Two approximations methods have been used, namely the phase-space cell approximation (PS) and the isomorphic approximation (I). They perform similarly for most mixtures and each of them displays stronger cases depending on the system concerned.

In this work, a single interaction parameter was not able to fit simultaneously experimental x_c - T_c and x_c - P_c data. The PC-SAFT RG could be improved by finding an alternative way to obtain its parameters (here fitted to critical coordinates). PC-SAFT RG is nevertheless able to provide good estimates of mixtures critical points using subcritical data for tuning the parameters of the model. In order to continue the work of Moussa Dicko [13] and Chien-bin Soo [14], a new thesis dealing with calculations and measurements in the critical region should begin shortly.

References

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