Simultaneous representation of critical point and phase equilibria with advanced thermodynamic models

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Outline

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- Motivation
- Thermodynamic Model
- Parametrization
- Mixtures

Introduction

The interest in systems near the critical region is increasing.

Importance of describing near-critical point (*C.P.*) properties:

1. Supercritical C_6 as a solvent for the production of methanol from syngas (Liu, 2003).
2. Use of near/supercritical alcohols to produce bio-fuel (Oliveira et al. 2010).
3. Implementation of EOR projects in *HTHP* fields with high CO_2 content (Pizzaro & Branco, 2012).
4. Extraction of non-volatile components in pharmaceutical, food and textile industries (Knez et al., 2014).

Introduction

Fluids present non-analytical / asymptotic behavior near *C.P.*

Analytical (*mean-field*) *EoS* fail to describe fluids close to *C.P.*

Density at microscopic regions vary substantially from the bulk (*vapor–liquid* transitions).

Order parameter (*density*) describes the interactions of the system.

Introduction

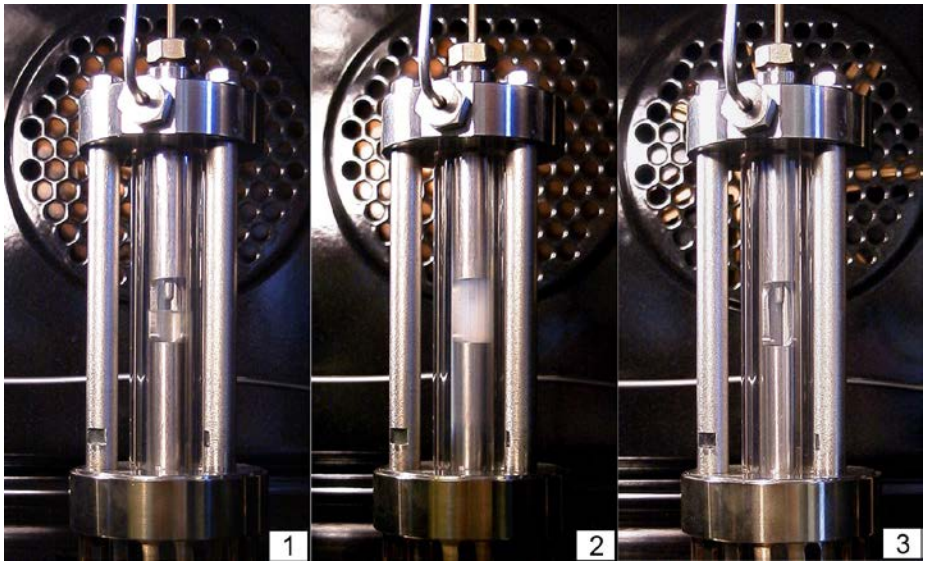
Global description of a fluid:

1. Regions far and close to *C.P.*

Crossover *EoS*:

1. Behave classically
   (Far from the critical region)

2. Incorporate fluctuations
   (Near the critical region)



Source: Horstmann, Sven (2000).

Motivation

Limited application in the Oil & Gas industry and other sectors.

Model useful for describing fluids both far and close to *C.P.*
(Renormalization group theory corrects the *mean-field EoS)*

Wilson's recursive procedure.
(Effective method to incorporate the density fluctuations)

Advantages and disadvantages of the crossover *SRK*.

Thermodynamic Model

White's approach:

1. Introduce density fluctuations into an *EoS* using a recursive procedure.
2. Based on the renormalization group theory (phase-space cell approx).
3. Longer wavelength fluctuations are added to the free energy of the fluid.
4. Non-analytical asymptotic behavior inside the critical region.
5. Reduces to the mean-field model far from the critical point.

Thermodynamic Model

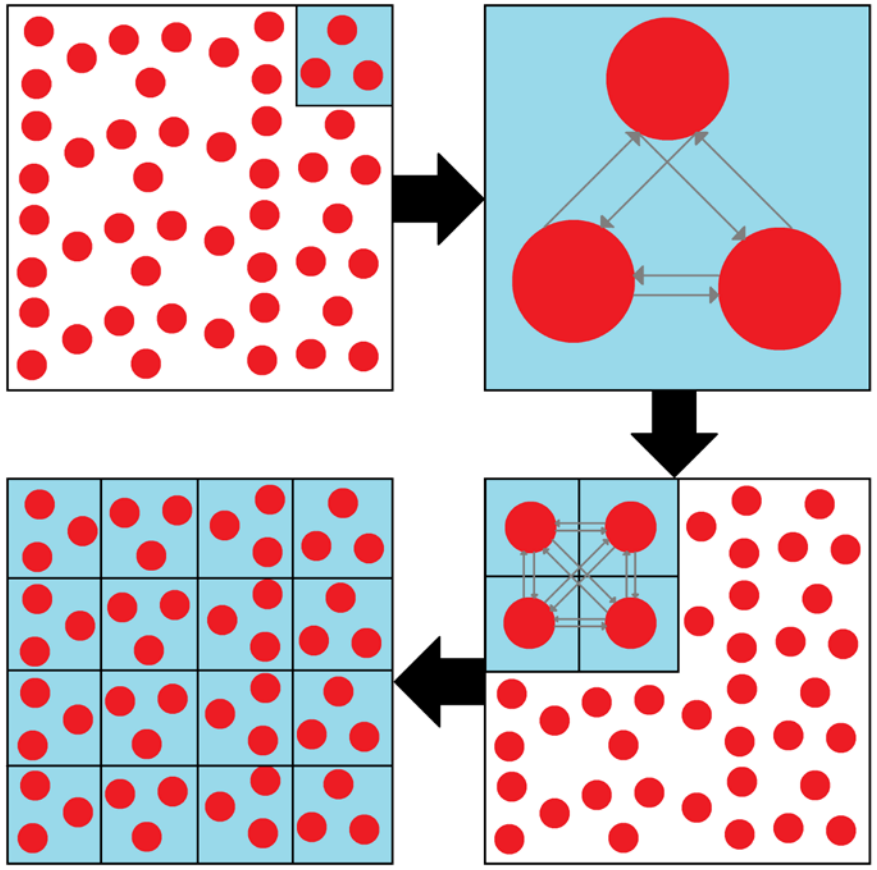
Phase-space cell approximation:

1. Calculate the cell's free energy. (Mean-field theory)

2. Include the fluctuations. (Non-mean-field model)

3. Neighbor cells are considered as a whole molecule.

4. Compute fluctuations among further molecules.



Thermodynamic Model

$$f_n(\rho) = f_{n-1}(\rho) + \delta f_n(\rho) \tag{1}$$

$$\delta f_n(\rho) = -K_n \ln\left(\frac{\Omega^s{}_n}{\Omega^l{}_n}\right) \tag{2}$$

$$K_n = \frac{k_b T}{2^{3n} L^3} \tag{3}$$

$$\Omega^\lambda{}_n = \int_0^{\min(\rho,\rho_{max}-\rho)} \exp\left(-\frac{\mathrm{G}^\lambda{}_n(\rho,y)}{K_n}\right) dy \tag{4}$$

$$\mathrm{G}^\lambda{}_n = 0.5\left(\bar{f}^\lambda{}_n(\rho+y) - 2\bar{f}^\lambda{}_n(\rho) + \bar{f}^\lambda{}_n(\rho-y)\right) \tag{5}$$

$$\bar{f}^s{}_n(\rho) = f_{n-1} + 2^{(-2n)}(a\rho^2\phi) \tag{6}$$

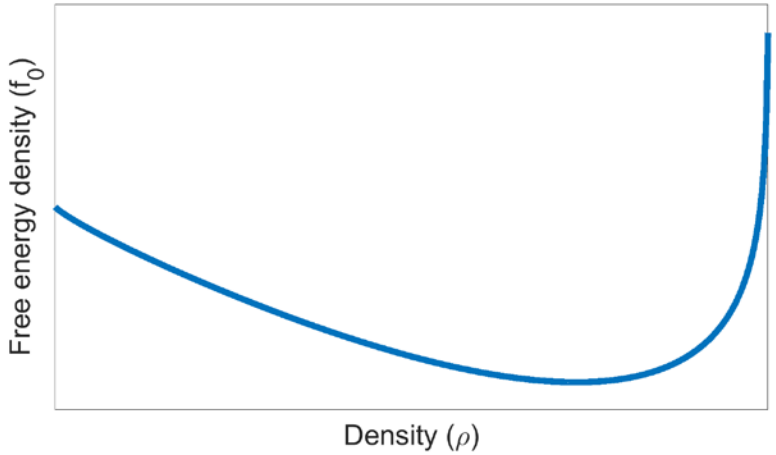
$$\bar{f}^l{}_n(\rho) = f_{n-1} + 2^{(-1)}(a\rho^2) \tag{7}$$

Thermodynamic Model

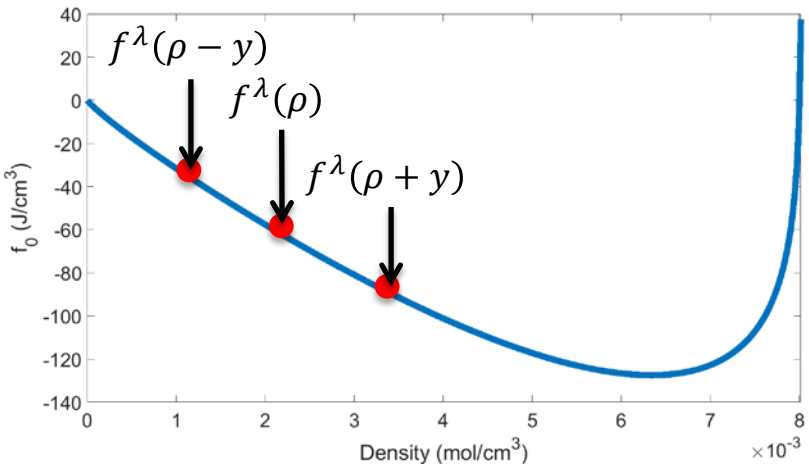
SRK

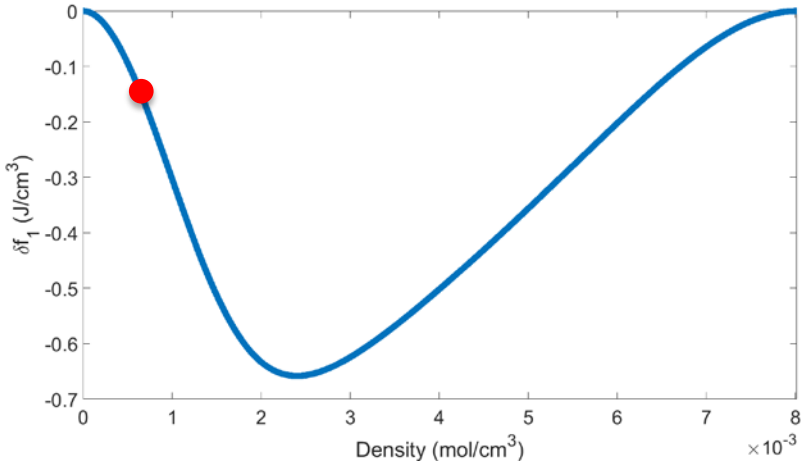
Initial free energy density:

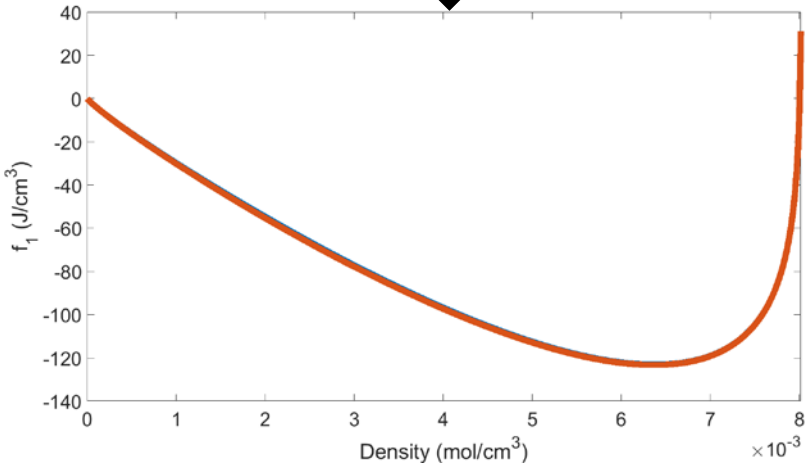
$$f_0 = -\rho RT ln\left(\frac{1-\rho b}{\rho}\right) - \frac{a\rho}{b}(1+\rho b) + \frac{a\rho^2}{2}$$

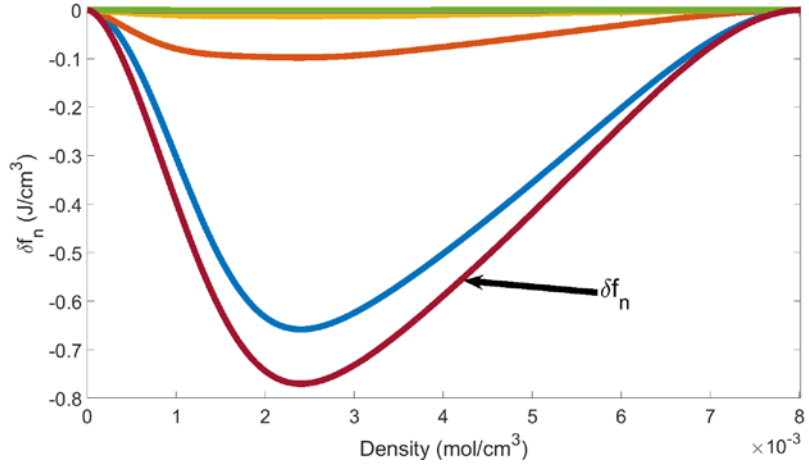


Thermodynamic Model









Thermodynamic Model

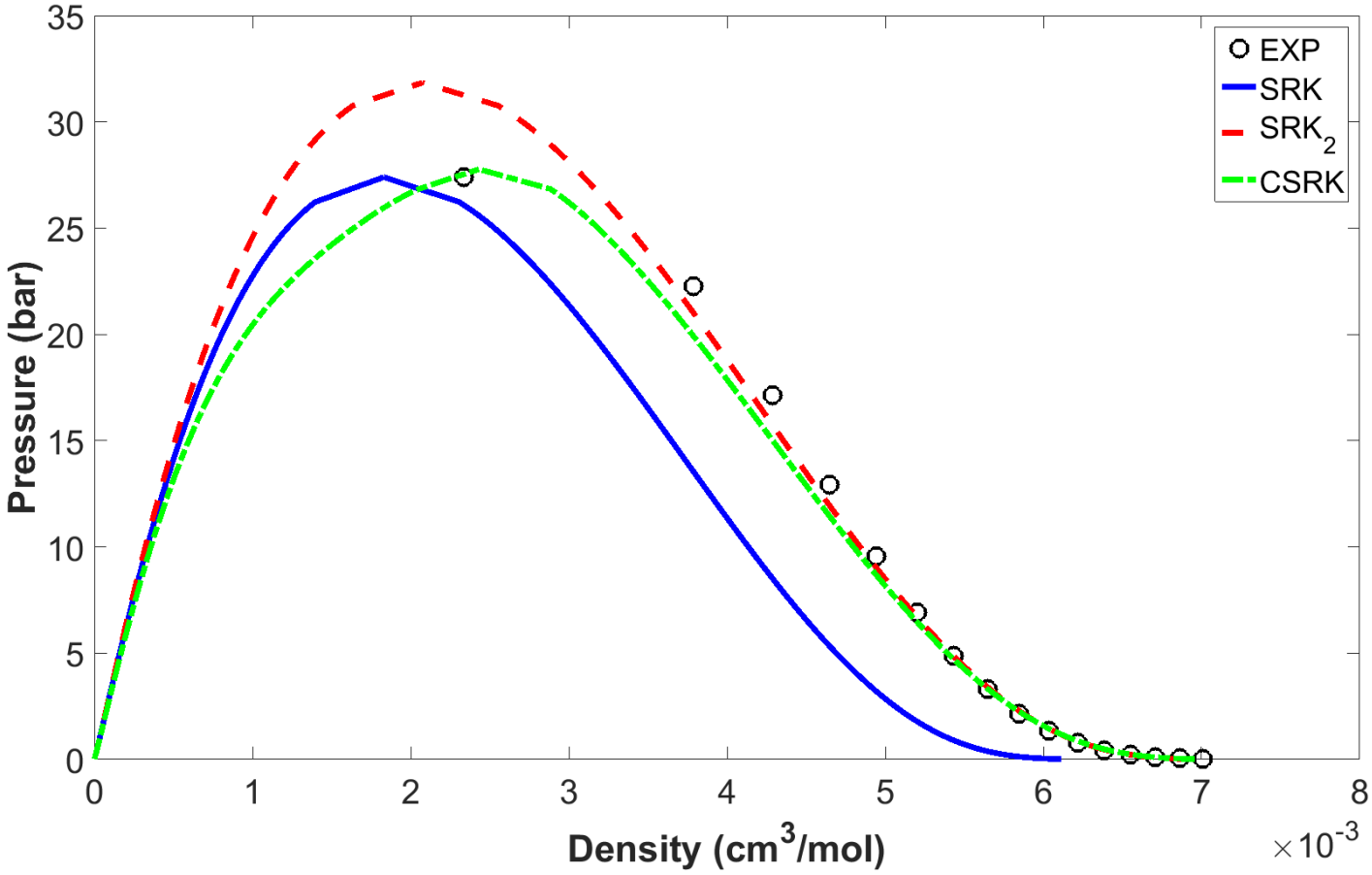
$$P = \rho^2 \left[\frac{\partial\left(f^{SRK}+\delta f\right)}{\partial \rho}\right]_T \quad (1)$$

$$\mu_i = \rho^{-1} \left[\frac{\partial\left(f^{SRK}+\delta f\right)}{\partial x_i}\right]_{T,V,x_{i\neq j}} \quad (2)$$

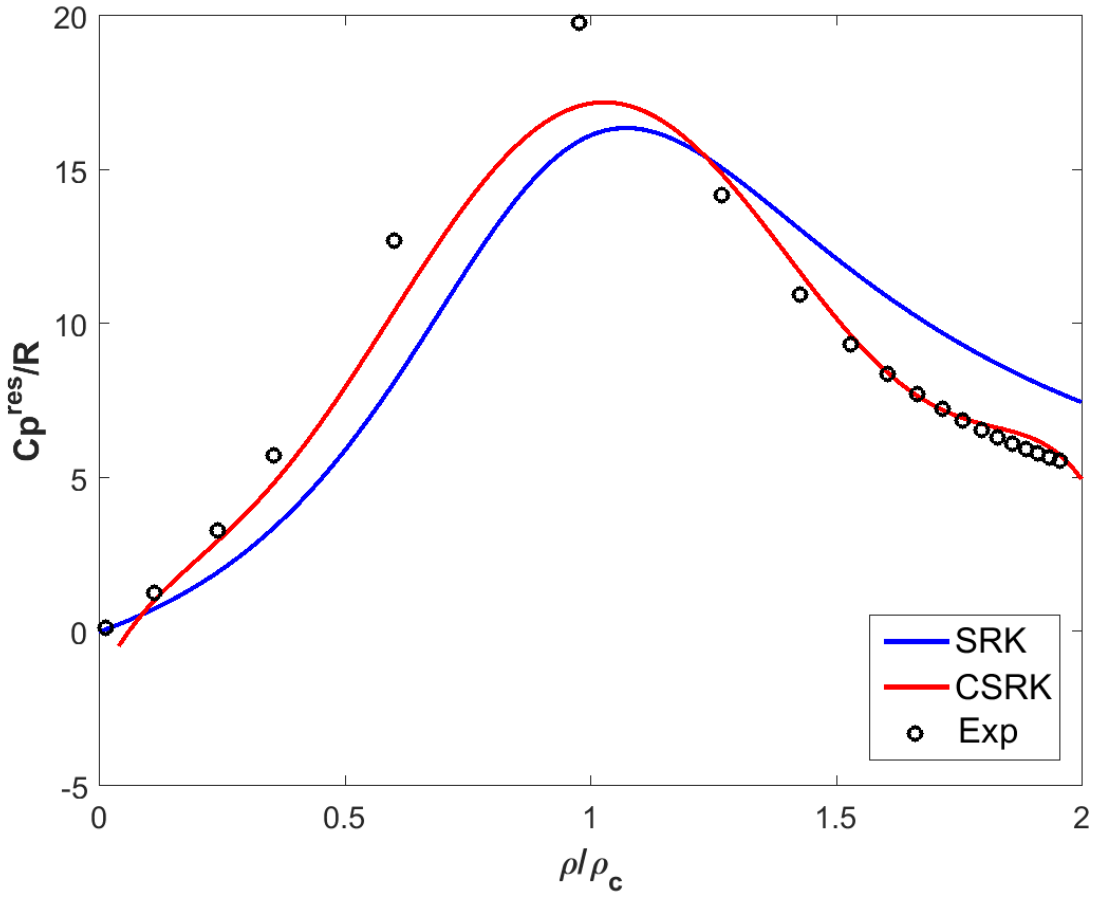
$$C_V = \frac{-T}{\rho} \left[\frac{\partial^2\left(f^{SRK}+\delta f\right)}{\partial T^2}\right]_V \quad (3)$$

…

Thermodynamic Model



Thermodynamic Model



Thermodynamic Model

Classical thermodynamic models: fail correctly describe the analytic form of the divergences.

$$C_v \propto A_0 \Delta T^{-\alpha}$$

$$\Delta\rho \propto B_0 \Delta T^{-\beta}$$

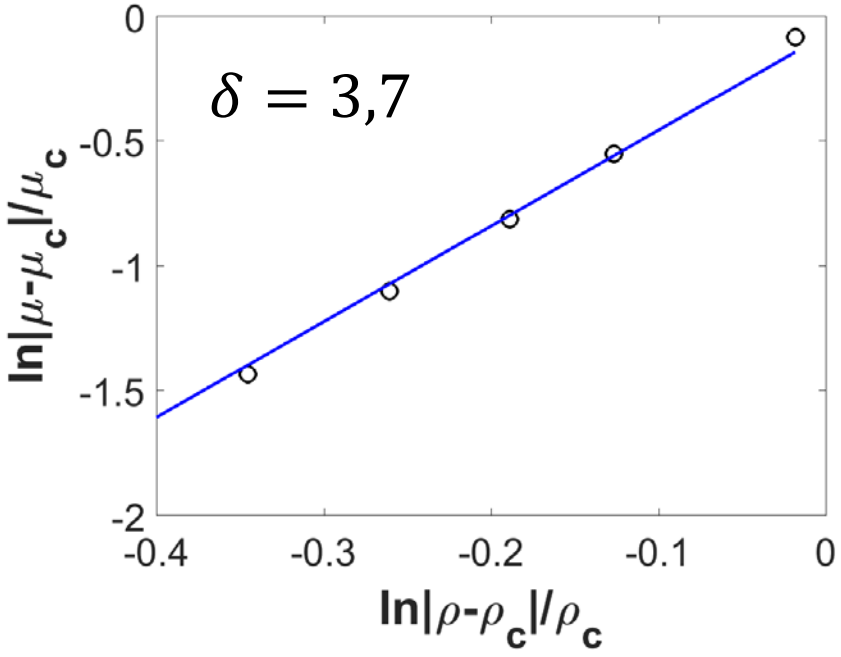
$$\kappa_T \propto C_0 \Delta T^{-\gamma}$$

$$\Delta\mu \propto D_0 \Delta\rho^{-\delta}$$

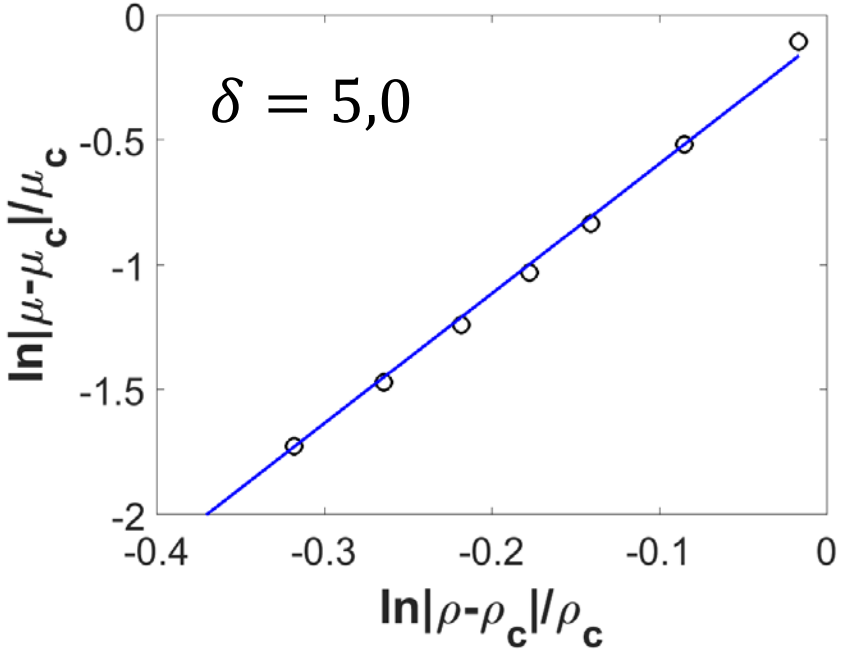
$$\Delta T = \frac{|T - T_c|}{T_c},\ \Delta\rho = \frac{|\rho - \rho_c|}{\rho_c},\ \Delta\mu = \frac{|\mu - \mu_c|}{\mu_c}$$

Thermodynamic Model

SRK



CSRK



Universal value: $\delta = 4{,}8$

Parametrization

Recursive procedure alters the *EoS* near the critical point.

Mean-field parameters are optimized with exp. saturation data.

Crossover parameters are optimized with near-critical exp. data.

Lack of standardization and straightforward implementations. (Hendriks, 2010)

Clear use of input data and numerical fitting procedures.

Parametrization

Model parameters:

Mean-field	Crossover
T_c': virtual critical temperature	L: cutoff length
P_c': virtual critical pressure	ϕ: shortest wavelength
ω': virtual acentric factor	

Parametrization procedures:

1. Simultaneous parametrization (mean-field and crossover).
2. Mean-field parameters from ***CPA*** and crossover from near-critical data.

Results

AAD for the saturated properties of several n-alkanes ($C_1 - C_{10}$) using different thermodynamic models

EoS	$\Delta P^{sat}(\%)$	$\Delta v^{liq}(\%)$
SRK	1.61	12.0
SRK2	0.97	1.29
CSRK	2.41	2.09
CSRK2	2.11	1.53
Cai (2004)	5.62	1.18

AAD for the critical properties of several n-alkanes ($C_1 - C_{10}$) using different thermodynamic models

EoS	$\Delta P_c(\%)$	$\Delta T_c(\%)$	$\Delta v_c(\%)$
SRK	0.00	0.00	24.7
SRK2	14.0	2.28	12.0
CSRK	1.08	0.36	3.22
CSRK2	0.23	1.69	3.76
Cai (2004)	3.00	0.60	3.35

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Conclusions

Precise description of critical and saturated properties data.

Strong correlation between the parameters.

Critical point is not matched if CPA parameters are used.

Parameter ϕ can be fixed for heavier hydrocarbons ($C_4 - C_{10}$).

Use of derivative properties to select the optimum parameters.

Mixtures

Isomorphism assumption:

1. Potential of a mixture has the same universal form as the pure fluid.
2. Mole fractions are used as independent variables.

Mixing rules:

Mean-field (vdW 1-fluid)

$$a_m = \sum\sum x_i x_j a_{ij}$$

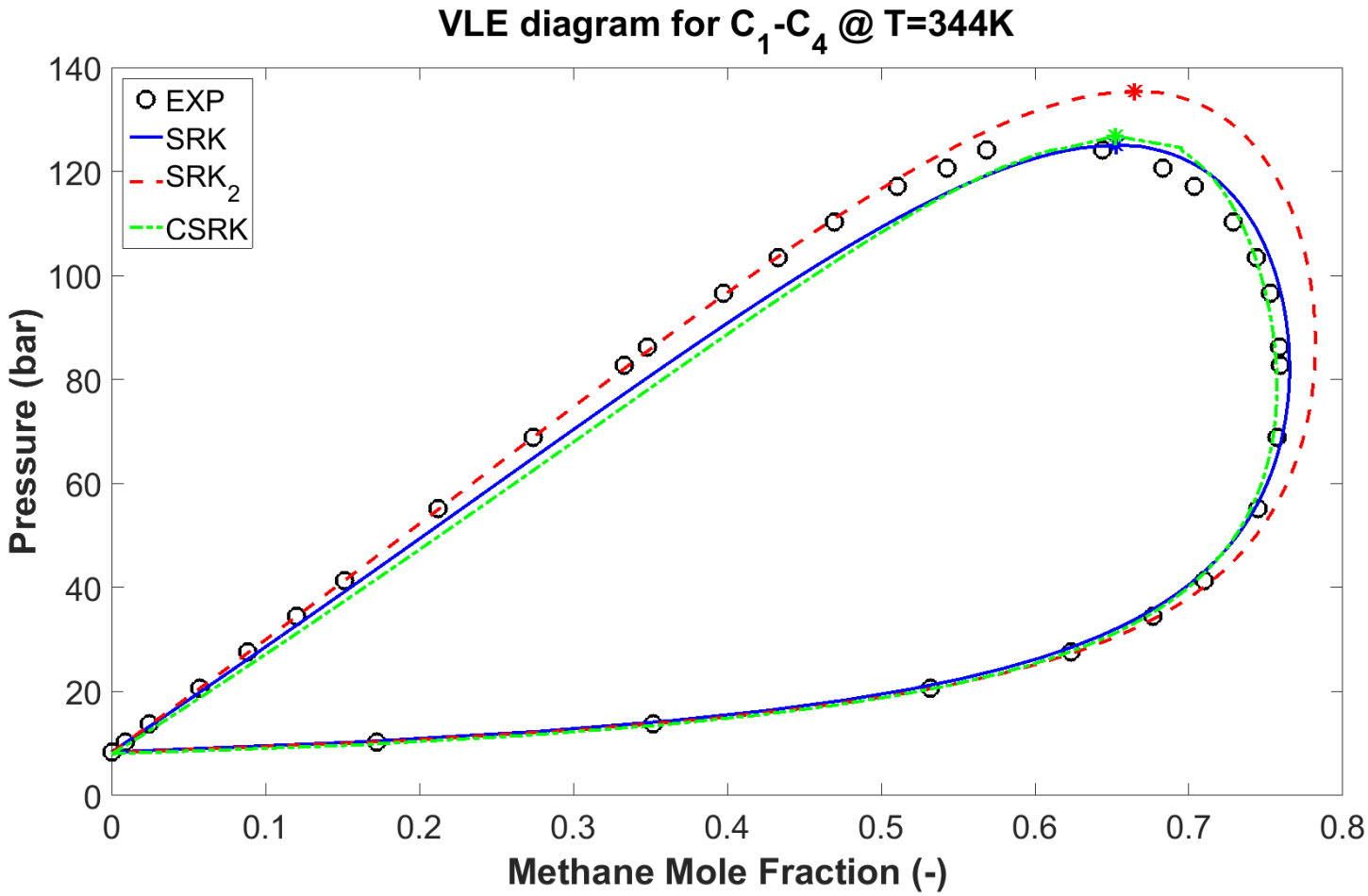
$$b_m = \sum x_i b_i$$

Crossover

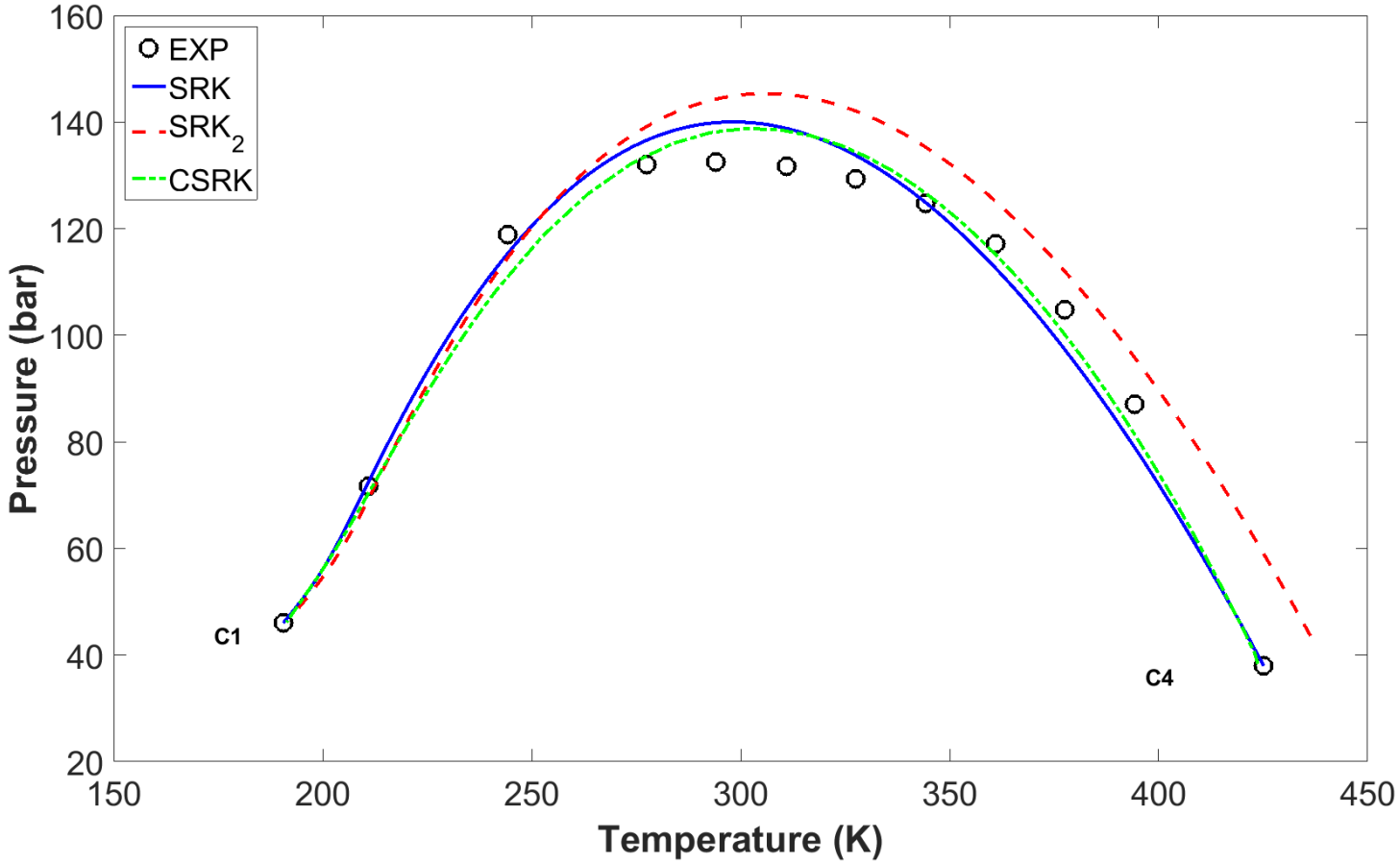
$$\phi_m = \sum x_i \phi_i$$

$${L_m}^3 = \sum x_i {L_i}^3$$

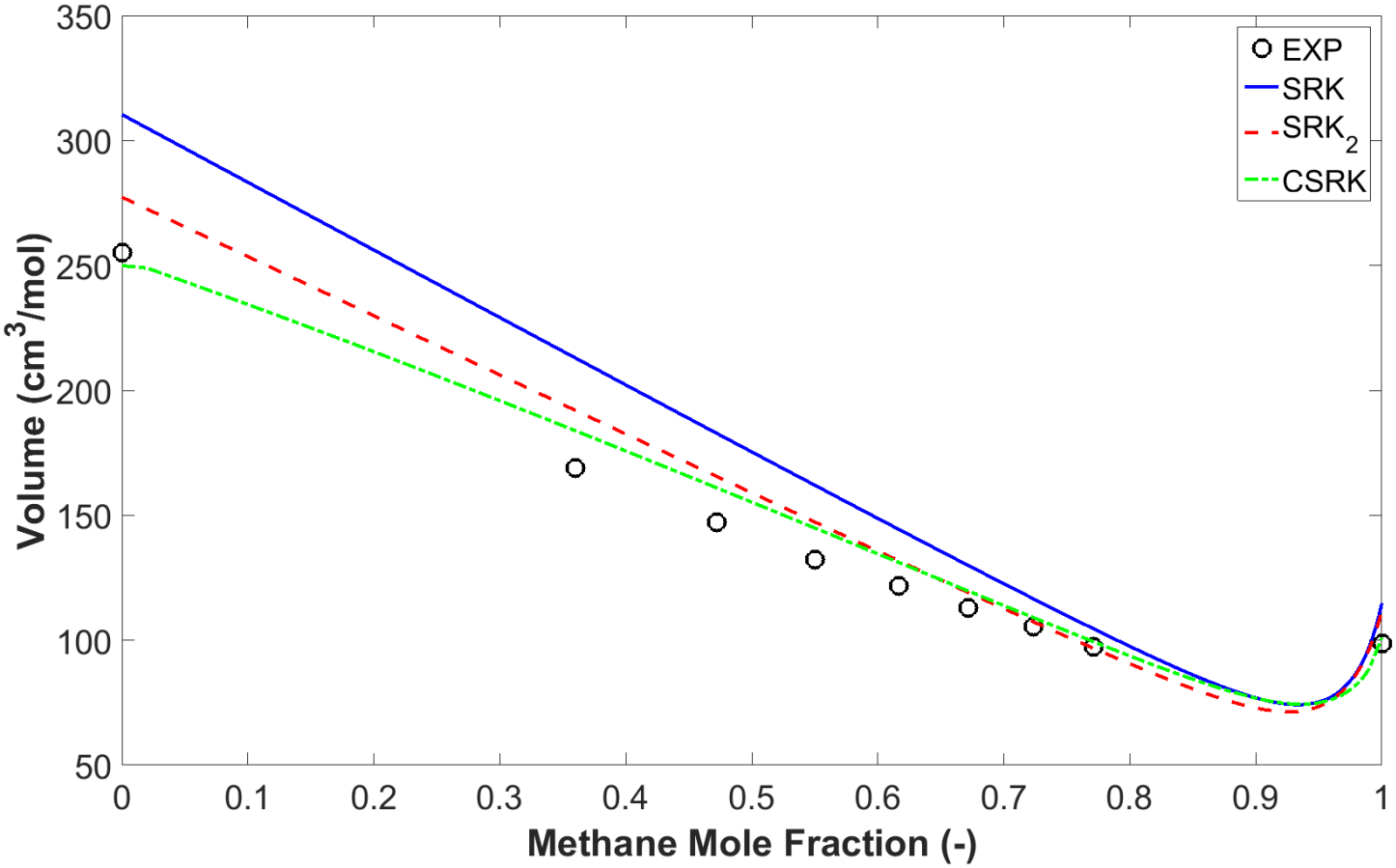
Results


VLE diagram for C1-C4 @ T=344K
EXP
SRK
SRK2
CSRK
Pressure (bar)
Methane Mole Fraction (-)
0
20
40
60
80
100
120
140
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

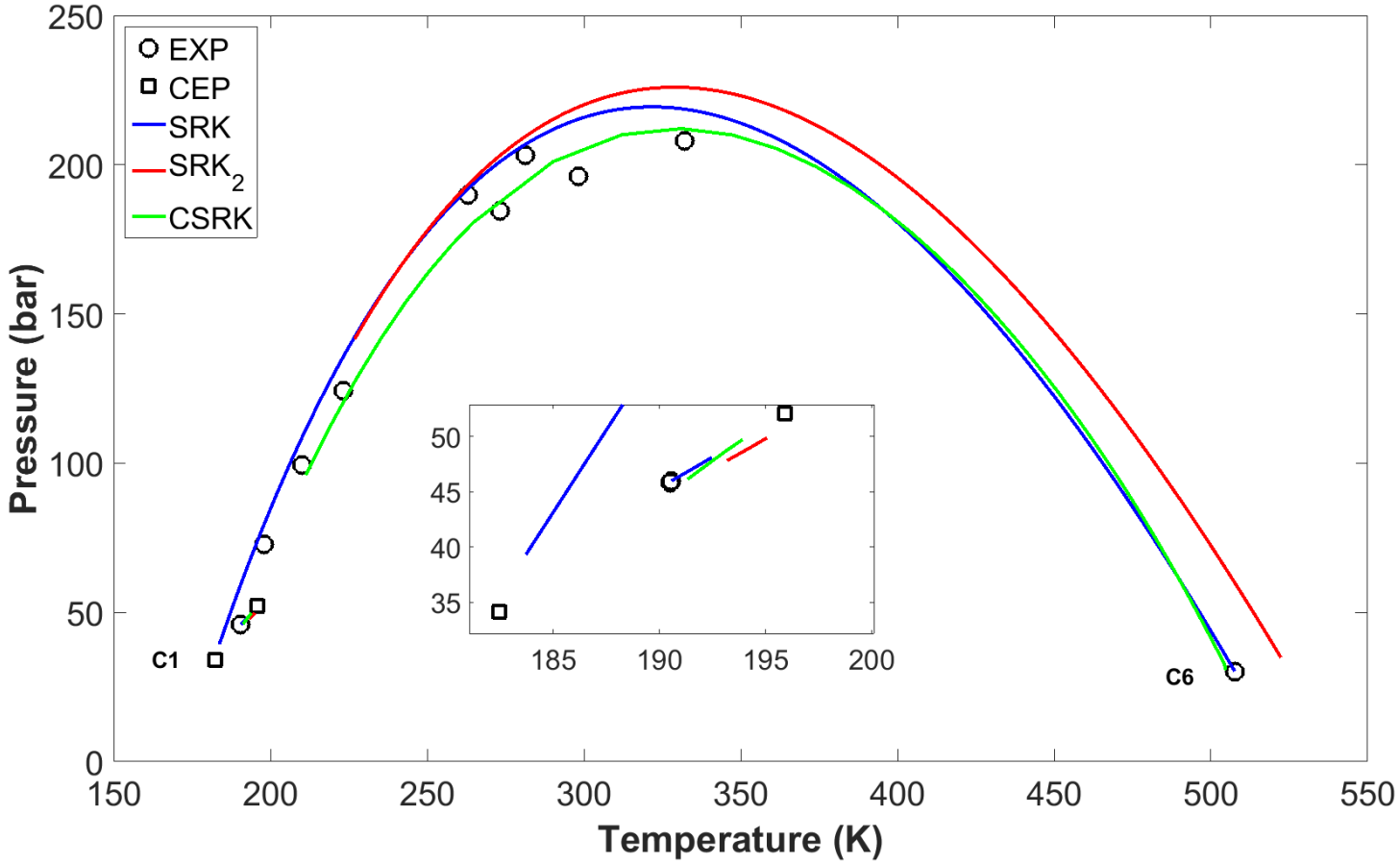
Results


EXP
SRK
SRK2
CSRK
C1
C4
Pressure (bar)
Temperature (K)
160
140
120
100
80
60
40
20
150
200
250
300
350
400
450

Results


EXP
SRK
SRK2
CSRK
Volume (cm3/mol)
Methane Mole Fraction (-)
350
300
250
200
150
100
50
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Results


EXP
CEP
SRK
SRK2
CSRK
Pressure (bar)
Temperature (K)
C1
C6
250
200
150
100
50
0
150
200
250
300
350
400
450
500
550
50
45
40
35
185
190
195
200

Conclusions

Phase behavior predictions of *HC* systems are similar to *SRK.* (Critical parameters)

Improved critical lines predictions with the crossover SRK. (Critical volume)

Binary interaction parameters or complex mixing rules for quantitative description.

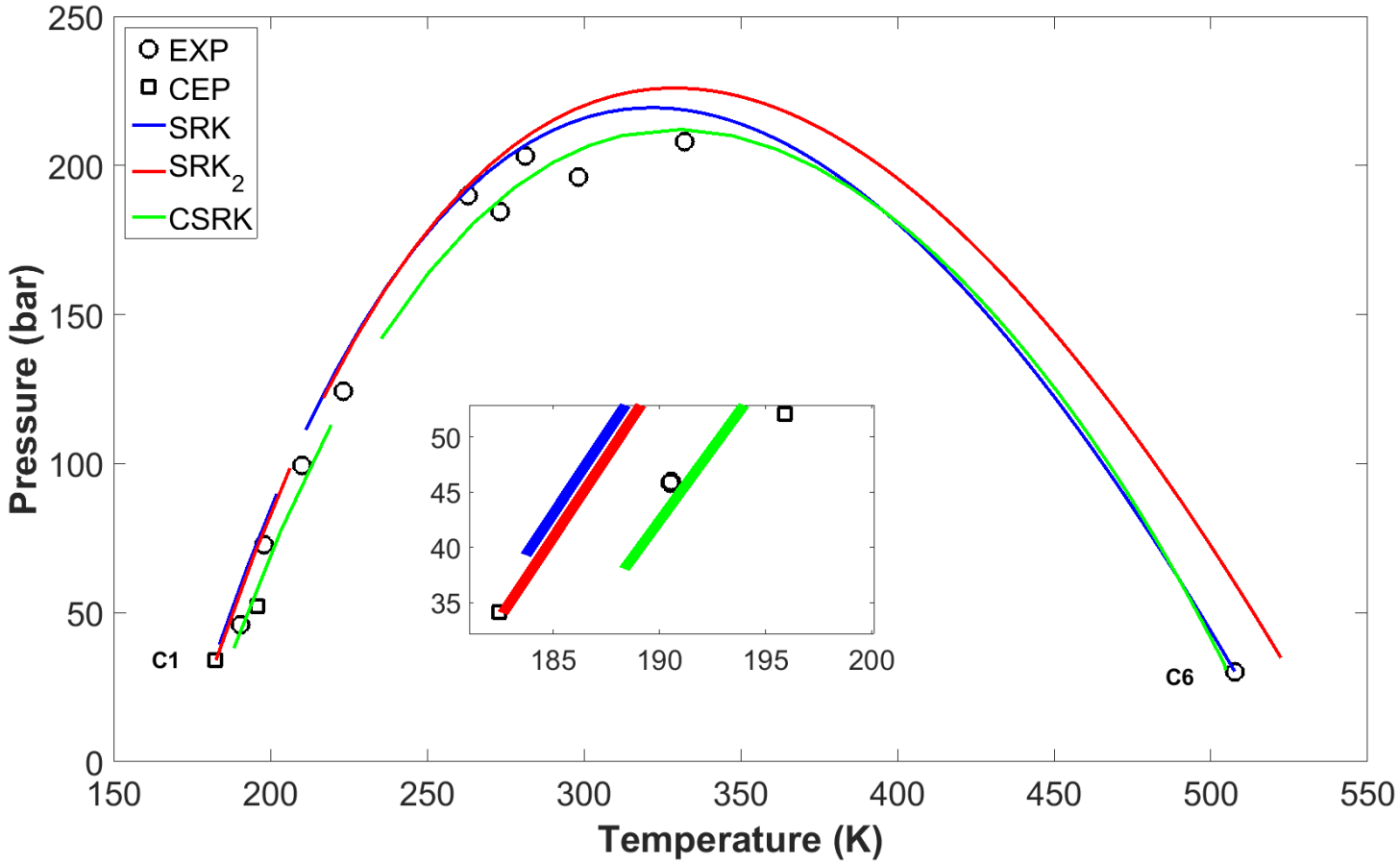
(Asymmetric mixtures: type V diagrams).

Inclusion of a hydrogen bonding term.

(Systems with associating species)

Acknowledgments

Results


EXP
CEP
SRK
SRK2
CSRK
Pressure (bar)
Temperature (K)
C1
C6
0
50
100
150
200
250
150
200
250
300
350
400
450
500
550
35
40
45
50
185
190
195
200