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ABSTRACT

In this work, two different Crossover Soave-Redlich-Kwong (*SRK*) Equations of State (*EoS*) were applied to incorporate the density fluctuations into the classical model for the representation of derivative properties of selected n-alkanes. Both methods, the first based on the renormalization of the Landau-Ginzburg expansion and the second based on the phase-space cell approximation, are capable of describing the non-classical behavior of the molar heat capacities and speed of sound close to the critical point. Nevertheless, the overall performance of the crossover equation is similar to the cubic model, since the non-mean-field *EoS* reduce to the classical model far from the critical region. Additionally, the comparison of the crossover equations indicates that the Kernel term is useful for the correct representation of the heat capacity at constant volume, as well as other properties related to the weak divergence at the critical point, over a wider range of conditions.

INTRODUCTION

The accurate description of the thermodynamic properties of fluids is a major task in several industrial applications. In fact, the representation of relevant phase equilibria is fundamental for the design and control of operation of many processes in the oil and gas, chemical and other sectors [1]. Additionally, reliable theoretical methods are of great need in the industry, in order to substitute correlative models and to predict the experimental data over a wide range of compositions, temperatures and pressures [2]. Aside from predicting primary, i.e. phase equilibrium properties, it is also important to correctly describe secondary properties, like heat capacities and speed of sound. However, these properties are more difficult to predict [3], and traditional cubic *EoS*, like Peng-Robinson (*PR*), which are frequently used in the oil and gas

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3 industry, fail to yield satisfactory results of the heat capacities in high pressure conditions,
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5 especially close to the critical point [4].
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8 Classical EoS fail to describe the thermodynamic properties of fluids close to the critical point
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10 because they do not take into account the asymptotic and non-analytical behavior of fluids due to
11
12 the critical fluctuations of density [5]. The non-classical behavior of fluids is characterized by
13
14 universal scaling laws with universal exponents that are in accordance to the Renormalization
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16 Group (*RG*) theory of the critical phenomena [6]. In order to represent the correct scaling behavior
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18 with EoS, it is necessary for a model to incorporate the fluctuations of the order parameter that
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20 arise in the critical region. Nonetheless, it is important that the model reduces to the classical
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22 analytic behavior far away from the critical point, where the density fluctuations are negligibly
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24 small [7]. There are two main *RG* approaches in the literature [8] that take into account such
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26 inhomogeneities. The *RG* corrections modify the Hamiltonian of a system into a renormalized one
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28 with reduced number of degrees of freedom, meaning that the microscopic degrees are integrated
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30 out as the characteristic length of the phenomenon becomes larger than the molecular interactions
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32 as the system approaches the critical point [5].
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38 The first method considers an extension of the Landau-Ginzburg equation, where the
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40 fluctuations are characterized on a local mesoscopic Hamiltonian, in which the solution of the
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42 renormalization transformation to the classical equation are mapped to a cutoff point [9]. The
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44 application of this procedure is done by decomposing the expression for the free energy in an
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46 analytical part and a non-analytical part that contains the fluctuations. Then, the utilization of a
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48 truncated expansion in temperature and density variables is rescaled by crossover transformations
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50 that explicitly incorporates the known asymptotic critical scaling laws. Two versions of this
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52 approach are found in the literature. The first uses the truncated classical Landau expansion, as
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done by Chen *et al.* [9] and more recently by Wyczalkowska *et al.* [7] with the van der Waals EoS instead of the truncated Landau expansion, while the second uses a more phenomenological approach in which the critical non-analytical part is also represented by the classical *EoS* [10–16].

The second technique is based on Wilson's phase-space cell approximation which applies a block averaging procedure for the qualitative analysis of the critical phase behavior [6,17]. The method reduces the degrees of freedom by decomposing the system in a sequence of cells, or renormalized Hamiltonians, in which the fluctuations are averaged, allowing the calculation of correct values of the universal critical exponents. White and co-workers [18–22] used this idea to develop a global RG EoS that extends the range of application of the original model to model fluids both far away and close to the critical point [18–22], since the original method was restricted to the vicinity of the critical point [6].

Thus, the objective of this study is to provide a comprehensive overview of the capabilities of *SRK EoS* using two RG method to describe the singular behavior of derivative properties for *n*-series alkanes near the critical point. Calculations have been performed over the defined temperature and pressure ranges and they are compared to the correlated experimental data [23]. In the process, the applicability of these models is considered by highlighting their strengths and weaknesses in representing the second order derivative properties.

We shall proceed as follows: In Section 2, we describe the crossover *EoS* using the two main methods to introduce density fluctuations in the classical thermodynamic model. In Section 3, we explain the parametrization procedure of the crossover *EoS*. The results are presented in Section 4, where we also compare the non-mean-field model with the classical *SRK EoS*, regarding the representation of the correlated experimental data. Finally, the last section contains the conclusions of this work.

CROSSOVER EQUATION OF STATE

The classical thermodynamic model, to which density fluctuations are incorporated into, used in this work is *SRK EoS* [24]. The pressure explicit expression of this model is given by:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (1)$$

where P is the pressure, v is the molar volume, and R is the universal gas constant. The parameters a and b are repulsive and attractive term constants and are calculated with the following equations:

$$a = \frac{0.4275R^2T_c^2}{P_c} \left[1 + k \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (2)$$

$$b = \frac{0.08664RT_c}{P_c} \quad (3)$$

where k is a function of the acentric factor (ω) defined as:

$$k = 0.480 + 1.574\omega - 0.175\omega^2 \quad (4)$$

As mentioned previously, traditional *EoS* fail to correctly describe the critical behavior of fluids because they do not take into account the density fluctuations that are significant close to the critical point. Therefore, in this work, we have applied two different crossover procedures based on the *RG* theory, in order to bridge the gap between the non-classical critical behavior to classical behavior far from the critical point.

The first method is a phenomenological procedure proposed by Kiselev and co-workers, and it is based on the renormalization of a Landau expansion originally proposed by Chen *et al.* [9]. The second method is a recursive procedure developed by White and co-workers [19–22], which is an extension of the work of Wilson [6], as explained in the previous section. In the next subsections, we describe in detail the application of the two *RG* methods to obtain two different Crossover *SRK EoS*.

Kiselev's method

To apply Kiselev's method to an *EoS*, one must first rewrite the classical expression for the Helmholtz free energy in the dimensionless form, as given by:

$$\bar{A}(T, v) = \Delta\bar{A}(\bar{\tau}, \bar{\eta}) + \bar{A}^{res}(T, v_{0c}) - \bar{\eta}\bar{P}_0(T) - \ln v_{0c} + \bar{A}_0(T) - K(\tau, \eta) \quad (5)$$

where $\bar{A}(T, v) = \frac{A(T, v)}{RT}$ is the total dimensionless Helmholtz energy, $\bar{P}_0(T) = P(T, v_{0c})v_{0c}/RT$ is the dimensionless pressure at the critical isochore, v_{0c} is the classical critical volume, $\bar{A}_0(T)$ is the dimensionless temperature dependent part of Helmholtz free energy for an ideal gas, and $K(\tau, \eta)$ is the Kernel term, which is used to provide the correct representation of the isochoric heat capacity. The critical Helmholtz energy, $\Delta\bar{A}(\bar{\tau}, \bar{\eta})$, is given by:

$$\Delta\bar{A}(\bar{\tau}, \bar{\eta}) = \bar{A}^{res}(\bar{T}, \bar{v}) - \bar{A}^{res}(\bar{T}, v_{0c}) + \bar{\eta}\bar{P}_0(\bar{T}) - \ln(\bar{\eta} + 1) \quad (6)$$

and $\bar{A}^{res}$ is the residual part of Helmholtz free energy which is a function of the renormalized temperature and volume, i.e. $\bar{T} = T_{0c}(1 + \bar{\tau})$ and $\bar{v} = v_{0c}(1 + \bar{\eta})$, and are calculated by the expressions:

$$\bar{\tau} = \tau Y^{\left(-\frac{\alpha}{2\Delta}\right)} + (1 + \tau)\Delta\tau_c Y^{\left(\frac{2(2-\alpha)}{3\Delta}\right)} \quad (7)$$

$$\bar{\eta} = \eta Y^{\left(\frac{\gamma-2\beta}{4\Delta}\right)} + (1 + \eta)\Delta\eta_c Y^{\left(\frac{2-\alpha}{2\Delta}\right)} \quad (8)$$

where, $\gamma = 1.24$, $\beta = 0.325$, $\alpha = 2 - \gamma - 2\beta = 0.110$ and $\Delta = 0.51$ are the universal non-classical critical exponents and T_{0c} is the classical critical temperature. The terms $\Delta\tau_c = (T_c/T_{0c} - 1)$ and $\Delta\eta_c = (v_c/v_{0c} - 1)$ are the dimensionless shifts of the critical parameters, while $\tau = T/T_c - 1$ and $\eta = v/v_c - 1$ are the dimensionless distance from the real critical temperature and volume (T_c and v_c), respectively.

The function $Y(q)$ plays an important role in the crossover EoS , and it is related to the parametric variable q , which represents the distance from the critical point. These two terms are calculated as the following:

$$Y(q) = \left(\frac{q}{1+q}\right)^{2\Delta} \quad (9)$$

$$\left(q^2 - \frac{\tau}{Gi}\right) \left[1 - \frac{p^2}{4b^2} \left(1 - \frac{\tau}{q^2 Gi}\right)\right] = \left\{ \frac{b(\eta(1 + v_1 e^{-10\eta}) + d_1 \tau)}{m_0 Gi^\beta} \right\}^2 Y^{(1-2\beta)/\Delta} \quad (10)$$

where Gi is the Ginzburg number, v_1 and d_1 are the system dependent parameters, p^2 and b^2 can be set equal the universal linear model parameter $p^2 = b^2 \cong 1.359$, and to reduce the number of adjustable parameters, m_0 is considered as a universal parameter equal to one.

Finally, the Kernel term is defined as:

$$K(\tau, \eta) = \frac{1}{2} a_{20} \tau^2 \left[Y^{-\frac{\alpha}{\Delta}} - 1 \right] + \frac{1}{2} a_{21} \tau^2 \left[Y^{-\frac{(\alpha-\Delta)}{\Delta}} - 1 \right] \quad (11)$$

where the coefficients a_{20} and a_{21} are calculated along the critical isochore at $\tau > 0$. The Kernel term is responsible for the divergent behavior of the isochoric heat capacity [25].

The crossover $SRK EoS$ using Kiselev's method is obtained by applying Eq. (1) to obtain Eq. (6), then the pressure explicit equation is obtained by differentiation of Eq. (6) with respect to volume, yielding:

$$P = - \left(\frac{\partial A}{\partial v} \right)_T = - \frac{RT}{v_c} \left(\frac{\partial \Delta \bar{A}(\bar{v}, \bar{\eta})}{\partial \eta} \right)_T + \bar{P}_0(T) - v_{0c}^{-1} \left(\frac{\partial K}{\partial \eta} \right)_T \quad (12)$$

The details of this crossover procedure can be found in the references [13,14].

White's method

One of the first authors to apply White's recursive procedure to a cubic EoS were Cai and Prausnitz [26], who have used the $SRK EoS$ as the underlying model to which the density fluctuations are

introduced. The recursive procedure for a pure fluid concerns of correcting the classical free energy density in the following way:

$$f = f_n - \alpha \rho^2 \quad (13)$$

$$f_n = f_{n-1} + \delta f_n \quad (14)$$

$$\delta f_n = -K_n \ln \left(\frac{\Omega_n^s}{\Omega_n^l} \right) \quad (15)$$

$$K_n = \frac{k_b T}{2^{3n} L^3} \quad (16)$$

$$\Omega_n^\lambda = \int_0^{\min(\rho, \rho_{max} - \rho)} \exp \left[-\frac{G_n^\lambda(\rho, y)}{K_n} \right] dy \quad (17)$$

$$G_n^\lambda = 0.5 [\overline{f_n^\lambda}(\rho + y) + \overline{f_n^\lambda}(\rho - y) - 2\overline{f_n^\lambda}(\rho)] \quad (18)$$

$$\overline{f_n^l} = f_{n-1} + \alpha \rho^2 \quad (19)$$

$$\overline{f_n^s} = f_{n-1} + \alpha \rho^2 \frac{\phi}{2^{2n}} \quad (20)$$

where the subscript n and the superscript λ represent the step in the recursive procedure and the long-range (l) and short-range (s) correlations, respectively; k_b is the Boltzmann constant, T is the temperature, α is a term related to the attractive Helmholtz energy density, ρ is the density, ρ_{max} is the maximum packing density in this work approximated to 0.999 b^{-1} , L and ϕ are parameters of the recursive procedure and represent the cut-off length and a function of the initial shortest wavelength of density fluctuations.

White's recursive procedure starts with the free energy density containing only the repulsive, *i.e.* short-range interactions, between the molecules, meaning that in the first step $f_0 = f_{rep}$. However, according to Cai and Prausnitz [26], the separation of the attractive and repulsive interactions in a phenomenological model like the *SRK EoS* is not clear. In other words, the first term on the right-hand side of Eq. (1) is not equivalent to the hard-sphere model [27]. Therefore,

the authors used experimental data to fit RG calculations, concluding that the attractive part of the free energy ($\alpha\rho^2$) corresponds to approximately:

$$-\alpha\rho^2 = -\frac{1}{2}a\rho^2 \quad (21)$$

where a is the attractive term constant of the SRK model calculated by Eq. (2). Consequently, the repulsive free energy density is given by f_{SRK} , *i.e.* the free energy density estimated with Eq. (1), subtracting the attractive contributions, which yields:

$$f_0 = f_{SRK} + \frac{1}{2}a\rho^2 \quad (22)$$

One of the limitations of the procedure adopted by Cai and Prausnitz [26], in order to accommodate the phenomenological character of the SRK EoS , is that the short-range correlation is not achieving its final form as n goes to infinity. It means that not all shortwave lengths are incorporated into the crossover equation, which limits the capacity of the model to represent properties like the heat capacity at constant volume and other weakly divergent thermodynamic properties, which mean-field models are unable to correctly describe [25]. This can be seen by substituting Eqs. (21) and (22) in the recursive procedure given by Eqs. (13) to (20). In the first step the corrected free energy densities are equal to:

$$\overline{f}_1^l = f_{SRK} + a\rho^2 \quad (23)$$

$$\overline{f}_1^s = f_{SRK} + \frac{1}{2}a\rho^2\left(1 + \frac{\phi}{2^2}\right) \quad (24)$$

After n iterations the values of the previous functions are:

$$\overline{f}_n^l = f_{SRK} + a\rho^2 + \sum \delta f_n \quad (25)$$

$$\overline{f}_n^s = f_{SRK} + \frac{1}{2}a\rho^2\left(1 + \frac{\phi}{2^{2n}}\right) + \sum \delta f_n \quad (26)$$

where we have used the expression $f_n = f_0 + \sum \delta f_n$ [21] to obtain the corrected short and long-range densities, *i.e.* Eqs. (25) and (26), at the final summand of the recursive procedure the n^{th}

order summation. This expression is defined by a simple manipulation of the recursive procedure given by Eq. (12) and it indicates that n^{th} order approximation to the free energy density is the sum of the initial free energy density and a sequence of the fluctuation contributions up to the order n .

The analysis of Eq. (24) shows that as $n \rightarrow \infty$, the term $\frac{\phi}{2^{2n}}$ becomes negligible; yet, an attraction contribution is still present in the short-range part of the free energy density. This limits the incorporation of increasingly longer wavelength density fluctuations as the order is increased, because an attractive term is added to Ω_n^s and $\frac{\Omega_n^s}{\Omega_n^l}$ in Eq. (15), which represents the ratio of non-mean-field contributions to mean field contributions, does not yield the full free energy density correction (δf_n), obtained from the recursion relations in the infinite order limit.

In order to correct this limitation, we defined $f_0 = f_{SRK}$ and the attractive part of the recursive procedure, *i.e.* $a\rho^2$, equal to $a\rho^2$. With these modifications, the corrected free energy densities, in the first step of the recursive procedure, are equal to:

$$\overline{f}_1^l = f_{SRK} + a\rho^2 \quad (27)$$

$$\overline{f}_1^s = f_{SRK} + a\rho^2 \frac{\phi}{2^2} \quad (28)$$

After n summands the values of the previous functions are:

$$\overline{f}_n^l = f_{SRK} + a\rho^2 + \sum \delta f_n \quad (29)$$

$$\overline{f}_n^s = f_{SRK} + a\rho^2 \frac{\phi}{2^{2n}} + \sum \delta f_n \quad (30)$$

The rest of the procedure is similar to the one developed by Cai and Prausnitz [26], and is given by Eqs. (13) to (18).

The comparison of Eqs. (23) and (24) with (27) and (28) indicates the modified procedure is similar for the long-range correction term of the free energy, but differs for the short-range

contributions, allowing the complete introduction of the density fluctuations and improving the representation of the properties that have a weak divergence at the critical point. In fact, this procedure is the same as the one used in *SAFT* implementations of White's recursive procedure [8,28] and it is similar to White's original development [18–20,22]. The difference is related to the interpretation of the critical phenomena.

In White's original method, L is defined as the cutoff length separating the repulsive and attractive contributions of the free energy, and $-a\rho^2$ is an approximation of the attractive interaction. In the usual *SAFT* implementation, L separates the mean-field and non-mean-field part of the free energy density, hence it is assumed that the initial f_0 , calculated with a *EoS* accurately describes the behavior of a system far away from the critical point. Apart from the differences in the interpretation, both approaches yield similar equations for the corrected free energy densities as described by Forte *et al* [28,29].

The application of the crossover *SRK* using White's procedure to represent the thermodynamic properties of fluids requires the numerical solution of the total free energy of the system. This is done by dividing the density range of the fluid in a pre-defined number of intervals. Following other works [21–23], we used 500 density points, from $\rho = \frac{10^{-12}}{b}$ to $\rho = \frac{1}{0.999b}$. Besides, a spline function is used to estimate $f(\rho)$ and five iterations were used in the numerical procedure for both procedures of White's method for most of the calculations performed in this work.

PARAMETRIZATION OF THE CROSSOVER *EOS*

In a previous work [30], we have thoroughly described the parametrization of the crossover *EoS* mentioned previously for the representation of the phase equilibria of pure n-alkanes (from methane to n-decane). In the case of White's procedure, we have kept the classical parameters that

were tuned to match the pure components' vapor pressure and liquid and vapor density curves both far away from and close to the critical point, i.e. the classical critical pressure (P_{0c}), temperature (T_{0c}) and acentric factor (ω_0). Nonetheless we have changed the value of the cutoff length (L), due to the modification of the recursive procedure as mentioned in the previous section. Although no significant changes are seen far from the critical point since the density fluctuations are negligible, the inclusion of additional short-range fluctuations requires refitting L for a correct description of the critical region. In fact, the values for the cutoff length are larger than the ones obtained previously, but follow a similar trend (Table 1 and Fig. 1). The crossover *SRK EoS* using the recursive procedure similar to Cai and Praunitz [26] is referred to as *CSRK* while the model using the modified procedure developed in this work is referred to as *CSRK2*.

Table 1. The values of the crossover parameters for the crossover *SRK EoS* using White's modified procedure (*CSRK2*) for the selected n-alkanes.

Comp.	$T_{0c}(K)$	$P_{0c}(\text{bar})$	$\omega_0(-)$	$L(\text{\AA})$	$\phi(-)$
C ₁	197.7	49.88	-0.049	6.454	2.000
C ₂	317.1	54.75	0.033	6.932	2.000
C ₃	383.3	47.65	0.086	7.575	2.000
C ₄	441.4	43.00	0.128	8.139	2.000
C ₅	488.0	38.63	0.174	8.431	2.000
C ₆	527.1	35.08	0.221	8.775	2.000
C ₇	560.5	32.10	0.271	9.052	2.000
C ₈	591.0	29.83	0.315	9.174	2.000
C ₉	618.4	27.58	0.354	9.504	2.000
C ₁₀	639.4	25.50	0.411	9.876	2.000

Fig. 1. Cut-off length for the crossover *SRK EoS* using White's procedure as a function of the molecular weight for selected n-alkanes. The blue triangles represents the optimum values with the approach given in [30] and the red circles are the ones obtained in this work.

On the other hand, the vapor pressure and coexistence diagrams are similar showing that for phase equilibrium calculations, the modified procedure does not substantially modify the representation of the experimental data (Fig. 2). Nevertheless, the same is not valid for the derivative properties, which will be addressed in the next section.

Fig. 2. Critical isotherm (a) and coexistence diagram (b) of ethane calculated with *SRK* and two versions of the crossover *SRK* using White's approach.

In the case of Kiselev's method, the procedure is similar to the one described in the previous work; however, we have added the Kernel term to improve the results for the derivative properties. This is an additive renormalization term given in Eq. (6), responsible for the divergent behavior of the isochoric heat capacity [25,31]. As seen in Eq. (11), it has two additional parameters, a_{20} and a_{21} , which are defined by fitting the critical isochore of the pure fluid. Table 2 shows the values of these parameters for the n-alkanes studied in this work. After the parametrization procedure, we have applied the models to describe some derivative properties and compared the crossover models with the classical *SRK EoS*, as well as experimental data.

Table 2. Kernel term parameters for the crossover SRK EoS using Kiselev’s method in Eq. (11) along the critical isochore in the selected temperature range.

Compound	T-range (K)	V(cm ³ /mol)	Parameters		AAD%
			a_{20}	a_{21}	C_v
C1	191-220	98.600	32.459	7.810	5.08
C2	306-350	145.56	25.930	5.372	4.25
C3	370-440	200.00	11.997	1.674	3.56
C4	426-480	254.92	21.557	3.782	1.60
C5	470-520	310.98	7.3640	-1.609	1.20
C6	508-540	369.56	2.6350	-3.428	0.29
C7	542-580	431.91	4.4420	-2.716	0.26
C8	570-600	486.29	3.1060	-3.001	0.13
C10	619-650	609.78	-5.8750	-6.764	0.15

RESULTS AND DISCUSSION

In order to evaluate the capability of the crossover *EoS* described previously to represent the derivative properties of selected hydrocarbons (methane to n-decane). These compounds have been chosen because they are normally used as a benchmark for studying the accuracy of the *EoS* [29]. Additionally, several crossover *EoS* have been applied in the literature to represent the derivative properties as a measure of the capability of the thermodynamic model [28,31–36]; nonetheless, there is a lack of direct comparison between the main *RG* approaches.

The models mentioned in Section 2 were applied to describe the heat capacities at constant pressures (C_p) for the substances shown in Tables 1 and 2. Due to the strong divergence of this property, it is expected that a classical *EoS* is able to reasonably describe the experimental data, although yielding incorrect critical exponents. This behavior is seen in Fig. 3, which shows the dimensionless residual C_p (C_p^{res}/R) at the critical volume and the temperatures greater than T_c for n-butane. It is also possible to observe that the classical model slightly overpredicts the

experimental data for the saturated liquid phase, while it underpredicts the points for the saturated vapor phase and the supercritical fluid.

Fig. 3. The correlated experimental C_p^{res}/R for n-butane taken from [23], and the calculated curves using *SRK EoS*. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

In an attempt to evaluate the improvements obtained with the introduction of the density fluctuations in the classical model, we have applied the crossover *SRK EoS*, using both White and Kiselev's approach to describe C_p^{res}/R of n-butane. Fig. 4 shows the results obtained using two approaches of the recursive method to incorporate density fluctuations in the classical model. The comparison of Figs. 3 and 4 indicates that *RG* corrections of the *SRK EoS* do not substantially improve the representation of experimental C_p . Additionally, both approaches of the recursive method yield similar results. Finally, the crossover *SRK EoS* using Kiselev's method was applied for the representation of the same data (Fig. 5). This non-mean-field model also yields to analogous estimations for C_p^{res}/R ; however, this method has less accuracy than the classical *SRK EoS* and both approaches of recursive method by approaching to the critical region.

Fig. 4. The correlated experimental C_p^{res}/R for n-butane taken from [23], as well as the calculated curves using the crossover *SRK EoS* with the two approaches of the White's procedure. The dashed and solid lines correspond to *CSRK* and *CSRK2*, respectively. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

In addition to calculations of C_p^{res}/R at the critical volume, we have applied the aforementioned models to calculate the same property at different pressures close to the critical point. Fig. 6 contains the calculated curves using the mean-field *SRK EoS* and the non-mean-field model with Kiselev's method. It is possible to observe from the figure that both models yield alike results and are capable of describing this property close to the critical point. The same behavior is seen with the application of White's method (Fig. 7); nonetheless, as the critical point is slightly modified, a shift of the curves is observed, especially for the heavier hydrocarbon. In fact, this difference is related to the parametrization procedure, which, as discussed in a previous paper [30], is done by fitting of the saturated pressure, liquid and vapor phase volume curves, and *PVT* data at the critical isotherm. Finally, Table 3 shows the average absolute deviations (*AAD%*) of the molar heat

capacity (C_p). In this case, the low $AAD\%$ of the classical model (Table 3) is a direct consequence of the ideal C_p correlation, which corresponds to a large amount of the C_p of a substance [30].

Fig. 5. The correlated experimental C_p^{res}/R for n-butane taken from [23], as well as the calculated curves using Kiselev's method to correct SRK . The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

Table 3. Calculated deviations for the molar heat capacity at constant pressure (C_p) for different pressures using different crossover methods applied on SRK EoS in comparison to classical SRK EoS .

Compound	P (MPa)	AAD% SRK	AAD% Kiselev's method	AAD% White's method CSRK	AAD% White's method CSRK2	T-range (K)
C1	4.5992	8.00	2.8	4.1	3.4	170-240
	4.8	8.2	3.6	11.4	4.6	
	5.1	8.0	4.4	3.6	3.8	
	5.4	8.0	5.4	3.9	3.9	
C2	4.8718	10.4	14.5	4.0	6.8	280-350
	5.0	10.9	6.2	5.8	7.7	
	5.3	10.6	4.8	6.5	8.4	
	5.6	10.7	5.6	7.2	8.1	
C3	4.2476	6.8	4.3	3.4	10.8	350-440
	4.5	6.9	2.9	11.0	15.0	
	4.8	7.2	3.4	5.4	13.1	
	5.1	7.3	3.9	6.2	11.4	
C4	3.7960	8.1	2.1	10.0	13.4	400-480
	4.0	8.2	3.4	10.4	22.6	
	4.3	8.3	4.8	9.3	17.4	
	4.6	3.8	5.3	9.0	14.5	
C5	3.37	8.3	4.2	9.3	16.1	450-520
	4.0	8.9	6.4	10.1	19.3	
	4.3	8.9	7.5	10.0	16.2	
	4.6	8.8	8.3	9.7	13.8	
C6	3.034	9.3	7.2	16.3	21.4	480-540
	3.3	9.5	6.0	16.4	32.4	
	3.6	9.5	7.5	14.6	25.1	
	3.9	9.2	8.8	12.9	19.4	
C7	2.7360	8.5	2.6	13.4	27.6	530-580
	3.0	9.0	4.9	16.6	35.0	
	3.3	9.0	6.0	14.8	27.6	
	3.6	8.6	7.0	13.4	21.5	
C8	2.497	9.5	3.3	13.6	25.0	550-600
	2.7	9.6	4.7	18.2	38.4	
	3.0	9.4	5.2	15.0	29.1	
	3.3	8.4	5.9	12.2	20.7	
C10	2.103	11.4	4.5	15.4	21.6	590-650
	2.4	11.3	7.6	19.6	32.9	
	2.7	10.7	8.9	33.3	24.2	
	3.0	8.6	7.8	21.8	16.3	
Average		8.8	5.6	11.6	18.0	

*Average Absolute Deviation ($AAD\% = (1/n) \left(\sum |X^{calc} - X^{exp}| / X^{exp} \right) * 100$)

Table 4. Calculated deviations for the molar heat capacity at constant volume (C_v) for different pressures using different crossover methods applied on *SRK EoS* in comparison to classical *SRK EoS*.

Compound	P (MPa)	AAD% SRK	AAD% Kiselev's method	AAD% White's method CSRK	AAD% White's method CSRK2	T-range (K)
C1	4.5992	6.9	4.7	7.1	5.6	170-240
	4.8	7.5	5.7	7.7	6.1	
	5.1	7.6	7.1	7.8	6.1	
	5.4	7.5	7.9	7.8	6.0	
C2	4.8718	6.8	4.2	6.7	5.1	280-350
	5.0	7.0	4.1	7.1	5.3	
	5.3	7.3	4.8	7.2	5.4	
	5.6	7.3	5.7	7.2	5.5	
C3	4.2476	4.3	2.0	4.7	3.7	350-440
	4.5	4.6	2.0	5.1	3.9	
	4.8	4.6	2.1	5.0	3.9	
	5.1	4.4	2.3	4.9	3.8	
C4	3.7960	3.4	1.3	3.6	2.9	400-480
	4.0	3.6	1.9	3.8	2.9	
	4.3	3.6	2.5	3.7	2.8	
	4.6	1.4	1.0	3.6	2.7	
C5	3.37	2.9	1.5	3.1	2.4	450-520
	4.0	3.1	2.7	3.3	2.4	
	4.3	3.0	2.8	3.2	2.4	
	4.6	2.8	2.7	2.9	2.2	
C6	3.034	2.8	1.5	2.8	2.2	480-540
	3.3	2.8	2.2	2.8	2.2	
	3.6	2.7	2.5	2.7	1.9	
	3.9	2.4	2.4	2.4	1.8	
C7	2.7360	2.6	0.7	3.3	2.6	530-580
	3.0	2.5	1.4	3.3	2.4	
	3.3	2.3	1.7	3.0	2.0	
	3.6	2.1	1.7	2.6	1.7	
C8	2.497	2.5	1.7	2.9	2.1	550-600
	2.7	2.4	1.8	2.9	2.0	
	3.0	2.1	1.8	2.5	1.6	
	3.3	1.7	1.8	2.0	1.3	
C10	2.103	2.4	0.9	2.7	2.3	590-650
	2.4	2.3	1.5	2.6	1.9	
	2.7	1.9	1.5	2.5	1.5	
	3.0	1.4	1.4	1.8	1.1	
Average		3.8	2.7	4.1	3.1

Fig. 6. The correlated experimental C_p^{res}/R for n-butane at the pressures shown in Table 3 taken from [23]. The dashed lines correspond to the classical *SRK EoS* and the solid lines to the crossover model with Kiselev's method.

Following the representation of C_p , we have applied the models to represent C_v . The latter property has a weak divergence at the critical point, which classical models are usually unable to correctly represent. In fact, the heat capacity at constant volume does not diverge in the mean-field approximation. Unlike C_p , which as a function of the isothermal compressibility, shows strong divergence caused by the long-range interactions between the particles of the system, the internal energy and its derivatives are determined by the short-range behavior of the short-range nature of the intermolecular potential [25]. Fig. 8 shows the dimensionless residual heat capacity at constant volume (C_v^{res}/R) for n-butane. The plot indicates that the model is unable to represent the divergence of the property close to the critical point.

Fig. 7. The correlated experimental C_p^{res}/R for n-butane at the pressures shown in Table 3 taken from [23]. The dashed and solid lines correspond to *CSRK* and *CSRK2*, respectively.

Fig. 8. The correlated experimental C_v^{res}/R for n-butane taken from [23], as well as the calculated curves using *SRK*. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

The same behavior is observed for *CSRK* (Fig. 9). Due to the addition of an attractive term on the short-range correction of the free energy density in the recursive procedure (Eqs. 22 and 24), which limits the incorporation of short wavelengths in the classical model, the representation of C_v^{res} is similar to the classical model. However, this limitation is corrected with the modified recursive procedure, yielding a superior representation of this property (Fig. 10).

Fig. 9. The correlated experimental C_v^{res}/R for n-butane taken from [23], as well as the calculated curves using *CSRK*. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

The calculations of the dimensionless residual C_v were also done with the crossover *SRK EoS* using Kiselev's method. Fig. 11 shows the experimental values and the calculated curves, indicating that this equation is also capable of representing the weak divergence of this property.

Fig. 10. The correlated experimental C_v^{res}/R for n-butane taken from [23], as well as the calculated curves using *CSRK2*. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

Fig. 11. The correlated experimental C_v^{res}/R for n-butane taken from [23], as well as the calculated curves using *SRK* with Kiselev's method. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

As previously done for C_p , we have applied the models to describe C_v for different pressures close to the critical point. A summary of the main results of C_v obtained with the crossover *EoS* and the classical *SRK EoS* is provided in Table 4 where *AAD%* is presented for selected constant pressures. Fig. 12 shows the results for the mean-field model and the non-mean-field model using Kiselev's method. It shows that the crossover equation corrects the behavior of the classical *SRK EoS* not only for the critical point, but also improves the description of the property below and above this point. This is due to the Kernel term, which provides the correct representation of the weak divergence. It is important to note that the classical model has an impact on the crossover *SRK* based on Kiselev's method. The figure indicates a descending trend below the critical temperature, which is intensified by the increase of pressure and carbon number of the hydrocarbon. This unphysical behavior is a limitation of the crossover *SRK EoS* based on Kiselev's approach to describe C_v^{res}/R at constant pressure in the asymptotic critical temperature range.

The crossover *SRK EoS* using White's method was also applied in the previous calculations. As expected, the approach similar to that of Cai and Prausnitz [26] is incapable of describing the weak divergence and the results are similar to the classical model, while the modified procedure is capable of representing the divergence (Fig. 13). Nevertheless, the comparison of this method with Kiselev's indicates that the Kernel term yields a superior description of this property, as it allows a correct description of the trend of the experimental data below the critical point. This behavior was also observed in other works using the crossover *SAFT-VR* [28] and *Soft-SAFT* [8] with the recursive procedure to include density fluctuations in the classical *EoS*. In both cases, the agreement for C_v was not as accurate as the other properties, since the Kernel term was not applied to represent the weakly divergent behavior of the property.

Fig. 12. Experimental C_v^{res}/R for n-butane at the pressures shown in Table 4 taken from [23]. The dashed lines correspond to the classical *SRK EoS* and the solid lines to the crossover model with Kiselev's method.

Fig. 13. Experimental C_v^{res}/R for n-butane at the pressures shown in Table 4 taken from [23]. The dashed and solid lines correspond to *CSRK* and *CSRK2*, respectively.

A final test of the models for the representation of the heat capacity at constant volume was made by comparing the results of C_v^{res}/R along the critical density at different reduced temperatures for n-butane (Fig. 14). The plot is given in terms of the reduced temperatures to facilitate the comparison of the models, as the simulated critical temperature using White's method deviates slightly from the experimental one, and to evaluate whether the crossover *EoSs* are capable of capturing the divergence at the critical temperature [32]. Fig.14 clearly shows that the second approach of recursive procedure (*CSRK2*) possesses a non-mean-field behavior. Moreover, the *AAD%* between the simulated C_v and the correlated supercritical data [23] is almost half of the first method, i.e. 5.26% and 10.15%, respectively. In addition, Fig. 14 also depicts the capability of the crossover *SRK EoS* based on Kiselev's approach to reproduce the divergence of C_v^{res}/R at the critical temperature. The calculated values of C_v^{res}/R along the critical density for n-butane show satisfactory agreement with the correlated experimental data and the *AAD%* for this isochore is 1.60%. The comparison of the crossover *EoS* using Kiselev's approach and the second approach of the recursive procedure indicates that the Kernel term is important to describe the asymptotic behavior of C_v^{res}/R near the critical region.

Finally, we applied the models to represent the speed of sound (V_s) of the selected hydrocarbons studied in this work. This property is related to both types of heat capacity and its correct representation is important in several processes [25]. Since the classical model is not capable of describing the weak divergence related to the heat capacity at constant volume, it is expected some inferior results for the representation of the speed of sound in comparison to the crossover procedures.

Fig. 14. Experimental C_v^{res}/R for n-butane at different reduced temperatures along the critical density close to the critical point. The blue, green and red lines correspond to *CSRK*, *CSRK2* and Kiselev's approach, respectively. The correlated experimental data was taken from [23].

Fig. 15. The correlated experimental V_s for n-butane taken from [23], as well as the calculated curves using the *SRK EoS*. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

Fig. 15 shows the experimental data for the speed of sound of n-butane and the results obtained with the classical *SRK EoS*. The comparison of the predicted curves with the experimental data shows that the larger deviations occur at the critical point, which is related to the limitation of the model to represent the weak divergence of the specific heat capacity at constant volume. The same behavior is observed when the first approach of the recursive procedure is applied to incorporate the density fluctuations into the classical *EoS* (Fig. 16). On the other hand, the second approach improves the results, yielding better agreement near the critical point. The same is observed when Kiselev's method is applied (Fig.17).

Fig. 16. The correlated experimental V_s for n-butane taken from [23], as well as the calculated curves using the crossover *SRK EoS* with both approaches of the recursive procedure. The dashed and solid lines correspond to *CSRK* and *CSRK2*, respectively. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

The comparison of the crossover *EoS* using Kiselev's method and the second approach of the recursive procedure indicates that the Kernel term is important for correcting the classical model

in the critical region. Fig. 17 shows a positive deviation of C_v^{res}/R , while there is a negative deviation when the other equations are applied.

Fig. 17. The correlated experimental V_s for n-butane taken from [23], as well as the calculated curves using the crossover *SRK EoS* with Kiselev's method. The red and green lines and points represent the saturated vapor and liquid phases, respectively, while the blue lines and points describe the supercritical fluid at the critical volume.

Following the previous calculations, we applied the models to describe V_s of the properties for different pressures close to the critical point. Fig. 18 shows the comparison between the classical *SRK* and the corrected model using Kiselev's method. Although the results are similar for supercritical conditions, superior results are obtained with the crossover model at the critical point and for the saturated liquid phase. On the other hand, the comparison of the mean-field model with the crossover *SRK* using White's method (Fig. 19) indicates that the second approach yields similar results at the critical point, but is inferior to the other *RG* method for the description of the property in subcritical conditions. According to the summary of the main results of V_s obtained with the crossover *EoSs* and the classical *SRK EoS* reported in Table 5, the importance of the Kernel term

to incorporate the short wavelength fluctuations not only at the divergence but also close to the critical point can be reflected [25].

Fig. 18. Experimental V_s at different pressures shown in Table 4 close to the critical point of n-butane, as well as the calculated curves using the classical *SRK EoS* (dash lines) and the model corrected with Kiselev’s method (solid lines). The correlated experimental data was taken from [23].

Fig. 19. Experimental V_s at different pressures shown in Table 4 close to the critical point of n-butane, as well as the calculated curves using the crossover *SRK EoS* with two approaches of

White's method. The dashed and solid lines correspond to *CSRK* and *CSRK2*, respectively. The correlated experimental data was taken from [23].

Table 5. Calculated deviations for *V_s* at constant pressures using different crossover methods applied on *SRK EoS* in compare to classical *SRK EoS*.

Compound	P (MPa)	AAD% SRK	AAD% Kiselev's method	AAD% White's method CSRK	AAD% White's method CSRK2	T-range (K)
C1	4.5992	5.7	4.9	4.0	3.8	170-240
	4.8	6.6	5.6	5.1	4.6	
	5.1	7.2	6.0	5.4	4.8	
	5.4	7.6	6.5	5.7	5.2	
C2	4.8718	6.7	2.6	4.9	4.8	280-350
	5.0	7.1	3.3	5.3	5.2	
	5.3	8.4	4.3	5.9	5.9	
	5.6	9.1	4.5	6.4	6.5	
C3	4.2476	4.7	3.9	3.4	4.2	350-440
	4.5	5.9	2.7	3.5	5.1	
	4.8	6.8	2.8	4.1	5.8	
	5.1	7.6	2.9	4.5	6.2	
C4	3.7960	5.9	6.8	4.0	7.7	400-480
	4.0	7.1	7.0	4.4	8.6	
	4.3	8.4	7.6	5.2	9.3	
	4.6	7.2	2.7	6.2	9.5	
C5	3.37	5.5	8.2	3.5	8.3	450-520
	4.0	9.3	9.4	5.6	11.1	
	4.3	10.5	9.1	7.2	11.4	
	4.6	11.3	8.2	8.4	11.4	
C6	3.034	7.9	11.7	5.8	14.4	480-540
	3.3	10.1	11.8	7.5	16.5	
	3.6	11.8	11.4	9.6	16.6	
	3.9	12.7	9.6	10.9	15.6	
C7	2.7360	7.0	10.8	1.7	12.2	530-580
	3.0	9.2	11.4	3.4	15.6	
	3.3	11.0	11.4	5.9	15.8	
	3.6	11.9	9.8	7.7	14.6	
C8	2.497	7.5	10.7	2.8	15.8	550-600
	2.7	9.6	11.2	4.1	18.9	
	3.0	11.4	11.5	6.2	18.6	
	3.3	11.4	10.1	7.2	15.9	

C10	2.103	7.5	10.7	3.8	16.4	590-650
	2.4	9.6	11.2	6.6	20.5	
	2.7	11.4	11.5	20.3	19.4	
	3.0	11.4	10.1	17.2	15.9	
Average		8.7	7.9	6.2	11.2	

The calculation of the critical exponent is an important test to evaluate the behavior of the *EoS*, as the mean-field models are unable to predict the correct values of the universal critical exponents. In this work, we focus on the estimation of the exponent α using the following expression:

$$\ln(C_v) = -\alpha \ln(\Delta T) + b \tag{31}$$

where α is the slope of the linear regression of the natural logarithm of C_v as a function of ΔT , which is $|T - T_c|/T_c$. Along the critical isochore, C_v asymptotically behaves proportionally to $\Delta T^{-\alpha}$, and the universal value of α is equal to approximately 0.11 [25]. On the other hand, the mean-field approximation predicts a value equal to 0 for this exponent.

Fig. 20 shows the critical exponent α calculated in the temperature range between $0.98 T_c$ and T_c with both crossover methods. It is possible to observe that *CSRK1* yields the classical value, while α simulated with *CSRK2* is close to the universal value. As explained previously, the critical behavior of the heat capacity at constant volume is determined by short-range interactions, hence the addition of the long-range term in *CSRK1* limits the incorporation of longer wavelength density fluctuations resulting in a critical exponent similar to the classical one. It is important to note that increasing the summand order does not modify this behavior. Besides, Kiselev's model cannot represent the divergent behavior of the isochoric heat capacity only based on the rescaling of the physical variables. In fact, it contains the Kernel term, an additive term related to the divergent behavior of C_v at the critical isochore, which normally improves the results for exponent α [9].

Fig. 20. Natural logarithm of the heat capacity at constant volume as a function of the dimensionless temperature distance for n-butane determined with the *CSRK1* (green triangles), *CSRK2* (blue squares) and Kiselev's (red circles) models. Critical exponent α is calculated from the slope of the linear regression of each model (solid lines).

In order to show the effect of the number of iterations in the representation of the derivative properties, a plot of C_p^{res}/R and C_v^{res}/R at the critical pressure is given in Fig. 21. The difference between the curves is marginal, as the corrections of the energy density after 5 iterations are marginal. Nonetheless, a small improvement is seen for C_p^{res}/R in comparison to C_v^{res}/R . This behavior is related to the fact that C_v is determined by the short-range interactions which are limited in *CSRK1*.

Fig. 21. The correlated experimental C_v^{res}/R (a and b) and C_p^{res}/R (c and d) for n-butane at critical pressure taken from [23]. Figures (a) and (c) show the calculated curves using $CSRK1$, while figures (b) and (d) are the results obtained with $CSRK2$, using 5 (solid lines) and 7 (dashed lines) iterations for the calculation of the free energy density function in White's procedure.

CONCLUSIONS

In this work, we applied two different methods to correct the classical *SRK EoS* for improving the representation of derivative properties in the critical region. First we used a procedure based on the Landau-Ginzburg expansion developed by Kiselev and co-workers [13–16,32,37]. Then we have used two different approaches based on White's recursive procedure. In both cases it was possible to observe an improvement of the results due to the incorporation of density fluctuations into the mean-field equation. Although the improvements are not substantial for the overall *AAD%* in comparison to the classical model, a superior description of the qualitative behavior of the derivative properties, specially for the isochoric heat capacity, is observed.

We have also shown that the procedure developed by Cai and Prausnitz [26] limits the introduction of short wavelengths, which hinders the description of the properties related to the weak divergence at the critical point, like the molar heat capacity at constant volume and the speed of sound. This behavior can be corrected by modifying the procedure in a way similar to that is used by many implementations in *SAFT-type EoS* [28,29].

The models were then used to describe the heat capacity at constant pressure and volume, as well as the speed of sound for selected n-alkanes. The comparison of the equations with experimental data showed that the crossover models yield similar results to the mean-field one for C_p^{res} due to the strong divergence of this property. On the other hand, in the case of C_v^{res} , only the non-mean-field models based on Kiselev's and the second approach of White's recursive procedure were capable of predicting the weak divergence related to this property. This is the reason the non-mean-field models are also superior in the description of the speed of sound.

Finally, the comparison of White's and Kiselev's method indicates that the Kernel term is important for describing the C_v^{res} and the speed of sound close to and far away from the critical

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3 region, since, although the crossover *SRK EoS* using White’s procedure is capable of capturing the
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5 divergence of the property at the critical point, the mean-field model using Kiselev’s method has
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7 a superior match regarding the trend of data in sub-critical conditions.
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