Development and application of a three-parameter RK–PR equation of state

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Abstract

In this work, we confirm the somehow previously expressed but not widespread idea that the limitations of cubic equations of state like Soave–Redlich–Kwong equation (SRK) or Peng–Robinson equation (PR) are a consequence of their two-parameter density dependence rather than of their empiric character. Moreover, it is shown that when combined with a simple generalized van der Waals attraction term, the van der Waals repulsion is more capable than the Carnahan–Starling term to follow the PvT behaviour of real fluids and, in particular, that the generalized Redlich–Kwong–Peng–Robinson (RK–PR) equation offers the best performance among cubic three-parameter density functionalities. A simple temperature dependence was developed and a straightforward parameterization procedure established. This simple – and optimized from pure compound data – three-parameter equation of state (3P-EoS) will allow in a later stage, by systematic study and comparison to other types of 3P-EoS, to find out what the actual possibilities and limitations of cubic EoS are in the modelling of phase equilibria for asymmetric systems.
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1. Introduction and objectives

As pointed out in our previous article [1], any given two-parameter equation of state (2P-EoS) will be intrinsically unable to quantitatively describe the PvT properties of different fluids and their asymmetric mixtures. These limitations, already observed, for example, in [2], are exemplified in Section 2 after identifying the general reasons behind them.

The three different classes of three-parameter equation of state (3P-EoS) were briefly introduced in our previous article [1]. While one equation from each of the two more theoretically based classes was already studied in the same article under the critical point constraints, we explore here the possibilities of cubic equations.

Our ultimate goal is the reproduction and prediction of phase equilibria in mixtures. Since pure compounds are the limiting cases of mixtures, during the development of the equation we put emphasis on volumetric properties of pure fluids for two reasons. First, because the reproduction of densities itself is an issue of practical importance in many cases. Secondly, because having a simple equation that reasonably describes the density behaviour of both small and large molecules (which implies high and low Z_c values, respectively) will allow us, by comparisons to 2P-EoS like Soave–Redlich–Kwong equation (SRK) [3] or Peng–Robinson equation (PR) [4], to address the question of whether the improvement on volumetric properties gained from a 3P approach is associated to an improvement on the

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correlative and predictive capabilities for phase equilibria calculations in asymmetric systems. This will be studied and analyzed further in a future publication but some promising preliminary results are shown in Section 6.

Throughout this work, the Span–Wagner equations [5–7] are used as the main source of reference data and critical constants. In all cases, the conditions of temperature and pressure were within the applicability range of the Span–Wagner equations. The MBWR equation [8] was used for carbon dioxide only when the comparisons included data up to 3000 bar.

2. Limitations of two-parameter equations of state

It is a well-known feature of two-parameter cubic equations of state that the critical compressibility factor Z_c is a characteristic constant for each model and we have shown [1] that this is a general feature also for non-cubic 2P-EoS. In addition, a 2P-EoS will also predict a unique universal PvT behaviour for all fluids in terms of reduced variables (see Appendix A for a demonstration), which is not in agreement with the properties of real fluids. Therefore, a given 2P-EoS might be accurate to estimate the properties of some compounds, while showing large systematic deviations for others.

Since the work of Soave [3] correlations for the energetic parameter, based on reduced temperature and the acentric factor, have overcome this limitation of corresponding states models for vapour pressure calculations, improving at the same time the prediction of volumetric properties, but only partially given that the co-volume is not affected.

Soave [9] observed that for a 2P-EoS with an alpha function like SRK [3] or PR [4] the ratio α/T_r is a universal function of the ratio P_r/T_r. Later, Zabaloy and Brignole [10] found some other important relations from which it can be deduced that the reduced saturated densities – and therefore also the relation $\rho_L^{sat}/\rho_V^{sat}$ – are universal functions of the ratio P_r^{sat}/T_r. These relations depend exclusively on the 2P density dependence of the equation, being absolutely independent of the alpha function for the energetic parameter. A universal relation of this kind is not in agreement with the behaviour of real fluids. Fig. 1 shows the relation $\rho_L^{sat}/\rho_V^{sat}$ at $T_r = 0.7$ for alkanes from methane to n-octane, along with the predictions from SRK and PR equations. It is evident that these predictions are accurate only for one or two particular compounds in the homologue series, while a third parameter that gradually changes the 2P density functionality is able to follow the proper trend. This 3P-EoS, labelled as generalized Redlich–Kwong–Peng–Robinson equation (RK–PR), is the model that we propose and discuss in later sections.

At high densities and pressures the disagreement between predictions from 2P-EoS and the data for certain components become more appreciable due to the wrong co-volumes. This explains the curves shown in Fig. 2 for the compressibility
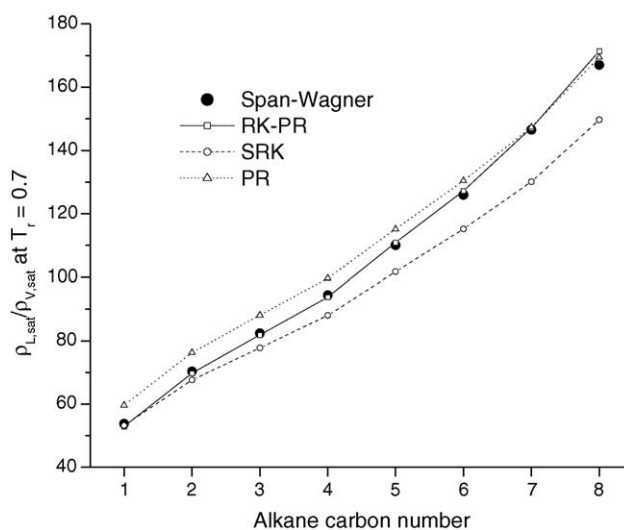

Fig. 1. Ratio of saturated densities at $T_r = 0.7$ predicted by the SRK and PR equations, compared to experimental values for alkanes. Predictions by the model proposed in this work are also included (see Section 4).

factors of different fluids at 300 K. SRK is better than PR in predicting the data of methane but the opposite is observed for octane and ammonia, and something intermediate for carbon dioxide. Similar results were found for other fluids and those shown in Fig. 2 are just some representative ones in order to cover the range of different Z_c in real fluids. The general trend is that the density dependence of the SRK is able to reasonably capture the behaviour of simple fluids like methane and different gases which have a high Z_c, i.e. between 0.28 and 0.29, while PR is more suitable for larger chains or polar compounds which exhibit considerable lower Z_c values, i.e. around 0.26. The same can be observed for fugacity coeffi-
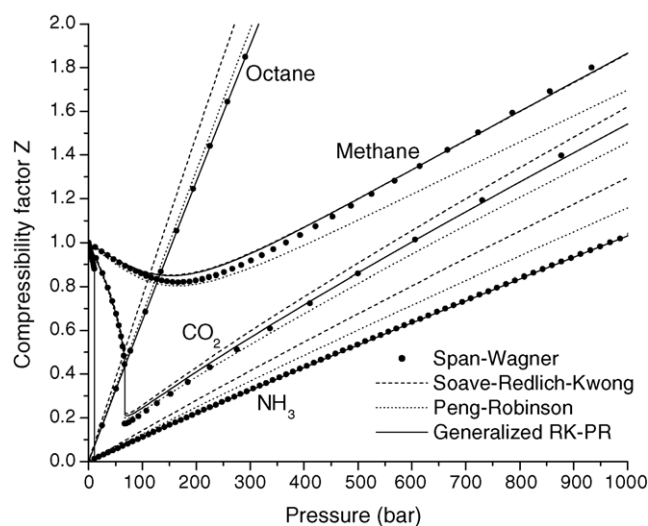

Fig. 2. Compressibility factors of four different fluids at 300 K and calculations with the SRK and PR equations. Calculations with the equation proposed in this work were also included (see Section 5 for the discussion).
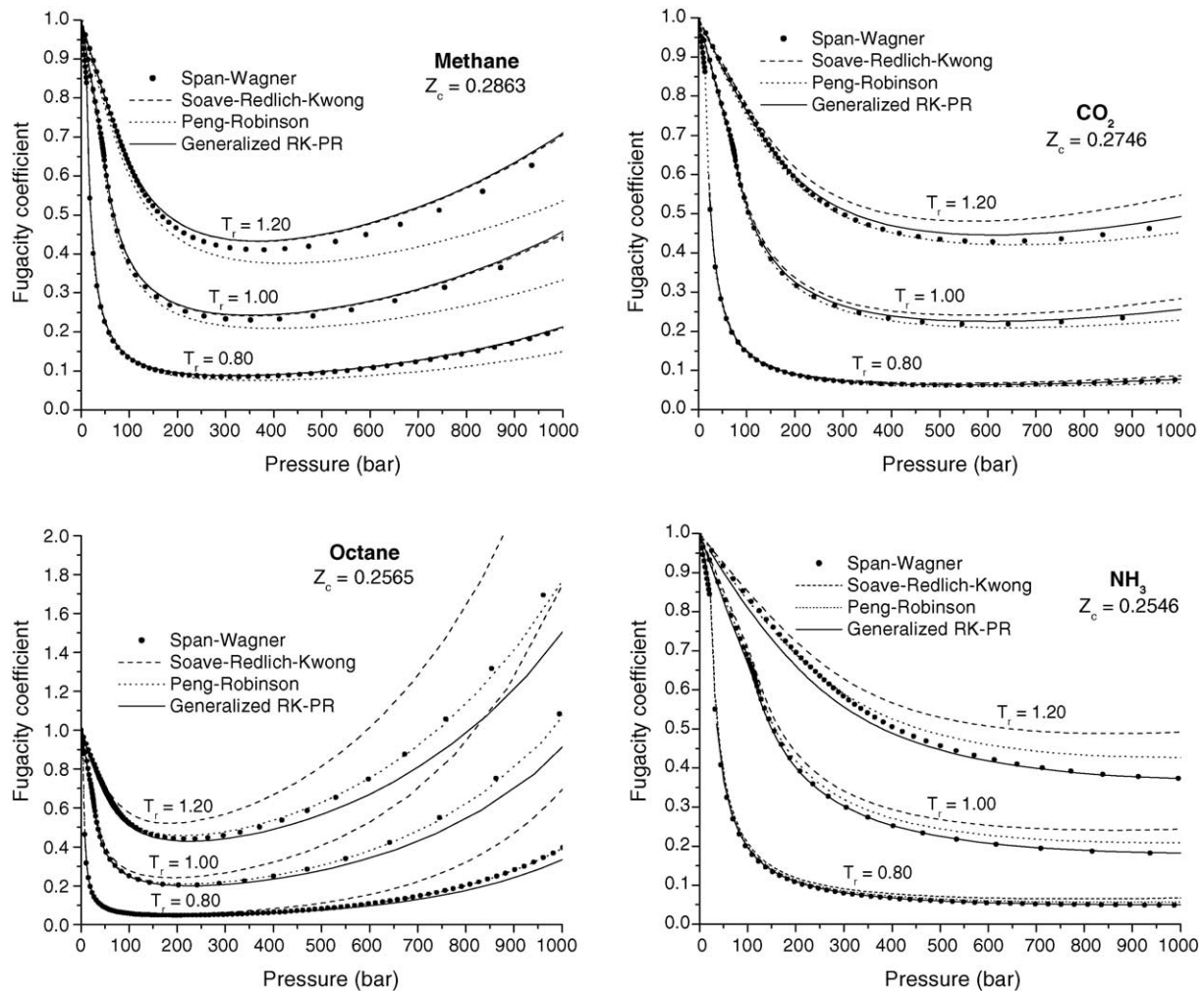
Fig. 3. Fugacity coefficients of different fluids at the reduced temperatures of 0.8, 1.0 and 1.2. Calculations with the SRK, PR and RK–PR EoSs.

cients in Fig. 3, where one subcritical and one supercritical isotherm were included along with the critical isotherm of each fluid.

The conclusion of this section is that the intrinsic limitations of 2P-EoS, rather than their empiric character, are the main reason behind the well-known inaccuracy of equations like SRK or PR for volumetric and derived properties. It must be clear that any theoretically based 2P-EoS will have the same problem and therefore a third compound-specific parameter in the density dependence of the equation of state is indispensable to model different types of fluids and their asymmetric mixtures.

It should be noted that volume translations in equations of state [11], which have been proposed to overcome the shortcomings discussed in this section, do not provide different models, i.e. the calculations could be performed with the original equation and then the reported volumes be shifted [12]. Therefore, and taking into account that the essential reason for engineering equations of state to exist is calculation of phase equilibria, volume translated 2P-EoS should not be regarded as 3P-EoS.

2.1. The necessary degree of freedom given by a third parameter

To show the qualitative effects of the flexibility gained from a third parameter we use here the generalized van der Waals (vdW) attraction term as introduced by Yelash and Kraska [13]:

$$P_{att, gvdw} = -\frac{a}{v(v + cb)} \quad \text{or}$$

$$Z_{gvdw} = 1 + Z_{rep}(\eta) - \frac{\tau}{\left(\frac{1}{4\eta} + c\right)}; \qquad \tau_{gvdw} = \frac{a}{RTb},$$

$$\eta_{gwdv} = \frac{b}{4v} \tag{1}$$

Using either the van der Waals repulsion term – which leads to the generalized vdW–RK EoS since it adopts the density dependence of the Redlich–Kwong equation for $c = 1$ – or the Carnahan–Starling (CS) expression [14] for Z_{rep} in Eq. (1), and fixing the third parameter in each case, we can solve the conditions of the critical point for η_c and τ_c (as explained
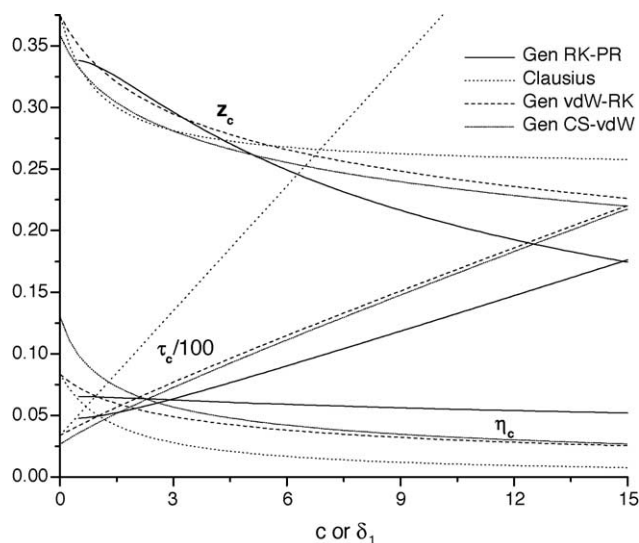
Fig. 4. Dimensionless variables of four different 3P density dependences in the critical point, as functions of the third parameter.

in [1]) and then introduce these values in the corresponding expression for explicit calculation of Z_c. Following this procedure, we obtained the curves in Fig. 4, showing that Z_c decreases with c. Since for a homologous series of compounds, decreasing values of Z_c correspond to increasing molecular weights, a larger c parameter corresponds in principle to a larger molecule.

Using these two 3P-EoSs without any temperature dependence and with c as the changing parameter, we observed trends for the pure compound critical isotherms, vapour pressures and saturated densities, that agree qualitatively with those experimentally observed for real fluids. In other words, the introduction of a third parameter in the way prescribed by Eq. (1) to the simple vdW or CS EoS provides a reasonable density dependence which is qualitatively in agreement with the behaviour of real fluids when going from small to large molecules. This observation, which we could not find in the literature, is also valid for other three-parameter density dependences and strongly supports the use of them to construct equations of state. So far, at least for non-associating compounds, we do not see any reason for using a fourth parameter in the density dependence.

Notice that a given value of c can be seen as defining a particular two-parameter EoS, e.g. $c = 0$ gives the attraction term of the vdW EoS while $c = 1$ the RK EoS. Thus, making this parameter compound-specific is equivalent to choose the 2P-EoS that best suits the behaviour of each fluid, but then – when applying the equation to mixtures – interpolating between the different 2P-EoSs through a mixing rule for c. From some previous results in the literature (see, for example, [15]), it can be deduced that this practice would significantly improve the reproduction of – at least – volumetric properties in mixtures. The same conclusions apply to other alternatives for the repulsive part. Here, we used the vdW and CS repul-

sive terms for illustration purposes since these two are very well known.

3. Evaluation of different alternatives and development of a 3P-EoS

Now, we face the fundamental questions when developing an equation of state: which repulsive and attractive terms to use? Which temperature dependences for the parameters? How to determine the parameters for each compound?

One could arbitrarily choose the van der Waals repulsion term for the sake of simplicity or the one by Carnahan and Starling [14] for – debatable – theoretical reasons and the lower c value required to match a given Z_c value (see Fig. 4). Then, adopt a particular temperature dependence for the a parameter, and eventually another one for b, and parameterize using the critical conditions to match T_c and P_c, while leaving the degree of freedom in c to minimize deviations in vapour pressures and liquid densities. This is a usual approach when evaluating a given model or comparing different equations [16–18].

However, when developing a 3P-EoS the repulsion term should be chosen from the volumetric performance. This can be done by examining the calculated critical isotherm, which is independent of the temperature dependence of the equation. The three parameters for each compound could then be determined from these data – critical isotherm – and finally, the temperature dependences defined, assuring that a good reproduction of vapour pressures, saturated densities and also densities in the one-phase region is achieved. As will be seen in Sections 3.3 and 3.4, we found more convenient instead to parameterize after defining the temperature dependence of the equation.

3.1. Choosing a repulsive term: comparison between the generalized vdW–RK and CS–vdW EoSs for critical isotherms

With the constraint of matching the experimental critical temperature and pressure – that we implement in this work exactly as in [1] – there is still one degree of freedom, i.e. the critical volume, to calculate a critical isotherm with a 3P-EoS. In Fig. 5, the critical isotherms of different fluids are shown as calculated from both vdW–RK and CS–vdW generalized equations, each of them with two different c values: one matching the experimental Z_c and the other one giving a better agreement at high densities. From this figure, we can clearly see two things. First, that the underestimation of the critical density is required for a reasonable reproduction of the whole isotherm. Secondly, that the vdW repulsion term performs better than the CS due to a steeper curve in the high density region which gets closer to the experimental data.

This seems to be related to the lower reduced critical packing fraction of the CS–vdW equation compared to the vdW–RK, as shown by Yelash and Kraska [13]. It might be
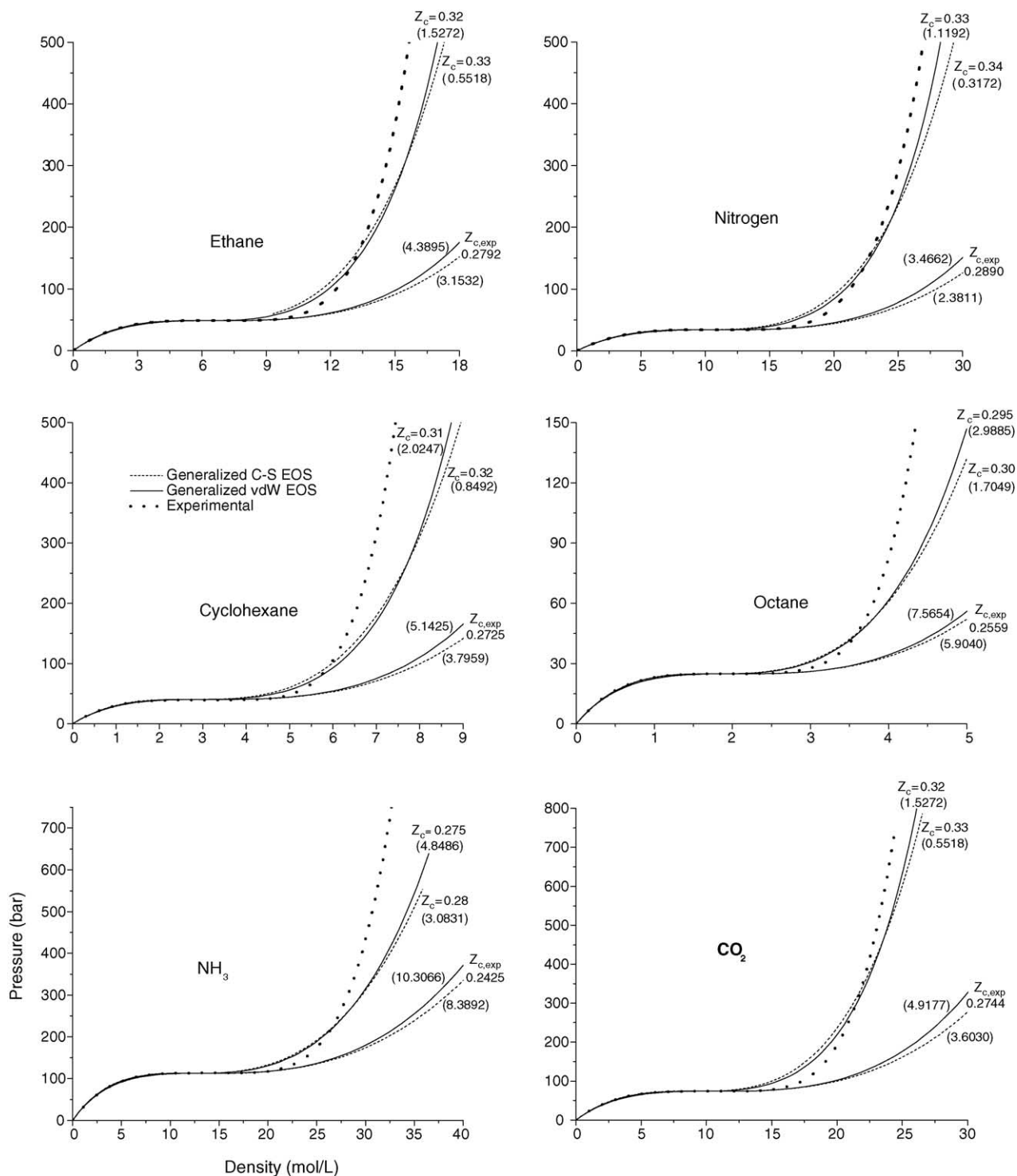
Fig. 5. Critical isotherms of different fluids calculated with the generalized vdW–RK and CS EoSs. In all the cases, experimental T_c and P_c are matched. The values of Z_c and c are indicated for each curve.

wrong to conclude that the repulsive term of van der Waals is better than the one of Carnahan–Starling. Nevertheless, it is clear that when combined with this simple attractive term the vdW repulsion performs better. Probably, a more complex density dependence could be found for the attractive term, such that combined with the CS repulsive term it would lead to better results. This is likely to be the case of the different SAFT equations.

3.2. Choosing an attractive term: a 3P density dependence connecting the RK and PR EoS

The generalized vdW–RK attractive term is one of the simplest alternatives for the implementation of a 3P-EoS. This approach had already been followed or studied in different ways by several authors [13,19–21]. In addition to the van der Waals and Carnahan Starling terms, we also tested other different alternatives for the repulsive part and no improvement was achieved over the combination of Eq. (1) with the vdW repulsion. Other approaches such as multiplying the attractive term by a density decreasing function or adding two extra terms with two extra parameters to make zero also higher derivatives at the critical point and get flatter curves did not yield significant improvements either.

Nevertheless, two other generalized attractive terms which lead to 3P-EoS have been proposed and studied in the literature. The first of them, the so-called Clausius EoS [22,23], is even simpler:

$$P_{Clau} = \frac{RT}{v - b} - \frac{a}{(v + cb)^2} \quad \text{or}$$

$$Z_{Clau} = \frac{1}{1 - 4\eta} - \frac{4\eta\tau}{(1 + 4c\eta)^2}; \qquad \tau = \frac{a}{RTb},$$

$$\eta = \frac{b}{4v} \tag{2}$$

The second one assumes the RK or PR density dependence for particular values of a third parameter in a similar way as Eq. (1) connects the vdW and the RK ones. Even though not attempting to use it for developing a 3P-EoS, Mollerup found this relation in the late 1970s [24]. He proposed the following general expression (see the book by Mollerup and Michelsen [25], for further details and discussion) in which all of the well-known cubic EoS are contained for particular pairs of values (δ_1, δ_2):

$$P = \frac{RT}{v - b} - \frac{a(T)}{(v + \delta_1 b)(v + \delta_2 b)} \tag{3}$$

Some characteristics of this double parameterized attraction term were studied by Yelash and Kraska [13], also combined with the CS repulsion. It is easy to see that for the delta parameters $(1 + \sqrt{2}, 1 - \sqrt{2})$ the PR equation is obtained, as $(0, 0)$ leads to the vdW and $(1, 0)$ to the RK. Then, if we add the restriction:

$$-\delta_1 \delta_2 = \delta_1 + \delta_2 - 1 = c \tag{4}$$

we have actually a 3P-EoS which connects the RK ($c = 0$) and PR ($c = 1$) density dependences with the following expression for the compressibility factor:

$$Z_{RKPR} = \frac{1}{1 - 4\eta} - \frac{4\eta\tau}{(1 + 4\delta_1\eta)\left(1 + 4\frac{1-\delta_1}{1+\delta_1}\eta\right)};$$

$$\tau = \frac{a}{RTb}, \qquad \eta = \frac{b}{4v} \tag{5}$$
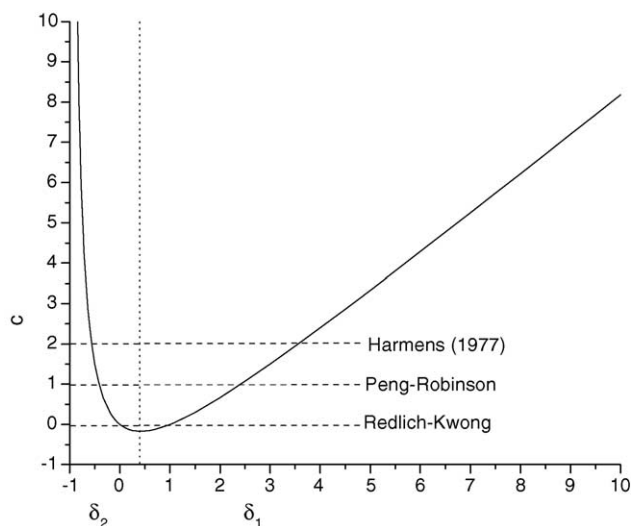

Fig. 6. The relation between c and the delta parameters in the RK–PR density dependence.

As Harmens and Knapp [26], we could use a different way of expressing the same equation which, using Mollerup's c parameter defined in Eq. (4), would be:

$$P_{RKPR} = \frac{RT}{v - b} - \frac{a(T)}{v^2 + (c + 1)bv - cb^2} \tag{6}$$

The last expression is used in the Patel–Teja equation [27], their c parameter being the product $c \times b$ here. Nevertheless, we will use Eq. (5) because of the simpler expression obtained through integration for the Helmholtz energy and also for its derivatives. In addition, it shows in a clearer manner the role of the delta parameters. In particular, one realizes the presence of a second pole, i.e. a given density at which the pressure contribution goes to infinity, when δ_2 is negative (or $\delta_1 > 1$). In Fig. 6, which shows the relation between the alternative parameters δ_1, δ_2 and c in this 3P-EoS, we can see that this attractive pole will always be located at higher densities than the repulsive one. This is due to the asymptotic approaching of δ_2 to -1 and guarantees that the physical requirement of an increasing pressure as the co-volume is approached will always be fulfilled for any value of δ_1 or c.

Fig. 4 shows the Z_c, η_c and τ_c curves for both Eqs. (2) and (5). One distinctive feature of Eq. (5) is the existence of a minimum value for the third parameter ($\delta_{1\ min} = \sqrt{2} - 1$ or $c_{min} = 2\sqrt{2} - 3$), which leads to a maximum Z_c value around 0.3384. The origin of this, which can be seen in Figs. 4 and 6, is in the constraint (Eq. (4)) and the symmetry of Eq. (3). Fortunately, as we will see later, this is not a limitation for modelling real fluids.

From the comparison of critical isotherms of CO_2 in Fig. 7, we can clearly see the superiority of the generalized RK–PR (Eq. (5)) over the generalized vdW–RK and Clausius EoS—Eqs. (1) and (2), respectively. The same results were obtained for other fluids.

It is important to note that in addition to providing lower deviations than the generalized vdW–RK along the whole
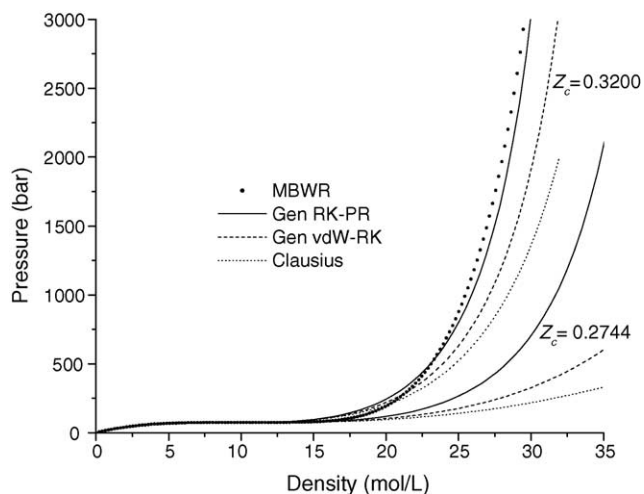
Fig. 7. Critical isotherms of carbon dioxide, calculated from three different 3P density dependences and for two different values of Z_c, including the experimental.

Table 1
Five different sets of parameters for CO_2, which reasonably approximate the experimental critical isotherm

Z_c	a_c	b_c	d_1	d_2
0.310	3.9353	0.0270	2.2800	−0.3902
0.315	3.8847	0.0275	2.0227	−0.3383
0.320	3.8340	0.0281	1.7638	−0.2763
0.325	3.7852	0.0287	1.4977	−0.1993
0.330	3.7363	0.0293	1.2134	−0.0964

curve, the generalized RK–PR EoS requires a lower Z_c to approach the high density data and therefore lower deviations in the critical density.

At this point, we can conclude that an attractive pole, which enlarges the attractive contribution to the pressure at high densities, is of great importance in the density dependence of the equation. This is valid at least when using the vdW repulsion, and is in agreement with what we found trying different approaches (these results are not included here): the attraction term density dependence has to be reinforced in order to allow for larger co-volumes (remember that, given the restriction of T_c and P_c, b changes with Z_c through the η_c curve) and consequently steeper curves in the high density region.

3.3. Defining the temperature dependence of the EOS

We have seen that a three-parameter density functionality itself gives already the proper qualitative evolution of vapour pressure and saturation density curves within a given family of compounds, e.g. *n*-alkanes. Nevertheless, as for every equation of state, a temperature dependence is required in order to achieve also a reasonable quantitative agreement with experimental data.

From the physical meaning of the repulsive and attractive parameters in every model, one can expect them to change with temperature, except the depth of pair potential or related parameters in theoretically based models. Since Soave [3] every cubic EoS includes a temperature dependence for a and models like perturbed chain SAFT equation (PC-SAFT) [28] or the GC-EOS [29] use a temperature dependent co-volume. Since to our knowledge no 3P-EoS has implemented so far a temperature dependence for the third parameter, and there seems to be no reason for that, we did not even considered such possibility. In addition, a soft temperature dependence for b should only be adopted in case it really improves the

performance of the equation while not violating any stability condition (see the analysis by Salim and Trebble [30]). We found that, when imposing the exact reproduction of vapour pressures and saturated liquid densities at subcritical temperatures and minimization of the deviations for supercritical isotherms, there is no unique trend that allows us to develop a temperature dependence for b.

Therefore, the temperature dependence for our model will be given by an alpha function like in most cubic EoSs. This function should correlate the optimum a values at different temperatures, which can be obtained after a set (δ_1, b, a_c) has been chosen from the critical isotherm. The latter is not a trivial matter. It will be clear that the co-volume in some curves is too big while it is too small for others. But which one to choose among all those that cross the experimental curve at high densities? We could minimize the average deviation in pressure, but the result would most likely change gradually depending on the maximum pressure considered. Another option is to impose the condition of matching a very high pressure value (e.g. the recommended pressure limit in the MBWR or Span–Wagner equation) or to define a general expression for the co-volume in terms of some tabulated property as suggested by Polishuk et al. [31].

Instead of applying one of those possibilities to arbitrarily fix the parameters, we will consider the five sets in Table 1, all of them providing a reasonable approximation to the experimental critical isotherm. This will allow us to see how the selected Z_c value affects the reproduction of data in the extended subcritical and supercritical regions and whether some values make it easier or not to correlate the different a values with a simple and general expression. By doing so, we will merge two steps in one, namely the determination of parameters at critical temperature and development of the temperature dependence.

3.3.1. Optimum a values versus reduced temperature for different Z_c

The optimum a parameters of carbon dioxide required to match vapour pressures and minimize pressure deviations for supercritical isotherms are shown in Fig. 8. It is interesting to note that by not imposing the exact reproduction of the saturated liquid density at subcritical temperatures, not much accuracy is lost, especially if a Z_c between 0.315 and 0.320 is used (see Fig. 9). This fact, together with the lower deviations in supercritical isotherms just above the critical temperature (also in Fig. 9) and a reasonable continuation of optimum

Table 2
Different fluids included in the determination of the Z_c ratio

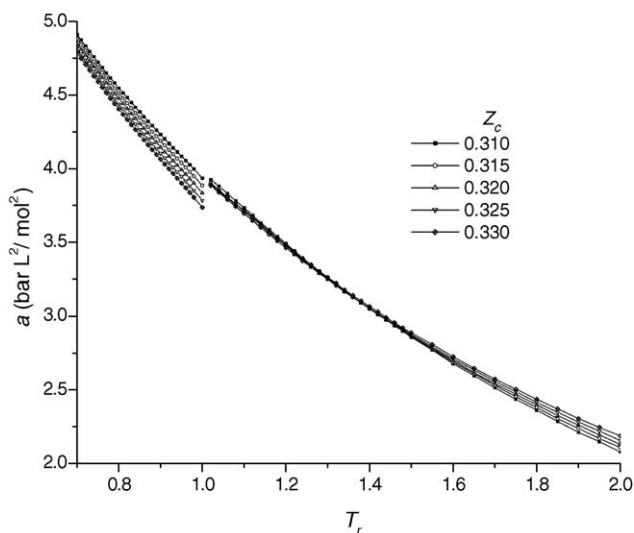| Compound	$Z_{c,exp}$	T_c (K)	T_{rtp}	T_{rmax}	Z_c range	1.16 $Z_{c,exp}$
Nitrogen	0.2894	126.19	0.50	8.51	0.330–0.335	0.3357
Ethylene	0.2812	282.35	0.37	1.68	0.320–0.325	0.3262
Propane	0.2763	369.83	0.24	1.68	0.317–0.322	0.3205
Carbon dioxide	0.2746	304.13	0.71	3.38	0.315–0.320	0.3185
n-Octane	0.2565	569.32	0.38	1.50	0.297–0.302	0.2975
Ammonia	0.2546	405.40	0.49	1.42	0.283–0.286	0.2953

Fig. 8. Optimum values of *a* (tuned to match vapour pressures or minimize deviations in supercritical isotherms), plotted against T_r.

a values between the two regions (Fig. 8) lead us to select this range of Z_c values as the most promising one for carbon dioxide. A similar procedure was followed for other fluids listed in Table 2 and the approximate ranges obtained in each case for Z_c are also given.

A very important observation is that if we take the ratios of the approximate optimum Z_c values with respect to the experimental ones, all of them take values around 1.15 or 1.16, with the only exception of ammonia (NH_3) in Table 2, which requires a ratio of about 1.11 or 1.12 and this can be explained by the volume contraction effect at high densities.

3.3.2. A simple temperature dependence for the a parameter

The same type of behaviour already seen in Fig. 8 for the optimum values of *a*, was found for all fluids. To correlate these values, we discarded Soave's quadratic function because of its behaviour at high temperatures and tried, among others, the following family of simple expressions, which are monotonically decreasing from a finite value at 0 K towards zero at infinite temperature:

$$\alpha = \frac{a}{a_c} = \left(\frac{n+1}{n+T_r} \right)^k, \qquad 0 < k \tag{7}$$

We found that $n = 2$ provides the best equation to correlate optimum *a* values. The *k* constant for each fluid can be obtained from least-squares regressions. Instead, since the range of reduced temperatures with available data is different for each compound, and in order to provide a simple and general procedure for the implementation of the equation, we decided to calculate the *k* constant from the *a* value required to match the vapour pressure at $T_r = 0.7$ (Soave [3]). The results, corresponding in this case to a fixed relation $Z_c^{EOS} = 1.16 Z_c^{exp}$, are shown in Fig. 10. It can be appreciated that due to an
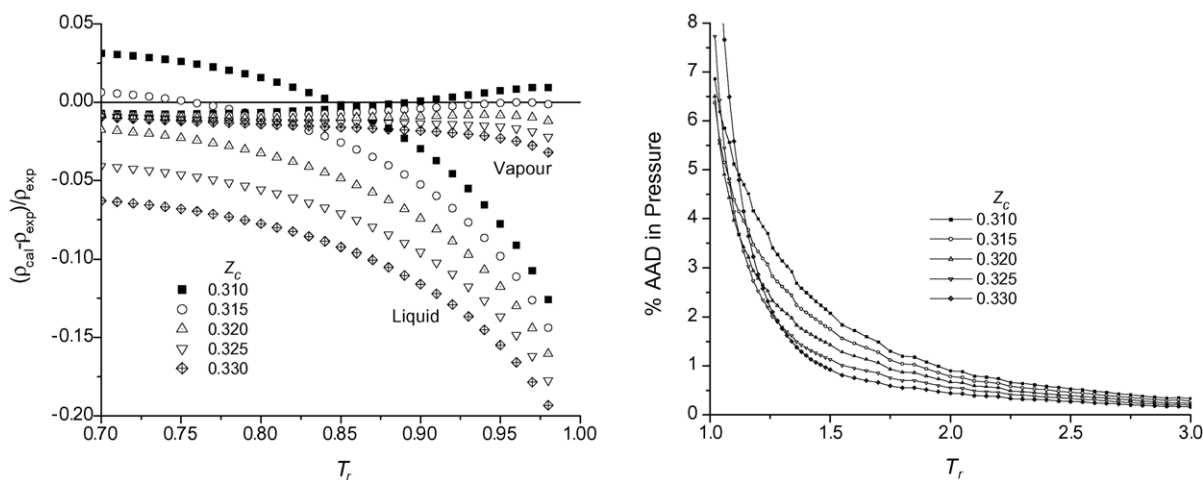

Fig. 9. Deviations in saturated densities of carbon dioxide when tuning *a* to match the vapour pressure and minimum AAD in pressures up to 1000 bar for supercritical isotherms.
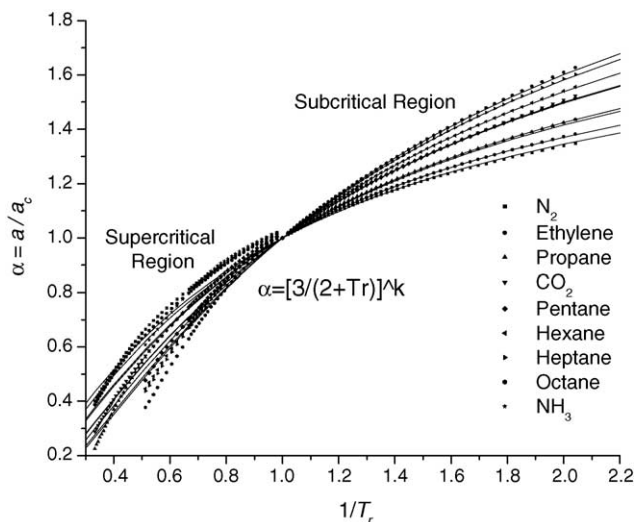
Fig. 10. Eq. (7) with $n = 2$ and constants k calculated from $T_r = 0.7$, compared to optimum values of a for different fluids.

excellent correlation at subcritical temperatures, any other available vapour pressure value will generally lead to essentially the same k. Even though we have not defined yet how to fix the critical compressibility factor – and therefore the three parameters – for each compound, it can be deduced from Fig. 8 that if some given temperature dependence works well once a specific ratio for Z_c has been specified, it will equally work for other different ratios. Therefore, from now on we will use Eq. (7) to calculate a. The value for the k constant is to be determined such that the vapour pressure at $T_r = 0.7$ is reproduced. Were this information not available, another vapour pressure can be used.

3.4. Parameterization: optimizing the reproduction of PvT behaviour through Z_c

Having already two constraints (T_c and P_c) for the determination of the three parameters at the critical point, having decided that both δ_1 and b will remain as constants and having also adopted a fixed procedure for determining the temperature dependence of a, our only degree of freedom left is the critical compressibility factor.

Instead of explicitly considering the particular values of Z_c for each fluid, we focus our study on the relation Z_c^{EOS}/Z_c^{exp}, given that equivalent results for different fluids were found for similar values of this ratio. We found that its variation affects only slightly the reproduction of vapour pressures – which is very good thanks to the adoption of Eq. (7) – while pressure deviations in the single-phase regions are more sensitive, specially at low temperatures. For this reason, and given that the representation of *PvT* properties is what we want to improve with this new equation of state, its optimization has been the criterion followed to select approximate values for the optimum Z_c ratio of each fluid.

In the high density region, where the isotherms approach vertical lines, the deviations in pressure or density along each

particular isotherm are almost exclusively determined by the co-volume or b parameter. Given the constraints of T_c and P_c, this value depends only on Z_c and this causes an extreme sensitivity of the deviations in pressure at low subcritical temperatures to the Z_c ratio. For this reason, we show instead average deviations of density at given pressures (from 0 to 1000 bar) in Fig. 11. The behaviour observed from propane to higher alkanes could be misinterpreted as suggesting a temperature dependence for the third parameter, but it must be remembered that the co-volume also changes with the Z_c ratio.

Despite the different kind of curves found for different fluids in Fig. 11, one can see that the optimum Z_c ratios are close to 1.17 for all fluids, with the only exception of associating fluids – like ammonia in this case – that require lower values. It can be argued that for large *n*-alkanes this ratio is appropriate only at low reduced temperatures, while higher ratios perform better at near critical and supercritical temperatures. Indeed, the heavier the *n*-alkane, the lower will be the reduced temperatures of practical interest. And still for octane, the larger alkane described by the Span–Wagner equation, the maximum average absolute deviation (AAD) at high temperatures is only 6%.

Given the restriction of a maximum Z_c predicted by the equation as already discussed in Section 3.2, and that some gases exhibit experimental values as high as 0.29, we will adopt a universal Z_c ratio of 1.168 for non-associating fluids.

4. The final equation and results for selected compounds

Inserting Eq. (7) with $n = 2$ into the density dependence defined by Eq. (5), we get the final expressions for the residual Helmholtz energy and pressure:

$$\frac{A^{res}}{RT} = -\ln\left(1 - \frac{b}{v}\right) - \frac{a}{RTb\left(\delta_1 - \frac{1-\delta_1}{1+\delta_1}\right)} \ln\left(\frac{v + \delta_1 b}{v + \frac{1-\delta_1}{1+\delta_1}b}\right),$$

$$a = a_c\left(\frac{3}{2 + T_r}\right)^k \tag{8}$$

$$P = \frac{RT}{v - b} - \frac{a_c\left(\frac{3}{2+T_r}\right)^k}{(v + \delta_1 b)\left(v + \frac{1-\delta_1}{1+\delta_1}b\right)} \tag{9}$$

Fugacity coefficients and all derivatives required for calculations are obtained from volume and temperature derivatives of Eq. (8) as described in [25]. Mixture calculations (see Section 6) also require mixing rules and composition derivatives.

The recommendations for a straightforward implementation of the equation are completed with the following relation for non-associating fluids:

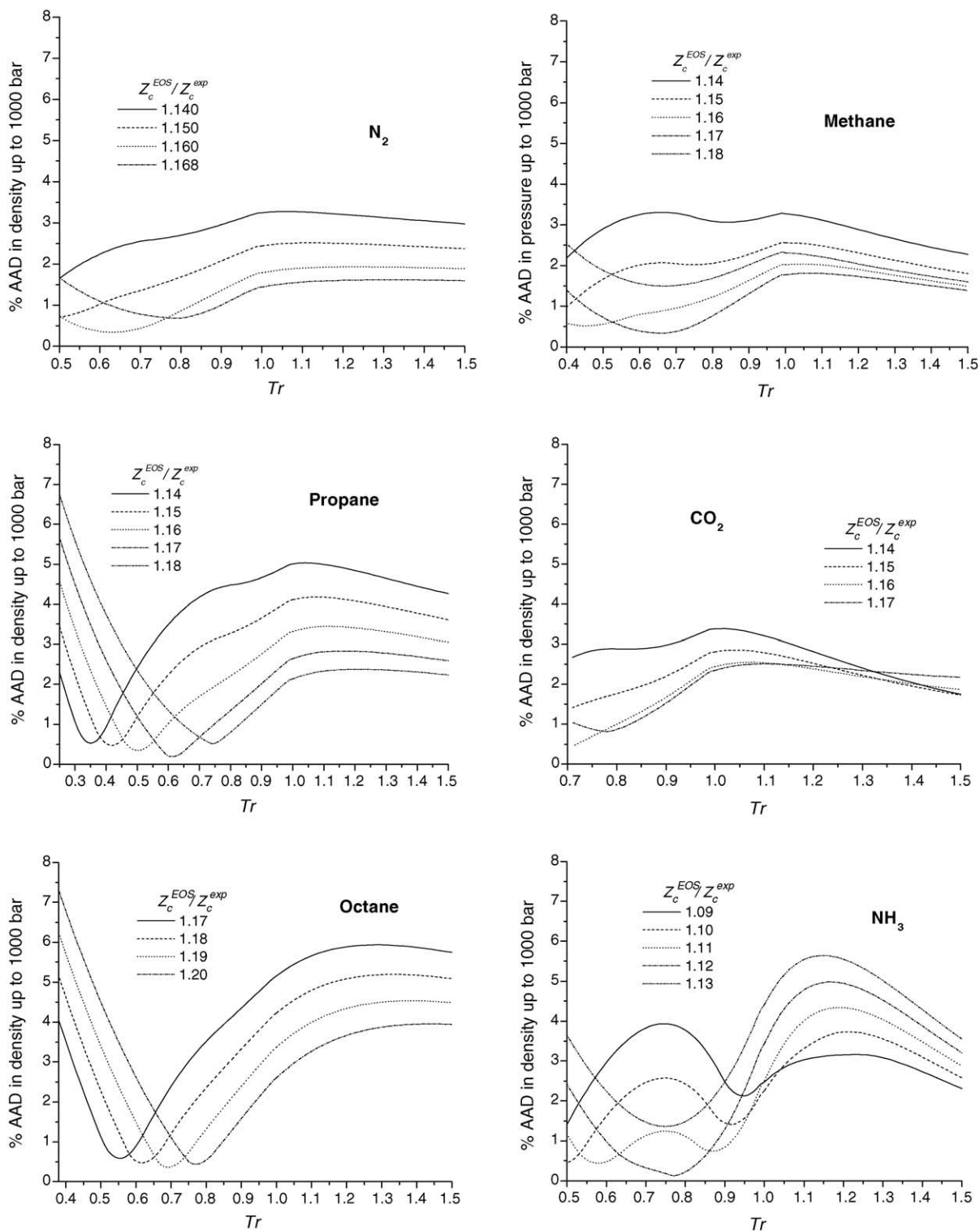$$Z_c^{EOS} = 1.168 Z_c^{exp} \tag{10}$$

Fig. 11. Influence of the Z_c ratio on the deviations in density for both subcritical and supercritical isotherms of different fluids.

This condition already determines the third parameter δ_1 for each fluid, while b and a_c are obtained from solving the critical conditions and fixing T_c and P_c to their experimental values. The k constant for the temperature dependence of the attractive parameter is readily determined from the acentric factor and critical constants. Explicit expressions for calculation of δ_1, b, a_c and k are provided in Appendix B. The corresponding parameters obtained in this way for different fluids, including ammonia with a Z_c ratio of 1.115, are given in Table 3. The average absolute deviations for vapour pres-

Table 3
Parameters and performance of the proposed RK–PR equation

Compound	δ_1	a_c	b	k	AADP$_V$	AADρ_L^{sat}	AADρ_V^{sat}
Methane	0.9253	2.3272	0.0300	1.49345	1.574	5.211	1.609
Ethane	1.4286	5.7597	0.0439	1.78590	1.113	4.447	1.236
Propane	1.6201	9.7810	0.0601	1.97064	0.892	4.243	1.040
n-Butane	1.7644	14.5670	0.0764	2.12852	0.891	4.339	0.960
n-Pentane	2.1026	20.3721	0.0925	2.25130	0.774	3.383	0.821
n-Hexane	2.2708	26.6747	0.1096	2.39294	0.610	3.302	0.754
n-Heptane	2.4173	33.7100	0.1277	2.54658	0.666	3.616	0.782
n-Octane	2.8220	41.8620	0.1425	2.60984	0.861	2.834	0.995
CO$_2$	1.7268	3.8290	0.0282	2.23854	0.501	6.875	0.537
NH$_3$	3.6926	4.8666	0.0208	1.89272	1.056	2.428	2.466

b is given in L/mol and a_c in bar L^2/mol^2. AAD in vapour pressures and saturated densities calculated from $T_r = 0.5$ to critical point, except carbon dioxide from $T_r = 0.71$. AADX $= 100 \times \sum |X_{cal} - X_{exp}|/X_{exp}$. Reference critical constants and experimental data according to Span and Wagner [5–7].
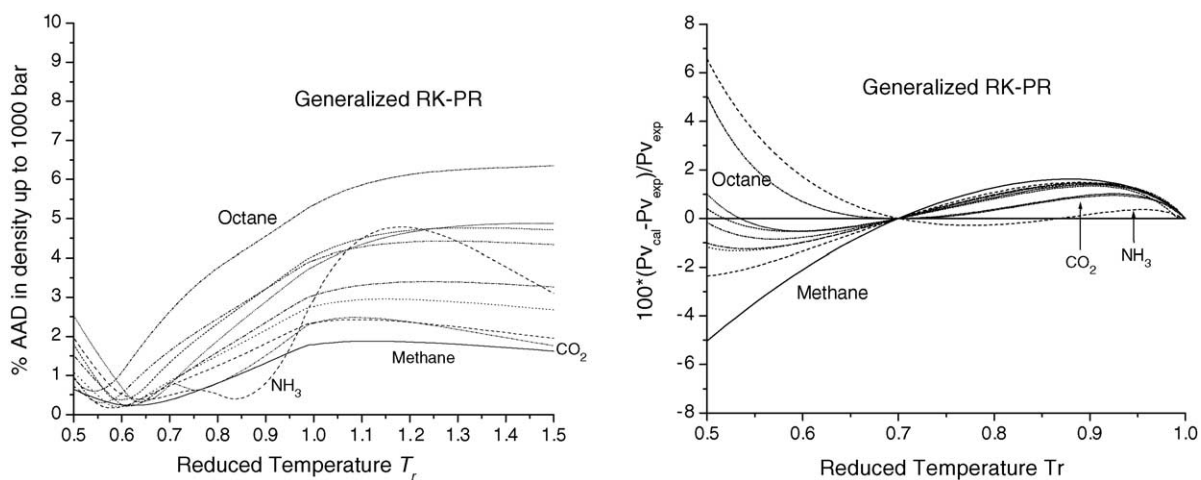

Fig. 12. Deviations in calculated vapour pressures and AAD in density for *n*-alkanes up to C8, carbon dioxide and ammonia. Generalized RK–PR EoS with parameters proposed in this work (Table 3).
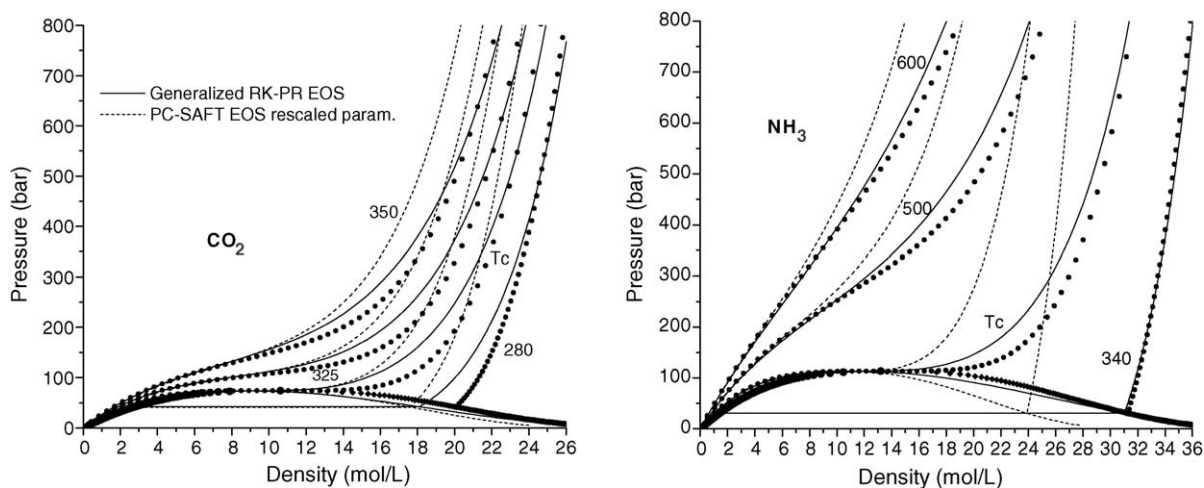

Fig. 13. *P*–*ρ* diagrams of carbon dioxide and ammonia. Parameters for PC-SAFT taken from [1].

sures and saturated densities are also informed in the same table. Further details of the performance of the model for estimation of vapour pressures and densities in the one-phase region are shown in Figs. 12 and 13, where it is compared to the PC-SAFT EoS with optimized rescaled parameters [1].

5. Discussion of the results for pure compounds

5.1. Comparisons with SRK and PR

Calculations with the generalized RK–PR EoS and parameters from Table 3 were also included in Figs. 1–3 in Section 2. From those comparisons with the SRK and PR equations, we can see that just by using a third parameter which allows making interpolations and extrapolations along the generalized density dependence defined by these well-known 2P-EoS the compressibility factors and fugacity coefficients of real fluids can be very well represented if appropriate values are chosen.

The curves for octane in Fig. 3 illustrate the higher inaccuracy of our equation for describing the properties of chain-like molecules at high temperatures (note the accuracy at 300 K in Fig. 2). The reason for this limitation is in the behaviour illustrated in Fig. 11 and this could probably be improved if temperature dependences for δ_1 and b were also adopted. Nevertheless, the insignificant practical importance of this limitation does not justify such increment in the complexity of the equation, which might even lead to thermodynamic inconsistencies.

5.2. Comparison with PC-SAFT

In a previous publication [1], we studied the possibilities of PC-SAFT under the constraint of reproducing T_c and P_c and presented optimized rescaled parameters, which retain the accuracy of original parameters for calculation of vapour

pressures. Here, from the results in Fig. 12, we see that the same level of accuracy in vapour pressures is achieved by our 3P-EoS and proposed parameters.

On the other hand, we do not pay the price of large systematic errors in predicted densities as it is seen from Fig. 13. One must be aware that this is possible thanks to a proper adjustable temperature dependence in the attractive term, which guarantees the representation of vapour pressures. Only in this case can the predicted Z_c be tuned to optimize the representation of volumetric properties, while for models with fixed temperature dependence it must be sacrificed for vapour pressures. In principle, although theoretically questionable, the same approach could be followed for PC-SAFT. Alternatively, a simple volume translation [11,12] can be implemented to get an acceptable description of densities. But so far, given the good results obtained for pure compounds with the very simple equation of state defined by Eq. (9), the disproportionate complexity of a model like PC-SAFT could only be justified for polymer systems or when high accuracy in densities is required and only conditions far away from the critical region are of interest, which permits the use of its original regressed parameters.

5.3. Comparison with the Patel–Teja EoS

As already mentioned in Section 3.2, other cubic 3P-EoS had already implemented the density dependence, which connects RK and PR. The Patel–Teja EoS is probably the best known and most used among them and therefore some comments on the differences with our new equation are necessary. The first noticeable difference is in the definition of the third parameter, which in principle could have some effect when a linear mixing rule is applied for mixtures, but this will be negligible given the high linearity observed between δ_1 and c in Fig. 6. Nevertheless, there are two important differences which do have an effect on pure compound properties and therefore also on mixtures.
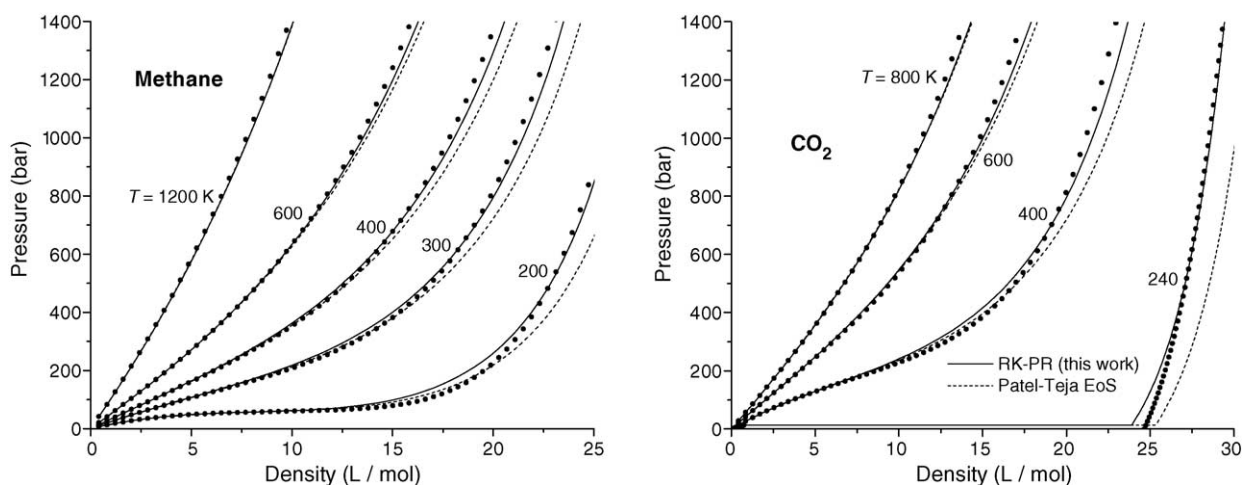

Fig. 14. Some isotherms in the P–ρ diagrams of methane and carbon dioxide as calculated by the Patel–Teja EoS [27] and the equation and parameters proposed in this work.

First, Patel and Teja [27] used the same quadratic function proposed by Soave and implemented also by Peng and Robinson for the temperature dependence of the attractive parameter. This function is capable of accurate correlations of vapour pressures, but some problems of thermodynamic consistency and unphysical results like multiple critical points [32,33] have been found for this type of functions. Instead, Eq. (7) results in an asymptotic vanishing of alpha at high temperatures, which prevents non-physical behaviour, and allows for a reasonable correlation of densities for supercritical isotherms – within the possibilities of the RK–PR density dependence with constant δ_1 and b – while the accuracy in vapour pressures is retained. One may notice from Fig. 10 that the optimum a values for supercritical temperatures up to $T_r = 1.5$ are higher than the ones predicted by Eq. (7) for most of the fluids. Nevertheless, some of those values are even higher than the critical value, which indicates that this is a limitation of the EoS in the critical region that cannot be overcome by any reasonable and consistent temperature dependence.

Secondly, the parameterization procedure adopted by Patel and Teja, and in consequence also their generalized correlations with the acentric factor, are based on the minimization of saturated liquid densities. This together with Fig. 9 explains why, for example, they choose a Z_c of 0.309 for carbon dioxide. But we have found that a small underestimation of saturated liquid densities is usually required for an optimum representation of densities in the one-phase region (see Fig. 13). Therefore, both our Z_c and co-volumes are in general higher than the ones given by Patel and Teja and as a consequence our equation is better for prediction of PvT properties of fluids, as it can be seen in Fig. 14. This last point discussed, namely the difference in co-volumes, is the main reason behind the systematic overestimation of densities by the Patel–Teja EoS.

6. Preliminary results for mixtures: critical lines of carbon dioxide + *n*-decane

A systematic investigation of the performance of the model for calculation of phase equilibria in mixtures is the object of further work. Nevertheless, we show in Fig. 15 these interesting preliminary results, which are analogous to those in pure compounds properties: the SRK equation describes better than the PR the region closer to pure carbon dioxide and the opposite is observed as we approach pure *n*-decane, while our three-parameter equation provides an optimum correlation in the whole range. Moreover, this correlation was obtained with $k_{ij} = 0$. Quadratic mixing rules were used, along with the classical van der Waals combining rules for a and b. A linear mixing rule was implemented for the third parameter δ_1. It is also important to note that the correlations obtained with PC-SAFT, although not showed in the figure, are of inferior quality, no matter whether original or rescaled parameters are used.
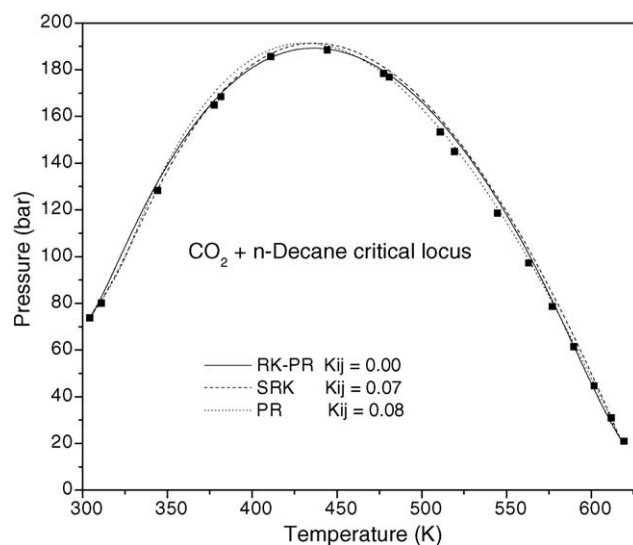

Fig. 15. Critical locus of the system carbon dioxide + *n*-decane, calculated by the SRK, PR and RK–PR equations. Experimental data from Reamer and Sage [35].

Although Fig. 15 shows the superiority of the proposed RK–PR equation in correlating the vapour–liquid critical line using only a k_{ij} parameter, the correct modelling of phase equilibria should take into account both the LLE and LVE regions, using also a l_{ij} interaction parameter for the co-volume. For this system, Fig. 16 shows that the upper critical end point (UCEP) can be reproduced and an even better prediction of the vapour–liquid critical locus obtained by using appropriate values of k_{ij} and l_{ij}. A detailed analysis of the effect of each interaction parameter and the strategy for their estimation will be provided in a future publication.
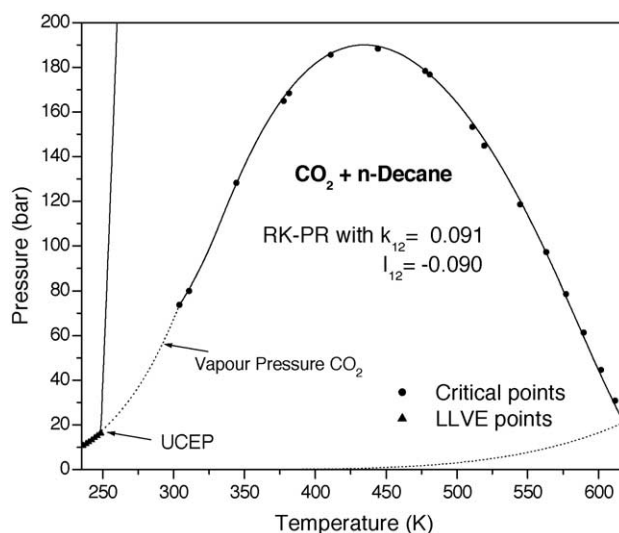

Fig. 16. Reproduction of global phase equilibria for the system carbon dioxide + *n*-decane with the RK–PR EoS and using both binary interaction parameters. Experimental critical points from Reamer and Sage [35] and LLVE data from Kulkarni et al. [36].

7. Conclusions

It was shown that in combination with a simple attractive term, the basic van der Waals repulsion is more accurate than the Carnahan–Starling equation to describe critical isotherms of real fluids. In particular, the RK–PR equation was found to be the best among the different cubic 3P density dependences found in the literature. The possibilities of this equation, connecting the density dependences of the SRK and PR EoS, have been explored in greater detail than previous studies for the modelling of PvT properties of pure fluids. The parameters δ_1 and b are constants for each compound, while a simple temperature dependence for the attractive parameter a is adjusted to reproduce the acentric factor.

The relation $Z_c^{EOS} = 1.168 Z_c^{exp}$ was adopted for all non-associating fluids. With the example of ammonia it was shown that very good results are also obtained for associating compounds, but the optimum Z_c ratio will be lower and need to be determined for each fluid.

The simple model thus obtained compares very favourable to the PC-SAFT equation when critical temperature and pressure are reproduced. At the same time, given that our 3P-EoS is essentially an extension of the SRK and PR equations, it was demonstrated that their limitations for prediction of densities are explained by their two-parameter nature rather than by their empiric character. Moreover, by comparison of their capabilities to correlate and predict phase equilibria of asymmetric systems, we will be able to identify the improvements due to the evolution from a corresponding states model to a one-parameter characterization of the length and/or polarity, which define the behaviour of a fluid in reduced variables. This will really be a test of cubic equations: to discriminate between the limitations of SRK or PR which are due to their 2P nature and those rooted in the empiricism of the vdW repulsions.

Although the proposed parameterization procedure requires T_c, P_c, Z_c and ω for each fluid, a group contribution approach is expected to provide good results for the heavier homologues of a given series, for which these constants are not known or cannot be measured. This is based on the trend observed for the relation a_c/b^2 which is analogous to the ratio $(\varepsilon/k)/(m\sigma^3)$ in SAFT models.

List of symbols

a	cohesive or energy parameter in an equation of state
b	general notation for the size-related parameter in an equation of state; co-volume
c	general notation for the dimensionless third parameter in an equation of state
k	parameter defining the temperature dependence of the attractive term in an EoS
P	pressure
R	universal gas constant ($R = 0.08314472$ bar L mol^{-1} K^{-1})
T	temperature
v	molar volume
Z	compressibility factor

Greek letters

δ_1	third parameter in the RK–PR EoS
δ_2	non-adjustable parameter defined in terms of δ_1
η	dimensionless variable relating the size parameter and the molar volume
ρ	molar density
τ	dimensionless variable relating the energetic parameter and the temperature
ω	acentric factor

Subscripts

c	critical property
L	liquid
r	reduced property
sat	saturated property
V	vapour

Appendix A. Demonstration of the uniqueness of the PvT behaviour predicted by a 2P-EoS

Mollerup [25,34] showed that every cubic two-parameter equation of state is a corresponding states model. Here, we provide a more general demonstration to the fact that every two-parameter equation of state shall predict a unique PvT behaviour in reduced variables and is therefore a corresponding states model.

In order to provide a reasonable qualitative behaviour, every 2P-EoS must have a size parameter and an energetic parameter, which serve to reduce the absolute volume and temperature, respectively.[1] Each of these equations can therefore be written in the dimensionless variables η and τ, defined in terms of those relations for the volume and temperature:

$$Z = \frac{P(b, v, a, T)v}{RT} = F(\eta, \tau) \tag{A.1}$$

Since η_c and τ_c are characteristic constants of a 2P-EoS [1] b and a will be directly proportional to v_c and T_c, respectively. Accordingly, η and τ turn out to be functions of v_r and T_r,

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[1] This includes, to the best of our knowledge, all published 2P-EoS in the literature with the only and particular exception of the Virial equation truncated after the third term, which nevertheless constitutes also a corresponding states model (see Appendix A.1).

respectively, and this implies that these two variables alone will determine the value of F in Eq. (A.1). Finally, we get:

$$P_r = \frac{T_r}{Z_c v_r} F(v_r, T_r) \tag{A.2}$$

which means unique PvT behaviour in reduced variables.

In order to apply this demonstration to some particular equations, and due to the way they are usually written, some transformations of parameters might be necessary in order to make things clearer. Taking the simple case of the van der Waals equation as an example, one may use $a = \frac{a_{vdW}}{Rb}$ to have the dimensionless variables

$$\eta = \frac{b}{v} = \frac{\eta_c}{v_r} \quad \text{and} \quad \tau = \frac{a}{T} = \frac{\tau_c}{T_r} \tag{A.3}$$

and the following expression for the compressibility factor

$$Z_{vdW} = \frac{1}{1-\eta} - \eta\tau = F_{vdW}(v_r, T_r) \tag{A.4}$$

It is important to note that the transformation of parameters is just an arbitrary matter, which does not affect the nature of the model or its predictions. It can also be useful, for example, for SAFT equations where the size parameter is a diameter and not a volume.

Finally, it should be pointed out that critical constants in this appendix – and therefore also reduced variables – refer to the values as predicted or estimated by the model. Accordingly, the conclusions apply to the models, independently of how their parameters are estimated.

A.1. The case when a size parameter and an energetic parameter cannot be identified

A good example of this situation is the Virial equation truncated after the third term:

$$P = \frac{RT}{v}\left(1 + \frac{B}{v} + \frac{C}{v^2}\right) \tag{A.5}$$

which can also be expressed as

$$Z = 1 + \eta_1 + \eta_2^2 \tag{A.6}$$

with $\eta_1 = \frac{B}{v}$ and $\eta_2 = \frac{\sqrt{C}}{v}$.

It is easy to see that for this equation of state, an equivalent result to Eq. (A.2), even simpler, is obtained:

$$P_r = \frac{T_r}{Z_c v_r} F(v_r) \tag{A.7}$$

and therefore, Eq. (A.5) is also a corresponding states model.

Summarizing, every two-parameter equation of state for which the compressibility factor can be expressed in terms of two dimensionless variables that are direct or inversely proportional to the molar volume and/or the temperature, is a corresponding states model.

Appendix B. Estimation of parameters for implementation of the generalized RK–PR EoS from Z_c, T_c, P_c and the acentric factor ω

The general case of estimation of parameters for a 3P-EoS implies, after fixing the critical compressibility factor, to solve the critical point conditions for the third parameter and the two dimensionless variables that relate the size and energetic parameters to the critical constants [1]. Nevertheless, cubic equations of state allow for the explicit calculation of a_c and b once the third parameter is obtained from a direct relation with Z_c. Most of the expressions given in this appendix are based on the second section of Chapter 3 in the book [25], where the reader is referred for further details and derivations.

In the RK–PR equation, the predicted Z_c is related to δ_1 by the following equation:

$$Z_c = \frac{y}{3y + d_1 - 1} \tag{B.1}$$

where y and d_1 are intermediate variables:

$$d_1 = \frac{1 + \delta_1^2}{1 + \delta_1} \tag{B.2}$$

$$y = 1 + [2(1 + \delta_1)]^{1/3} + \left(\frac{4}{1 + \delta_1}\right)^{1/3} \tag{B.3}$$

For non-associating fluids, we suggest to use $Z_c = 1.168 Z_c^{exp}$. Those fluids with $Z_c^{exp} = 0.29$ or higher must use $\delta_1 = \sqrt{2} - 1$, which corresponds to $Z_c = 0.3384$. Unfortunately, Eq. (B.1) cannot be solved analytically for δ_1. Nevertheless, the following correlation can be safely used for Z_c in the range 0.20–0.3384:

$$\delta_1 = d_1 + d_2(d_3 - Z_c)^{d_4} + d_5(d_3 - Z_c)^{d_6} \tag{B.4}$$

The coefficients for Eq. (B.4) as well as those for the correlation of k in Eq. (B.10) are given in Table B.1. The co-volume and the critical value of the attractive parameter are calculable from the following expressions:

$$b = \Omega_b \frac{RT_c}{P_c} \tag{B.5}$$

$$a_c = \Omega_a \frac{(RT_c)^2}{P_c} \tag{B.6}$$

Table B.1
Coefficients for estimation of δ_1 and k

Eq. (B.4)		Eq. (B.10)	
d_1	0.428363	A_1	−2.4407
d_2	18.496215	A_0	0.0017
d_3	0.338426	B_1	7.4513
d_4	0.660000	B_0	1.9681
d_5	789.723105	C_1	12.504
d_6	2.512392	C_0	−2.7238

Ω_a and Ω_b are functions of the third parameter δ_1:

$$\Omega_a = \frac{3y^2 + 3yd_1 + d_1^2 + d_1 - 1}{(3y + d_1 - 1)^2} \tag{B.7}$$

$$\Omega_b = \frac{1}{3y + d_1 - 1} \tag{B.8}$$

The k constant for the temperature dependence of the attractive parameter is obtained from the relation

$$k = \frac{\ln(a_{0.7}/a_c)}{\ln(3/2.7)} \tag{B.9}$$

where $a_{0.7}$ is the value required to match the experimental vapour pressure at $T_r = 0.7$.

To avoid the iterative calculation of that value one can use the following correlation in terms of the acentric factor and the predicted Z_c:

$$k = (A_1 Z_c + A_0)\omega^2 + (B_1 Z_c + B_0)\omega + (C_1 Z_c + C_0) \tag{B.10}$$

A simple recommendation for associating fluids is to estimate δ_1 and k simultaneously by reproducing the experimental vapour pressure and saturated liquid density at a reduced temperature of 0.7 or lower. a_c and b are given by δ_1 through Eqs. (B.5) and (B.6).

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