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Understanding Cubic Equations of State: A Search for the Hidden Clues of Their Success

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This work investigates the hidden details that are responsible for the practical success of cubic equations of state (EOS) in phase equilibrium calculations. A detailed consideration of the van der Waals method for evaluating the pure compound EOS parameters sheds new light on the reasons why the elimination of the actual critical volume as parameter was also adopted in the Redlich–Kwong and the Peng–Robinson (PR) frameworks. It is shown that an interesting relationship for the critical compressibility factor arising from the Martin–Hou method opens a new door for future exploration of different frameworks. A consideration of the key steps of Soave's reasoning for determining the temperature dependence of the attractive parameter explains the larger success of the Stryjek–Vera modification of PR EOS over the PR EOSs. A reference to the extension of cubic EOS to calculate liquid densities and enthalpies and a ready to use algorithm for the evaluation of the roots of a cubic equation are included for instructional purposes. *AIChE J*, 61: 2824–2831, 2015
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Introduction

It is surprising that in times when computer simulations of fluid phase systems are so advanced, cubic equation of state (EOS) are still the "working horse" for the design of industrial separation processes.[1] Moreover, although a recent study[2] has shown a potential use of cubic EOS for detecting errors in the values of the critical constants of complex compounds, it is difficult to imagine that there are some other interesting aspects of these EOS which still remain insufficiently explored. This work deals only with the case of pure compounds and identifies some surprising facts responsible for making cubic EOS so successful in engineering practice.

No attempt is made here to review the plethora of cubic or other EOS available in the literature. According to Valderrama,[3] at the time of publication of the Redlich–Kwong (RK) EOS,[4] 65 years ago, there were already more than 400 publications on cubic EOS available in the literature. As the RK EOS was the first-cubic EOS widely used for practical applications, after its proposal the number of publications on the subject dramatically increased.

Cubic EOS are of common use due to the simplicity in evaluating the volume roots at given values of the independent variables pressure and temperature. Exact equations for the evaluation of the roots of a cubic equation are well known and given in standard texts. A ready to use calculation algorithm is presented in the Appendix.

In this work, we discuss details that are common to three cubic EOS of practical use: the van der Waals (VW),[5] the RK,[4] and the Peng–Robinson (PR)[6] forms. For the RK EOS, we include its Soave modification, the RKS EOS,[7] and for the PR, we include the variation proposed by Stryjek, the PRSV EOS.[8] All these equations can be written in any of the following equivalent forms:

$$P=\frac{RT}{(v-b)}-\frac{a_c\alpha(T_r)}{v^2+c_1bv+c_2b^2} \tag{1a}$$

$$z\equiv\frac{Pv}{RT}=\frac{v}{(v-b)}-\frac{va_c\alpha(T_r)/RT}{v^2+c_1bv+c_2b^2} \tag{1b}$$

or

$$v^3+\left[(c_1-1)b-\frac{RT}{P}\right]v^2+\left[(c_2-c_1)b^2-c_1\frac{RT}{P}b+\frac{a_c\alpha(T_r)}{P}\right]v-\left[c_2b^2+c_2\frac{RT}{P}b+\frac{a_c\alpha(T_r)}{P}\right]b=0 \tag{1c}$$

The values of the constants c_1 and c_2 for the three basic cubic EOS are given in Table 1. The parameter b is usually interpreted as representing the volume occupied by the molecules, and the parameter a_c multiplied by the function of reduced temperature $\alpha(T_r)$ can be thought as representing the attractive effect of intermolecular forces. Thus, the second terms of the right-hand side of Eqs. 1a and 1b are usually referred to as the attractive term. Both the RKS and the PRSV modifications of the corresponding basic EOS, RK, and PR, affect only the form used for the function $\alpha(T_r)$. In all cases, however, at the critical isotherm the function $\alpha(T_r)$ is equal to unity.

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Table 1. Comparison of the Three Basic Cubic EOS

EOS	c_1	c_2	λ_b	λ_a	$z_{c,eq}$	$\Omega_b = \lambda_b z_{c,eq}$	$\Omega_a = \lambda_a z_{c,eq}$
VW	0	0	1/3=0.333	9/8=1.125	3/8=0.375	1/8=0.125	27/64=0.4218
RK/RKS	1	0	0.2599	1.2824	1/3=0.333	0.08664	0.42748
PR/PRSV	2	−1	0.2531	1.4874	0.3074	0.07780	0.45724

$$\alpha(T_r=1)=1 \tag{2}$$

Key Observations Common to the Three Basic Cubic EOS and Their Variations

The cubic EOS proposed by van der Waals was the first EOS capable of representing the vapor–liquid phase transition of pure compounds at temperatures below the critical and giving a single phase at temperatures above the critical. At temperatures below the critical, the equation has three roots for the molar volume. At the saturation pressure,* the largest and the smallest roots qualitatively represent the molar volumes of the gas and the liquid phases, respectively, while the intermediate root, which is quite close to the liquid volume root, has no physical meaning. At a temperature below the critical temperature and pressures below the saturation pressure, only the larger root in volume has physical sense and at pressures above the saturation pressure, the reverse is true. All three basic cubic EOS have used the method proposed by van der Waals for the evaluation of the constants b and a_c. This approach considers that the analytical representation of a pure compound critical isotherm has an inflexion point when the pressure equals the value of the actual critical pressure. At this inflection point, the molar volume is equal to a value $\bar{v}_c$ that is not necessarily equal to the experimental critical volume v_c of the compound under consideration. The fact that $\bar{v}_c$ is a pseudocritical volume and is the most important observation for the understanding of the study that follows. For simplicity, the following two definitions are introduced for the calculation of the values of the parameters b and a_c:

$$\lambda_b \equiv \frac{b}{\bar{v}_c} \tag{3}$$

and

$$\lambda_a \equiv \frac{a_c}{RT_c\bar{v}_c} \tag{4}$$

The mathematical requirement to satisfy the condition of an inflexion point of the critical isotherm, when the value of the pressure equals the value of the critical pressure, is that the two first derivatives of the pressure with respect to the volume be equal to zero. After simple algebra, using the definitions (3) and (4) and setting the first and second derivatives of Eq. 1a equal to zero, one obtains, respectively,

$$\lambda_a=\frac{(1+c_1\lambda_b+c_2\lambda_b^2)^2}{(1-\lambda_b)^2(2+c_1\lambda_b)} \tag{5}$$

and

$$\lambda_a=\frac{(1+c_1\lambda_b+c_2\lambda_b^2)^3}{(1-\lambda_b)^3\left[3+3c_1\lambda_b+\lambda_b^2(c_1^2-c_2)\right]} \tag{6}$$

Thus, eliminating λ_a from these two expressions, one obtains,

$$[c_1(c_1+c_2)-c_2]\lambda_b^3+3(c_1+c_2)\lambda_b^2+3\lambda_b-1=0 \tag{7}$$

The value of λ_b is then directly obtained from the solution of this cubic equation that for all cases of the cubic EOS considered here, gives only one real root and two complex conjugate roots. At this point, to clarify ideas, it is useful to consider the value of the compressibility factor that can be calculated from Eq. 1b in terms of the reduced variables $v_r=v/v_c$. and $T_r=T/T_c$, where v_c and T_c are the actual critical molar volume and critical absolute temperature of the compound under consideration. Introducing the definitions given by Eqs. 3 and 4, we obtain,

$$z_{\text{calculated}}=\frac{v_r}{\left[v_r-\lambda_b\left(\frac{\bar{v}_c}{v_c}\right)\right]}-\frac{v_r\lambda_a\left(\frac{\bar{v}_c}{v_c}\right)\alpha(T_r)}{T_r\left[v_r^2+c_1v_r\lambda_b\left(\frac{\bar{v}_c}{v_c}\right)+c_2\lambda_b^2\left(\frac{\bar{v}_c}{v_c}\right)^2\right]} \tag{8}$$

For the critical isotherm, Eq. 8 takes the form

$$z_{\text{calculated}\,(T_r=1)}=\frac{v_r}{\left[v_r-\lambda_b\left(\frac{\bar{v}_c}{v_c}\right)\right]}-\frac{v_r\lambda_a\left(\frac{\bar{v}_c}{v_c}\right)}{\left[v_r^2+c_1v_r\lambda_b\left(\frac{\bar{v}_c}{v_c}\right)+c_2\lambda_b^2\left(\frac{\bar{v}_c}{v_c}\right)^2\right]} \tag{9}$$

and for the critical point of a compound, at $v_r=1$,

$$z_{c,\text{calculated}}=\frac{1}{\left[1-\lambda_b\left(\frac{\bar{v}_c}{v_c}\right)\right]}-\frac{\lambda_a\left(\frac{\bar{v}_c}{v_c}\right)}{\left[1+c_1\lambda_b\left(\frac{\bar{v}_c}{v_c}\right)+c_2\lambda_b^2\left(\frac{\bar{v}_c}{v_c}\right)^2\right]} \tag{10}$$

If $\bar{v}_c$ were considered equal to the critical volume v_c of the compound under consideration, that is, if the inflection point of the analytical critical isotherm obtained from the cubic EOS would correspond with the actual critical point of the compound, Eqs. 8 and 11 would take the forms,

$$z_{\text{calculated},\bar{v}_c=v_c}=\frac{v_r}{(v_r-\lambda_b)}-\frac{v_r\lambda_a\alpha(T_r)}{T_r(v_r^2+c_1v_r\lambda_b+c_2\lambda_b^2)} \tag{8a}$$

and

$$z_{\text{calculated},\bar{v}_c=v_c,T_r=1}=\frac{v_r}{(v_r-\lambda_b)}-\frac{v_r\lambda_a}{(v_r^2+c_1v_r\lambda_b+c_2\lambda_b^2)} \tag{9a}$$

With the assumption of $\bar{v}_c=v_c$, Eq. 10 gives the values of $z_{c,eq}$ which we will call the intrinsic value of the critical compressibility factor given by Eq. 11. This intrinsic compressibility factor is characteristic for particular cubic EOS defined by the values of its constants c_1 and c_2,

$$z_{c,eq}=\frac{1}{(1-\lambda_b)}-\frac{\lambda_a}{1+c_1\lambda_b+c_2\lambda_b^2} \tag{11}$$

Thus, the intrinsic critical isotherm can be calculated as:

$$P_{r,\text{calculated}}=\frac{z_{\text{calculated},\bar{v}_c=v_c,T_r=1}}{z_{c,eq}v_r} \tag{11a}$$

For the VW EOS, as $c_1=c_2=0$, Eq. 7 directly gives

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*As discussed in the next section, cubic EOS of practical use are designed to give the saturation pressure of pure compounds.

$$\lambda_b = \frac{1}{3}$$

and from (6) and (11)

$$\lambda_a = \frac{9}{8} \text{ and } z_{c,eq} = \frac{3}{8}.$$

For the RK and the PR EOS, it is necessary to solve the cubic equation for λ_b. Direct application to Eq. 7 of the exact solution of a cubic equation (see the Appendix) shows that it corresponds to the case of a single real root and two imaginary roots. Thus, for the real root in the RK case,

$$\lambda_b = \sqrt[3]{2} - 1 = 0.25992, \lambda_a = 1 + \frac{\lambda_b{}^2}{3} + \lambda_b = 1.28244$$

and from (11),

$$z_{c,eq} = \frac{1}{3} = 0.33333$$

A similar exercise for the PR EOS gives

$$\lambda_b = 0.25308, \lambda_a = 1.48742, \text{ and } z_{c,eq} = 0.30740$$

These values are included in Table 1. The effect of the constants c_1 and c_2 on lowering the calculated value of the critical compressibility factor is evident. As there are two equations to evaluate the two parameters b and a_c, there is no additional flexibility to adjust the value of the critical compressibility factor to the proper value for each pure compound. The value of the critical compressibility factor for most compounds is lower than 0.29, thus, clearly, the introduction of the constants c_1 and c_2 given in Table 1, originated from the desire of lowering the value of compressibility factor given by the VW form.

In fact, although it seems that everything is in order, and there is not much to add, it is exactly at this point where van der Waals, knowingly or not, made his master move. Arguing that the critical volume was not easily available, what was true at the time of van der Waals proposal, he used the intrinsic critical compressibility factor given by Eq. 11 with the critical pressure and the critical temperature as reducing parameters.

Considering Eq. 11, van der Waals wrote

$$\bar{v}_c = z_{c,eq} \frac{RT_c}{P_c} \tag{12}$$

This change of variables is far from trivial as it explains the main factor supporting the success of cubic EOS. As the literature has largely ignored what is behind the evaluation of parameters for cubic EOS, we give some detailed consideration to this aspect here.

From Eq. 12, we write

$$\frac{\bar{v}_c}{v_c} = \frac{z_{c,eq}}{z_c} \tag{13}$$

where we repeat, v_c and z_c are the experimental critical volume and compressibility factor of the compound under consideration. Also, according to Eq. 3, the parameter b is now given by

$$b = (\lambda_b z_{c,eq}) \frac{RT_c}{P_c} \equiv \Omega_b \frac{RT_c}{P_c} \tag{14}$$

Similarly, from Eq. 4, the value of the parameter a_c is now given by

$$a_c = (\lambda_a z_{c,eq}) \frac{(RT_c)^2}{P_c} \equiv \Omega_a \frac{(RT_c)^2}{P_c} \tag{15}$$

The values of Ω_b and Ω_a as defined by Eqs. 14 and 15, are included in Table 1. Table 1 does not include any information that is not easily available in the literature. The purpose of reproducing it here is to show that in what follows we use exactly the forms of the cubic EOS applied in practice.

Most notably, the values of the parameters b and a_c obtained from Eqs. 14 and 15 are different from the values obtained from Eqs. 3 and 4 if $\bar{v}_c$ were considered equal to the critical volume v_c of the compound under consideration.

With van der Waals suggestion, Eqs. 8, 9, and 10 now take the forms:

$$z_{\text{calculated,vW}} = \frac{v_r}{\left(v_r - \frac{\Omega_b}{z_c}\right)} - \frac{v_r \frac{\Omega_a}{z_c} \alpha(T_r)}{T_r \left[v_r^2 + c_1 v_r \frac{\Omega_b}{z_c} + c_2 \left(\frac{\Omega_b}{z_c}\right)^2 \right]} \tag{16}$$

or

$$P_{\text{r,calculated,vW}} = \frac{z_{\text{calculated,vW}} T_r}{z_c v_r} \tag{16a}$$

For the critical isotherm, Eq. 9a takes the form

$$z_{\text{calculated at } T_r=1\text{,vW}} = \frac{v_r}{\left(v_r - \frac{\Omega_b}{z_c}\right)} - \frac{\frac{\Omega_a}{z_c} v_r}{v_r{}^2 + c_1 \frac{\Omega_b}{z_c} v_r + c_2 \left(\frac{\Omega_b}{z_c}\right)^2} \tag{17}$$

or

$$P_{\text{r,calulated,vW}}(T_r = 1) = \frac{z_{\text{calculated at } T_r=1\text{,vW}}}{z_c v_r} \tag{17a}$$

and for the critical point of a compound, at T_c, P_c, and v_c, Eq. 17 gives

$$z_{\text{c,calculated,vW}} = \frac{1}{\left(1 - \frac{\Omega_b}{z_c}\right)} - \frac{\frac{\Omega_a}{z_c}}{1 + c_1 \frac{\Omega_b}{z_c} + c_2 \left(\frac{\Omega_b}{z_c}\right)^2} \tag{18}$$

The letters "vW" added to the subscripts indicate that these equations follow the van der Waals suggestion. So, in fact, in van der Waals algebra, we have to distinguish three values of "critical compressibility" factors: (a) the experimental value for the compound under consideration, z_c; (b) the intrinsic value given by Eq. 11, $z_{c,eq}$; (c) the value $z_{\text{c,calculated,vW}}$ calculated from Eq. 18 in the way that cubic EOS are used in practice once a_c and b are determined from Eqs. 14 and 15.

Although the van der Waals' suggestion is the universally accepted treatment, we call the attention to its flagrant mathematical inconsistency. We note that Eq. 11 is obtained from Eq. 10 considering that $\bar{v}_c$ corresponds to the critical volume, v_c, and that the value of $z_{c,eq}$ was obtained using precisely Eq. 11. This very same value of $z_{c,eq}$ is the one used by van der Waals in Eq. 12 to calculate a new value for $\bar{v}_c$ that is obviously going to be different from the critical volume, v_c. If the treatment is so inconsistent, one may ask why the cubic equation of RK and also the cubic equation of PR, followed the exact path proposed by van der Waals even when at the time of their proposals values for the critical volumes of compounds were easily available in the literature. To understand the reason for these choices, Figure 1 presents the plots of Eqs. 9a and 17 for a compound with $z_c = 0.29$.

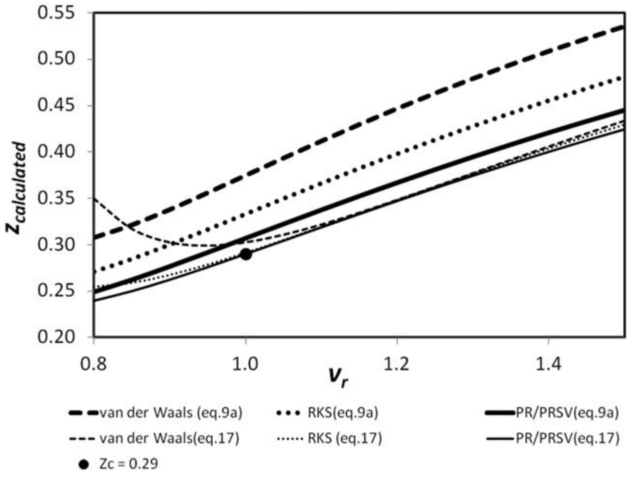

Figure 1. Comparison of compressibility factor *z* calculated with basic EOS when Eq. 9a (thick lines) or Eq. 17 (thinner lines) are used. $z_c=0.29$.

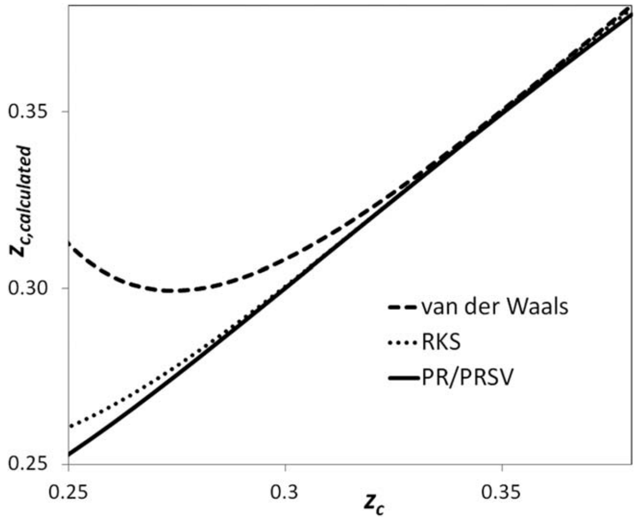

Figure 2. Comparison of results of Eq. 18 with experimental values.

The displacement of z_{calc} at $v_r=1$ toward the value of $z_c=0.29$ is evident.

As a further example of the effect of the change in the parameters, Figure 2 presents the values for the critical compressibility factor calculated with Eq. 18 as a function of the critical compressibility factor of the compounds. It is obvious that the values of the constants b and a_c obtained with Eqs. 14 and 15 will be different from the values obtained from Eqs. 3 and 4. While these latter values satisfy the mathematical conditions for the critical isotherm having an inflexion point at the critical point, the former values, that are those actually used in practice, do not. Conversely, the displacement of the calculated critical point obtained with b and a_c evaluated from Eqs. 14 and 15 seems to be more important for practical applications than the rigorous satisfaction of the mathematical requirements of a critical point. The displacement of the calculated critical point toward the actual critical point moves the critical isotherm, as a whole, toward the values closer to that of the compound in question and this effect propagates to lower temperatures. Figure 3 depicts the behavior of the calculated reduced pressure for the critical isotherm as a function of reduced volume.

Thus, the change in parameters tends to improve the results obtained with cubic EOS for the calculation of fugacities at saturation, which are basic for phase equilibrium calculations.

The impressive results presented in Figure 2 can be explained by observing that the van der Waals method of using Eq. 12 to calculate $\bar{v}_c$ is in fact introducing a third-pure compound parameter, z_c. This is what it is done in practice when cubic EOS are used with the parameters b and a_c calculated in terms of of Ω_b and Ω_a with Eqs. 14 and 15.

Equations Obtained from the Martin–Hou Method

Martin and Hou[9] proposed an alternative method to evaluate the pure compound parameters b and a_c, which is simpler and produces useful intermediate equations. This method considers that at the point of inflection of the analytical critical isotherm, the cubic equation gives three equal roots for the molar volume. Thus, at this inflection point,

$$(v-\bar{v}_c)^3=0$$

or after expansion,

$$v^3-3\bar{v}_c v^2+3\bar{v}_c^2 v-\bar{v}_c^3=0 \tag{19}$$

We observe that again we use the special symbol $\bar{v}_c$ to distinguish the molar volume at which the inflection point occurs from the actual critical volume, v_c, of a compound under consideration. Equation 1c, at the critical temperature, when the pressure is equal to the critical pressure, takes the form

$$v^3+\left[(c_1-1)b-\frac{RT_c}{P_c}\right]v^2+\left[(c_2-c_1)b^2-c_1\frac{RT_c}{P_c}b+\frac{a_c}{P_c}\right]v-\left[c_2b^2+c_2\frac{RT_c}{P_c}b+\frac{a_c}{P_c}\right]b=0 \tag{20}$$

Comparison of the coefficient for the second power of volume of Eqs. 19 and 20 gives

$$(c_1-1)b-\frac{RT_c}{P_c}=-3\bar{v}_c$$

Thus, combining with Eqs. 3 and 12, after rearranging, we get

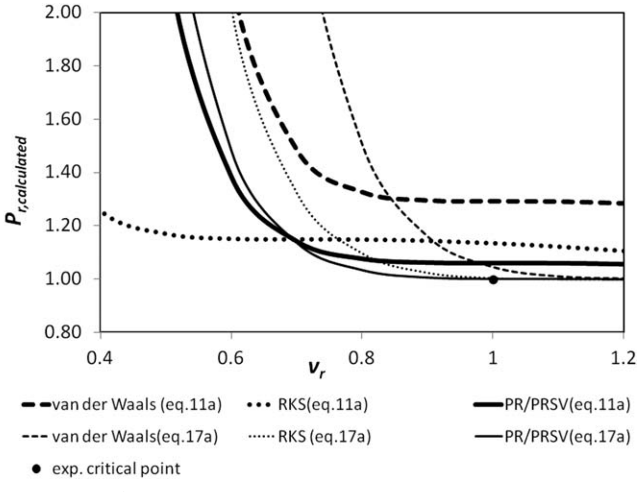

Figure 3. Comparison of critical isotherms calculated by different EOS using Eqs. 11a and 17a.

$$z_{c,eq} \equiv \frac{P_c \bar{v}_c}{RT_c} = \frac{1}{3+(c_1-1)\lambda_b} \tag{21}$$

To the best of our knowledge, this extremely interesting equation has passed unnoticed in the literature. While Eq. 11 requiring the values of constantsc_1 and c_2, it is a function of both λ_a and λ_b, Eq. 21 gives the value of $z_{c,eq}$ as a function of c_1 and λ_b only. Conversely, for each value of c_1, giving the desired value of $z_{c,eq}$ with Eq. 21, there is a conjugate value of c_2 necessary to satisfy Eq. 7.

Similarly, comparison of the coefficients of the volume to the first power of Eqs. 19 and 20, combining with Eq. 4 gives,

$$\lambda_a = \frac{3+(c_1-c_2)\lambda_b^2}{3+(c_1-1)\lambda_b} + c_1\lambda_b \tag{22}$$

Again, this interesting new form of the relation between λ_a and λ_b is simpler than Eqs. 5 and 6. Although not immediately obvious, combination of Eqs. 11 and 22 gives the same results as the simpler Eq. 21. Finally, completing the presentation of the results obtained by the method of Martin–Hou, it suffices to say that the comparison of the constant terms of Eqs. 19 and 20, after rearrangement, gives a cubic equation identical to Eq. 7 used to evaluate λ_b.

Answers to Two Important Questions

After the above exercise, one question naturally arises. What would have happened if van der Waals and all his followers had done all the exercise considering the actual critical volume $v_c = z_c \frac{RT_c}{P_c}$ of a compound instead of considering the fictitious value $\bar{v}_c = z_{c,eq} \frac{RT_c}{P_c}$? In this case, Eqs. 14 and 15 will have been simplified to the forms

$$b = (\lambda_b z_c)\frac{RT_c}{P_c}$$

$$a_c = (\lambda_a z_c)\frac{(RT_c)^2}{P_c}$$

and Eq. 11 would have been recovered, as expected. Thus, the convenient displacement introduced that the use of Eq. 12 would have been lost.

A second-natural question is whether there is any way to further lower the calculated critical compressibility factor by a cubic EOS in comparison with the values reported in Table 1. The answer is that this is possible and simple to do. Van der Waals, Redlich and Kwong, and also Peng and Robinson did not have the advantage of having the treatment of Martin–Hou, so presumably, they found the values for the constants c_1 and c_2 by trial and error. In addition, following the treatment of van der Waals, they obtained the values of λ_b and λ_a using the simultaneous solution of equations generated from the first and second derivative of the pressure with respect to the molar volume equated to zero. The solution of these two simultaneous equations is cumbersome and gives Eqs. 5 and 6. For the critical compressibility factor, the only form these authors had at their disposal was Eq. 11, which is the form directly obtained from Eq. 1b. Conversely, the treatment of Martin–Hou gives separately the two components of Eq. 11, namely Eqs. 21 and 22. Notably, Eq. 21 shows that the value of the calculated critical compressibility factor is only a function of the constant c_1. The fact that the calculated critical compressibility factor is not a function of the constant c_2, as given by Eq. 11, suggests a simple form to lower the value of the calculated critical compressibility factor without necessary using a fictitious critical volume as van der Waals and all his followers did. Although using Eq. 21, it would be possible to adjust the value of the constant c_1 so to give any desired value of the critical compressibility factor for each particular compound, it is desirable to have the same values of c_1 and c_2 for all compounds, otherwise the mixing rules necessary for the treatment of mixtures would become too complex. Thus, let us say that we fix the value of the critical compressibility factor at 0.290. Giving values to c_1, we then calculate λ_b from Eq. 21, from Eq. 7 we obtain c_2, and from Eq. 22 we finally obtain λ_a. Although it is not a necessary condition, for elegance, it is desirable that the constantsc_1 and c_2, be integers. A few trials using Excel gave $c_1=4$, $c_2=3$, $\lambda_b=0.14937$ and $\lambda_a=1.4740$. As far as we know, this set of values has not been used in the literature.

On the Temperature Dependence of the Attractive Term

Even when the proposal of a cubic EOS describing the vapor–liquid transition earned van der Waals the Nobel Prize, for practical purposes the VW EOS is of limited use. As discussed by Abbott,[10] no cubic EOS can give simultaneously good values for vapor pressure, molar volumes, enthalpies, or heat capacities without introducing additional parameters or displacements. A decision must be made on the property that is desirable to reproduce and then adjust the parameters accordingly. Due to the importance of phase equilibrium in the design of separation processes, cubic EOS of common use has been designed to reproduce vapor pressures. Following this line of thought, major steps forward were the modifications of the volume dependence. As shown in Table 1, the RK EOS lowered the value of the critical compressibility factor through the introduction of the constant c_1 and the PR EOS lowered it further by changing the value of c_1 and introducing the constant c_2. In addition, the VW EOS considered the function $\alpha(T_r)$ to be equal to unity at all temperatures while the RK EOS considered it equal to the inverse of the reduced temperature elevated to a power 0.5.

A first step toward a better representation of the pure compound vapor pressure was done by Wilson[11] by modifying the temperature dependence of $\alpha(T_r)$. The next leap forward was given by Soave[7] who incorporated the acentric factor into the temperature dependence of the RK EOS and formulated what is now called the Redlich-Kwong-Soave (RKS) EOS. To follow Soave's reasoning, we consider first the information he had at hand. The main use of EOS is for the phase equilibrium calculations. For the case of vapor–liquid equilibrium of a pure compound, it is desirable to calculate the saturation pressure of the compound at temperatures below the critical. This is done by satisfying the equality of pressure calculated by the EOS for the vapor and the liquid at the temperature of interest and also the equalities of the fugacity coefficients of the compound in both saturated phases. The algebraic forms of the pure compound fugacity coefficients for the EOS included in Table 1 are listed in Table 2.

Thus, the saturated volumes of the vapor and of the liquid phases should satisfy the following two equations,

$$P^{sv}(v^{sv},T) = P^{sl}(v^{sl},T)$$

$$\varphi^{sv}(v^{sv},T) = \varphi^{sl}(v^{sl},T)$$

Soave observed that for any given value of $\alpha(T_r)$, there is a single value of pressure that is obtained from this set of

Table 2. Expressions for the Fugacity Coefficients of the Three Basic Cubic EOS

EOS	$\ln\phi=(z-1)-\ln z-\int_{\infty}^{v}(z-1)\frac{dv}{v}$
VW	$\ln\phi=(z-1)-\ln(z-B)-A/z$ with $A=Pa/(RT)^2$, $B=Pb/RT$
RK/RKS	$\ln\phi=(z-1)-\ln(z-B)-\frac{A}{B}\ln\left(\frac{z+B}{z}\right)$ with A and B as above
PR/PRSV	$\ln\phi=(z-1)-\ln(z-B)-\frac{A}{2B\sqrt{2}}\ln\left(\frac{z+B(1+\sqrt{2})}{z+B(1-\sqrt{2})}\right)$ with A and B as above

equations, and thus, he concluded that for a given value of the saturation pressure there is only a single value of α that satisfies both equations. He then took correlations for the saturation pressure of different hydrocarbons. For each hydrocarbon, he followed a trial and error procedure to find the values of $\alpha(T_r)$ at different reduced temperatures. At each temperature, starting from the RK approximation of $\alpha=1/T_r^{0.5}$, he guessed a value of α, and knowing the vapor pressure, he obtained the values of the two-saturated volumes by the exact solution of the cubic equation for each phase. Subsequently, he checked whether these values satisfied the equality of fugacities or not and continued until a solution was found. A plot of $\alpha^{0.5}$vs. ${T_r}^{0.5}$ gave straight lines for each of the hydrocarbons studied, so Soave proposed the following relation satisfying the condition of $\alpha_{T_r=1}=1$,

$$\alpha=\left[1+\kappa(1-{T_r}^{0.5})\right]^2 \tag{23}$$

where κ is the slope of the straight line obtained for each of the hydrocarbons. The next step of Soave's reasoning was the most significant as it directly relates the slope to the acentric factor ω of each compound. The acentric factor ω, was defined by Pitzer[12] as:

$$\omega\equiv-\log_{10}\left(\frac{P^s}{P_c}\right)_{at\,T_r=0.7}-1 \tag{24}$$

Writing Eq. 23 for $T_r=0.7$, and rearranging,

$$\kappa=\frac{1-\alpha^{0.5}_{T_r=0.7}}{1-(0.7)^{0.5}} \tag{25}$$

The value of ω fixes the value of the saturation pressure at reduced temperature 0.7, and this value of the saturation pressure uniquely fixes the value of $\alpha_{T_r=0.7}$ which in turn uniquely fixes the value of the slope κ, according to Eq. 25. Therefore, Soave correlated the values of κ with ω, and obtained

$$\kappa_{RKS}=0.480+1.574\omega-0.176\omega^2 \tag{26}$$

This brilliant step forward made all the difference in the use of the RK, now RKS EOS, for applications in the petroleum industry.

As discussed above, the PR EOS[6] modified the volume dependence of the attractive term, so to give still a lower value of the critical compressibility factor, closer to that of compounds around hexane and heptane that were of special interest for the petroleum industry. For the temperature dependence of $\alpha(T_r)$, the authors fitted a polynomial formally similar to Eq. 26 using values of $\alpha(T_r)$ in all the range of reduced temperature for which they had vapor pressure data and proposed the form

$$\kappa_{PR}=0.37464+1.54226\omega-0.2699\omega^2 \tag{27}$$

As shown elsewhere,[13] Eq. 27 fails to reproduce the value of κ given by Eq. 25. Conversely, Stryjek[8] realizing this shortcoming of the PR EOS followed exactly the path proposed by Soave for the RK EOS and obtained the following correlation for κ, to be used in Eq. 29 in a modified PR EOS, called PRSV:

$$\kappa_{PRSV}=\kappa_0+\kappa_1(1+T_r^{0.5})(0.7-T_r) \tag{28}$$

with

$$\kappa_0=0.37889+1.48971\omega-0.17132\omega^2+0.01965\omega^3 \tag{29}$$

Clearly, κ_0 is the slope given by Eq. 25 and κ_1 is an individual parameter for each compound, which effect cancels out at reduced temperature 0.7. Values of κ_1 have been presented in the literature for compounds of industrial interest.[8,14,15]

Zabaloy[13] compared the values of $\alpha(T_r)$ given by the different approximations. The original PR EOS gives large errors at low and high values of the acentric factor. The error in κ propagates exponentially in the vapor pressure. The RKS EOS has an acceptably error for low values of the acentric factor, but the error increases as the acentric factor increases while the PRSV EOS gives an error of virtually 0% in all the range of acentric factors. These results explain why the RKS EOS is satisfactory for light nonpolar fluids, say from methane to butane, and the PR EOS is satisfactory for medium weight hydrocarbons, say from pentane to heptane, while the PRSV extended the use of cubic EOS to alcohols, acids, and all other kinds of functional compounds. As discussed elsewhere,[15] although not immediately evident, it can be shown that the combination of Eqs. 23 and 28 gives a temperature dependence for α of the PRSV EOS formally similar to a temperature dependence that had been previously proposed by Mathias[16] for a modified RKS EOS. However, most notably, in the same year Mathias and Copeman[17] proposed a different temperature dependence for a modified PR EOS and this suggests that the temperature dependence that had worked well for the modified RKS EOS did not produce equally good results for the modified PR EOS. As the combination of Eqs. 23 and 28 produced excellent results in the PRSV form, the clear explanation is that the under performance of the modified PR EOS was due to the failure of the PR form to satisfy the all important Eq. 25. Conversely, the PRSV modification of the PR EOS meets this condition by construction.

Although the understanding of the factors determining the performance of cubic EOS presented in this work has been restricted to their use for calculation of vapor pressures and fugacities, once the EOS produced satisfactory results for these properties, it was possible to extend its use for the calculation of pure compounds saturated volumes and enthalpies.[15] Similarly, Mathias and Klotz[18] have shown that if so desired, the function $\alpha(T_r)$ can be fitted to closely reproduce liquid heat capacities without a major deterioration of the fitting of vapor pressures.

Discussion and Conclusions

To explain the surprising effects clearly seen in Figures 1 and 2, it has been necessary to distinguish between the critical volume of the compound under consideration, v_c, and the molar volume at which the analytical critical isotherm presents an inflection point, $\bar{v}_c$. Additionally, it has been necessary to identify three compressibility factors: the critical compressibility factor of the compound under consideration, z_c, the intrinsic compressibility factor given by EOS,

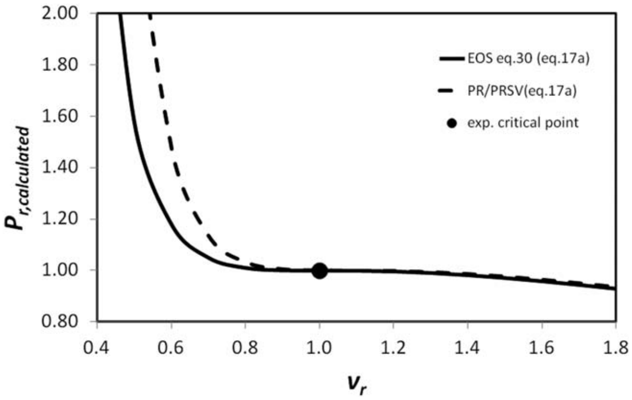

Figure 4. Comparison of critical isotherms for the new proposed equation and the PR/PRSV equation.

$z_{c,eq}$, and the critical compressibility factor calculated from the EOS in the form that is actually used in practice, $z_{c,calculated}$.

In this study, we have emphasized the difference between the VW and the Martin–Hou approaches for obtaining the EOS parameters. Although both approaches give the same answers, as they should, the latter treatment is more direct and explicit. The Martin–Hou treatment has the additional advantage of showing in an explicit way that $\bar{v}_c$ is molar volume at which the inflection point occurs in the analytical representation of the critical isotherm and not necessarily it corresponds with the actual critical volume of a compound under consideration. Important as this distinction is, perhaps the most surprising result produced by the method of Martin–Hou is Eq. 21. This equation shows that the value of the calculated critical compressibility factor is only a function of the constant c_1 and λ_b while Eq. 8, obtained following the van der Waals method, seems to indicate that the calculated critical compressibility factor is not only a function of c_1 and λ_b but it also requires the values of c_2 and λ_a. In this work, we also have explored the effect of using a fictitious critical volume as defined by Eq. 12 instead of the actual critical volume of a compound for the evaluation of the EOS parameters a_c and b. The mathematical conditions of having an inflection point in the critical isotherm at the critical point are violated, but the value of the calculated critical compressibility factor tends to follow the actual value of the compressibility factor of the compound. Until now, this intriguing result has been totally ignored in the literature. Finally, we have emphasized the difference between the temperature dependence used by the PR EOS and the form proposed by Stryjek for the PRSV EOS, which makes the PRSV EOS so superior to the original PR form.

In conclusion, using Eq. 21, the following new framework, among other possibilities, looks interesting:

$$P=\frac{RT}{v-b}-\frac{a_c\alpha(T_r)}{v^2+4bv+3b^2} \tag{30}$$

This form gives $z_{eq}=0.29$ with $\lambda_a=1.4740$, $\lambda_b=0.1494$ or equivalently $\Omega_a=$ 0.42748 and $\Omega_b=$ 0.04332. Thus, from Eqs. 14 and 15

$$a_c=0.42748\ \frac{(RT_c)^2}{P_c}$$

$$b=0.04332\frac{RT_c}{P_c}$$

As the fitting of $\alpha(T_r)$ at the ω point is independent of the framework, exactly the same approach used in PRSV can be used (Figure 4). The detailed study of this particular form or any other, arising from the same reasoning, is well beyond the aims of the present exploratory search.

The application of EOS to mixtures is beyond the scope of this study as it requires the use of mixing rules. A study of the performance of a two-parameter mixing rule is available elsewhere.[19] When using mixing rules, it is important to test their invariance to the subdivision of one component into quasi-identical components.[20]

As a closing comment, we observe that the most important ideas included in this analysis of the cubic EOS are absent in the presentation of these EOS in standard texts for students.[21,22] The text of Smith et al.[21] gives a simplified version of the Martin–Hou method, without giving a reference, and it applies it only to the van der Waals framework which has c_1 and c_2 equal to zero, thus it misses the important form of Eq. 21.

Notation

a = attractive parameter
b = covolume
c_1, c_2 = EOS constants
P = pressure
R = universal gas constant
T = absolute temperature
v = molar volume
v_c = critical molar volume
$\bar{v}_c$ = pseudo critical molar volume obtained from the inflexion point of the critical isotherm at P_c
z = compressibility factor

Greek letters

α = temperature functionality of the attractive parameter
ϕ = fugacity coefficient
κ = slope of α as a function of $T_r^{0.5}$
κ_0 = function of the acentric factor
λ_a = proportionality constant for the attractive parameter
λ_b = proportionality constant for the covolume
Ω_a = $\lambda_a z_{c,eq}$
Ω_b = $\lambda_b z_{c,eq}$
ω = acentric factor

Subscripts and superscripts

c = critical state
eq = intrinsic value characteristic of the EOS
exp = experimental
r = reduced property
s = value at saturation
sl = saturated liquid
sv = saturated vapor
vW = following the van der Waals approach, Eq. (12)

Abbreviations

EOS = equation of state
PR = Peng–Robinson[6]
PRSV = Stryjek–Vera modification of PR EOS[8]
RK = Redlich–Kwong[4]
RKS = Soave modification of RK EOS[7]
VW = van der Waals[5]

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Appendix : Exact Solution of a Cubic Equation

The following simplified presentation of the exact method to evaluate the solutions to a cubic equation has been adapted from the version presented in Perry's Handbook.[23] Consider the general form of a cubic equation

$$x^3+Ax^2+Bx+C=0$$

where A, B, and C are numeric coefficients. For simplicity, define

$$D=(A/3)^3-(AB/6)+(C/2)$$

$$E=(B/3)-(A/3)^2$$

and

$$\Delta=D^2+E^3$$

If $\Delta=0$, there are three real roots with at least two equal roots:

$$x_1=2\sqrt[3]{(-D)}-(\mathrm{A}/3)$$

$$x_2=x_3=-\sqrt[3]{(-D)}-(\mathrm{A}/3)$$

If $\Delta>0$, there is one real root and two complex conjugate roots. In this case define

$$F=\sqrt[3]{(-D)+\sqrt{\Delta}}$$

and

$$G=\sqrt[3]{(-D)-\sqrt{\Delta}}$$

$$x_1=F+G-(A/3)$$

$$x_2=-\left[\frac{1}{2}(F+G)+\frac{A}{3}\right]+\frac{\sqrt{3}}{2}(F-G)i$$

$$x_2=-\left[\frac{1}{2}(F+G)+\frac{A}{3}\right]-\frac{\sqrt{3}}{2}(F-G)i$$

If $\Delta<0$, there are three real and unequal roots. In this case define

$$\theta(\text{radians})=\arccos\left(\frac{-D}{\sqrt{-E^3}}\right)$$

$$x_1=2\sqrt{-E}\,\cos\,(\theta/3)-A/3$$

$$x_2=2\sqrt{-E}\,\cos\,[\theta/3+(2/3)\pi]-A/3$$

$$x_3=2\sqrt{-E}\,\cos\,[\theta/3+(4/3)\pi]-A/3$$

Readers interested in efficient use of an iterative algorithm can consult the recent work by Deiters and Macías-Salinas[24] (2014).

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