

Simple modifications of the van der Waals and Dieterici equations of state: vapour–liquid equilibrium properties

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Recent studies have considered simple (*i.e.*, no adjustable parameters) modifications to the van der Waals and Dieterici equations of state. It is still unclear, however, at least for the calculation of vapour–liquid equilibrium properties, whether the appropriate repulsive term is that of the classical van der Waals equation or that given by the Carnahan–Starling equation for hard spheres. Moreover, the studies on the Carnahan–Starling–Dieterici equation of state have raised the interesting question of the comparison between the van der Waals (summed terms) and Dieterici (multiplied terms) approaches. We study here the suitability of six families of equations of state in obtaining the main vapour–liquid properties of simple fluids. These families include, together with the aforementioned equations, a variable exponent in the power-law temperature dependence. The main aims are to identify the best choice of a simple predictive equation of state, and to determine whether the Carnahan–Starling repulsive equation is a clearly acceptable alternative to the traditional van der Waals repulsive term, and whether the Dieterici-type equations can give better results than those based on the van der Waals equation.

1. Introduction

Since the time of van der Waals, there have appeared an almost uncountable number of equations of state (EoS's) for industrial and academic uses (see for *e.g.* refs. 1–3). A few of the academic EoS's, including the van der Waals or the Redlich–Kwong⁴ cases, can be considered as simple and predictive, since they contain only two fixed parameters that are calculated from the critical properties. Their simple mathematical structure allows one to calculate thermodynamic properties analytically. Although they are generally less accurate, they have served as the basis for the development of more complex empirical equations, which, while they usually give an improved description of a fluid's properties, have the drawback of mathematical complexity and additional adjustable parameters.

Recent papers^{3,5–8} have reconsidered simple analytical expressions for the EoS's, raising two interesting and still unanswered questions. On the one hand, there is the question of whether the Carnahan–Starling hard-sphere EoS is an acceptable alternative to the traditional van der Waals (vdW) term for the repulsive part of the complete EoS. And on the other, there is an unresolved issue about two possible separations for the EoS's, with the papers of Sadus^{3,7} and Cachadiña *et al.*⁶ arguing in opposite directions. The Dieterici-type separation considers the complete EoS to be a product of two factors, one attractive and one repulsive. The vdW-type separation considers the more usual additive scheme of contributing terms.

While there have been very many equations of state developed following the vdW scheme, only the Redlich–Kwong⁴ EoS has led to an improvement in the results without increasing the mathematical complexity or the number of input parameters. Both the vdW and the Redlich–Kwong (RK)

equations require only the critical pressure and temperature as input. The improvement in results for the vapour–liquid equilibrium properties (which is perhaps the most important reason for the development of a new equation of state) is significant, and the RK equation has been the foundation of numerous further improvements based on empirically modifying the attractive term by introducing new coefficients or input parameters (see for *e.g.* refs. 1, 2, 9–11). In most cases, the proposed equations of state are cubic in volume, so that the van der Waals idea is maintained. The disadvantage of cubic EoS's is that both the repulsive and the attractive terms are inaccurate, as shown by molecular simulations.^{1,12–14} These inaccuracies cancel out each other when the EoS's are used to calculate fluid properties, in particular the VLE.¹ A sounder theoretical basis for the coupling of repulsive and attractive terms in simple EoS's would make them more suitable for extrapolation purposes than the empirical equations.^{3,15,16}

The possibilities for the choice of expressions other than the vdW one for the repulsive term are many,^{2,17–19} but the most commonly used is the well-known Carnahan–Starling (CS) equation for hard-spheres.^{20,21} Carnahan and Starling²² incorporated their repulsive term into the vdW and RK attractive terms, proposing the so-called CSvdW and CSRK equations. This latter combination improved the prediction of hydrocarbon densities²² and several properties of other pure fluids.²³ Moreover, according to Prausnitz²⁴ the “CSRK equation gives better values than the CSvdW one for the compressibility factor for argon along the critical isotherm at intermediate densities somewhat above the critical, but it is poor at high densities”. These results do not clarify whether the predictions of other vapour–liquid equilibrium properties are improved or not. Indeed, whereas Kontogeorgis *et al.*²⁵ state that “the van der Waals repulsive term is a reasonable choice and attempts to

use other repulsive terms, typically the hard-sphere one, lead to no improvement”, Yelash and Kraska³ indicate that “it appears that the vdW repulsion accidentally yields better results than the CS repulsion” with respect to the saturation liquid density, “what is caused by the low pole packing fraction of the vdW repulsion. It, however, fails to describe thermodynamic and structure properties of dense phases”. Moreover, whereas from practical considerations it has been argued that most modifications to the repulsive term give rise to non-cubic equations,¹ there is a clear exception in the recent proposal of Mohsen-Nia *et al.*²⁶

The possibility of simple changes maintaining the quadratic dependence on volume for the attractive term has been amply studied by Yelash and Kraska in ref. 3. In particular, the authors investigate the effect of the density dependence of an attractive term by using a generalized quadratic volume dependence, but maintaining the vdW temperature dependence. The generalization is accomplished by introducing two (substance independent) parameters which allow several families of generalized simple cubic EoS's to be considered. Both the vdW and the CS repulsions were studied. Unfortunately, the results of that work³ do not shed any light on whether the use of the CS expression is an adequate alternative for the calculation of the VLE properties at least for simple fluids. Moreover, other forms of temperature dependence, such as that proposed by Redlich and Kwong,⁴ were not considered. In this sense, Mathias²⁷ has found that using a dependence on T^{-1} instead of $T^{-1/2}$ in the attractive RK equation gives better results for substances' second virial coefficient. As far as we know, there has been no consideration of other simple temperature power laws in either the vdW or the RK equations and of their influence on VLE properties. Other studies of possible changes to the repulsive and/or attractive part of the vdW-type equations of state (see for *e.g.* refs. 1, 2, 15, 16, 26, 28, 29) include new input parameters or adjustable coefficients.

Recently,^{5,7,30} Sadus has revisited the alternative approach suggested by Dieterici in which the attractive part of the equation is not a summed term, but is an exponential term in temperature and density. Sadus suggests that suitably modifying the Dieterici equation by introducing the modern understanding of intermolecular interactions, it might be possible to find a new type of equation that could yield more accurate predictions of the phase coexistence properties of fluids than the traditionally used additive approach.

In particular, Sadus proposes using the Carnahan–Starling EoS²⁰ to represent the repulsive term in combination with the exponential term suggested by Dieterici. That equation is both simple (involving only two parameters) and predictive since only the critical properties are required. The multiplicative separation of the EoS increases the curvature of the liquid branch of the VLE temperature–density diagram, leading to more accurate liquid saturation densities.⁶ In contrast, it is well-known that whereas the vdW-type equations, such as the RK equation, do not give adequate results for the liquid saturation density, they do reproduce very accurately the saturation pressure.^{1,6} It is also clear that both the vdW and the Dieterici schemes lead to mean field critical exponents.^{6,31} These results do not clarify whether the Dieterici approach can lead to new equations with improved results for the VLE properties. Moreover, no results for other important properties such as the vaporization enthalpy have yet been obtained from the Carnahan–Starling–Dieterici (CSD) equation proposed by Sadus,^{5,30} and there have been no studies of the possibility of considering a simple generalized CSD equation with the introduction of other simple temperature laws. In this present work we made a more detailed analysis of the validity of simple modifications (in the sense of only including terms that can be calculated from a knowledge of the critical properties of a given fluid, without having to fit empirical data) of the van der Waals, the Redlich–Kwong, and the Dieterici equations. In all

cases, we considered two forms of including the repulsive part: that given in the vdW equation and the CS expression for hard spheres. For the attractive part we took into account the possibility of introducing simple changes in the temperature dependence, studying six families of equations in which the exponent of the temperature is varied. In particular, four of these families were of the van der Waals repulsive-plus-attractive type, and two of the Dieterici repulsive-times-attractive type. In each case, we calculated the VLE saturation densities, the saturation pressure, and the vaporization enthalpy, and compared the results with data for simple fluids.

The main aims were: (i) to determine whether the Dieterici-type equations can give better results than those of the van der Waals type; (ii) to clarify whether the Carnahan–Starling repulsive equation represents an acceptable alternative to the traditional van der Waals repulsive term; and (iii) to study the possibility of finding a best choice among these six families of simple and predictive EoS's.

The paper is structured as follows. In section 2, we present the different families of EoS's and the thermodynamic functions needed to determine the VLE. In section 3, we present the main results and a discussion of the study, and compare those results with data of real simple fluids. Finally, section 4 presents the main conclusions.

2. Families of equations of state

In this section we present six families of EoS's which are based on different combinations and choices for the repulsive and attractive terms. Following the idea of Redlich and Kwong, in all cases the temperature dependence for the attractive term is taken to be a power law of the form $T^{-\beta}$. All the combinations (and the abbreviations used to refer to them) are listed in Table 1.

As can be seen, both the vdW and CS expressions have been considered for the repulsive part. Four families are based on the most widely used vdW additive separation $z = z_{\text{rep}} + z_{\text{att}}$, taking the vdW and the RK attractive terms as possible choices. The other two families follow the proposal of Sadus⁵ in which the compressibility factor of the fluid factorizes as in the Dieterici EoS $z = z_{\text{rep}} \exp[z_{\text{att}}]$.

Note that in all cases we introduce a new parameter β as the exponent of the temperature in the attractive term. Also note that the choice $\beta = 0$ recovers the original EoS's for the vdW and Dieterici families and $\beta = 1/2$ recovers the RK EoS, and that the critical compressibility factor is not dependent on β . We calculated the critical parameters and the analytic expressions for the chemical potential and the excess enthalpy for all of the families, which allowed us to obtain the VLE properties, including the enthalpy of vaporization.

For the sake of simplicity, we use the dimensionless variable $y = b/4v$ instead of the molar volume v , with b being the so-called co-volume. The definition of variable y , as $y = b/v$ becomes simpler for the families of EoS's containing the vdW repulsive term, nevertheless we prefer to unify the notation with respect to the families which contain the CS repulsive term, where the proposed definition $y = b/4v$ takes the sense of packing fraction.^{3,5,30} For the analytical calculation of the chemical potential μ and the excess enthalpy Δh , we used the

Table 1 Repulsive (vertical: vdW, CS) and attractive (horizontal: vdW, RK, D) terms leading to the six families of EoS studied in this work. The label β refers to the power law temperature dependence that was considered

	vdW	RK	D
vdW	vdW- β	RK- β	D- β
CS	CSvdW- β	CSRK- β	CSD- β

following relations:

$$\mu = \int \frac{P}{4y} \left(\frac{\partial P}{\partial y} \right)_T dy + \phi(T), \quad (2.1)$$

where ϕ only depends on the temperature, and

$$\frac{\Delta h}{R} = T(z-1) - T^2 \int_0^y \frac{1}{y} \left(\frac{\partial z}{\partial T} \right)_y dy \quad (2.2)$$

respectively. In these equations P , T , z , and R are the pressure, temperature, compressibility factor $z = bp/4yRT$, and molar universal gas constant, respectively.

2.1. The van der Waals (vdW- β) family

The vdW- β family of EoS's is constructed by using the repulsive and attractive terms of the classical vdW EoS. The compressibility factor is written as

$$z = \frac{1}{1-4y} - \frac{4ay}{bRT^{1+\beta}} \quad (2.3)$$

Note that $\beta = 0$ reproduces the vdW EoS, $\beta = 1$ the classical Berthelot EoS, and $\beta = 1/2$ the Fox EoS.³² The critical point conditions can be solved to yield the critical parameters:

$$y_c = 1/12, \quad (2.4)$$

$$z_c = 3/8, \quad (2.5)$$

$$a = \lambda bRT_c^{1+\beta}, \quad (2.6)$$

where $\lambda = 27/8$. Using eqns. (2.1) and (2.2), one obtains the following useful relations

$$\mu(y, T) = \frac{RT}{1-4y} - \frac{8ay}{bT^\beta} + RT \log \left| -\frac{y}{1-4y} \right| + \phi(T), \quad (2.7)$$

and

$$\frac{\Delta h}{R} = \frac{4Ty}{1-4y} - \frac{4(2+\beta)ay}{bRT^\beta}. \quad (2.8)$$

2.2. The Carnahan–Starling–van der Waals (CSvdW- β) family

The CSvdW- β family comes from replacing the classical vdW repulsive term in eqn. (2.3) by the CS hard sphere fluid EoS. The temperature dependence of the attractive term of the EoS remains unchanged as in eqn. (2.3). The CSvdW- β EoS's can hence be written as

$$z = \frac{1+y+y^2-y^3}{(1-y)^3} - \frac{4ay}{bRT^{1+\beta}}. \quad (2.9)$$

Note that $\beta = 0$ reproduces the usual form of the CSvdW EoS.²² The critical point conditions for this EoS yield

$$y_c = 0.1304439, \quad (2.10)$$

$$z_c = 0.3589562, \quad (2.11)$$

$$a = \lambda bRT_c^{1+\beta}, \quad (2.12)$$

where $\lambda = 2.6503068$. Note that the compressibility factor of the critical point is slightly improved relative to the vdW- β EoS when the CS repulsive term is considered.³ From eqns. (2.1) and (2.2), one has the chemical potential and the excess enthalpy:

$$\mu = \frac{RT(3-y)}{(1-y)^3} - \frac{8ay}{bT^\beta} + RT \log(y) + \phi(T), \quad (2.13)$$

and

$$\frac{\Delta h}{R} = \frac{2(2-y)y}{(1-y)^3} T - \frac{4a(2+\beta)}{bRT^\beta} y. \quad (2.14)$$

These expressions will be used in their reduced form in the calculations.

2.3. The Redlich–Kwong (RK- β) family

The vdW approach was originally modified by Redlich and Kwong⁴ by taking a $T^{-1/2}$ temperature dependence for the attractive term of the pressure, and including a volume displacement. These modifications are not based on a microscopic theory but they are phenomenological approaches that improve the results. In the present work, we allow the exponent of the temperature to vary, again as a phenomenological approach. The RK- β family can then be written as

$$z = \frac{1}{1-4y} - \frac{4ay}{bRT^{\beta+1}(1+4y)}. \quad (2.15)$$

Note that $\beta = 1/2$ recovers the original idea of Redlich and Kwong.⁴ For this EoS the critical parameters are:

$$y_c = 0.0649803, \quad (2.16)$$

$$z_c = 1/3, \quad (2.17)$$

$$a = \lambda bRT_c^{1+\beta} \quad (2.18)$$

where $\lambda = 4.9339625$. After a little algebra, one obtains the following expressions for the chemical potential and the excess enthalpy of the RK- β EoS's:

$$\begin{aligned} \mu = & \frac{RT}{1-4y} + \frac{a}{bT^\beta(1+4y)} + T \log \left| -\frac{y}{1-4y} \right| \\ & - \frac{a}{bT^\beta} \log(1+4y) + \phi(T), \end{aligned} \quad (2.19)$$

and

$$\begin{aligned} \frac{\Delta h}{R} = & \frac{4Ty}{1-4y} - \frac{4ay}{bRT^\beta(1+4y)} \\ & - \frac{a(1+\beta)}{bRT^\beta} \log(1+4y). \end{aligned} \quad (2.20)$$

2.4. The Carnahan–Starling–Redlich–Kwong (CSRK- β) family

Following the work of Carnahan–Starling,²² de Santis *et al.*,²³ and Prausnitz,²⁴ we also consider the CSRK- β family of EoS's:

$$z = \frac{1+y+y^2-y^3}{(1-y)^3} - \frac{4ay}{bRT^{\beta+1}(1+4y)}. \quad (2.21)$$

As in the preceding case, $\beta = 1/2$ recovers the CSRK equation. The critical parameters can be obtained by solving the usual critical point equations, giving:

$$y_c = 0.0831444, \quad (2.22)$$

$$z_c = 0.3157144, \quad (2.23)$$

$$a = \lambda bRT_c^{1+\beta}, \quad (2.24)$$

where $\lambda = 4.3989089$. As is pointed out in ref. 3 the compressibility factor is not affected if the attractive term is multiplied by a temperature-dependent function. As was the case for the CSvdW- β family, the substitution of the CS hard sphere EoS for the repulsive term in the pressure slightly improves the value of the compressibility factor at the critical point.

Useful analytical functions for the VLE can be obtained. The chemical potential is

$$\begin{aligned} \mu = & \frac{3-y}{(1-y)^3} RT + \frac{a}{bT^\beta(1+4y)} + RT \log(y) \\ & - \frac{a}{bT^\beta} \log(1+4y) + \phi(T), \end{aligned} \quad (2.25)$$

and the excess enthalpy is

$$\frac{\Delta h}{R} = \frac{2(2-y)y}{(1-y)^3} T - \frac{4ay}{bRT^\beta(1+4y)} - \frac{a(1+\beta)}{bRT^\beta} \log(1+4y). \quad (2.26)$$

2.5. The Dieterici (D- β) family

The preceding families of EoS's were based on the additive separation of the pressure. Multiplicative factorization of the EoS has been less used, but recent works^{5-7,30} indicate that this type of separation needs to be taken into account for the calculation of various thermodynamic properties. In this sense, our first family with multiplicative separation is the classical Dieterici EoS modified in its attractive term with the by-now customary temperature power law. Expanding the exponential term, one recovers the van der Waals behaviour from the Dieterici EoS in the low-density limit. The family of EoS's proposed in this paper based on the Dieterici EoS is

$$z = \frac{1}{(1-4y)} \exp\left[-\frac{4ay}{bRT^{1+\beta}}\right]. \quad (2.27)$$

The critical values provide information about the two parameters of the EoS's:

$$y_c = 1/8, \quad (2.28)$$

$$z_c = 2/e^2 \approx 0.27067, \quad (2.29)$$

$$a = \lambda bRT_c^{1+\beta}, \quad (2.30)$$

where $\lambda = 1/4$. In this case, due to the temperature dependence of the attractive term, we also find a fixed value for z_c . This value, eqn. (2.29), is much closer to the mean value reported for a large number of substances, $z_c = 0.262$,³ than that given by the previous four families.

The calculation of μ and $\Delta h/R$ is not as straightforward as in the previous cases. The final analytical expressions are

$$\mu = \frac{RT}{1-4y} \exp\left[-\frac{4ay}{bRT^{1+\beta}}\right] + RTEi\left[-\frac{4ay}{bRT^{1+\beta}}\right] - RT \exp\left[-\frac{a}{bRT^{1+\beta}}\right] Ei\left[\frac{a(1-4y)}{bRT^{1+\beta}}\right] + \phi(T). \quad (2.31)$$

and

$$\frac{\Delta h}{R} = T(z(y, T) - 1) - \frac{a(1+\beta)}{bRT^\beta} \times \exp\left[-\frac{a}{bRT^{1+\beta}}\right] \left(Ei\left[\frac{a}{bRT^{1+\beta}}\right] - Ei\left[\frac{a(1-4y)}{bRT^{1+\beta}}\right] \right) \quad (2.32)$$

where $Ei(x)$ is the exponential integral function defined as

$$Ei(x) = - \int_{-x}^{\infty} \frac{e^{-t}}{t} dt. \quad (2.33)$$

2.6. The Carnahan–Starling–Dieterici (CSD- β) family

Finally, we studied the proposal of Sadus,⁵ of modifying the power law temperature dependence of the attractive term. This proposal uses the CS repulsive term in the factorization of the Dieterici form of the EoS. The compressibility factor for the modified proposal is

$$z = \frac{1+y+y^2-y^3}{(1-y)^3} \exp\left[-\frac{4ay}{bRT^{1+\beta}}\right]. \quad (2.34)$$

Calculation of the values of the parameters of the EoS gives:

$$y_c = 0.3821319, \quad (2.35)$$

$$z_c = 0.2545401, \quad (2.36)$$

$$a = \lambda bRT_c^{1+\beta}, \quad (2.37)$$

where $\lambda = 2.0932572$. As was the case for the preceding families of EoS's, the use of the CS repulsive term slightly improves the value of z_c , and this value is independent of the form of the temperature dependence function that multiplies the attractive term. The thermodynamic functions to use in the VLE calculations can also be obtained:

$$\mu = \left(\frac{4a}{bT^\beta(1-y)} + RT \frac{4-4y+3y^2-y^3}{(1-y)^3} \right) \exp\left[-\frac{4ay}{bRT^{1+\beta}}\right] + RTEi\left[-\frac{4ay}{bRT^{1+\beta}}\right] - \frac{8a(2a+bRT^{1+\beta})}{b^2RT^{1+2\beta}} \times \exp\left[-\frac{4a}{bRT^{1+\beta}}\right] Ei\left[\frac{4a(1-y)}{bRT^{1+\beta}}\right] + \phi(T), \quad (2.38)$$

$$\Delta h/R = T(z(y, T) - 1) - (1+\beta)(f(y, T) - f(0, T)) \quad (2.39)$$

where

$$f(y, T) = \left(\frac{4a}{bR(1-y)^2T^\beta} + \frac{16a^2}{b^2R^2(1-y)T^{1+2\beta}} - T \right) \times \exp\left[-\frac{4ay}{bRT^{1+\beta}}\right] + \left(\frac{8a}{bRT^\beta} - \frac{64a^3}{b^3R^3T^{2+3\beta}} \right) \times \exp\left[-\frac{4a}{bRT^{1+\beta}}\right] Ei\left[\frac{4a(1-y)}{bRT^{1+\beta}}\right]. \quad (2.40)$$

3. Results and discussion

We tested the behaviour of the six families of EoS's proposed in the above section by calculating the main thermodynamic properties at the vapour–liquid equilibrium, and comparing them with those results derived from real data³³ for some simple fluids. In particular, we calculated the coexistence lines in the $y_r - T_r$ and $P_r - T_r$ diagrams (all properties being in terms of adimensional units relative to their values at the critical point), and the reduced enthalpy of vaporization $\Delta h_v/RT_c$ versus the temperature. The calculations were made varying β within the range $\beta \in (0, 2)$, an interval that we had observed to include the best choice for comparison with real data. In the numerical calculation of the VLE of each family of EoS's, we used the analytical form of the chemical potential, finding the intersection of the loop of the isotherm in the $\mu - P$ diagram. This avoids the numerical errors involved in using Maxwell's equal area rule.

Figs. 1–3 show the results for the VLE densities, pressures, and vaporization enthalpies (in reduced units) versus the reduced temperature. The points represent the data for various simple fluids,³³ and the lines represent the predictions obtained with the vdW- β and CSvdW- β (Fig. (a)), RK- β and CSRK- β (Fig. (b)), and D- β and CSD- β (Fig. (c)) families of EoS's. The continuous lines correspond to the families containing the classical vdW repulsive term, and the dashed lines correspond to the families containing the CS repulsive term. The selected values of the parameter β are indicated in each case.

As can be seen in the figures, our proposal of introducing simple modifications in the temperature dependence of the attractive term improves the results for the saturation

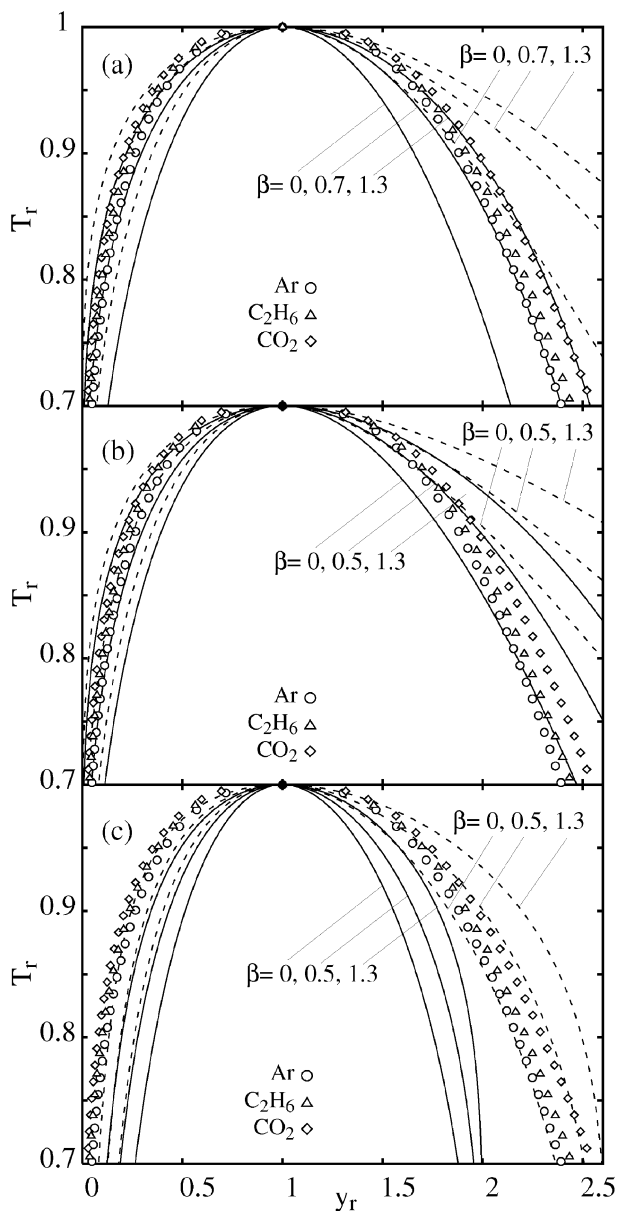


Fig. 1 Plot of the reduced temperature *versus* reduced density for the VLE. The symbols represent data for Ar, C₂H₆, and CO₂.³³ The plots (a), (b), and (c) are of values calculated from the vdW- β and CSvdW- β , RK- β and CSRK- β , and D- β and CSD- β , respectively. Solid lines correspond to the family of EoS's containing the vdW repulsive term, and dashed lines correspond to the cases with the CS repulsive term.

properties as obtained from simple EoS's. Indeed, it seems to be an acceptable alternative to other proposals such as that of Eubank and Wang³⁴ in which, because the parameters a and b in cubic EoS's are obtained from saturation pressure and enthalpies of vaporization data, the EoS's are not predictive. A more detailed discussion of the results is given below.

Finally, in order to complete Table 1 we have also studied two more families, not included in the paper, by using the Dieterici multiplicative scheme with the Redlich-Kwong z_{att} term as the argument of the exponential. These families, namely RKD- β and CSRKD- β , have not been included due to the following reasons. On the one hand the analytical results become more complex due to the non-linear argument of the exponential, specially for the CSRKD- β family. On the other hand the results obtained with this couple of families do not improve the results of the more standard D- β and CSD- β families. Moreover the values of the critical compressibility factor given by the RKD- β and CSRKD- β families are $z_c =$

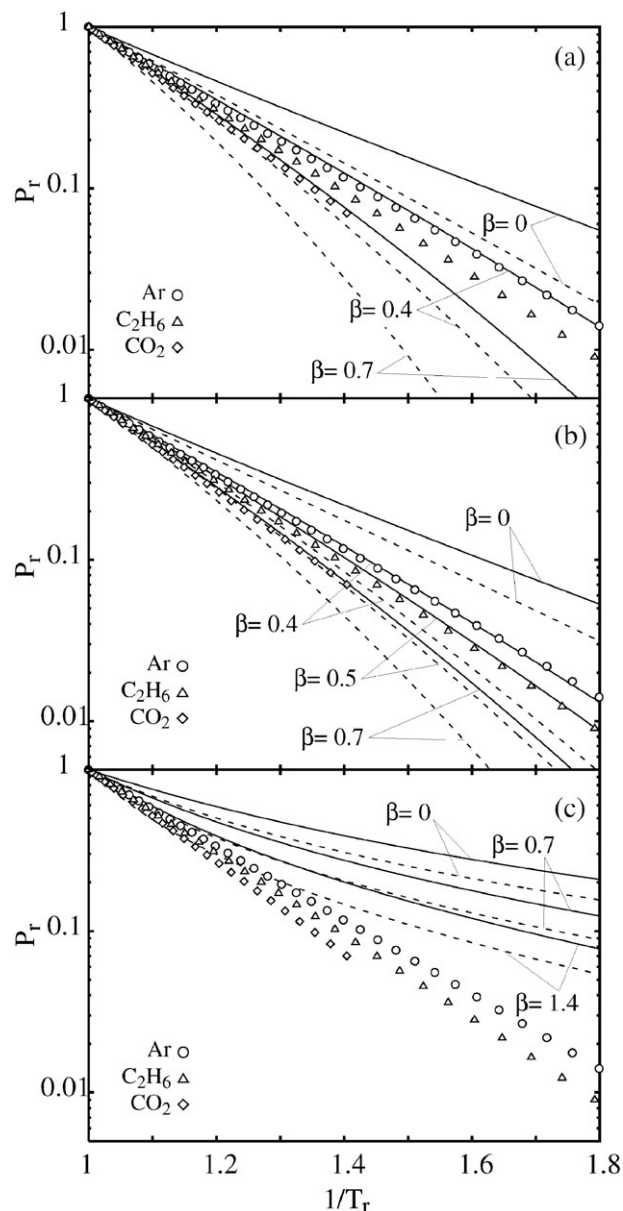


Fig. 2 As for Fig. 1 except that the plot is of the reduced pressure *versus* inverse reduced temperature.

0.203003 and $z_c = 0.179520$ respectively. These values are far from the most accepted value of $z_c = 0.262$.

3.1. Temperature-density diagram

As is well-known, and can also be seen in Fig. 1(a), the saturation densities obtained with the classical vdW EoS ($\beta = 0$) are very poor. The figure also shows that the use of the CS EoS for the repulsive term in this EoS, *i.e.* the CSvdW EoS, only improves numerically the results on the liquid branch over a small temperature range. Nevertheless, the curvature of the theoretical liquid saturation density is qualitatively clearly different from that of the real data.

One also observes that the consideration of several β exponents other than $\beta = 0$ in the classical vdW EoS is able to locate both the liquid and vapour branches in good agreement with the data for fluids, but that this is not the case for the CSvdW family of EoS's. This result suggests that for the vdW- β family of EoS's there is an optimal value for β for each fluid. For simple fluids such as considered here, this optimal value is in the range 0.7 to 1.5, so that it is close to the value $\beta = 1$ used in the classical Bertheloth EoS, but far from the value $\beta = 1/2$

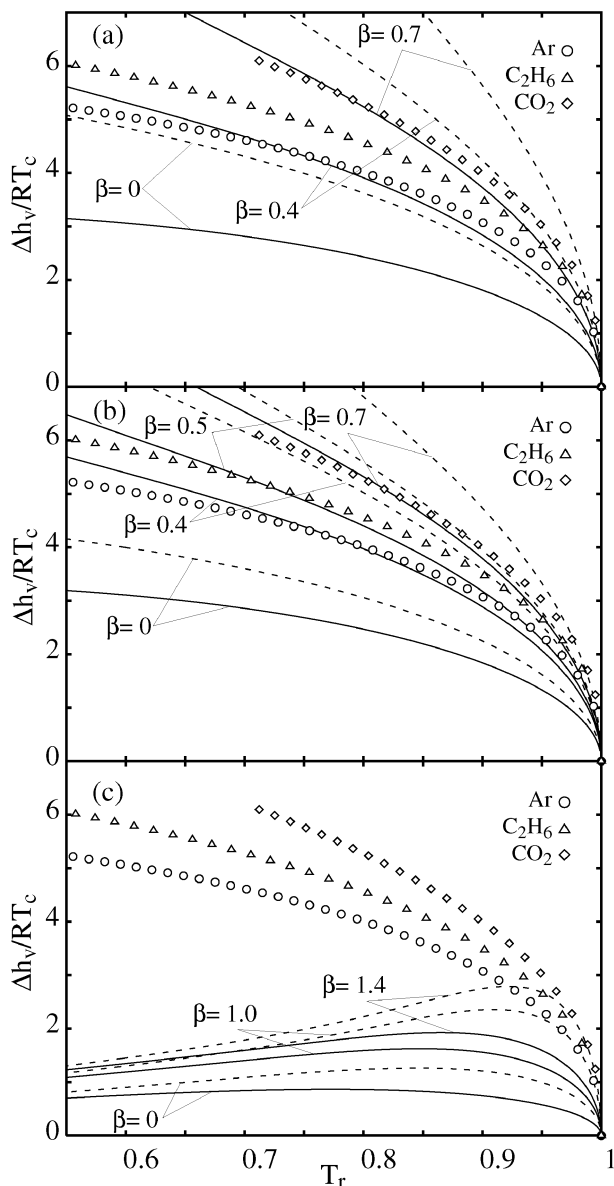


Fig. 3 As for Fig. 1 except that the plot is of the reduced enthalpy of vaporization versus reduced temperature.

used in the Redlich–Kwong⁴ and the Fox³² EoS's. The good agreement obtained with very simple vdW EoS's has been interpreted³ as the consequence of an error cancellation between the repulsive and attractive terms. The present results show that one still has this cancellation in the vdW EoS for different values of β , leading to good results for several values of the β exponent. Our results confirm, at least for the calculation of the saturation VLE densities, the recommendations of Kontogeorgis *et al.*²⁵ and Yelash and Kraska³ that the vdW repulsive term should be used, not the CS one.

Fig. 1(b) shows the results from the RK- β (solid lines) and CSRK- β (dashed lines) EoS's. As is well-known, the original value of $\beta = 0.5$ proposed by Redlich and Kwong⁴ improves the prediction of the liquid branch relative to the vdW EoS. Moreover, the exploration of different values for the exponent β showed that, although the data can be matched over some temperature intervals, it is impossible to obtain any overall improvement for the behaviour of the liquid branch. Note also that the assumption of the CS EoS for the repulsive term is not able to improve the results for the liquid saturation density: only for $\beta = 0$ are the CSRK EoS predictions similar to, although still poorer than, those obtained with the original RK equation. One must conclude, therefore, that the improve-

ments found by Carnahan and Starling,²² de Santis *et al.*,²³ and Prausnitz²⁴ in using the CSRK EoS instead of the CSvdW do not extend to the saturation VLE densities.

With respect to the Dieterici-type families of EoS's, one observes in Fig. 1(c) that the D- β family is a very poor approximation for the saturation densities, but, as claimed by Sadus,⁵ the CSD ($\beta = 0$) EoS reproduces the liquid branch fairly accurately. We would add here that, from a practical standpoint, a certain numerical improvement in the prediction of the saturation densities of simple fluids can be attained by changing the temperature dependence attractive exponential term in the CSD EoS proposed in ref. 5 from $\beta = 0$ to a slightly higher value (less than $\beta = 0.5$). A clear numerical improvement in the prediction of the vapour saturation density is also possible using a value of β near 1.3, but at the cost of losing the liquid branch improvement. In general terms, the multiplicative separation of the EoS gives a greater curvature for the liquid branch than do the additive vdW- β , CSvdW- β , RK- β , and CSRK- β EoS's. On the other hand, the vapour branch predictions of the multiplicative-scheme EoS's are poorer than those of the additive scheme.

In any case, the vdW EoS with β near 1 (with the optimal value in the range 0.7 to 1.3) gives better overall results for the saturation densities than the CSD EoS with β ranging from 0 to 0.5. These results indicate that, at least for the calculation of saturation densities of simple fluids, the analytically more complex Dieterici scheme is no improvement over the EoS based on the vdW separation of terms, not even for the liquid saturation density which has been considered to be the main advantage of the CSD EoS.^{6,7}

3.2. Pressure–temperature diagram

We shall start with the discussion of the effect of the CS repulsive term on the prediction of the saturation pressure. As is shown in Fig. 2(a), comparison of the original vdW and CSvdW ($\beta = 0$) EoS's showed that the CS repulsive term significantly improves the prediction of the saturation pressure for simple fluids. Moreover, in both cases the results can be improved by modifying the temperature dependence in the attractive term, in particular that an appropriate choice of the β exponent can lead to better agreement. The difference between choosing between the CS and the vdW repulsive terms is simply a shift of the value of the optimal β exponent. Thus, for the vdW- β family, the optimal β of from 0.4 to 0.7 seems to be the appropriate choice, whereas for the CSvdW- β case the range is from 0 to 0.4. For the RK- β and CSRK- β families, the behaviour was qualitatively similar. As can be seen, the original EoS's ($\beta = 0.5$) reproduce the data well (Fig. 2(b)), but an optimal value of β could be found for each fluid. Fig. 2(c) shows that the D- β and CSD- β families are unable to reproduce the saturation pressure except very close to the critical temperature. Also we would note that the CS repulsive term does not significantly improve the results. The lack of even qualitative accuracy of the original CSD EoS⁵ in the calculated saturation pressure has already been noted in refs. 6 and 7. That conclusion can be extended to the Dieterici-scheme-based families studied here. In summation, one could generalize with respect to the scheme of separation of the EoS's that the families based on a multiplicative separation of the pressure terms present a pronounced curvature (see Fig. 2(c)) and fail in their prediction of the VLE pressure–temperature data even for simple fluids. Although the β exponent allows one to approximate the behaviour in the critical region, the rest of the curve greatly overestimates the pressure. On the contrary, the behaviour of the families based on additive separation is more appropriate (Fig. 2(a) and 2(b)). For these families it is possible to find an optimal β exponent that gives an adequate representation of a particular fluid.

3.3. Enthalpy of vaporization

Once the temperature and densities of the coexistence lines were calculated, we used the expression for the excess enthalpies to obtain the enthalpy of vaporization. For the sake of completeness, and in order to verify the expressions of the excess enthalpy ((2.8), (2.14), (2.20), (2.26), (2.32), and (2.39)), we tested the enthalpy of vaporization results by using the Clapeyron equation. As was expected, the results were identical to those obtained using the excess enthalpy except for the expected numerical error introduced in the calculation of the numerical derivative dP_r/dT_r .

The differences between the enthalpies of vaporization predicted by the additive and multiplicative schemes of separation of the equation of state are really large. As one can see in Fig. 3, the vdW- β , CSvdW- β , RK- β , and CSRK- β EoS's are better approximations than the D- β and CSD- β ones. Indeed, these last equations are unsuitable even using a β value as large as 1.4 instead of the original value of zero. We would remark that this is the first report of results for the enthalpy of vaporization using the original CSD. A high value of β slightly improves the results in a temperature interval close to the critical point, although no critical exponents are reproduced. In conclusion, the simple modifications to the temperature dependence of the Dieterici EoS proposed in this present work cannot be used to calculate the enthalpy of vaporization even for simple fluids. On the contrary, the additive scheme EoS's lead to better results, although neither of the approaches accurately reproduces the curvature of the data.

With respect to the families with a vdW attractive term, the enthalpy of vaporization was greatly improved by introducing the CS repulsive term into the original ($\beta = 0$) vdW EoS. Nevertheless, it was also possible to obtain a good result with the vdW EoS by using an optimal value between 0.4 and 0.7 of the exponent β for the selected fluids. The results were then similar to those given by the CSvdW EoS, which is not a cubic equation, with values of β from 0 to 0.4. As also was the case for the previous properties, for each fluid studied by varying the exponent β , one finds a theoretical curve that reproduces the data over a certain interval, again suggesting that there exists an optimal value of β that depends on the fluid. The same effect was found with the RK- β and CSRK- β families, although now Redlich and Kwong's original choice, ($\beta = 0.5$), seems to be accurate enough for some fluids. In any case, the RK families do not significantly improve the accuracy of the vdW families.

4. Conclusions

We have tested several single-parameter families of EoS's by calculating the main properties of simple fluids at the liquid–vapour equilibrium. In particular, we calculated the VLE densities, pressure, and latent heat of vaporization. Obviously, because of the simplified analytical character of the VLE for all the EoS's studied in this present work, the critical exponents are the classical ones, which are far from the experimental values. Nevertheless, the results clearly seem to indicate, conversely to that suggested in ref. 5, that the EoS's obtained by additive decomposition of the compressibility factor $z = z_{\text{rep}} + z_{\text{att}}$ are preferable to those using the decomposition $z = z_{\text{rep}} \exp[z_{\text{att}}]$, at least for the six families of EoS's proposed here. On the other hand the values of the critical compressibility factor of the RKD- β and CSRKD- β families indicate that the goodness of the critical compressibility factor of the D- β and CSD- β families is not a characteristic of the Dieterici scheme but a property of these two families of EoS's.

The excellent relationship between the simplicity of the vdW- β family of EoS's and the goodness of their predictions of VLE properties suggests that one way to further improve the predictions might be to introduce simple modifications to the

functional form of the temperature dependence of the attractive term. Although this idea was originally explored by Redlich and Kwong, the present findings indicate that the results from using their well-known EoS can be improved in the case of the saturation densities, and are practically the same in the case of the saturation pressure and the enthalpy of vaporization, relative to those obtained using a slightly modified and simpler vdW- β EoS. In particular, a mean value of around 0.7 for that exponent gives reasonable agreement with the VLE properties studied here. In any case, the results for a specific property or fluid can be numerically improved by finding an optimal value of that exponent for each case. Our results indicate that such an improvement is impossible for all the properties if the other families of simple and predictive EoS's are used. Extension of this treatment to different compounds other than those studied here requires the calculation of the β exponent appropriate for each VLE property. Once the best choice of the β exponent is found the study of mixtures and mixing rules will be considered in further work.

We have shown that the improvements reported by other workers from using the CSRK EoS instead of the CSvdW one cannot be extended to the VLE properties.

We also found that for the families of EoS's proposed and studied here, the use of the Carnahan–Starling hard sphere EoS for the repulsive term can be replaced by using an appropriately chosen exponent of the temperature in the attractive term. This allows one to avoid using the non-cubic EoS's that appear when the repulsive CS term is considered. Unfortunately, the optimal choice of the β exponent depends on the property under study, *i.e.*, given a real simple fluid there exists no universal optimal choice of β that allows one to calculate the entire set of VLE properties.

In order to find a better agreement near the critical point, and then to reproduce the critical exponents, crossover transformations must be considered.³¹ Thus, the method used by Wyczalkowska *et al.*³¹ for the vdW EoS could be successfully applied to an optimal EoS of the vdW- β family proposed here, in which better results were also obtained far from the critical point.

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