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# Search for the optimal expression of the volumetric dependence of the attractive contribution in cubic equations of state.

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## ABSTRACT

The 2<sup>nd</sup> degree polynomial volume function ( $v^2 + ubv + wb^2$ ), involved in the attractive term of cubic equations of state, has a strong influence on the calculated volumetric properties and, to a lesser extent, influences the calculated vapor-liquid equilibrium properties such as vapor pressure and enthalpy of vaporization. This function contains two parameters ( $U$  and  $w$ ) that were either selected constant or constituent-dependent in the literature. In this work, it is analyzed through a systematic methodology how parameters  $U$  and  $w$  influence the accuracy of predicted volumetric and vapor-liquid equilibrium properties, both for untranslated and translated cubic equations of state. It was thus possible to determine the optimum values of such parameters and to discuss if the values selected in well-known cubic equations of state are the most relevant.

**Keywords:** volumetric properties; cubic equation of state; volume translation; attractive term; universal constants.

## 1. INTRODUCTION

Today, computer-aided-process-design software allow virtually any engineer to simulate large flowsheets with considerable detail. Such simulators embed many thermodynamic models, and among these, equations of state (EoS) play a major role. The proper selection of these latter determines in large part the accuracy of the simulation. Indeed, as explained by Agarwal et al. [1], *if we have an equation of state (EoS) and the ideal-gas heat capacities, we can calculate not only phase equilibria, but also all the needed thermodynamic properties for a comprehensive model of an entire flowsheet.* Among these properties, vapor pressures are paramount, liquid densities are fundamental for mass balances whereas enthalpies, entropies and heat capacities are key properties for energy and exergy balances. Among different types of equations of state, the so-called cubic equations of state (CEoS), usually written in pressure-explicit form, arise as a widespread choice due to their accuracy, the low number of required experimental parameters and their availability as well, ease of implementation, ability to provide reasonable estimation of enthalpies and entropies and robustness. In a generalized form, CEoS can be expressed as:

$$P(T, v) = \frac{RT}{v - b} - \frac{a(T)}{v^2 + ubv + wb^2} \quad (1)$$

where parameter  $a$  is a measure of the attractive forces between molecules; parameter  $b$  is the so-called covolume, which attempts to correct the perfect-gas law for the fact that molecules have a non-zero effective volume; and the constants  $U$  and  $w$  are either universal real numbers (the same values apply to all compounds) or substance-dependent quantities. The temperature-dependent  $a(T)$  parameter is classically written as:

$$a(T) = a_c \cdot \alpha(T) \quad (2)$$

It is the product of the value of the attractive parameter at the critical temperature ( $a_c$ ) multiplied by a so-called  $\alpha$ -function, which is dimensionless. Such an  $\alpha$ -function has a great influence on the calculated vapor-liquid equilibrium properties like vapor pressure, enthalpy of vaporization and saturated-liquid heat capacity. On the other hand, the volume function of the attractive term ( $v^2 + ubv + wb^2$ ) and, in particular, the numerical values assigned to  $U$  and  $w$ , govern essentially the accuracy of the predicted volumetric properties. To parametrize this function, two options are on the table. The first option is to consider  $U$  and  $w$  as universal (component-independent) constants. By doing so, the critical compressibility factor returned by the EoS ( $\frac{P_c}{z_c P_c^{\text{EoS}}}$ ) is the same for all components. However, known experimental values of  $z_c$  range between 0.0144 (for magnesium oxide) and 0.637 (for triethyl phosphate); therefore, by selecting this first option, the predicted saturated liquid densities, and particularly those in the critical region, are inevitably going to deviate from their experimental values. However, to the best of our knowledge, a systematic study of how the selection of  $U$  and  $w$  values (that can be chosen in a very large range of values) influence the accuracy of CEoS for property predictions was never conducted. The second option is to consider  $U$  and  $w$  as component-dependent factors. A first possibility is to correlate  $U$  and  $w$  to a readily available property like the acentric factor. Alternatively, the volume-translation concept, as initially developed by P eneloux et al. [2], can be used: the addition of a component-specific volume translation parameter entails that the  $U$  and  $w$  parameters become component-specific themselves. But, are these two alternatives equivalent? Would it be an interest to combine them? (i.e., to use component-dependent  $U$  and  $w$  parameters and to simultaneously translate the EoS). Here again, we did not find in the literature any systematic study comparing the usefulness to correlate  $U$  and  $w$  to  $\omega$  or to use of a volume-translated EoS.

Bearing this in mind, the first part of this paper presents a historical background of the most popular modifications of the volume function proposed to improve the ability of CEoS to predict volumetric properties. The second part of this paper explores the possibility to correlate  $U$  and  $w$  to the acentric factor and to simultaneously translate the EoS. In the last part of this paper, a map reporting deviations between EoS predictions and experimental properties in the  $U - W$  space is screened in order to deem how such parameters influence the accuracy of the predicted volumetric and vapor-liquid equilibrium properties, both for untranslated and translated CEoS. This map made it possible to determine the optimal ( $U, W$ ) values and to discuss the parametrization of the volume function in the attractive term of well-known cubic equations of state.

## 2. HISTORICAL BACKGROUND

An overview of the various modifications operated on the volume function of the attractive term of CEoS is presented below. A particular attention is devoted to the choice for the  $U$  and  $w$  parameters.

### 2.1. Selection of constant ( $U, W$ ) values

In 1873, J.D. van der Waals [3] proposed the first, simplest and best known cubic equation of state:

$$P(T, v) = \frac{RT}{v-b} - \frac{a_c}{v^2} \quad \text{with:} \quad \begin{cases} a_c = \frac{27 R^2 T_{c,\text{exp}}^2}{64 P_{c,\text{exp}}} \\ b = \frac{1 RT_{c,\text{exp}}}{8 P_{c,\text{exp}}} \end{cases} \quad (3)$$

It is a so-called 2-parameter CEoS because its application to a pure component requires the preliminary knowledge of two experimental (exp) component-dependent parameters (the critical temperature  $T_{c,\text{exp}}$  and pressure  $P_{c,\text{exp}}$ ). In Eq. (3),  $R$  is the gas constant,  $T$ , the temperature,  $P$ , the pressure and  $v$ , the molar volume. The Van der Waals EoS gives a qualitatively correct description of fluid properties and phase behavior [4], but it predicts a too large critical compressibility factor of  $3/8$  and thus leads to very poor correlation of densities in the critical region. By identification with Eq. (1), it is noticeable that  $u$  and  $w$  were set to  $u = w = 0$ . Although numerous modifications of the Van der Waals equation were proposed, very few different  $(u, w)$  pairs were tested out.

As a matter of fact, the two EoS which received most attention in the last 50 years are those proposed by Soave [5] (he introduced the so-called Soave-Redlich-Kwong EoS denoted SRK) and Peng-Robinson [6–8] (PR). For a given pure component, such modern EoS require the specification of three macroscopic properties ( $T_{c,\text{exp}}$ ,  $P_{c,\text{exp}}$  and  $\omega_{\text{exp}}$ ) and they are thus equivalent to a 3-parameter corresponding states principle [9,10]. In this paper, they are simply referred as 3-parameter EoS. The equation developed by Harmens [11] (Ha) to predict the properties of air also received substantial attention.

Without clear explanation or theoretical foundations, all these authors assumed that  $U$  and  $w$  are subject to the constraint:  $u+w=1$ . As a first example, the SRK EoS is characterized by  $u=1$  and  $w=0$  and the corresponding critical compressibility factor is equal to  $1/3$ . The SRK EoS is defined by:

$$P(T, v) = \frac{RT}{v-b} - \frac{a_c \cdot \alpha(T)}{v(v+b)} \quad \begin{cases} \alpha(T) = \left[1 + m(1 - \sqrt{T/T_c})\right]^2 \\ m = 0.480 + 1.574\omega_{\text{exp}} - 0.176\omega_{\text{exp}}^2 \\ a_c = \Omega_a \frac{R^2 T_{c,\text{exp}}^2}{P_{c,\text{exp}}} \\ b = \Omega_b \frac{RT_{c,\text{exp}}}{P_{c,\text{exp}}} \\ \Omega_a = \frac{1}{9(\sqrt[3]{2}-1)} \approx 0.42748 \\ \Omega_b = \frac{\sqrt[3]{2}-1}{3} \approx 0.08664 \\ \text{corresponds to: } u = 1 ; w = 0 \text{ and } z_c = 1/3 \end{cases} \quad (4)$$

In 1976, Peng and Robinson selected  $u = 2$  and  $w = -1$  so that the corresponding critical compressibility factor is equal to  $0.3074$ . The PR EoS expression is:

$$P(T, v) = \frac{RT}{v-b} - \frac{a_c \cdot \alpha(T)}{v(v+b) + b(v-b)} \left\{ \begin{array}{l} \alpha(T) = \left[ 1 + m \left( 1 - \sqrt{T/T_c} \right) \right]^2 \\ m = 0.37464 + 1.54226 \omega_{\text{exp}} - 0.26992 \omega_{\text{exp}}^2 \\ a_c = \Omega_a \frac{R^2 T_{c,\text{exp}}^2}{P_{c,\text{exp}}} \\ b = \Omega_b \frac{RT_{c,\text{exp}}}{P_{c,\text{exp}}} \\ X = \left[ 1 + \sqrt[3]{4 - 2\sqrt{2}} + \sqrt[3]{4 + 2\sqrt{2}} \right]^{-1} \approx 0.25308 \\ \Omega_a = \frac{8(5X+1)}{49-37X} \approx 0.45724 \\ \Omega_b = \frac{X}{X+3} \approx 0.07780 \\ \text{corresponds to: } \begin{cases} u = 2 ; w = -1 \\ z_c = 1/(X+3) \approx 0.3074 \end{cases} \end{array} \right. \quad (5)$$

In 1977, focusing on the reproduction of vapor-liquid equilibria (VLE) of the nitrogen-argon-oxygen system, Harmens selected  $u=3$  and  $w=-2$ . He claimed that the strength of the equation lied in the fact that for nitrogen  $z_c = 0.2883$ , which is very close to the value returned by his model:  $z_c = 0.2862$ .

## 2.2. Selection of component-dependent ( $u, w$ ) pairs

As previously stated, assigning universal values to  $u$  and  $w$  entails the prediction by the EoS of a unique  $z_c$  value for all components. In order to improve the prediction of liquid densities in the critical region, the  $z_c$  parameter must be made component-dependent and no longer universal. One way to reach this goal is to use component-dependent values for  $u$  and  $w$ . A possibility is to correlate  $u$  and  $w$  to a readily available property. This is exactly what Schmidt and Wenzel [12] decided to do in 1980 after noticing that the SRK EoS better describes liquid molar volumes (at  $T_r = 0.7$ ) of spherical molecules like methane (for which  $\omega=0$ ) than the PR EoS while, conversely, the PR EoS yields better results for n-heptane (the acentric factor of which is about 0.35) than the SRK EoS. Both the SRK ( $u=1 ; w=0$ ) and PR ( $u=2 ; w=-1$ ) EoS satisfy  $u+w=1$  so that Schmidt and Wenzel kept this relationship. Moreover, in order to find back the SRK EoS ( $w=0$ ) when  $\omega=0$  and the PR ( $w=-1$ ) EoS when  $\omega \approx 0.35$ , they set:  $w = -3\omega$ . This led them to the following expression:

$$P(T, v) = \frac{RT}{v-b} - \frac{a_c \cdot \alpha(T)}{v^2 + (1+3\omega)bv - 3\omega b^2} \quad (6)$$

The same year, a similar methodology was applied by Harmens and Knapp [13]. They also kept  $u+w=1$  and, following Schmidt and Wenzel, they developed a complex correlation to estimate  $u$  from the mere knowledge of the acentric factor. They proposed:

$$\left\{ \begin{array}{l} u = 1 + \frac{1 - 3z_c}{0.10770z_c + 0.76405z_c^2 - 1.24282z_c^3 + 0.96210z_c^4} \\ \text{with: } z_c = 0.3211 - 0.080\omega_{\text{exp}} + 0.0384\omega_{\text{exp}}^2 \end{array} \right. \quad (7)$$

For small-size molecules characterized by  $z_c = 1/3$ , Eq. (7) returns  $u=1$  and  $w=0$  corresponding to the SRK EoS. Similarly, by setting  $z_c = 0.3074$  (corresponding to intermediate-size molecules like n-hexane), the PR EoS constants are obtained ( $u=2$  and  $w=-1$ ).

In 1982, Patel and Teja [14] also followed the footsteps of Schmidt and Wenzel and selected  $u + w = 1$ . For non-polar molecules,  $w$  was correlated to the acentric factor and a Soave-type  $\alpha$ -function was used. In particular, in order to determine  $w$ , it is first necessary to calculate the smallest positive root (noted  $x_{\min}$ ) of the following cubic equation:

$$\begin{cases} x^3 + (2 - 3z_c)x^2 + (3z_c^2)x - z_c^3 = 0 \\ \text{with: } z_c = 0.329032 - 0.076799\omega_{\text{exp}} + 0.0211947\omega_{\text{exp}}^2 \end{cases} \quad (8)$$

Once done: 
$$w = \frac{3z_c - 1}{x_{\min}} \quad (9)$$

For a light non-polar substance characterized by  $\omega=0$ , Eq. (9) returns a value of  $w$  close to zero so that the new equation is comparable to the SRK equation and, for components whose acentric factors are close to 0.3, we get  $w \approx -1$  so that the proposed equation is comparable to the PR EoS. As previously observed with the works by Schmidt and Wenzel or Harmens and Knapp, characteristics of both the SRK and PR equation are implicit in the new formulation by Patel and Teja.

For polar molecules, Patel and Teja failed to correlate  $w$  and the shape parameter  $m$  of the  $\alpha$ -function (see, e.g., Eq. (4)) with the acentric factor. They thus decided to work with a 4-parameter CEoS.  $m$  and  $w$  were considered as adjustable parameters and were fitted component by component on experimental vapor-pressure and liquid-density data. In the end, their EoS requires the knowledge of  $T_{c,\text{exp}}$ ,  $P_{c,\text{exp}}$ ,  $m$  and  $w$ .

In 1976, Fuller [15] published a 5-parameter EoS that requires the knowledge of  $T_{c,\text{exp}}$ ,  $P_{c,\text{exp}}$ ,  $V_{c,\text{exp}}$ ,  $\omega_{\text{exp}}$  and  $\bar{P}_{\text{exp}}$  (the experimental value of the parachor) for a given pure component. With the aim of accurately correlating the liquid densities of polar and non-polar components, he decided to set  $w=0$  and to make  $u$  component and temperature-dependent. Fuller also selected a temperature-dependent covolume and we know today that such a choice is thermodynamically inconsistent since it leads to the crossing of isotherms in a (P,v) plane and to negative heat capacities [16–18]. His final equation takes the form:

$$P(T, v) = \frac{RT}{v - b(T)} - \frac{a_c \cdot \alpha(T)}{v^2 + u(T, T_{c,\text{exp}}, P_{c,\text{exp}}, V_{c,\text{exp}}, \omega_{\text{exp}}, \bar{P}_{\text{exp}}) \cdot bv} \quad (10)$$

In 1992, Twu *et al.* [19] carried out an analysis of the CEoS on a  $u - w$  diagram with the aim of discussing the representation of volumetric properties. 21 possible combinations of  $u$  and  $w$  were checked for a number of alkanes, alcohols and glycols. They established that the relationship between  $u$  and  $w$  should be:  $u - w = 4$  for the best representation of saturated-liquid densities. The following expression was obtained:

$$P(T, v) = \frac{RT}{v - b} - \frac{a_c \cdot \alpha(T)}{v^2 + (w + 4)bv + wb^2} \quad (11)$$

In Eq. (11),  $w$  is treated – component by component – as an adjustable parameter. It is obtained by minimizing the deviations between calculated and experimental liquid densities. In order to simultaneously get accurate vapor pressures, Twu used a 3-parameter (noted  $L$ ,  $M$ , and  $N$ )  $\alpha$ -function [20] so that in the end, each pure component is characterized by 6 parameters ( $T_{c,\text{exp}}$ ,  $P_{c,\text{exp}}$ ,  $w$ ,  $L$ ,  $M$ ,  $N$ ).

At this step, we believe it is important to recall that the brilliant concept to make  $u$  and  $w$  substance-dependent in order to get better liquid densities was first introduced by Clausius who proposed the following equation in 1880 [21]:

$$P(T,v) = \frac{RT}{v-b} - \frac{a_c \cdot \alpha(T_r)}{(v+c)^2} \quad \text{with: } \alpha(T_r) = \frac{1}{T_r} \quad (12)$$

where  $c$  is a component-dependent parameter. For such an EoS, we immediately get:

$$u = 2\frac{c}{b} \quad \text{and} \quad w = \left(\frac{c}{b}\right)^2.$$

Another method to obtain component-dependent  $L$  and  $w$  parameters (and thus to get  $z_c$  component-dependent in order to achieve better representation of volumetric properties) is to translate the EoS. This simple and ingenious concept, proposed by P eneloux [2], corresponds to a translation of the whole P-v isotherm (of the amount  $-c$ ) along the volume axis. Indeed, for a given component, the saturated-liquid volume calculated by a CEoS at a given temperature is usually notably different from the experimental value but the difference between the calculated and the experimental volume is approximately constant when varying the temperature. Consequently, a temperature-independent volume translation (all the calculated molar volumes are translated by a constant amount  $C$ ) significantly improves the description of saturated-liquid densities. Assuming that subscripts  $o$  and  $t$  refer to the original (i.e. untranslated) and translated equations of state, respectively, the shifted volume  $V_t$  (closer to the experimental value than  $V_o$ ) is linked to  $V_o$  by:

$$V_t = V_o - C \quad (13)$$

In Eq. (13), the substance-dependent volume-translation parameter,  $C$ , is often determined in order that the translated EoS exactly reproduces the experimental saturated liquid volume at  $T_r = 0.8$ . At this step it is possible to determine the relationship between  $U_o$  and  $W_o$  stemming from the untranslated EoS and  $U_t$  and  $W_t$  from the translated EoS.

Starting with a non-translated EoS with the form of Eq. (1) in which  $U_o$  and  $W_o$  are constant:

$$P_o(T,v_o) = \frac{RT}{v_o - b_o} - \frac{a_c \cdot \alpha(T)}{v_o^2 + u_o b_o v_o + w_o b_o^2} \quad (14)$$

the expression of the translated EoS is obtained by replacing in Eq. (14)  $V_o$  by  $(V_t + C)$  and  $b_o$  by  $(b_t + C)$  [22,23]. This gives the form:

$$P_t(T,v_t) = \frac{RT}{v_t - b_t} - \frac{a_c \cdot \alpha(T)}{(v_t + c)^2 + u_o(b_t + c)(v_t + c) + w_o(b_t + c)^2} \quad (15)$$

By rearranging Eq. (15), in the form of Eq. (1), we get:

$$P_t(T, v_t) = \frac{RT}{v_t - b_t} - \frac{a_c \cdot \alpha(T)}{v_t^2 + u_t b_t v_t + w_t b_t^2} \quad \text{with:} \quad \begin{cases} u_t = u_o + (2 + u_o) \left( \frac{c}{b_t} \right) \\ w_t = w_o + (u_o + 2w_o) \left( \frac{c}{b_t} \right) + (1 + u_o + w_o) \left( \frac{c}{b_t} \right)^2 \end{cases} \quad (16)$$

Depending on the component-dependent parameters  $C$  and  $b_t$ , the  $U_t$  and  $W_t$  parameters are now component-dependent, and thus  $Z_{c,t}$ , the critical compressibility factor of the translated CEoS, is component dependent too. Indeed, as a direct consequence of having translated the critical volume ( $V_{c,t} = V_{c,o} - C$ ), we immediately get:  $z_{c,t} = z_{c,o} - \frac{P_{c,\text{exp}}}{RT_{c,\text{exp}}} c$ .

Finally, in Table 1, the values of  $u$  and  $w$  are reported for all the CEoS previously mentioned.

**Table 1.** Selected values of  $u$  and  $w$  for the volume function of the attractive term in cubic equations of state.

EoS	$u$	$w$
Van der Waals (1873) [3]	0	0
Clausius (1880) [21]	$2 \frac{c}{b}$	$\left( \frac{c}{b} \right)^2$
Soave-Redlich-Kwong (1972) [5]	1	0
Peng and Robinson (1976) [6]	2	-1
Harmens (1977) [11]	3	-2
Schmidt and Wenzel (1980) [12]	$1+3\omega$	$-3\omega$
Harmens and Knapp (1980) [13]	component-dependent	$1-u$
Patel and Teja (1982) [14]	$1-w$	component-dependent
Fuller (1976) [15]	component-dependent	0
Twu, et al. (1992) [19]	$4+w$	component-dependent
<i>translated</i> EoS (1982) [2]	$u_o + (2 + u_o) \left( \frac{c}{b_t} \right)$	$w_o + (u_o + 2w_o) \left( \frac{c}{b_t} \right) + (1 + u_o + w_o) \left( \frac{c}{b_t} \right)^2$

This table highlights that very few ( $u, w$ ) pairs of constant parameters were explored. It is however well-established that the SRK and PR EoS predict the saturated liquid volumes with an average deviation of about 16% and 8% respectively. This means that by changing the ( $u, w$ ) pair from (1; 0) to (2; -1), the deviations are divided by 2. Thus, by screening all the possible ( $u, w$ ) pairs, the optimal one, leading to the most accurate reproduction of volumetric data, could be determined. This table also shows that the volume-translation concept was never applied to an EoS expressing  $u$  and  $w$  as generalized functions of the acentric factor. For all these reasons, in the next sections the usefulness of using functions of the acentric factor for the ( $u, w$ ) parameters in a translated EoS is first discussed. Then, a large screening of ( $u, w$ ) pairs for both untranslated and translated CEoS will be performed to identify the optimal one.



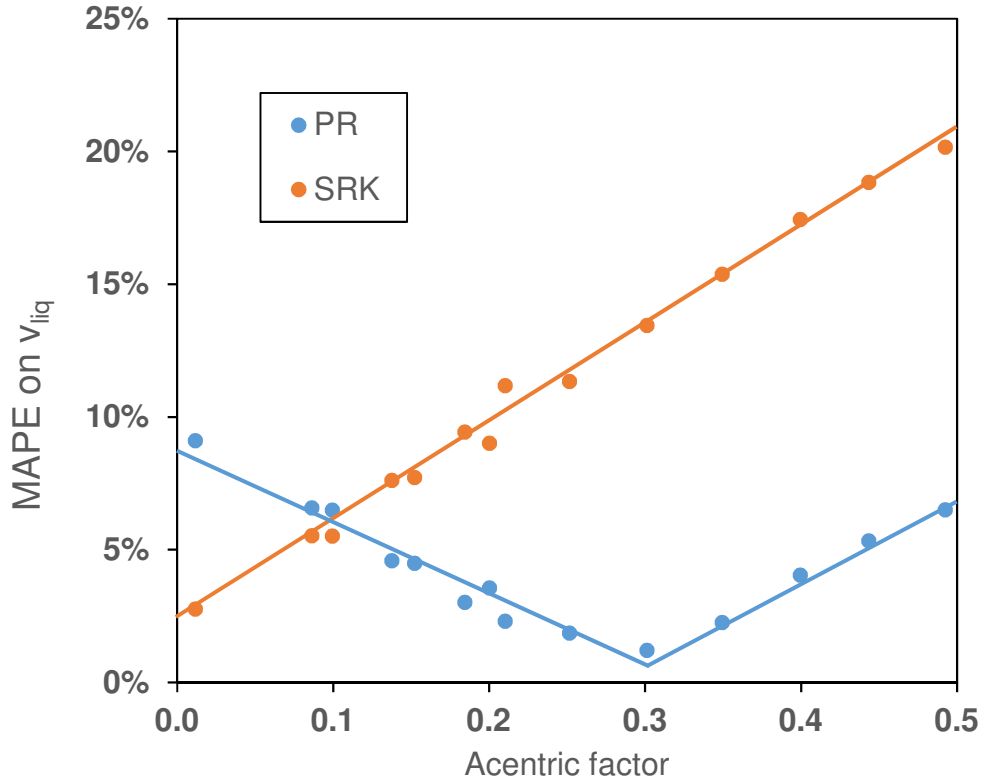
### 3. ON THE INTEREST TO COMBINE $\omega$ -DEPENDENT ( $u,w$ ) PARAMETERS AND A VOLUME-TRANSLATION PARAMETER IN A CEoS

#### 3.1. On the interest to select $\omega$ -dependent ( $U,W$ ) pairs in untranslated CEoS

In order to highlight the interest of selecting  $\Omega$ -dependent ( $U,W$ ) parameters for a better correlation of liquid-density data, let us illustrate that the selection of universal ( $U,W$ ) constants entails that minimum deviations over liquid-density data are solely obtained for molecules having a specific acentric factor. To do so, the SRK ( $u=1, w=0$ ) and PR ( $u=2, w=-1$ ) EoS, that embed a generalized  $\alpha$ -function, are considered. Note that a similar study was conducted by Schmidt and Wenzel 40 years ago but these authors only calculated the deviation over one kind of datum: the molar volume at  $T_r=0.7$ . Here, our plan is to consider a larger range of temperatures to get more reliable conclusions. Following Schmidt and Wenzel, 14 hydrocarbons ranging from  $\text{CH}_4$  ( $\omega=0.01$ ) to n-decane ( $\omega=0.49$ ) were selected. For each of them, the correlation reported by the DIPPR database to estimate the molar liquid volume at saturation was used to generate 50 equidistant data points between  $T_{\min}$  and  $T_{\max} = 0.9T_c$ . Here,  $T_{\min}$  is the minimum temperature at which  $v_{liq}^{sat}$  can be estimated from the DIPPR correlation. Once done, the MAPE (Mean Absolute Percentage Error) on  $v_{liq}^{sat}$  was calculated as:

$$MAPE = \frac{100}{50} \sum_{i=1}^{50} \left| \frac{v_{liq}^{sat,DIPPR} \left( T_i^{v_{liq}^{sat}} \right) - v_{liq}^{sat,CEoS} \left( T_i^{v_{liq}^{sat}} \right)}{v_{liq}^{sat,DIPPR} \left( T_i^{v_{liq}^{sat}} \right)} \right| \quad (17)$$

The results shown in Fig. 1 highlight that, for a given acentric factor value, deviations on  $v_{liq}^{sat}$  are strongly impacted by the choice of the EoS i.e. by the values assigned to  $u$  and  $w$ . Fig. 1, in which a large range of temperature was considered, differs significantly from the one published by Schmidt and Wenzel but leads to similar conclusions: the SRK EoS ( $u=1, w=0$ ) describes well the liquid volume at low values of  $\omega$ ; while the PR EoS ( $u=2, w=-1$ ) yields the best results around  $\omega=0.30$  (for n-hexane).



**Figure 1.** Deviation on saturated liquid molar volume up to  $T_r = 0.9$  as a function of the acentric factor  $\omega$ , calculated by the SRK and PR EoS. The 14 substances are by order of  $\omega$ : CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, but-1-ene, n-butane, benzene and the n-alkanes from n-pentane to n-decane.

What can be said for  $\omega$  values different from 0 and 0.3? For sure, Fig. 1 does not help to determine which  $(U, W)$  pair is suitable when, e.g.,  $\omega = 0.5$ . Schmidt and Wenzel assumed  $w = -3\omega$  and  $u = 1 + 3\omega$  although they had no argument justifying that  $u$  and  $w$  should be linear functions of  $\omega$ .

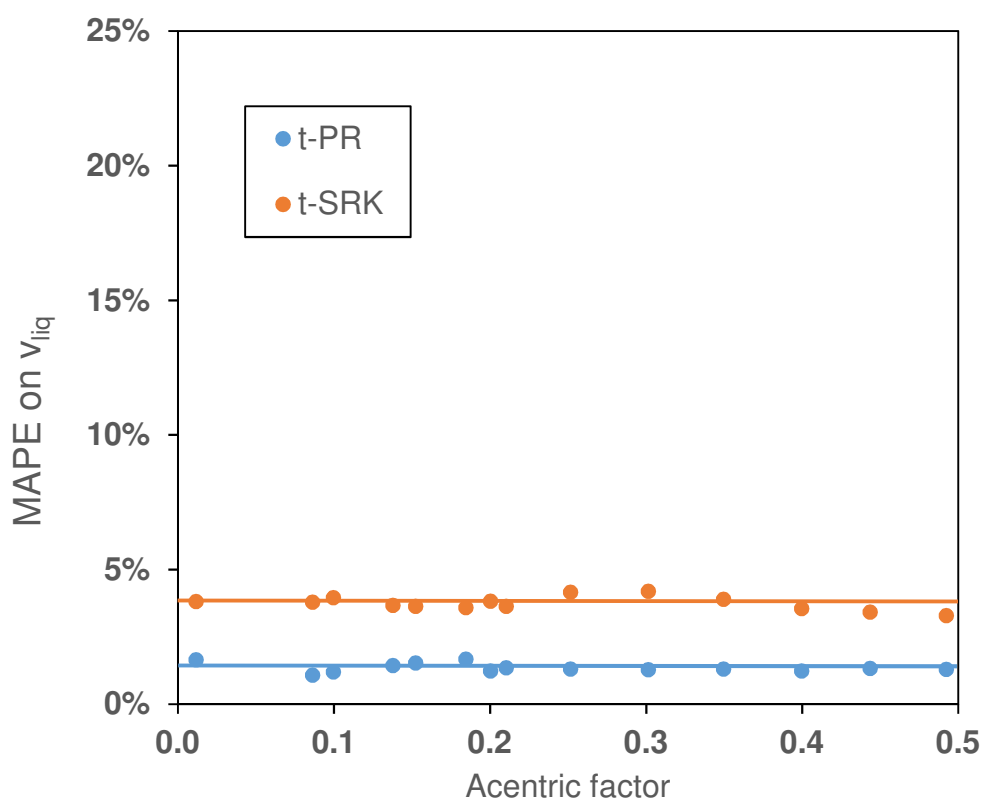
### 3.2. On the interest to select $\omega$ -dependent $(U, W)$ pairs in translated CEoS

The second possibility to make  $z_c$  component-dependent is to translate the EoS explaining why it was now decided to check the influence of the acentric factor on the correlation of saturated-liquid volumes with translated versions of the SRK and PR EoS. In this study, the substance-dependent volume-translation parameter,  $C$ , was determined, component by component, in order the translated EoS exactly reproduces the experimental saturated liquid volume at a reduced temperature of 0.8,  $[v_{liq,exp}^{sat}(T_r = 0.8)]$ , that is:

$$c = v_{liq}^{sat, u-CEoS}(T_r = 0.8) - v_{liq,exp}^{sat}(T_r = 0.8) \quad (18)$$

where  $v_{liq}^{sat, u-CEoS}(T_r = 0.8)$  is the molar volume calculated with the original (*untranslated*) CEoS at  $T_r = 0.8$ .

The results are visible in Fig. 2 and, in comparison to Fig. 1, the change is drastic: for both the translated SRK and PR EoS, the MAPE on  $v_{liq}^{sat}$  is more or less constant regardless of the acentric factor value.



**Figure 2.** Deviation on saturated liquid molar volume ( $v_{liq}^{sat}$ ) up to  $T_r = 0.9$  as a function of the acentric factor  $\omega$ , calculated by the *translated*-SRK and *translated*-PR EoS. The scale has intentionally been kept identical to the one of Fig. 1 and the 14 substances are those of Fig. 1.

It is no longer possible to assert that the SRK EoS is more suitable for spherical molecules and the PR EoS is more suitable for larger molecules. Independently of the acentric factor value, the *translated*-PR (*t*-PR) EoS leads to smaller deviations on liquid densities than the *translated*-SRK (*t*-SRK). We can thus conclude that  $L$  and  $W$  strongly affect the correlation of liquid densities but have to be selected as universal constants ( $\omega$ -independent) when CEoS are translated. There is thus no benefit to select component-dependent ( $L, W$ ) pairs and to simultaneously translate the EoS. Such a result is extremely important and opens the way to the search for an optimal ( $L, W$ ) set of universal constants that would potentially lead to better results than those obtained with the *t*-PR EoS (about 2% on liquid molar volumes according to Fig. 2).

**Remark:** although not shown, the results depicted in Fig. 2 were confirmed by considering an extended database of 1,300 pure compounds – including all families of chemical species – and for which accurate pseudo-experimental liquid densities could be extracted from the DIPPR database.

3.3. Search for  $\omega$ -dependent ( $L, w$ ) parameters to be used with untranslated CEoS that lead to the same performance as ( $u_o, w_o$ ) universal constants used in translated CEoS

What have we learnt?

1) In section 3.2, it has been shown that the combination of constant universal parameters ( $u_o = 2$ ,  $w_o = -1$ ) of the PR EoS and a component-specific volume-translation parameter leads to quite low deviations over liquid-density data (around 2%).

2) As stated in section 2.2, by translating an EoS characterized by constant universal parameters ( $u_o$ ,  $w_o$ ), we obtain component-dependent  $u$  and  $w$  parameters, noted ( $u_t, w_t$ ).

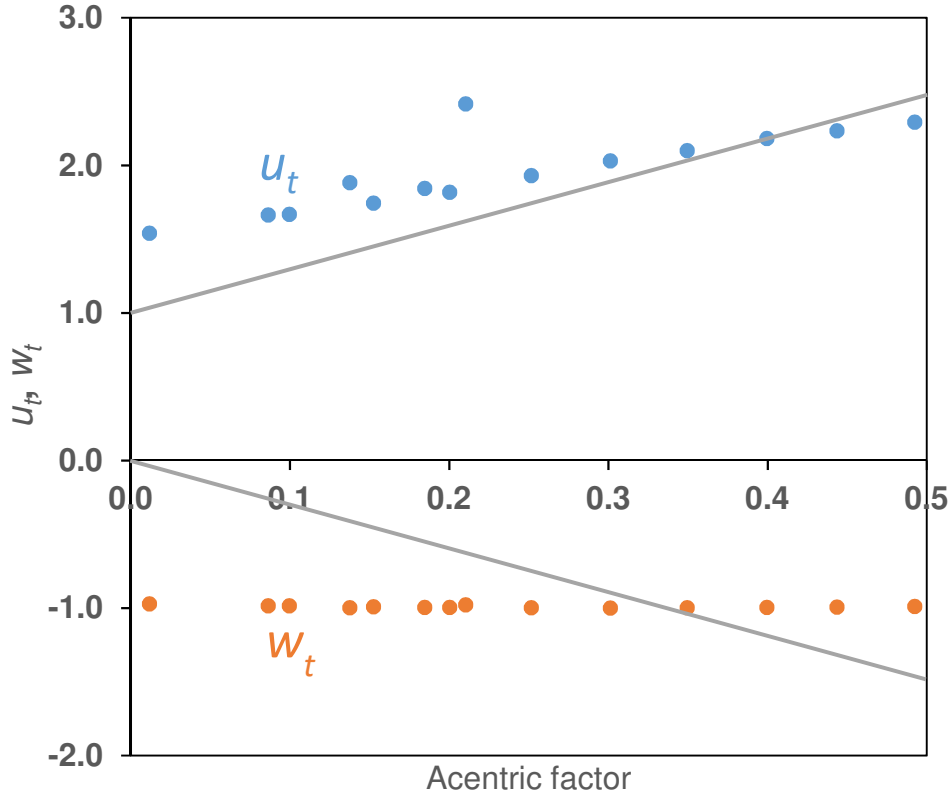
The relationship between the ( $u_o, w_o$ ) and ( $u_t, w_t$ ) sets of parameters has been derived (see Eq. (16)). For the PR EoS ( $u_o = 2$ ,  $w_o = -1$ ), one obtains:

$$\begin{cases} u_t = u_o + (2 + u_o) \left( \frac{c}{b_t} \right) = 2 + 4 \left( \frac{c}{b_t} \right) \\ w_t = w_o + (u_o + 2w_o) \left( \frac{c}{b_t} \right) + (1 + u_o + w_o) \left( \frac{c}{b_t} \right)^2 = -1 + 2 \left( \frac{c}{b_t} \right)^2 \end{cases} \quad (19)$$

Once again, although ( $u_o$ ,  $w_o$ ) are constant parameters, ( $u_t$ ,  $w_t$ ) are component specific, since  $c$  and  $b_t$  are component specific: the substance-dependent volume-translation parameter,  $c$ , is indeed determined by Eq. (18) and according to Eqs. (5) and (13)

$$b_t = 0.07780 \frac{RT_{c,\text{exp}}}{P_{c,\text{exp}}} - c.$$

Component-dependent ( $u_t, w_t$ ) parameters stemming from Eq. (19) lead to an average deviation over liquid-density data of about 2% and can thus be considered as reference values. Consequently, for 14 pure components, they were plotted versus  $\omega$  in Fig. 3 in order to highlight the relationship between the component-specific parameters ( $u_t$ ,  $w_t$ ) on one hand, and  $\omega$  on the other hand. Doing so, it will be possible to evaluate the empirical correlations proposed by Schmidt and Wenzel ( $w = -3\omega$  and  $u = 1 + 3\omega$ ) and see if they moved in the right direction.



**Figure 3.** Plot of  $U_t$  (●) and  $w_t$  (●) stemming from the  $t$ -PR EoS as a function of the acentric factor  $\omega$ . With such  $U$  and  $w$  parameters, the MAPE on  $v_{liq}^{sat}$  is about 2% (see Fig. 2) so that such pairs can be considered as *optimal* values. The 14 substances are those of Fig. 1. The two straight lines ( $w = -3\omega$  and  $u = 1 + 3\omega$ ) recall the values recommended by Schmidt and Wenzel.

Fig. 3 highlights that to get accurate densities (the same as those obtained with the  $t$ -PR EoS), it is enough to select  $U$  acentric factor-dependent and to keep  $w$  constant ( $w = -1$ ). It is noticeable that  $U$  must be an increasing function of  $\omega$  but the relationship proposed by Schmidt and Wenzel ( $u = 3\omega + 1$ ) has a too steep slope. After considering a database of 1300 components, it was found that a good fit of  $U$  and  $w$  with respect to  $\omega$ , was:

$$\begin{cases} u = 0.7\omega + 1.9 \\ w = -1 \end{cases} \quad (20)$$

Eq. (20) clearly establishes that  $(u + w) = 0.9 + 0.7\omega$  is not constant. It takes a value equal to one (as recommended by Schmidt and Wenzel) only for a small molecule like the propane. In 1992, Twu et al. [19] recommended  $(u - w) = 4$  but this relationship deviates significantly from Eq. (20).

#### 4. SEARCH FOR THE OPTIMAL ( $u, w$ ) SET FROM A MAP REPORTING DEVIATIONS BETWEEN EOS PREDICTIONS AND EXPERIMENTAL PROPERTIES IN THE ( $u, w$ ) SPACE

As previously discussed, very few pairs of constant ( $U, W$ ) parameters were tested. For untranslated CEoS, we find (0,0) for the VdW EoS, (1,0) for the SRK EoS, (2, -1) for the PR

EoS and (3, -2) for the Harmens EoS. Such pairs are however not equivalent at all in terms of correlation of liquid-density data. As an example, we know that the deviations on liquid densities are twice smaller with the PR EoS than with the SRK EoS. It seems thus pertinent to wonder what are the optimal values of  $(U, W)$ , i.e., what are the  $(U, W)$  values that lead to the best correlation of both volumetric and VLE equilibrium data. For clarity, let us recall that  $u$  and  $w$  only have a small influence on the accuracy of VLE predictions.

The previous section also highlighted that the volume translation technique was certainly the best option to make  $u$  and  $w$  component-dependent. Such a technique indeed avoids to develop a correlation between  $(U, W)$  and  $\Omega$ . In turn, it necessitates the knowledge of the experimental molar volume at  $T_r = 0.8$ . The strong impact of  $u$  and  $w$  on *translated*-CEoS was also emphasized. As an example, deviations on liquid densities were found to be close to 2% with the *t*-PR EoS and about 4% with the *t*-SRK EoS.

For all these reasons, it was decided to meticulously explore the  $u - w$  space in order to determine the optimal values of these two parameters for both an *untranslated* and a *translated* CEoS.

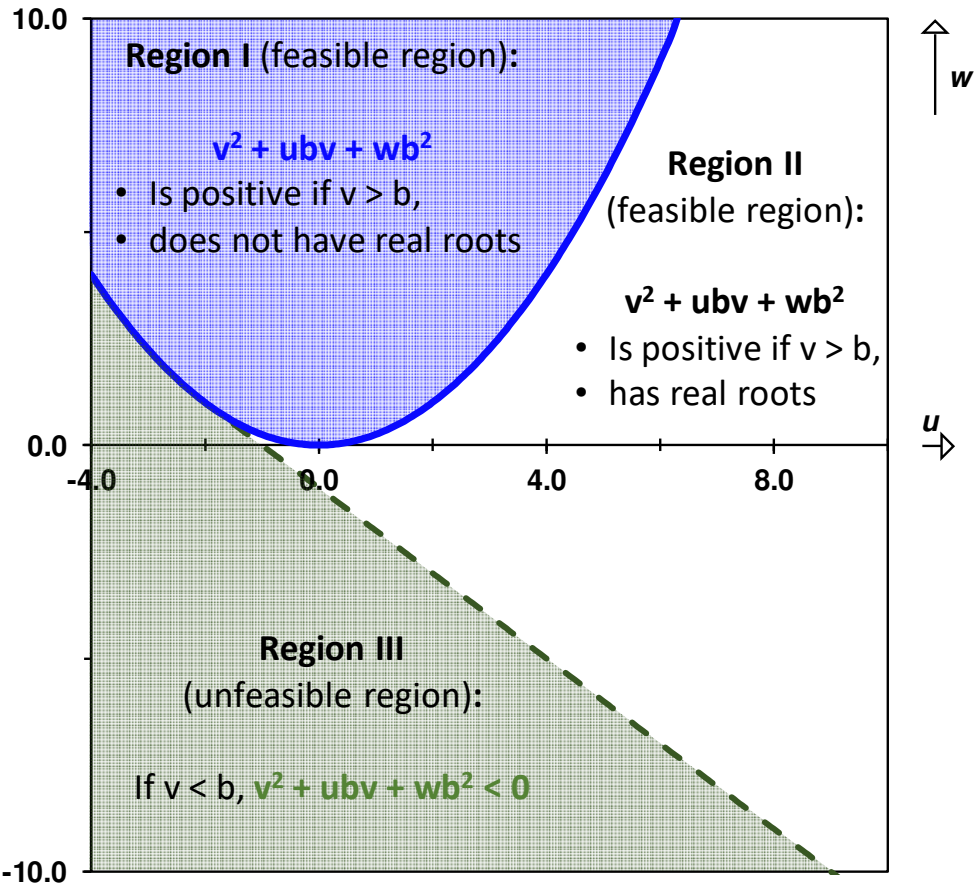
Note that optimal values of the  $(U, W)$  universal parameters for an untranslated CEoS are searched for comparative purpose only. We know from the previous section that a better strategy exists for improving the reproduction of liquid-density data (i.e., the use of universal  $(U, W)$  constants in a translated CEoS). However, as mentioned previously, the untranslated PR EoS is currently the best CEoS using universal  $(U, W)$  constants in terms of reproduction of liquid-density data and it is interesting to determine if better  $(U, W)$  values could be found for this kind of untranslated EoS.

#### 4.1. Exploration of map reporting deviations between EoS predictions and experimental properties in the $u - w$ space

In order to explore the  $u - w$  space, it is necessary to identify the feasible values of  $u$  and  $w$ . According to Segura et al. [24], these parameters must be selected in order to ensure that the volume function of the attractive term ( $v^2 + ubv + wb^2$ ) remains strictly positive in the molar volume range of applicability of the EoS (i.e., for any  $v \geq b$ ) and therefore, that the attractive term of the EoS remains positive and finite, as physically expected. Segura et al. obtained the following set of constraints:

$$\begin{cases} u + w > -1 & \text{if } u > -2 \\ u^2 < 4w & \text{if } u \leq -2 \end{cases} \quad (21)$$

These constraints are represented in Fig. 4 (see the dashed line) and separate the  $U-W$  space in two parts: a first one called “Region III” defines all the unfeasible  $(U, W)$  pairs (i.e., the  $(U, W)$  pairs leading to negative values of  $v^2 + ubv + wb^2$  for  $v \geq b$ ), while the remaining region corresponds to the feasible  $(U, W)$  pairs. This latter can be divided in two sub-regions denoted Region I and Region II in Fig. 4. Region I is such that the polynomial  $v^2 + ubv + wb^2$  exhibits complex roots while region II is associated with real roots. In practice, the representative points of CEoS of the literature all belong to Region II.



**Figure 4.** Representation of the feasible and unfeasible regions of CEoS in the  $U-W$  space.

In this study, in order to realize a very large screening of  $(U, W)$  pairs, i.e. to explore a very large part of Region II,  $u$  was varied between  $-2$  and  $10$ , while  $w$  was subject to the two above constraints (see Eq. (21)).

To build the  $u - w$  map, a variation step equal to  $0.05$  was selected for each parameter so that more than  $50,000$   $(U, W)$  combinations were tested.

Clearly, each  $(U, W)$  pair defines a new EoS for which a mathematical expression of the  $\alpha$ -function is required. However, the open literature only defines generalized  $\alpha$ -functions for the RK and PR EoS. In other words,  $\alpha$ -functions are only available for 2 single combinations of the  $(U, W)$  parameters. These well-known expressions are recalled below:

$$\left\{ \begin{array}{l} \left\{ \begin{array}{l} u = 1 \\ w = 0 \end{array} \right. ; \text{SRK EoS} ; \left\{ \begin{array}{l} \alpha(T) = \left[ 1 + m \left( 1 - \sqrt{T/T_c} \right) \right]^2 \\ \text{with: } m(\omega_{\text{exp}}) = 0.480 + 1.574\omega_{\text{exp}} - 0.176\omega_{\text{exp}}^2 \end{array} \right. \\ \left\{ \begin{array}{l} u = 2 \\ w = -1 \end{array} \right. ; \text{PR EoS} ; \left\{ \begin{array}{l} \alpha(T) = \left[ 1 + m \left( 1 - \sqrt{T/T_c} \right) \right]^2 \\ \text{with: } m(\omega_{\text{exp}}) = 0.37464 + 1.54226\omega_{\text{exp}} - 0.26992\omega_{\text{exp}}^2 \end{array} \right. \end{array} \right. \quad (22)$$

In order to overcome this lack of information, for each  $(U, W)$  pair, the  $m(\omega_{\text{exp}})$  expression to be used in the Soave  $\alpha$ -function ( $\alpha(T) = \left[ 1 + m \left( 1 - \sqrt{T/T_c} \right) \right]^2$ ) has to be re-determined. For

this purpose, a procedure similar to the one used by Soave for the development of the SRK EoS was followed [5]:  $\Omega$  values ranging from zero to 1.4 with a step of 0.05 were assumed. For each of these  $\Omega$  values, the *experimental* reduced vapor pressures at  $T_r = 0.7$  was determined from the definition of the acentric factor:  $P_r^{sat}(T_r = 0.7) = 10^{-\Omega-1}$ . Once done, the  $m$  value enabling to reproduce exactly this latter quantity is determined. This procedure is possible, i.e., does not require to specify values of  $T_c$  and  $P_c$  because generalized CEoS obey the 3-parameter corresponding states theorem which stipulates that the calculated values of  $P_r^{sat}$  only depend on  $T_r$  and  $m$ . Finally, the  $m$  values were correlated with respect to  $\Omega$  using a third-order polynomial expression:

$$m(\Omega) = A + B\Omega + C\Omega^2 + D\Omega^3 \quad (23)$$

The accuracy of each EoS, i.e. of each  $(U, W)$  combination is assessed by evaluating the deviations between calculated and experimental vapor pressures ( $P^{sat}$ ), enthalpies of vaporization ( $\Delta_{vap}H$ ) and saturated molar liquid volumes ( $v_{liq}^{sat}$ ) for a huge number of pure components. Indeed, thanks to the DIPPR database, we were able to find 1721 compounds belonging to many different chemical families (hydrocarbons, halogenated, oxygenated, sulfur, nitrogen compounds, etc.) for which at least vapor pressure data could be accurately generated from a temperature-dependent correlation. More information about this database can be found in one of our previous papers [25]. This initial number of 1721 was reduced to 1525 because the behavior of 196 non-classical compounds could not be described properly by the 1-parameter Soave  $\alpha$ -function. They were removed to avoid introducing a bias in the results. We also know that a 1-parameter  $\alpha$ -function cannot catch simultaneously  $P^{sat}$ ,  $\Delta_{vap}H$  and liquid heat capacity ( $C_{p,liq}^{sat}$ ) data, explaining why this latter property was disregarded here. Table 2 summarizes the available property data for the 1525 components considered in this study.

**Table 2.** Available properties for the 1525 components that are used to determine the optimum values of  $u$  and  $w$ .

Property	Number of compounds
$P^{sat}$	1525
$\Delta_{vap}H$	1318
$v_{liq}^{sat}$	1300

For each property, the DIPPR correlations are used to generate 50 equidistant data points following the rules explained in the Appendix. In the end, for each  $(U, W)$  combination, a kind of "global mean percent error (GMPE) per property" expressed through Eqs. (24) and (25) for the untranslated and translated EoS, respectively, are calculated:

$$GMPE_{untranslated} = \frac{2 \cdot \overline{MAPE} P^{sat} + \overline{MAPE} \Delta_{vap}H + \overline{MAPE} v_{liq}^{sat}}{4} \quad (24)$$

$$GMPE_{translated} = \frac{\overline{MAPE} P^{sat} + \overline{MAPE} \Delta_{vap}H + \overline{MAPE} v_{liq}^{sat}}{3} \quad (25)$$



where:

$$\overline{MAPE}^{P^{sat}} = \frac{\sum_{j=1}^{NC^{P^{sat}}} MAPE_j^{P^{sat}}}{NC^{P^{sat}}} \quad (26)$$

$$\overline{MAPE}^{\Delta_{vap}H} = \frac{\sum_{j=1}^{NC^{\Delta_{vap}H}} MAPE_j^{\Delta_{vap}H}}{NC^{\Delta_{vap}H}} \quad (27)$$

$$\overline{MAPE}^{v_{liq}^{sat}} = \frac{\sum_{j=1}^{NC^{v_{liq}^{sat}}} MAPE_j^{v_{liq}^{sat}}}{NC^{v_{liq}^{sat}}} \quad (28)$$

$NC^{P^{sat}}$ ,  $NC^{\Delta_{vap}H}$  and  $NC^{v_{liq}^{sat}}$  are given in Table 2. These are the number of components for which experimental  $P^{sat}$ ,  $\Delta_{vap}H$  and  $v_{liq}^{sat}$  could be extracted from the DIPPR database. The  $MAPE_j$  on a given property for a component  $j$  is calculated as:

$$MAPE_j^{prop} = \frac{100}{50} \sum_{i=1}^{50} \left| \frac{prop^{DIPPR}(T_i^{prop}) - prop^{CEoS}(T_i^{prop})}{prop^{DIPPR}(T_i^{prop})} \right| \quad (29)$$

#### 4.2. Optimal ( $U, W$ ) values for untranslated CEoS

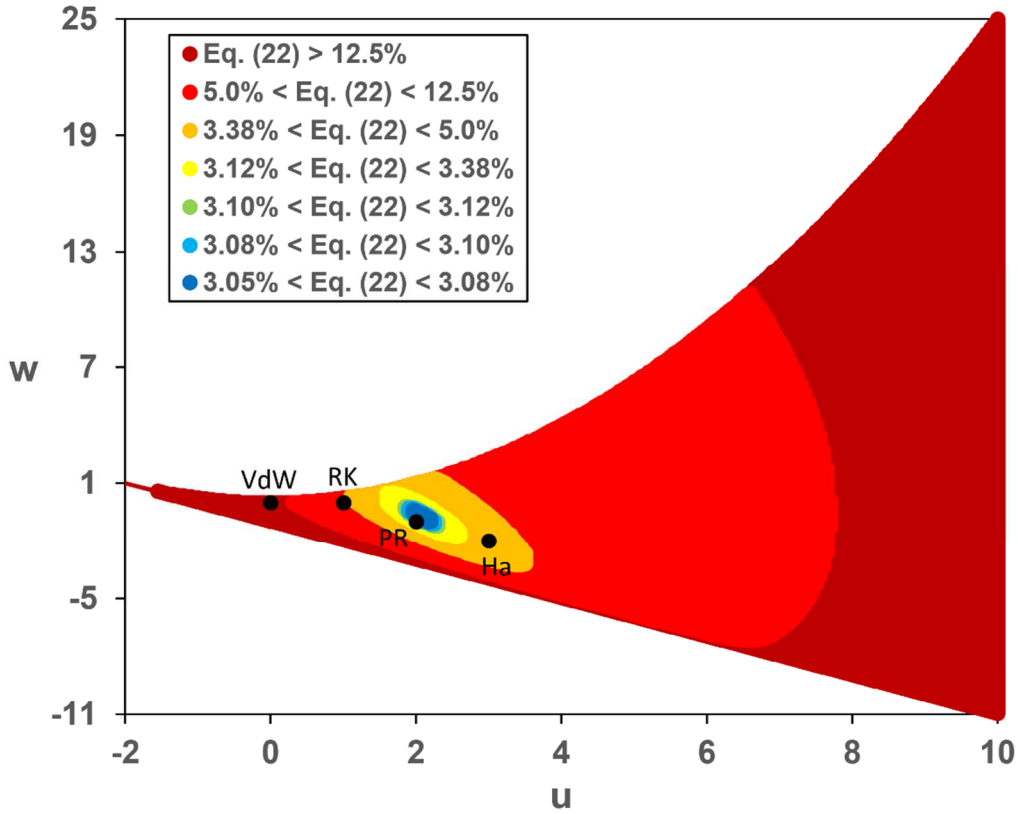
The results obtained for all the tested ( $U, W$ ) combinations (more than 50,000 with a variation step equal to 0.05) are visible in Fig. 5. The ( $U, W$ ) pair leading to the smallest value of  $GMPE_{untranslated}$  (Eq. (24)) is:

$$\begin{cases} U_{opt} = 2.10 \\ W_{opt} = -0.75 \end{cases} \quad (30)$$

It is however possible to define in Fig. 5 a small region of ( $U, W$ ) parameters for which the difference between the values of the parameters is not significant in terms of  $GMPE_{untranslated}$  value. In other words, such parameters lead to equivalent minima for the  $GMPE_{untranslated}$  value defined in Eq. (24). Such a region is characterized by:

$$U \in [1.95, 2.20] \text{ and } W_{opt} = -1.89U + 3.22 \quad (31)$$

It is noticeable that the PR EoS is quite close to this zone (see Fig. 5). On the other hand, the VdW and RK EoS, as expected, yield to higher values of  $GMPE_{untranslated}$  due to the limitations to reproduce liquid molar volumes. This is particularly true for the VdW EoS and to a lesser extent for the SRK EoS.



**Figure 5.** Values of the *global mean percentage error per property* (see Eq.(24)) as a function of the parameters  $u$  and  $w$  for untranslated CEoS.

For a better comparison, Table 3 shows the MAPE on  $P^{sat}$ ,  $\Delta_{vap}H$  and  $v_{liq}^{sat}$  obtained with the VdW, SRK, PR and the optimized untranslated EoS characterized by  $u=2.10$  and  $w=-0.75$ . All EoS use the Soave  $\alpha$ -function. It is noticeable that the optimized EoS developed in this work makes it possible to gain 1% of accuracy on the prediction of liquid molar volumes in comparison with the PR EoS which was until now the most accurate untranslated CEoS for  $v_{liq}^{sat}$ .

**Table 3.** Comparison of the main untranslated CEoS (VdW, SRK, PR) with the optimized untranslated CEoS developed in this work. Note that all EoS are combined with a Soave-type  $\alpha$ -function.

EoS	$u$	$w$	GMPE <sub>untranslated</sub> (Eq. (24))	MAPE on $P^{sat}$ (1525 fluids)	MAPE on $\Delta_{vap}H$ (1318 fluids)	MAPE on $v_{liq}^{sat}$ (1300 fluids) ( $T_r < 0.9$ )
VdW	0	0	17%	2.0%	2.7%	60%
SRK	1	0	6.1%	1.8%	2.6%	18%
PR	2	-1	3.3%	1.5%	2.6%	7.6%
<b>This work</b>	<b>2.10</b>	<b>-0.75</b>	<b>3.1%</b>	<b>1.5%</b>	<b>2.5%</b>	<b>6.7%</b>

**Remark:** in this study the CEoS are parameterized classically, i.e. in order to exactly get:  $P^{sat,EoS}(T_{c,exp}) = P_{c,exp}$ . It is however well-known that by constraining a CEoS to pass through the experimental critical coordinates, the compressibility of saturated liquids cannot be represented correctly [10]. The unique solution to get a better accuracy would be to fit the

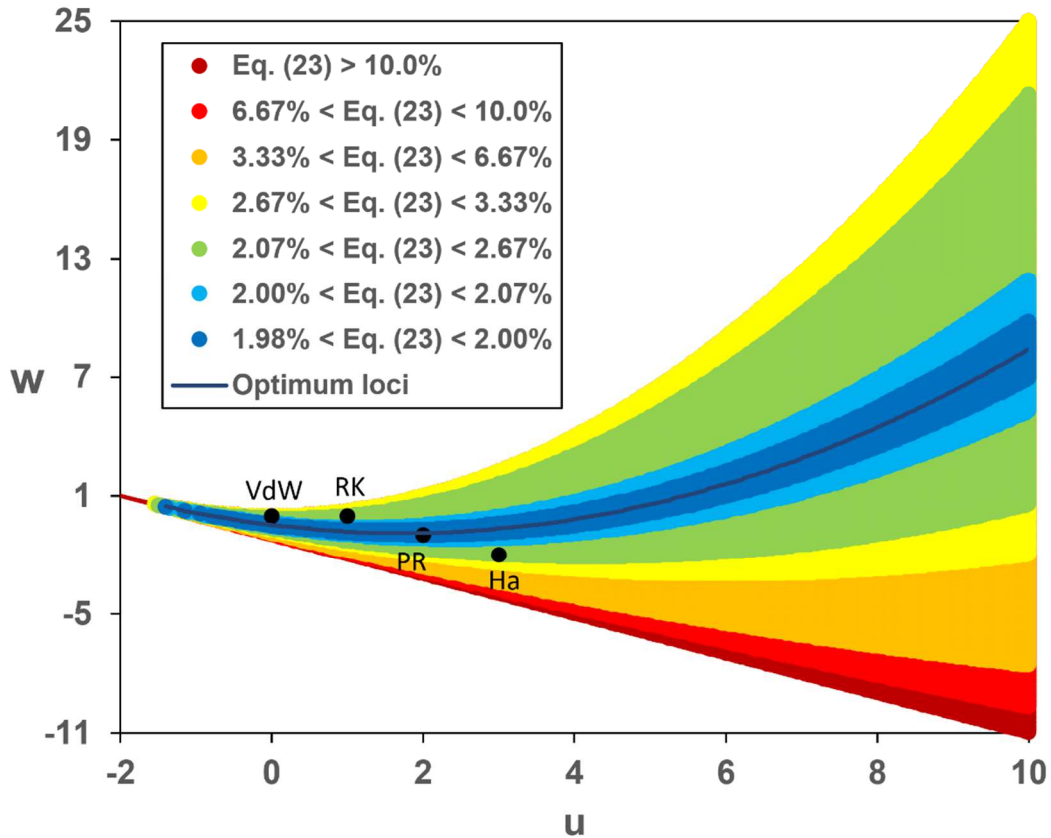
three pure-component parameters (let us say  $b$ ,  $a_c$  and  $m_{Soave}$ ) of a given CEoS to saturated liquid densities and vapor pressures as is conventionally done with SAFT-type EoS. In addition, as explained by Polishuk [26–28], incorrect compressibility values may lead to higher deviations on density data at very high pressures (much higher deviations than those reported in Table 3 for the saturated liquid).

#### 4.3. Optimal ( $U, W$ ) values for translated CEoS

It is recalled that the volume correction was determined in order to exactly reproduce the liquid molar volume at  $T_r = 0.8$ , for each pure component. The results obtained for all the tested ( $U, W$ ) pairs are shown in Fig. 6. It is noticeable that they differ notably from those obtained for untranslated CEoS. In the present case, there is not a unique ( $U, W$ ) combination leading to a minimum (or a specified) value of Eq. (25) but instead a valley of ( $U, W$ ) combinations all located along a second-order polynomial line. As an example, in Fig. 6, the ( $U, W$ ) pairs that minimize the  $GMPE_{translated}$  quantity defined by Eq.(25) are identified by a dark blue line the equation of which is:

$$W_{opt} = 0.14U_{opt}^2 - 0.47U_{opt} - 0.47 \quad (32)$$

The following couples of parameters:  $\begin{cases} u=0 \\ w=-0.47 \end{cases}$ ,  $\begin{cases} u=1 \\ w=-0.80 \end{cases}$ ,  $\begin{cases} u=2 \\ w=-0.85 \end{cases}$  or  $\begin{cases} u=3 \\ w=-0.62 \end{cases}$  are thus equivalent and all minimize Eq. (25).



**Figure 6.** Values of the *global mean percentage error per property* (see Eq. (25)) as a function of the parameters  $u$  and  $w$  for translated CEoS.

By superimposing Fig. 5 and Fig. 6, it is noticeable that the locus of optimal values drawn in Fig. 6 overlaps the small region in Fig. 5 that minimizes Eq. (24). By selecting an  $(U, W)$  pair in this overlapping zone, we get simultaneously the most accurate untranslated and translated CEoS. The  $U$  and  $W$  values satisfying simultaneously Eq. (31) and Eq. (32) are:

$$\begin{cases} U_{opt} = 2.16 \\ W_{opt} = -0.86 \end{cases} \quad (33)$$

In the rest of the paper, the translated CEoS using the  $(U, W)$  values reported in Eq. (33) is called the  $t$ -OptiM EoS. Table 4 shows the MAPE on  $P^{sat}$ ,  $\Delta_{vap}H$  and  $v_{liq}^{sat}$  obtained with the  $t$ -VdW,  $t$ -SRK,  $t$ -PR and the  $t$ -OptiM EoS. All EoS use the Soave  $\alpha$ -function. Since a volume translation does not change the phase equilibrium conditions [2,22,23], the MAPEs on  $P^{sat}$ , and  $\Delta_{vap}H$  reported in Table 4 are strictly the same as those given in Table 3. Only the deviations on  $v_{liq}^{sat}$  are modified.

**Table 4.** Comparison of the main translated CEoS ( $t$ -VdW,  $t$ -SRK,  $t$ -PR) with the optimized translated CEoS developed in this work and called  $t$ -OptiM. All EoS use a Soave-type  $\alpha$ -function.

EoS	$u$	$w$	GMPE <sub>translated</sub> (Eq. (25))	MAPE on $P^{sat}$ (1525 fluids)	MAPE on $\Delta_{vap}H$ (1318 fluids)	MAPE on $v_{liq}^{sat}$ (1300 fluids) ( $T_r < 0.9$ )
$t$ -VdW	0	0	2.9%	2.0%	2.7%	4.1%
$t$ -SRK	1	0	2.6%	1.8%	2.6%	3.5%
$t$ -PR	2	-1	2.0%	1.5%	2.6%	1.9%
<b><math>t</math>-OptiM</b>	<b>2.16</b>	<b>-0.86</b>	<b>2.0%</b>	<b>1.5%</b>	<b>2.5%</b>	<b>1.9%</b>

The comparison of Table 3 and Table 4 highlights the colossal positive impact of a volume translation. As an example, the MAPE on  $v_{liq}^{sat}$  are reduced from 60% to 4% for the VdW EoS. Similarly, they are reduced from 18 to 3.5% for the SRK EoS. Both the  $t$ -PR and the  $t$ -OptiM EoS show deviations on  $v_{liq}^{sat}$  that are as low as 2%. Such a table makes it also possible to conclude that by selecting  $(u = 2 ; w = -1)$ , Peng and Robinson made a very good choice. This couple of values is indeed extremely close to the optimal one so that the  $t$ -PR EoS is certainly the most accurate CEoS today available. As a direct consequence, there is only a minor difference between the  $t$ -PR and  $t$ -OptiM EoS in Table 4. The  $t$ -SRK and  $t$ -VdW EoS lie outside but near the region of optimal parameters [see Fig. 6 and Eq. (32)].

#### 4.4. Optimal translated and consistent CEoS

As stated in the introduction, the second-order polynomial volume function ( $v^2 + ubv + wb^2$ ) has a strong influence on the calculated volumetric properties whereas the  $\alpha$ -function has a strong influence on the calculated VLE properties like  $P^{sat}$ ,  $\Delta_{vap}H$  and  $c_{P,liq}^{sat}$ . It was thus decided to couple the optimized  $(U, W)$  parameters determined in this study ( $U_{opt} = 2.16$ ,  $w_{opt} = -0.86$ ) with the highly flexible 3-parameter  $\alpha$ -function proposed by Twu in 1991 [20]:

$$\alpha(T_r) = T_r^{N(M-1)} \exp\left[L(1 - T_r^{MN})\right] \quad (34)$$

This association should enable to define the most accurate CEoS ever published. In this study, the three  $L, M, N$  parameters were determined for the 1721 pure components recommended by Piña-Martinez et al. [25] following the fitting procedure these authors advised to implement. In order to guarantee safe property predictions in both subcritical and supercritical domains, the parameters were fit to experimental data in order that the resulting  $\alpha$ -function obeys the following list of constraints:

$$\alpha(T_c) = 1 \text{ and for all } T: \begin{cases} \alpha \geq 0 & \text{and } \alpha(T_r) \text{ continuous} \\ \frac{d\alpha}{dT_r} \leq 0 & \text{and } \frac{d\alpha}{dT_r} \text{ continuous} \\ \frac{d^2\alpha}{dT_r^2} \geq 0 & \text{and } \frac{d^2\alpha}{dT_r^2} \text{ continuous} \\ \frac{d^3\alpha}{dT_r^3} \leq 0 \end{cases} \quad (35)$$

An  $\alpha$ -function that fulfills all of the conditions reported in Eq. (35) can be considered as *consistent* (according to Le Guennec et al. [29–31]). In addition to the  $t$ -OptiM CEoS, and for possible comparison with well-acknowledged CEoS, such a procedure was also applied to the  $t$ -PR,  $t$ -RK and  $t$ -VdW thus defining the  $tc$ -OptiM,  $tc$ -PR,  $tc$ -RK and  $tc$ -VdW CEoS. Here  $tc$  stands for *translated* and *consistent* to state that the CEoS is used both with a volume translation and the consistent version of the Twu 91  $\alpha$ -function. It is worth including the Schmidt and Wenzel (SW) EoS in the comparison, i.e., to set  $L$  and  $w$  as a function of the acentric factor in order to see the potential advantage of such a procedure. The comparison of all these *translated-consistent* models is presented in Table 5 from which it is possible to highlight that all the  $tc$ -CEoS give similar and very small deviations on  $P^{sat}$ ,  $\Delta_{vap}H$  and  $C_{P,liq}^{sat}$  thus demonstrating the benefit of using the 3-parameter Twu 91  $\alpha$ -function.

**Table 5.** Comparison of the most famous *translated-consistent* CEoS ( $tc$ -VdW,  $tc$ -RK,  $tc$ -PR,  $tc$ -SW) with the optimized one developed in this work and called  $tc$ -OptiM. All EoS are combined with the Twu 91  $\alpha$ -function.

EoS	MAPE on $P^{sat}$ (1721 fluids)	MAPE on $\Delta_{vap}H$ (1453 fluids)	MAPE on $C_{P,liq}^{sat}$ (829 fluids)	MAPE on $v_{liq}^{sat}$ (1489 fluids) ( $T_r < 0.9$ )	MAPE on $v_c$ (1489 fluids)	Untranslated	
						MAPE on $v_{liq}^{sat}$ (1489 fluids) ( $T_r < 0.9$ )	MAPE on $v_c$ (1489 fluids)
$tc$ -VdW	1.2%	2.0%	2.2%	4.2%	25%	60%	48%
$tc$ -RK	1.2%	1.9%	2.2%	3.7%	24%	19%	31%
$tc$ -PR	1.0%	1.9%	2.0%	2.2%	20%	8.5%	21%
$tc$ -SW	0.9%	1.9%	1.9%	2.9%	18%	7.6%	19%
<b><math>tc</math>-OptiM</b>	<b>1.0%</b>	<b>1.9%</b>	<b>2.0%</b>	<b>2.2%</b>	20%	7.6%	20%

Without getting into the details, the error on  $P^{sat}$  is 1% whereas the errors on  $\Delta_{vap}H$  and  $C_{P,liq}^{sat}$  are both 2%. For  $v_{liq}^{sat}$  data, it is not surprising to find back in Table 5 the deviations previously obtained with the  $t$ -CEoS (see Table 4) since the  $\alpha$ -function has a minor impact on the calculation of liquid densities. In Table 5, the deviations on  $v_{liq}^{sat}$  are however slightly higher than those reported in Table 4 because the number of compounds was significantly

increased. It is thus not surprising to see that the *tc*-PR and the *tc*-OptiM EoS give similar deviations on  $v_{liq}^{sat}$  that are also the smallest ones (about 2%). It was indeed concluded in the previous section that the values of  $u$  and  $w$  selected by Peng and Robinson were very close to the optimal ( $u_{opt}, w_{opt}$ ) values determined in this study.

The *translated-consistent* form of the SW EoS cannot achieve the same results for  $v_{liq}^{sat}$  as *tc*-PR and *tc*-OptiM (but performs better than *tc*-RK or *tc*-VdW). This confirms our previous conclusions that it is not relevant to select component-dependent ( $U, W$ ) parameters and to simultaneously translate the EoS.

The VdW EoS, with the introduction of an efficient temperature-dependence of the attractive term, can reproduce vapor pressure data of 1721 pure fluids, both polar and non-polar, with a deviation of 1.2%. At the same time, the enthalpies of vaporization and liquid heat capacities are correlated with a deviation of about 2%. With the introduction of a constant volume correction, the VdW EoS can reproduce liquid densities with a deviation close to 4% (such deviations reach no less than 60% without volume correction!). Contrary to a priori beliefs, the *tc*-VdW EoS is thus accurate enough to be used for process design and simulation purposes. These conclusions totally agree with the previous findings of Soave [32] and Tassios [33–36] who brilliantly explained how the VdW EoS could be improved.

## 5. CONCLUSION

In this work, we studied how the  $L$  and  $w$  parameters [involved in the volume function of the attractive term in cubic equations of state ( $v^2 + ubv + wb^2$ )] influence the accuracy of the description of saturated-liquid molar volume data. We concluded that:

- As already reported [19], the ability for a CEoS to predict vapor pressure and vapor-liquid equilibrium (VLE) data requires the selection of an appropriate  $\alpha$ -function while the accuracy of the predicted volumetric properties is governed by the volume function of the attractive term.
- The unique solution to predict accurate volumetric properties is to make  $L$  and  $w$  component-dependent.
- The volume translation technique is certainly the best option to make  $L$  and  $w$  component-dependent. Such a technique indeed avoids the development of a correlation between ( $U, W$ ) and  $\omega$ . Moreover, its application is straightforward.
- When cubic EoS are translated,  $L$  and  $w$  must be  $\omega$ -independent. There is indeed no benefit to select  $\omega$ -dependent ( $U, W$ ) pairs and to simultaneously translate the EoS.
- The empirical relationships between  $u$  and  $w$  proposed in the open literature:  $u+w=1$  or  $u-w=4$  were not deemed as optimal to get the smallest deviations over liquid densities.
- Selecting  $u=2.16$  and  $w=-0.86$ , the most accurate untranslated and translated CEoS are simultaneously obtained. By coupling such parameters with (i) a temperature-independent volume translation in order to exactly reproduce the liquid molar volume at  $T_r = 0.8$  and (ii) the highly-flexible Twu 91  $\alpha$ -function, we were able to propose the most accurate CEoS ever published. It was named *tc*-OptiM and is able to correlate the vapor pressures with an error of 1% whereas errors on  $\Delta_{vap}H$ ,  $C_{P,liq}^{sat}$  and  $v_{liq}^{sat}$  are close to 2%.
- Results obtained with the *tc*-OptiM EoS are however only slightly better than those obtained with the *tc*-PR [30] CEoS. This is because the values of  $u$  and  $w$  associated

with the Peng-Robinson EoS are very close to the optimal  $(u_{opt}, w_{opt})$  values determined in this study.

- The  $tc$ -VdW EoS (i.e. the *translated*-VdW EoS coupled with the Twu 91  $\alpha$ -function) is accurate enough to be used for process design and simulation purposes.

Our plans it to extend the  $tc$ -PR (or  $tc$ -OptiM) to mixtures by using, e.g., advanced mixing rules like those involved in the  $E$ -PPR78 model [37].

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## APPENDIX

In this study, generation of the pseudo-experimental data from the DIPPR database obeys the following rules:

- 1) Regardless of the considered property among  $P^{sat}$ ,  $\Delta_{vap}H$ ,  $C_{P,liq}^{sat}$  and  $v_{liq}^{sat}$ , 50 equidistant pseudo-experimental data points are generated in their valid temperature range,  $[T_{min}; T_{max}]$ .
- 2) For the  $\Delta_{vap}H$  and  $C_{P,liq}^{sat}$  correlations, in the case that  $T_{max}$  exceeds  $0.98T_c$ ,  $T_{max} = 0.98T_c$  is set. The reason for this choice is simple:  $\Delta_{vap}H$  goes to zero at the critical temperature and the calculation of the relative deviation with the experimental data induces a division by zero. Similarly,  $C_{P,liq}^{sat}$  goes to infinity at the critical temperature so that, once again, the relative deviation with the experimental value cannot be calculated.
- 3) For the  $P^{sat}$  correlations,  $T_{max} = T_c$  is set. However, in the case where  $P^{sat}(T_{min}) < 0.1 \text{ bar}$ , the value of  $T_{min}$  is increased to enforce that  $P^{sat}(T_{min}) = 0.1 \text{ bar}$ . The reason for such a choice is twofold:
  - First and as previously discussed the  $(L, w)$  parameters we want to optimize have a strong influence on the calculated liquid densities and to a much smaller extent an influence on the calculated vapor pressures. Consequently, our conclusions are very insensitive to the choice of  $P_{min}$  (here 0.1 bar).
  - We also know that the 1-parameter Soave  $\alpha$ -function can lose accuracy at very low temperatures. Consequently,  $P_{min} = 0.1 \text{ bar}$  seems a good compromise to avoid a bias when determining the optimal values of the parameters  $u$  and  $w$ .
- 4) For the  $v_{liq}^{sat}$  correlations,  $T_{max} = 0.9T_c$  is set (it is indeed well-known that it is not possible to properly catch the critical region with a CEoS).

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