Fluid Phase Equilibria 279 (2009) 56–63

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Density-and-temperature-dependent volume translation for the SRK EOS: 1. Pure fluids

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ARTICLE INFO

Article history:
Received 1 October 2008
Received in revised form 30 January 2009
Accepted 7 February 2009
Available online 20 February 2009

Keywords:
Volume translation
Equation of state
Property estimation

ABSTRACT

A mathematical framework for applying a density-and-temperature-dependent volume translation in a thermodynamically consistent manner was developed. Volumetric equations of state (EOS)s that incorporate this translation procedure can be used to generate derived properties, such as fugacity and enthalpy departure, that are based on isothermal departure or residuals from ideal gas state conditions. This kind of translation serves to improve the original EOS and not simply act as a correlation for molar volumes. A density-and-temperature-modified translation of this type was applied to the Soave–Redlich–Kwong EOS and was shown to possess accuracy for saturation pressure predictions equivalent to the untranslated EOS, as well as greatly improved density predictions compared to what is available when using only constant valued translation. The EOS translated in this manner retains many of the important features of the untranslated EOS, such as explicit calculation of volume roots, while having the representation capabilities of substantially more complicated models, such as the extended virial equation of Benedict, Webb, Rubin, and Starling.

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1. Introduction

Analytic van der Waals-type equations of state (EOS)s are pressure explicit functions used to describe the relationship between the pressure, volume, temperature, and composition of fluid systems. These equations have clearly identifiable repulsive and cohesive contributions and provide a convenient way of simultaneously representing all fluid phases over a wide range of pressures and temperatures. Cubic EOSs, relations that can be arranged so all terms are at most third order in volume, have become indispensable for process calculations when dealing with systems containing gaseous or compressible components [1]. Unfortunately, these EOSs also tend to be less accurate for modeling condensed liquid phases than activity coefficient models or other auxiliary relations that can be more finely tuned to a narrower range of operating conditions.

One of the most significant improvements to EOS models was provided by Soave [2], building off the work of Wilson [3]. They demonstrated that the vapor pressure of a pure component could be reproduced exactly by incorporating an appropriately regressed, temperature-dependent function, the alpha function, into the cohesive term of the EOS. Prior to this modification, EOS methods were only of questionable use in industrial applications. The Soave-modified Redlich–Kwong equation (SRK), along with other similarly constructed equations such as the Peng–Robinson (PR) EOS [4], are still today the most widely used EOS models in the chemical and petrochemical industries [5].

Nonetheless, these EOS methods do not provide accurate density estimates at all conditions, particularly in the liquid phase [6]. This difficulty can be partially attributed to the manner in which the two EOS parameters, a and b, are calculated. For a pure component, these parameters are determined by enforcing stability criteria at the vapor–liquid critical point using the measured critical temperature and pressure (T_C and P_C). Away from the critical point, the b parameter is typically left constant while the a parameter is given temperature dependence with an alpha function. At the critical point, the alpha function is unity to ensure that the value of the a parameter at the critical point, a_C, continues to satisfy the stability criteria. The measured critical volume (V_C) is not used because only two critical properties are needed to determine the values of the two EOS parameters. The critical temperature and critical pressure can be determined more precisely than the critical volume, and the former also tend to give the EOS superior overall performance [7]. Unfortunately, excluding the experimental critical volume causes the EOS-predicted critical volume to disagree significantly with the measured value.

Abbreviations: BWRS, Benedict–Webb–Rubin–Starling; EOS, volumetric equation of state; MT, density-modified translation; OT, optimized constant translation; PR, Peng–Robinson; PR-DC, Peng–Robinson with Mathias' density correction; PVT, pressure, volume, and temperature; SRK, Soave–Redlich–Kwong; UT, untranslated.

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doi:10.1016/j.fluid.2009.02.005

The use of only two critical properties is necessitated by having only two adjustable parameters in the EOS. For any two-constant equation, the third critical property is fixed in a constant ratio with the other two properties (e.g., the critical compressibility factor for the SRK EOS has a constant value of one-third). Over 40 years ago, Martin proposed introducing a third parameter as a means of correcting the discrepancy in critical volume [8]. This parameter was formulated as a mathematical translation of the volume coordinate at a fixed temperature and pressure. Martin determined that exactly matching the volume at the critical point was not the best approach because that translation uniformly underestimated the volume at all other conditions. An intermediate translation value that slightly overestimates the critical volume was selected instead.

Applying a constant volume translation leaves the EOS calculated vapor pressure unaffected, which implies that the required alpha correction is also unchanged under translation [9]. Although the translation alters the absolute value of the calculated fugacity in both phases, each phase is affected equally and the equilibrium condition of fugacity equality remains unchanged.

Improvements to the volumetric accuracy of an EOS are not restricted to translation parameter approaches. The most widely recognized approach of incorporating a third parameter was introduced by Pitzer et al. [10] and employed by Lee and Kesler [11]. Both the repulsive and cohesive components of the EOS are grouped together as a single term, with additional terms included as coefficients in a power series expansion about a third fluid parameter. Many authors have successfully applied this strategy [12,13], or similar strategies [14], to model fluid systems. However, it is important to note that Pitzer's approach was formulated to model only particular classes of fluids with respect to a reference fluid. Broader applicability is possible, but usually involves substantially increased complexity. Other methods of introducing a third parameter [15], or a third and fourth parameter [16], typically change only the form of the cohesive term in a van der Waals-type EOS model. Parameters introduced in this manner provide a substantial increase in the flexibility; however, they also require significant modification of the original equation and are not easily transferred between different models [17]. A volume translation approach both avoids the need for a reference fluid and can be easily incorporated into an EOS without significantly affecting the base equation.

Unfortunately, a fixed value for the volume translation has a limited effect on the accuracy of pure component saturated liquid volumes [18,19]. Several authors have applied temperature-dependent translations [20,21], although translations that depend only on temperature can lead to serious inconsistencies in the pressure, volume, and temperature (*PVT*) representation [22]. Incorporating density dependence into the volume translation is necessary to achieve increased accuracy at all operating conditions and to avoid potential thermodynamic inconsistencies [23,24].

2. Theory

2.1. Formalism for density-dependent volume translation

The mathematical formalism of volume translation for constant or temperature-dependent translations [25] can be easily extended to density-dependent translations. A pressure explicit EOS can be expressed as in Eq. (1), where the pressure, P, is an explicit function, fxn_1, of the temperature, T, the total untranslated volume, $\underline{V}_{UT}$, and the molar quantity, N. In this study only pure components are considered.

$$P = fxn_1(T, \underline{V}_{UT}, N) \tag{1}$$

The volume translation function then expresses the actual volume, $\underline{V}$, according to Eq. (2).

$$\underline{V} = \underline{V}_{UT} - fxn_2(T, \underline{V}_{UT}, N) \tag{2}$$

For constant volume translations, the function fxn_2 will only depend on the total number of moles, while in temperature-dependent translations fxn_2 will depend on both the number of moles and the temperature. For translations that do not depend on density (i.e., the function fxn_2 is independent of $\underline{V}_{UT}$), Eqs. (1) and (2) are typically combined in order to eliminate the need for the untranslated volume to appear explicitly, as in Eq. (3).

$$P = fxn_1(T, \underline{V} + fxn_2(T, N), N) \tag{3}$$

Algebraic elimination of the untranslated volume is not an option when the translation is density-dependent because Eq. (2) would need to be solved for $\underline{V}_{UT}$. Density-dependent translation requires working with the untranslated volume as an intermediate variable when calculating thermodynamic properties derived from the EOS, such as fugacity or enthalpy departure.

Eq. (4) provides the exact definition, without any simplifying assumptions, of the fugacity for a pure component i, f_i, that is convenient for use with pressure explicit EOSs such as Eq. (1) [26]. In Eq. (4), R is the universal gas constant.

$$f_i = P \cdot \exp\left(\frac{1}{RT}\int_{\underline{V}}^{\infty}\left(\left(\frac{\partial P}{\partial N}\right)_{T,\underline{V}} - \frac{RT}{\underline{V}}\right) d\underline{V} - \ln\left(\frac{P\underline{V}}{RTN}\right)\right) \tag{4}$$

When it is possible to eliminate the untranslated volume as demonstrated in Eq. (3) then the use of Eq. (4) is straightforward. Unfortunately, when such elimination is not possible, it is necessary to change the variable of integration in Eq. (4) in order to work in the untranslated volume.

$$\begin{aligned} f_i &= P\exp\left(\frac{1}{RT}\int_{\underline{V}_{UT}}^{\infty} fxn_3(\underline{V}_{UT}, T, N)\, d\underline{V}_{UT} - \ln\left(\frac{P\underline{V}}{RTN}\right)\right) \\ fxn_3(\underline{V}_{UT}, T, N) &= \left(\frac{\partial P}{\partial N}\right)_{T,\underline{V}_{UT}}\left(\frac{\partial \underline{V}}{\partial \underline{V}_{UT}}\right)_{T,N} - \left(\frac{\partial P}{\partial \underline{V}_{UT}}\right)_{T,N}\left(\frac{\partial \underline{V}}{\partial N}\right)_{T,\underline{V}_{UT}} - \frac{RT}{\underline{V}}\left(\frac{\partial \underline{V}}{\partial \underline{V}_{UT}}\right)_{T,N} \end{aligned} \tag{5}$$

The method of calculating the enthalpy departure may be altered in the same manner, as demonstrated in Eqs. (6) and (7), where the real fluid enthalpy is given as $\underline{H}$ and the ideal gas state enthalpy is given as $\underline{H}^{\circ}$.

$$\underline{H} - \underline{H}^{\circ} = RT\left(\frac{P\underline{V}}{RTN} - 1\right) + \int_{\infty}^{V}\left(T\left(\frac{\partial P}{\partial T}\right)_{\underline{V},N} - P\right) d\underline{V} \tag{6}$$

$$\begin{aligned} \underline{H} - \underline{H}^{\circ} &= RT\left(\frac{P\underline{V}}{RTN} - 1\right) + \int_{\infty}^{\underline{V}_{UT}} fxn_4(\underline{V}_{UT}, T, N)\, d\underline{V}_{UT} \\ fxn_4(\underline{V}_{UT}, T, N) &= T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}_{UT},N}\left(\frac{\partial \underline{V}}{\partial \underline{V}_{UT}}\right)_{T,N} - T\left(\frac{\partial P}{\partial \underline{V}_{UT}}\right)_{T,N}\left(\frac{\partial \underline{V}}{\partial T}\right)_{\underline{V}_{UT},N} - P\left(\frac{\partial \underline{V}}{\partial \underline{V}_{UT}}\right)_{T,N} \end{aligned} \tag{7}$$

Working with the volume translation in this manner retains many of the characteristics of the original EOS. In particular, when applying a density-dependent volume translation to a cubic EOS, both the untranslated and translated volume can be calculated explicitly in the normal manner [27]. The additional operations required in determining the fugacity or enthalpy departure increases the computational intensity somewhat, but no implicit solutions are required. However, applying a density-dependent volume translation does change the calculated phase equilibrium because the contributions of the translation to the fugacity in each phase are no longer equal at a given temperature. Thus, the alpha function for the translated EOS needs to be adjusted to correct for the changes to equilibrium caused in translation. Changes to the value of the alpha function have a very small impact on the calculated densities [24], so iterating between corrections to the alpha function and volume translation is not necessary.

2.2. Motivation for a new formulation

Using the EOS to represent both the volumetric properties and the derived properties such as the fugacity is very important in retaining the overall consistency of the equation. A volumetric EOS, when coupled with supplementary data for ideal gas state heat capacities, contains essentially, to within an arbitrary constant, all the information that is present in Gibbs' Fundamental Equation of thermodynamics [26]. From this perspective, the EOS can be viewed as a model of the fluid region of the Fundamental Equation. For this reason, care needs to be taken when augmenting EOSs because empirical changes to increase accuracy in observable properties (e.g., vapor pressure or molar volumes) may also impair the ability of the EOS to approximate the Fundamental Equation.

The form of the repulsive term in most cubic EOSs has been discounted as inherently theoretically deficient [28], which has motivated many volume translation approaches intended to only improve the molar volumes [29]. Corrections that target a single property can provide impressive increases in the accuracy of that property, but may also result in decreased accuracy for other properties. Mathias' volume translation for the PR EOS [30], is a density-dependent volume translation of the form described in Eq. (2) that reduces the average error in predicted volumes to less than 3% for a wide range of fluids (e.g., see Fig. 1 for a representation of CO_2 at 5 °C). This translation can only be applied *ad hoc* to the molar volumes because the derived properties, such as fugacity, demonstrate severe discontinuities depending on the method of calculation. These problems in the derived properties arise because of the behavior of the translation function in the unstable region, where it is not possible to fit the translation to volumetric data.

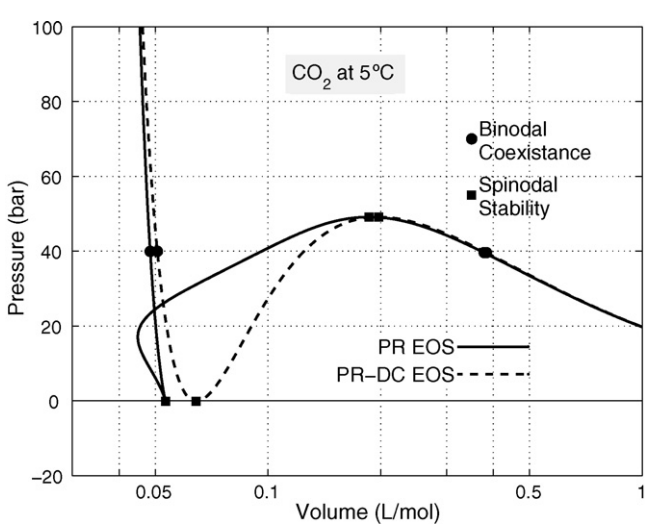

Fig. 1. The 5 °C isotherm for carbon dioxide as modeled by the Peng–Robinson (PR) EOS [4] and Mathias' density correction to the Peng–Robinson (PR-DC) EOS [30]. The circles represent the limit of normal stability (i.e., the vapor pressure of carbon dioxide at 5 °C is about 40 bar) and the square symbols represent the limit of mechanical stability.

The translation provides excellent accuracy for molar volumes in the stable regions for carbon dioxide, but between the limits of spinodal stability, where no stable volume roots exist, the translation value grows unreasonably large and creates numerical problems. In order to calculate the saturation pressure from an EOS, the EOS must be smoothly integrable throughout the unstable region [31]. Translations that create loops or discontinuities along an isotherm, such as the original Mathias translation, preclude the use of the translated equation in calculating the saturation pressure. In this kind of situation, the volume translation can only be used as a correlation for liquid densities. Ideally, an EOS that is able to provide an improved volumetric representation should also provide improvements to all other properties derived from the EOS, such as the saturation pressure, fugacity, or enthalpy. The isotherm looping behavior depicted in Fig. 1 is caused by the density dependency of the volume translation. Differentiating Eq. (2) yields the rate of change of the volume translation with respect to the untranslated volume, given as Eq. (8), which has several important implications [24].

$$\left(\frac{\partial \underline{V}}{\partial \underline{V}_{UT}}\right)_{T,N} = 1 - \left(\frac{\partial fxn_2}{\partial \underline{V}_{UT}}\right)_{T,N} \tag{8}$$

The quantity represented in Eq. (8) is used to relate the translated and untranslated volumes, and arises naturally in Eqs. (5) and (7) when transforming the variable of integration from the translated volume to the untranslated volume. Mathematically, this transformation of variables is only valid when the quantity expressed in Eq. (8) is not equal to zero; evaluation of Eq. (5) is still possible at this point, although the values calculated are not physically meaningful.

When the derivative of the volume translation function, fxn_2, with respect to the untranslated volume becomes equal to one, the isotherm demonstrates points of infinite pressure response to volume change (i.e., the isotherm is vertical). When the derivative of the volume translation function, fxn_2, becomes greater than one, isotherms exhibit multiple pressure roots for a single volume. The looping behavior, shown in Fig. 1, is characteristic of translations where the derivative of fxn_2 becomes much larger than one. Mathematically, the process of volume translation described in Eqs. (1) and (2) creates a parametric representation of both P and $\underline{V}$ as functions of $\underline{V}_{UT}$, T, and N. As long as Eq. (8) does not evaluate to zero (i.e., $(\partial fxn_2/\partial \underline{V}_{UT})_{T,N} < 1$) then P remains a function of $\underline{V}$ as in Eq. (3), even if it not convenient to analytically represent it in such a manner. If Eq. (8) does evaluate to zero at any point (i.e., $(\partial fxn_2/\partial \underline{V}_{UT})_{T,N} \geq 1$) then an analytic representation is no longer possible and the pressure, P, is no longer a function of the volume, $\underline{V}$. For the Mathias function, the derivative of the volume translation value not only exceeds the threshold established in Eq. (8), but is also undefined at several points.

2.3. Mathematical development of the translation

The Mathias translation was formulated using a distance parameter that is related to a fluid's proximity to its critical point. Overall, this approach provides a good foundation for a density-dependent volume translation. However; several issues, as indicated previously, remain to be addressed. Here, density-dependent volume translation will be applied to the SRK EOS [32,2], which is reproduced in Eq. (9). The variable V_{UT} represents the untranslated molar

volume; it is equivalent to the untranslated total volume divided by the total number of moles in the system.

$$P = fxn_1(T, V_{UT}) = \frac{RT}{V_{UT} - b} - \frac{a_C \cdot \alpha}{V_{UT}(V_{UT} + b)} \tag{9}$$

The constants a_C and b are determined in the usual manner by satisfying the stability criteria presented in Eq. (10) at the critical point, using the critical temperature and pressure.

$$\left(\frac{\partial P}{\partial V_{UT}}\right)_T = \left(\frac{\partial^2 P}{\partial V_{UT}^2}\right)_T = 0 \tag{10}$$

Density-dependent volume translation necessarily leaves the stability conditions given in Eq. (10) satisfied post-translations, as long as they are satisfied pre-translation and the translation meets the validity condition described in Eq. (8) at the critical point [24]. As that validity condition should be met everywhere in the translated function and not just the critical point, the critical coordinates of T_C and P_C, denoting the temperature and pressure at the vapor–liquid critical point of the pure component, will be retained in the translated equation. The values for the constants a_C and b that satisfy Eq. (10) are given in Eq. (11).

$$a_C = \frac{R^2 T_C^2}{9(\sqrt[3]{2} - 1)P_C}, \qquad b = \frac{(\sqrt[3]{2} - 1)RT_C}{3P_C} \tag{11}$$

A simple one-term alpha function equivalent to Soave's model [2], given in Eq. (12), is used in this study. The parameter m_0 is a constant used in regression.

$$\alpha = \left(1 + m_0\left(1 - \sqrt{\frac{T}{T_C}}\right)\right)^2 \tag{12}$$

The value of the alpha function parameter, m_0, is affected by the application of density-dependent volume translation. The alpha function presented in Eq. (12) is sufficient to provide vapor pressure predictions accurate to within a few percent both before and after translation. Greater accuracy can be achieved using an alpha function with additional parameters, such as proposed by Mathias [33].

The volume translation function, given in Eq. (13) is based on a distance parameter approach, amended to account for the consistency issues previously mentioned. The variable V is the molar volume. The variable V_C denotes the molar volume at the vapor–liquid critical point of the pure component, and the value c_0 is a constant, substance-dependent parameter. The distance function, δ, has been used by other authors [30,34]. It is similar to the bulk modulus and serves as a gauge of the fluid's compressibility or proximity to its critical point.

$$V = V_{UT} - fxn_2(T, V_{UT}) = V_{UT} - \left(\frac{RT_C}{3P_C} - V_C\right) - c_0\left(\frac{1}{1 + 2\delta} - 1\right) \tag{13}$$

The first term of the volume translation function in Eq. (13) is a constant that accounts for the disagreement between the SRK predicted critical volume (i.e., $RT_C/3P_C$) and the actual critical volume. The second term contains all of the temperature and density dependence of the translation.

The distance function δ presented in Eq. (14) differs from the one that has been used by other authors.

$$\delta = -\frac{V_{UT}^2}{RT}\left(\frac{\partial P}{\partial V_{UT}}\right)_T + \frac{V_{UT} - (RT_C/4P_C)}{(RT_C/3P_C) - (V_{UT}^3/RT)(\partial P/\partial V_{UT})_T + \tau} + \tau V_{UT} \tag{14}$$

Mathias noted that the distance parameter approach was only tested for saturated liquid densities, but that its performance over the entire density range was expected to be reasonable [35]. Evaluation over a wide range of fluid densities has found that the translation provides good accuracy [36], although there are some concerns in the vicinity of the pure fluid's critical point. Mathias' expression appears as the first term in Eq. (14); the second term has been introduced to account for the difference between the EOS predicted compressibility and real fluid compressibility, while the empirical temperature function τ is used to ensure that the expression given in Eq. (8) remain strictly positive. The pressure derivative is calculated according to the SRK EOS in Eq. (9).

At the critical point, the empirical temperature function τ is equal to zero, the derivative of the pressure with respect to the untranslated volume is zero, and the untranslated SRK volume is equal to $RT_C/3P_C$. The distance function in Eq. (14) then evaluates to 1/4 and the second term of the volume translation function in Eq. (13) evaluates to $c_0/3$. Therefore, unlike the specified critical pressure and specified critical temperature, P_C and T_C, which are reproduced exactly at the critical point, the specified critical volume, V_C, is not reproduced exactly at the critical point. The critical volume predicted by the translated EOS exceeds the specified critical volume by $c_0/3$. This is equivalent to an overestimation of 5–8% in molar volume at the critical point. By slightly overestimating the molar volume at the critical point, a higher overall accuracy can be achieved. This tradeoff in accuracy is acceptable for the purposes of this study since the actual value of V_C is typically only known to within an accuracy of 2–4% [37–40].

The empirical temperature function τ was included in Eq. (14) because the derivative of the pressure with respect to the untranslated volume becomes positive for unstable volume roots. Positive values of this derivative can potentially cause near-zero values in the denominator of the translation function resulting in rapidly changing translation values or discontinuities. Near-zero values in the denominator of the translation function are the main cause of the inconsistencies discussed earlier in Section 2.2. The temperature correction is given in Eq. (15).

$$\tau = \frac{\begin{array}{l}0.001316 \cdot \exp(10.24(1 - (T/T_C))) \\ +0.8782 \cdot \exp(2.543(1 - (T/T_C))) - 0.879516\end{array}}{1 + \exp(-1000(1 - (T/T_C)))} \tag{15}$$

The value of τ is graphically illustrated in Fig. 2. This value is substance independent. The value of this function was specified in order to make the maximum value of the derivative of the distance parameter δ in Eq. (14) with respect to the untranslated volume

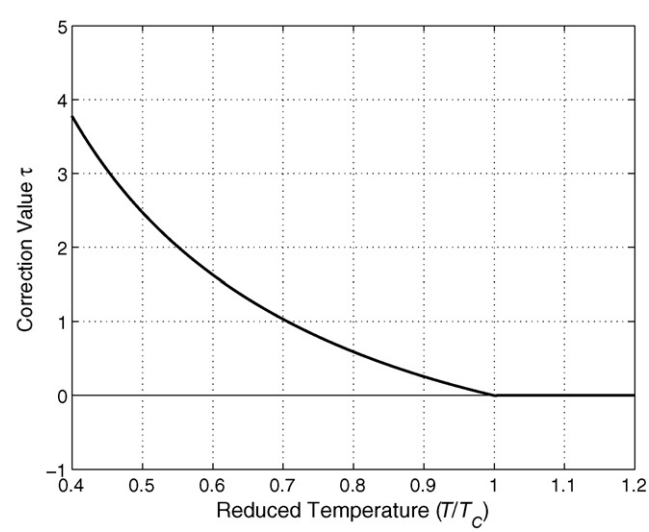

Fig. 2. The empirical temperature correction τ as described by Eq. (15). The value of this function is substance independent. The value of this function was specified in order to make the maximum value of the derivative of the distance parameter δ in Eq. (14) with respect to the untranslated volume close to constant.

Table 1
Parameters for the density-modified translation to the SRK EOS. The reference indicated is the data source for the critical properties as well as *PVT* and saturation data used to determine the parameters in the alpha and volume translation functions.

Fluid	T_C (K)	P_C (bar)	V_C (L/kmol)	c_0 (L/kmol)	m_0	m_0 – UT	Reference
CH_4	190.56	45.99	99	16.5	0.515	0.497	[40]
C_2H_6	305.33	48.72	146	26.5	0.670	0.643	[41]
C_3H_8	369.83	42.47	202	36.5	0.762	0.716	[42]
n-C_4H_{10}	425.13	37.96	255	50.0	0.834	0.804	[37]
n-C_5H_{12}	469.70	33.70	311	65.5	0.920	0.864	[37]
n-C_6H_{14}	507.82	30.34	370	80.5	0.991	0.935	[37]
n-C_7H_{16}	540.13	27.36	432	95.5	1.073	1.008	[37]
n-C_8H_{18}	569.32	24.97	486	120.	1.146	1.071	[37]
N_2	126.19	33.96	89	14.0	0.558	0.541	[43]
O_2	154.57	50.43	73	11.5	0.538	0.513	[44]
H_2S	373.10	90.00	98	16.0	0.662	0.636	[48]
CO_2	304.13	73.77	94	18.0	0.825	0.825	[39]
CF_4	227.51	37.5	141	27.5	0.801	0.755	[50]
NH_3	405.40	113.3	76	17.0	0.905	0.871	[49]
H_2O	647.10	220.6	56	19.0	1.046	1.001	[38]

For comparison, values for the alpha constant m_0 are given for both before and after the translation.

close to constant. For temperatures at and above the critical temperature, the derivative of the pressure with respect to the untranslated volume is non-positive and the temperature function is not needed. At these conditions the temperature function τ is forced to effectively zero using the expression in the denominator of Eq. (15).

The empirical temperature function described in Eq. (15) was selected so that the maximum value of the derivative of the translation function with respect to the untranslated volume is roughly constant. By making this selection, the original one-parameter SRK alpha function given in Eq. (12) can still be used to provide a satisfactory level of accuracy in vapor pressure predictions. Many other selections of the empirical temperature are possible in order to meet the derivative criteria of Eq. (8), but most would require a significantly more complicated alpha function in order to provide vapor pressure accuracy equivalent to that of the untranslated SRK EOS.

3. Results and discussion

The density-modified translation to the SRK EOS is represented by Eqs. (9)–(15).

For each pure fluid, five parameters are required: two critical properties; T_C and P_C, one constant for the volume translation function, c_0, and one constant for the alpha function, m_0. In addition, a specified or measured value of V_C is needed to fix the volume translation, although this value will not be reproduced exactly by the EOS. Parameters for the translated EOS in this study are summarized in Table 1, along with references to the critical coordinate data, *PVT* data, and saturation data used during this study. The constant used in the alpha function for the untranslated SRK has also been included for comparison. These untranslated values were taken from Soave's original correlation [2].

Parameter estimation for the density-modified translation to the SRK EOS for fluids not included in Table 1 is not expected to be difficult. The critical temperature and pressure are routinely used in EOS calculations; these values are tabulated, or provided through correlation, from several sources [45]. The critical volume is not as readily available, although correlations are available and predictions from the translated EOS are not highly dependent on precise estimates of the critical volume. The two remaining parameters require further comment. If vapor pressure data are available, the alpha parameter can be regressed directly. Examination of Table 1 suggests that the alpha parameter m_0 for the translated equation is only slightly greater than for the untranslated SRK EOS. If no other data are available, increasing the value obtained by Soave's correlation by about 6% should provide a reasonable estimate. The accuracy in vapor pressure predictions for propane from both the translated and untranslated EOSs is illustrated in Fig. 3; all other fluids are similar.

Using a single parameter alpha function for the translated EOS provides roughly the same level of accuracy in vapor pressure as is provided by a single parameter in the untranslated EOS, although at low reduced temperatures ($T/T_C < 0.4$) the translated EOS has a tendency to overestimate the vapor pressure.

The volume translation parameter c_0 can be estimated using liquid phase densities, such as those along the saturated liquid curve. In addition, the volume translation parameter was found to be very highly correlated to the predicted critical volume of the untranslated EOS (i.e., $RT_C/3P_C$). This correlation is illustrated in Fig. 4.

The correlation provided in Fig. 4, ($c_0 = 0.185(RT_C/3P_C) - 4$) should provide a useful initial estimate of the volume translation parameter if no other data are available.

Accurate density predictions across the entire fluid range are provided by the translated EOS. Other properties, such as the Helmholtz or Gibbs energies were not examined. In Table 2, the density predictions of the density-modified translation to the SRK EOS (MT) are compared against the untranslated SRK, the SRK

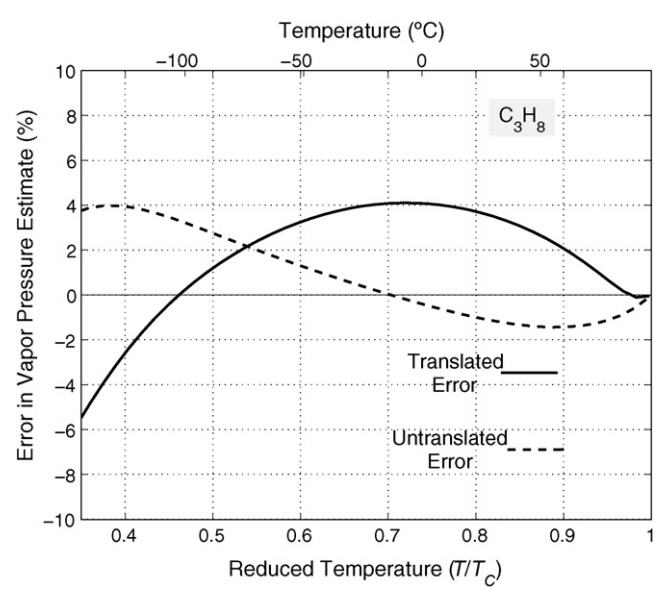

Fig. 3. The errors in the predicted vapor pressure of propane estimated by the untranslated SRK EOS and the SRK EOS with a density-modified translation as presented in this paper. All other fluids are similar.

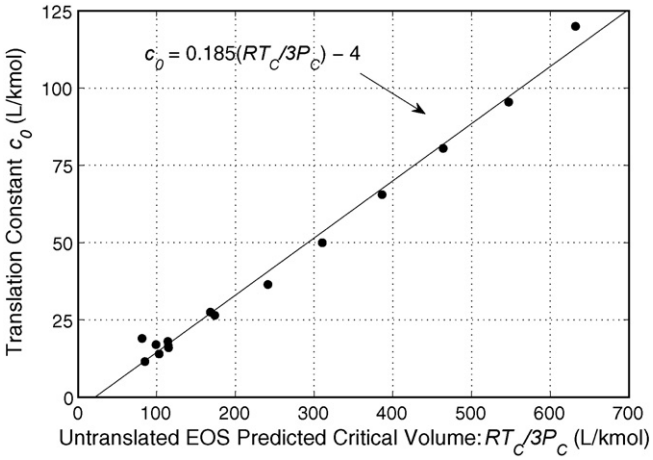

Fig. 4. The volume translation parameter, c_0, presented in relation to a fluid's critical volume as predicted by the untranslated SRK EOS. The linear regression depicted in the figure is provided in order to estimate the translation parameter in absence of other data.

EOS with an optimal constant translation value (OT), and the Benedict–Webb–Rubin–Starling (BWRS) model [46]. The optimal constant translation value for the SRK EOS was selected to minimize the absolute average error reported for this comparison. The BWRS model is an extended virial equation frequently used to provide a high accuracy density representation for pure fluids; it requires 11 parameters and a rich data set to specify them. The temperature at each pressure condition indicated ranges from the freezing temperature up to well above the critical temperature where the fluid begins to behave ideally (i.e., fluid behavior is considered ideal when the compressibility approaches unity; $PV/RT > 0.95$).

Translation functions that depend only on temperature, such as proposed by Duan and co-workers [21], were not considered here. These translation functions provide excellent accuracy along the saturation curve but can provide poor and sometimes aphysical predictions at other conditions [22]. Average deviations for water from the BWRS equation are reported in Table 2 using Starling and Han's correlation [47]. This correlation is not well suited for water, but it provides parameter estimates that are valid for the entire fluid region. Other implementations of BWR-type EOSs that may provide superior accuracy are available [51].

At lower pressures, the density-modified translation may demonstrate roughly equal or slightly greater average error when compared an optimal constant translation, as is shown for methane and propane in Table 2. Density estimates along isobars below the critical isobar incorporate both the liquid and vapor phases. The translation function presented in this work does not provide an increase in molar volume accuracy for low density vapors; it was designed to give consistent accuracy at all pressures. Most EOSs, including the translated EOS proposed here, already provide good

Table 2
Accuracy in the density predicted by the Soave–Redlich–Kwong (SRK), the SRK using optimal constant translation (OT), the SRK using the density-modified translation developed here (MT), and the Benedict–Webb–Rubin–Starling (BWRS) models.

Fluid	Pressure (bar)	Average absolute deviation (%)			
		SRK	OT	MT	BWRS
Methane (P_C = 46.0); OT value = −0.3 L/kmol	20	0.63	0.51	0.66	0.35
	30	0.93	0.85	0.73	0.43
	40	1.45	1.38	0.80	0.54
	50	1.90	1.89	0.87	0.75
	60	2.33	2.33	0.89	0.74
	70	2.68	2.69	0.92	0.67
	80	2.96	2.97	0.95	0.61
Propane (P_C = 42.5); OT value = 4.3 L/kmol	18	3.34	0.89	1.28	0.85
	27	3.62	1.14	1.24	0.80
	36	4.05	1.59	1.23	0.82
	45	4.56	2.09	1.23	0.91
	54	5.00	2.51	1.21	0.96
	63	5.38	2.85	1.23	1.00
	72	5.69	3.12	1.27	1.04
n-Octane (P_C = 25.0); OT value = 25.6 L/kmol	16	8.58	1.48	1.03	1.22
	20	9.01	1.93	1.06	1.56
	24	9.52	2.40	1.11	1.85
	28	9.99	2.84	1.12	1.84
	32	10.47	3.25	1.13	1.85
	36	10.94	3.63	1.14	1.92
	40	11.37	3.97	1.14	1.98
Carbon dioxide (P_C = 73.8); OT value = 3.6 L/kmol	30	2.03	0.83	0.41	0.99
	45	2.83	1.12	0.51	1.28
	60	3.67	1.64	0.60	1.63
	75	4.49	2.26	0.64	2.72
	90	5.29	2.87	0.60	2.81
	105	5.96	3.37	0.58	2.59
	120	6.51	3.78	0.60	2.46
Water (P_C = 221); OT value = 6.4 L/kmol	75	18.19	2.05	1.88	3.81
	125	18.01	2.85	2.22	3.90
	175	18.56	3.55	2.54	4.12
	225	19.41	4.14	2.83	6.63
	275	20.36	4.65	2.95	7.10
	325	21.35	5.35	2.93	6.55
	375	22.34	6.06	2.91	6.28

At each pressure condition the deviation is calculated at every degree Celsius ranging from the freezing point of the fluid at that pressure to above the critical temperature where the fluid begins to behave ideally (i.e., ideal behavior is considered equivalent to $PV/RT > 0.95$).

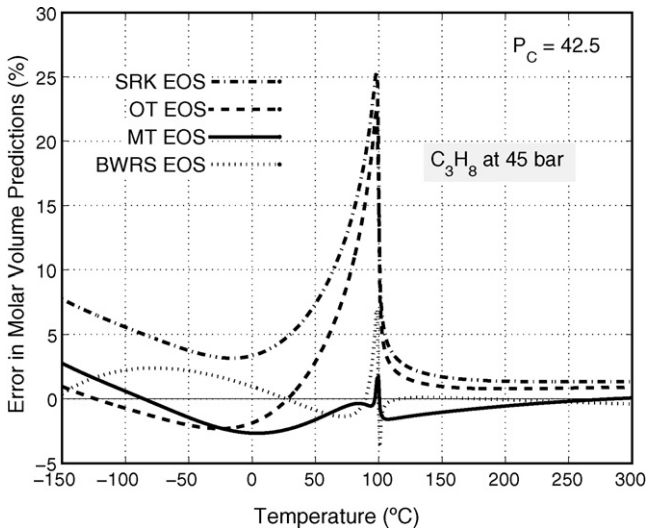

Fig. 5. The error in molar volume predictions for the 45 bar isobar of propane. Molar volume predictions are provided by the SRK, OT, MT and BWRS models. The temperature ranges from near the freezing point at −185 °C to temperatures where the fluid begins to behave as an ideal gas (i.e., $PV/RT > 0.95$) 345 °C.

accuracy for low density vapors because their behavior at very high molar volumes reduces to the ideal gas EOS.

The density-modified translation presented in this study provides accuracy that is comparable to that of the 11-parameter BWRS EOS, but with the numerical simplicity similar to that of a cubic EOS for the hydrocarbons analyzed. The volume translation approach is applicable to any fluid that can be represented by the untranslated EOS, and all volume roots of the translated EOS can be determined explicitly.

The pattern of errors in molar volume predictions along a single isobar, propane at 45 bar, is presented in Fig. 5. The temperature range shown reflects the range of temperature used for the analysis in Table 2. At 45 bar, the freezing point is approximately −185 °C, while the minimum temperature for ideal behavior (i.e., $PV/RT > 0.95$) is 345 °C.

The 45 bar isobar for propane was selected for its proximity to the critical pressure of 42.5 bar. With regard to density predictions, the two translated EOSs and BWRS perform comparably well over most of the temperature range; the difference between models is most apparent near the critical point. For propane, a constant volume translation provides very good representation of densities except in the near-critical region, but is unable to provide accurate density estimates in that region regardless of the volume translation value. The density-modified translation presented here is able to provide substantially improved accuracy in the critical region without loss of accuracy at other conditions.

4. Conclusions

The density-dependent volume translation described in this work provides a robust means for improving the prediction accuracy of EOS models, particularly in the dense, near critical fluid and compressed liquid regimes. For example, appropriate formulation of the translation function ensures that all derived properties, such as the fugacity and enthalpy, are both calculable and physically meaningful using a translated SRK EOS. The translation function does not need to be restricted to only correlation of molar volumes. A density-modified translation of this type, applied to any cubic EOS, has been shown to possess equivalent accuracy to the untranslated EOS for saturation pressure, and greatly improved density predictions in the vicinity of the pure component critical point. The modified translation retains many of the important features of the untranslated EOS, such as explicit calculation of volume roots, while having the modeling capabilities of substantially more complicated EOS formulations.

List of symbols

a	EOS parameter, cohesive term
a_C	EOS parameter, cohesive term, evaluated at critical point
b	EOS parameter, repulsive term
c_0	volume translation parameter
fxn_1, fxn_2	functions representing an EOS and a volume translation
fxn_3, fxn_4	functions representing the integrand in untranslated volume
$\hat{f}_i$	fugacity of component i
$\underline{H}$	total enthalpy of real fluid
$\underline{H}^\circ$	total enthalpy of fluid in ideal gas state
m_0	alpha function parameter
N	molar quantity
P	pressure
P_C	pressure at critical point
T	temperature
T_C	temperature at critical point
V	molar volume
$\underline{V}$	total volume
V_C	molar volume
V_{UT}	untranslated molar volume
$\underline{V}_{UT}$	untranslated total volume

Greek

α	alpha function vapor pressure correction
δ	distance function for volume translation
τ	translation function temperature correction

Acknowledgements

The authors would like to thank Bob Robinson, Charles Greco, Judy Wagner, Roger Humphreville. Especial gratitude to due to Richard Bailey, Malcolm Woodman, Fatosh Gozalpour, Alan Stephens, Mike Roffey, and Sue Little for their comments and suggestions. Financial support from BP America, Incorporated through Project Academy 926-4101 is gratefully acknowledged.

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