

## Volume translation in equations of state as a means of accurate property estimation

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### Abstract

Molar volumes predicted by cubic volumetric equations of state (EOS)s over a range of reduced temperatures and pressures from  $T_r = 0.5$ – $2.0$  and  $P_r = 0.5$ – $10.0$  were compared to reference molar volume values for water, carbon dioxide, hydrogen sulfide, ammonia, nitrogen, oxygen, argon, and the first eight normal paraffin alkanes. A similarity of molar volume residuals was observed for predictions by the Soave–Redlich–Kwong EOS, indicating that volume translation can be used to improve the accuracy of these molar volume predictions. The necessity of both density and temperature dependence in the volume translation is established; guidelines for maintaining thermodynamic consistency and a correlation for identifying the maxima in molar volume residuals are provided.

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**Keywords:** Volume translation; Equation of state; Property estimation

### 1. Introduction

Designing and piloting a new process is a costly undertaking that typically requires the investment of millions of dollars over multiple years. Process simulation is an essential tool for both reducing costs and guiding design and development. The level of confidence that can be placed in these simulations is completely dependent on the accuracy with which unknown properties may be predicted. In particular, there will always be a dearth of satisfactory thermodynamic property data and a need for reliable ways to estimate fluid behavior in poorly characterized operating regimes. There are many different property methods available that describe fluid density, phase equilibrium, and other quantities such as enthalpies and entropies. Commonly these property methods are based on a selected set of constitutive property models including a volumetric (*PVT*) equation of state (EOS). *PVTEOS*-based property methods are attractive because

of the consistency they provide by representing both the liquid and vapor phases using a single equation. The *PVTEOS* model, along with an ideal gas state heat capacity model correlated as a function of temperature, allows for the calculation of all thermodynamic properties of interest over the entire fluid region. Using this approach avoids many inconsistencies that may occur when applying other, property specific, correlations. In particular, activity coefficients can be very accurate and are well suited for many liquid mixtures, but are inappropriate for systems with gaseous or highly compressible components [1]. EOS-based methods are required for systems involving near-critical and supercritical fluids.

Near-critical and supercritical fluid use is becoming much more common; many novel process pathways and operating environments can take advantage of the rapidly changing properties that occur in fluids and fluid mixtures near the vapor–liquid critical point. Examples of processes include using supercritical fluids as solvents in organic synthesis [2], as media for destruction of organic compounds [3], and the extraction and re-injection of naturally occurring fluids in petroleum and geothermal reservoirs [4]. Accurate modeling makes a substantial contribution to the rapid development and implementation of these and other processes, but balancing the dual needs of accuracy and convenience in process simulation can be difficult.

**Abbreviations:** EOS, equation of state; PR, Peng–Robinson; *PVT*, volumetric, involving pressure, volume, and temperature; SRK, Soave–Redlich–Kwong; TST, Twu–Sim–Tassone

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Present day simulation software has substantially reduced the need for mathematical simplicity of form; regression techniques that are incorporated within most simulators provide a means to fit a large number of parameters when modeling individual pure compounds. Additional parameters simply require more extensive data for regressions. Today, as compared to 20 years ago, there exists a very large body of data that can be used in regressing complicated relations with many parameters. This has already been done for a growing number of compounds. The major problem with the resulting equations is that they do not have a unified functional form, without which they cannot readily be extended to mixtures. Specifically, mixing rules are required for each new parameter introduced. If the equations do not have a consistent mathematical form, it is difficult, if not impossible, to define appropriate mixing rules. Thus, there is a need for a unifying EOS that can be applied to diverse classes of compounds, and for which appropriate mixing rules can be developed.

Cubic EOS models are the simplest class of EOSs that can be used to represent the vapor–liquid critical point, but these models are inaccurate for predicting liquid densities [5]. Nonetheless, cubic EOSs are still valuable and extensively used because they can be enhanced using fitted alpha functions to successfully reproduce phase equilibria while retaining the mathematical simplicity of the original equation [6]. Other authors have also proposed that molar volume accuracy from cubic EOSs can be improved by using volume translation [7,8].

While many different methods of volume translation are possible, to date the most successful methods for accurate prediction of saturated liquid volumes are those involving a constant [9,10] or temperature-dependent [11–15] translation that is fit to experimental data. However, reported problems with consistency, such as prediction of negative heat capacities or isotherm crossover, can occur when using a temperature-dependent volume translation function with a cubic EOS. These problems may limit the applicability of the EOS in process simulation [16]. In order to be useful in process simulation, volume translation must be applied in a consistent manner.

When using cubic EOSs, we show that volume translation using only a temperature correction is not sufficient to predict molar volumes in the liquid, vapor, and supercritical region to within 5% accuracy. Although no new volume translation functions are being proposed in this work, we will demonstrate that both temperature and density dependence are required for a thermodynamically consistent volume translation. Furthermore, we show that there is a consistent pattern of volume correction required for diverse classes of compounds, ranging from hydrocarbons and non-polar gases to polar gases and water.

## 2. Models and calculation methods

### 2.1. Cubic EOSs

The importance of EOSs in modeling pure fluids and mixtures is especially evident when dealing with compressible systems (components with  $P_r > 0.5$ ) where proximity to a vapor–liquid critical point or locus is an issue; no other methods are avail-

able. The most common EOSs used in process simulation are based on the Soave–Redlich–Kwong (SRK) equation [6], the Peng–Robinson (PR) equation [17], or any one of a number of other closely related equations that can be expressed as a cubic polynomial in volume. The primary advantage of the cubic model is that it can be extended to mixtures with relative ease. Commonly, only two mixing rules are required, and a large body of empirical constants supporting those mixing rules is available. The gains in accuracy resulting from using more complicated EOS forms that involve additional parameters have typically been insufficient to compensate for the decrease in availability of empirically fitted constants [18]. In recent years, modern advances in computing have lessened these concerns somewhat.

The PR and SRK EOSs give very similar predictions over a wide range of temperature and pressure conditions [19] and have been identified as specific cases of a more general family of equations [20,5]. One instance of this general formulation is given in the following equation [5]:

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2} \quad (1)$$

The PR EOS form can be regenerated from Eq. (1) by setting  $u=2$  and  $w=-1$  while the SRK EOS form is obtained with  $u=1$  and  $w=0$ . The term “form” is used to here emphasize that both the PR and SRK EOSs have entire families of equations based upon them that are created by applying various correction terms (e.g., alpha functions). Neither family of equations has a clear advantage in the accuracy of its property predictions; equation selection is usually driven by other factors. The most commonly used heuristic is how well the equation’s critical compressibility matches the critical compressibilities of the fluids being modeled. The critical compressibility factor, given in Eq. (2), is determined explicitly in a cubic EOS as a direct consequence of satisfying the volumetric stability criteria in Eq. (3) at the critical point using  $T_c$  and  $P_c$  values.

$$Z_c = \frac{P_c V_c}{RT_c} \quad (2)$$

$$\left( \frac{\partial P}{\partial V} \right)_T = 0, \quad \left( \frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (3)$$

The predicted values of  $Z_c$  are constant for the PR ( $Z_c = 0.3074$ ) and SRK ( $Z_c = 0.3333$ ), while actual compressibilities vary widely and are typically lower ( $Z_c = 0.23$ – $0.29$ ). Exactly matching the predicted critical compressibility with the experimental compressibility does not yield the most accurate property predictions. Twu et al. [21] developed a cubic EOS (TST) that optimized the critical compressibility ( $Z_c = 0.2963$ ) over many polar and non-polar fluids by minimizing the relative error in predicted saturated liquid volumes. Their EOS is equivalent to setting  $u=2.5$  and  $w=-1.5$  in Eq. (1).

We have defined the absolute deviation in molar volume as the difference between a reference value taken from a multiparameter correlation that has been fit to experimental data and a value predicted by an EOS at a particular state point. Absolute deviations for propane at a reduced pressure  $P_r = 0.7$ , using a correlation by Miyamoto and Watanabe [22] and predictions from

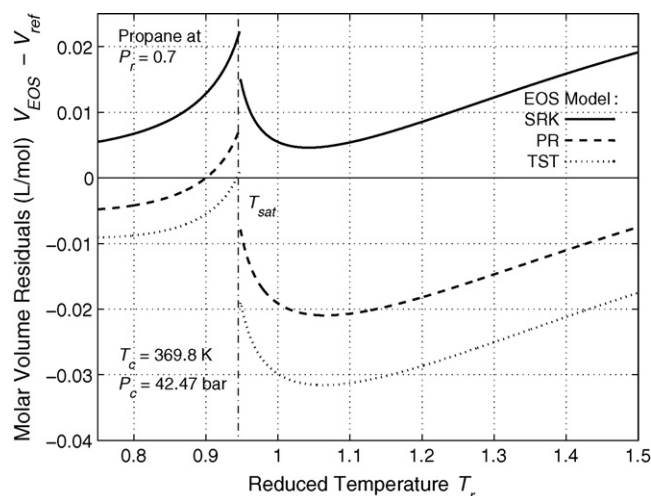


Fig. 1. The difference between reference molar volumes and molar volumes predicted by the SRK, PR, and TST EOSs for propane at  $P_r = 0.7$ .

the Peng–Robinson, Soave–Redlich–Kwong, and Twu EOSs, are presented in Fig. 1.

In this figure, an alpha function, as presented in Eq. (4), is applied to ensure accurate vapor pressure predictions. The constant  $a_c$  in Eq. (4) is equal to the constant  $a$  in Eq. (1) while the alpha function becomes unity at the critical temperature ( $T_r = 1.0$ ) in order to preserve the critical stability criteria established in Eq. (3).

$$P = \frac{RT}{V - b} - \frac{a_c \alpha(T_r)}{V^2 + u b V + w b^2} \quad (4)$$

A Mathias-type alpha function [23] is used at subcritical temperatures ( $T_r < 1.0$ ) and a Boston–Mathias-type extrapolation [24] is used at supercritical temperatures ( $T_r \geq 1.0$ ). The effect of the alpha function correction on the molar volume residuals was found to be small (<1%).

Varying the equation used to predict molar volumes results in shifting the residuals and has no effect on the pattern of deviations. The discontinuity that appears in Fig. 1 at  $T_r = T_{sat}$  is the separation between the liquid phase (lower temperature) and vapor phase (higher temperature) residuals. The deviations along a supercritical isobar,  $P_r = 1.1$  is shown in Fig. 2, are continuous from the compressed liquid ( $T_r < 1$ ) to the supercritical fluid ( $T_r > 1$ ) states for the three different EOSs examined.

Adjustment of the EOS-predicted critical compressibility to a more representative value does not represent a major improvement in the performance of the EOS; the pattern of molar volume residuals is simply shifted. Exactly matching the experimental critical compressibility results in an under prediction of the molar volumes at all non-critical temperatures and pressures; the ‘optimal’ compressibility for a cubic EOS is one that centers the molar volume residuals on zero. The PR EOS and the TST EOS provide more accurate molar volume estimation for propane than the SRK EOS at the conditions depicted in Figs. 1 and 2. However, this accuracy appears to be exclusively a consequence of those equations having a critical compressibility factor that more nearly centers their predicted molar volume deviations about zero. If a fluid with a different critical compressibility

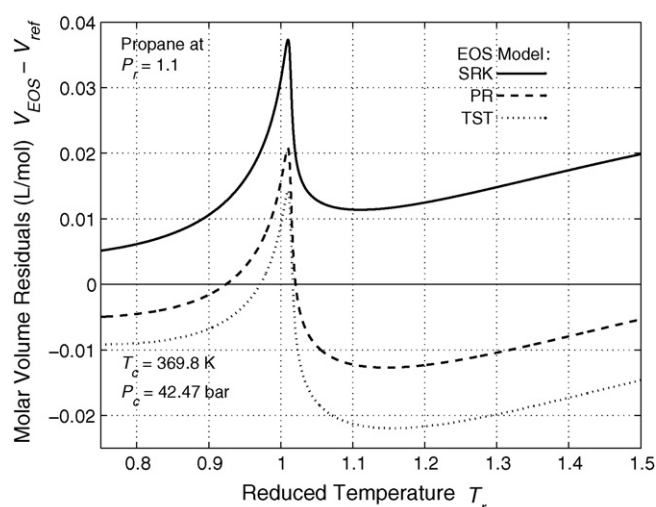


Fig. 2. The difference between reference molar volumes and molar volumes predicted by the SRK, PR, and TST EOSs for propane at  $P_r = 1.1$ .

factor were selected, then the preferred equation would also be changed. For example, molar volumes for methane ( $Z_c = 0.286$ ) are predicted most accurately by the SRK EOS. None of the cubic EOSs examined appear capable of providing an improvement in accuracy beyond a constant shift in the molar volume residuals.

Both Martin [7] and Peneloux and Rauzy [8] were able to show that the critical compressibility can be adjusted using volume translation. Vidal [25] demonstrated that the differences in molar volume prediction between the PR, SRK, and the van der Waals EOSs (Eq. (1) with  $u = w = 0$ ) were mostly attenuated using a constant volume translation. Further, Yu and Lu [26] were able to show that a constant volume translation is equivalent to continuously varying the parameters  $u$  and  $w$  in Eq. (1). When employing volume translation, the specific instance of the untranslated cubic used is not important.

## 2.2. Volume translation

Martin’s approach to volume translation [7] was constructed to follow the exact mathematical definition of volume translation, which is a transformation of the volume coordinate in an EOS by a constant value with no distortion of the other coordinates. Eq. (5) represents this symbolically.

$$f(P, V_{UT} + t, T, N) = f(P, V_T, T, N) \quad (5)$$

In Eq. (5),  $P$  is the pressure,  $T$  the temperature,  $N$  the number of moles,  $V_{UT}$  the untranslated volume,  $V_T$  the translated volume, and  $t$  is the volume translation. Because of the insensitivity of molar volume residuals to the selected form of the general cubic EOS, only one will be considered for the remainder of this study. The EOS function selected for all subsequent calculations in this work is the SRK EOS, given in its intensive, volume translated form as Eq. (6).

$$P = \frac{RT}{V - c - b} - \frac{a_c \alpha(T_r)}{[V - c][V - c + b]} \quad (6)$$

In Eq. (6),  $V$  is the molar volume. The parameter  $c$  is used as a substitute for the volume translation parameter  $t$  in order to emphasize that volume translations dependent on temperature are frequently used with the SRK equation. The constants  $a_c$  and  $b$  are fixed in order to meet the mechanical stability criteria of Eq. (3) at the vapor–liquid critical point. These values are given for pure components in the following equation:

$$a_c = \frac{R^2 T_c^2}{9[\sqrt[3]{2} - 1]P_c}, \quad b = \frac{[\sqrt[3]{2} - 1]RT_c}{3P_c} \quad (7)$$

This study focuses on pure fluids; the mixture formulation of these constants depends on the selection of mixing rules and was not considered here. The alpha function originally proposed by Soave (Eq. (8)) was used.

$$\alpha(T_r) = f(\omega, T_r) = \left[ 1 + [0.480 + 1.574\omega - 0.176\omega^2] \left[ 1 - \sqrt{\frac{T}{T_c}} \right] \right]^2 \quad (8)$$

Rather than utilize a specific closed form for the volume translation value, represented by  $c$  in Eq. (6), this work analyzes the volume residuals that are required to create a volume translation function that can correct the SRK equation (or equivalently, any cubic equation). In all of our calculations to determine the residuals from Eq. (6) (i.e., the difference between the pure component reference values and values predicted by the equation), the value of  $c$  was set to zero. This approach was also used in 1989 by Mathias et al. [27]. However, accurate reference values were not as readily available in 1989, nor were sophisticated regression techniques. Thus their results were limited to a smaller number of compounds.

### 2.3. Reference values

The pure component reference values used herein are taken from multiparameter equations of state. These equations are typically created using a Helmholtz free energy formulation and should not be confused with the pressure explicit volumetric equations (EOSs) that are more easily used in engineering calculations. Multiparameter equations provide a means for correlating and interpolating highly accurate thermophysical property data and are routinely used to create reference tables and charts of property data [28]. Unfortunately these equations are not suited for mixture calculations. The sources of the pure component reference values used in this study are presented in Table 1 along with their reported ranges of validity.

The multiparameter equations in the references cited in Table 1 are not unique and are only as reliable as the data sets used in their creation. The accuracy reported for each equation only involves the representation of the data sets selected by the respective authors. A comparison between different multiparameter equations of state for the same fluid [36,39] reveals that the uncertainty in the predicted density tends to be greater than the uncertainty values reported by the authors. This discrepancy is possibly due to the data sets selected when fitting parameters

Table 1

Sources of pure component reference values and their reported ranges of validity in reduced temperature and pressure coordinates

Fluid	$T_c$ (K)	$P_c$ (bar)	$T_r$ min	$T_r$ max	$P_r$ max	Source
Methane	190.56	45.99	0.476	3.28	217.4	[29]
Ethane	305.33	48.72	0.296	2.05	14.37	[30]
Propane	369.83	42.47	0.231	1.74	24.25	[22]
<i>n</i> -Butane	425.13	37.96	0.317	1.39	18.18	[31]
<i>n</i> -Pentane	469.70	33.70	0.305	1.22	20.47	[31]
<i>n</i> -Hexane	507.82	30.34	0.518	1.08	30.32	[31]
<i>n</i> -Heptane	540.13	27.36	0.338	1.28	36.55	[31]
<i>n</i> -Octane	569.32	24.97	0.453	0.96	38.45	[31]
Nitrogen	126.19	33.96	0.500	7.92	647.9	[32]
Oxygen	154.57	50.43	0.352	1.94	16.22	[33]
Argon	150.69	48.63	0.556	4.65	205.6	[34]
Carbon dioxide	301.13	73.77	0.712	4.93	108.4	[35]
Hydrogen sulfide	373.37	89.63	0.503	2.04	18.97	[36]
Ammonia	405.40	113.3	0.482	1.85	44.11	[37]
Water	647.10	220.6	0.423	1.97	45.32	[38]

and is not a source of concern for this study. The uncertainty trends for all of the reference equations cited in Table 1 are similar; data in the single phase regions are consistent to within a few tenths of a percent, while molar volumes near the critical point and saturation conditions are consistent to within 1–2%. The maximum uncertainty in the molar volume is always found around the critical point and reflects the difficulty in experimentally measuring critical and near-critical volumes. The increased uncertainty at saturated conditions is mitigated through the use of auxiliary equations fit exclusively to saturation data. For this study, deviations between reference volumes and the molar volumes predicted by the SRK EOS are only considered significant when the relative disagreement exceeds 3%. The multiparameter equations are able to provide this level of accuracy over the entire range of reduced temperature and pressure.

### 2.4. Uncertainty trends in molar volume predictions

The absolute deviations between reference molar volumes for propane at  $P_r = 0.7$  and molar volumes predicted by the SRK equation that were originally presented in Fig. 1 are reproduced in Fig. 3a (using the original Soave alpha function of Eq. (8) instead of the Boston–Mathias-type extrapolation) along with the relative intensity of those deviations. Comparing the curves created using the SRK EOS from Fig. 1 and the absolute deviation curve from Fig. 3a, the minor differences in molar volume residuals due to variations in the alpha function become apparent. The maximum absolute discrepancy of 0.01 L/mol occurs at high temperatures ( $T_r \geq 1.5$ ), but still corresponds to a relative difference of less than 1.0%. The low-relative intensity of deviations at high temperatures is a general result. The absolute deviations between predicted and reference molar volumes in the liquid phase (low-temperature branch of Fig. 3a) are significant, but the deviations in the vapor phase (high-temperature branch) are not significant. Although the absolute magnitude of the molar volume deviation appears to increase at higher temperatures ( $T_r > 1.1$ ), this deviation is not appreciably different from zero and there is no actual trend to the deviations at these tem-



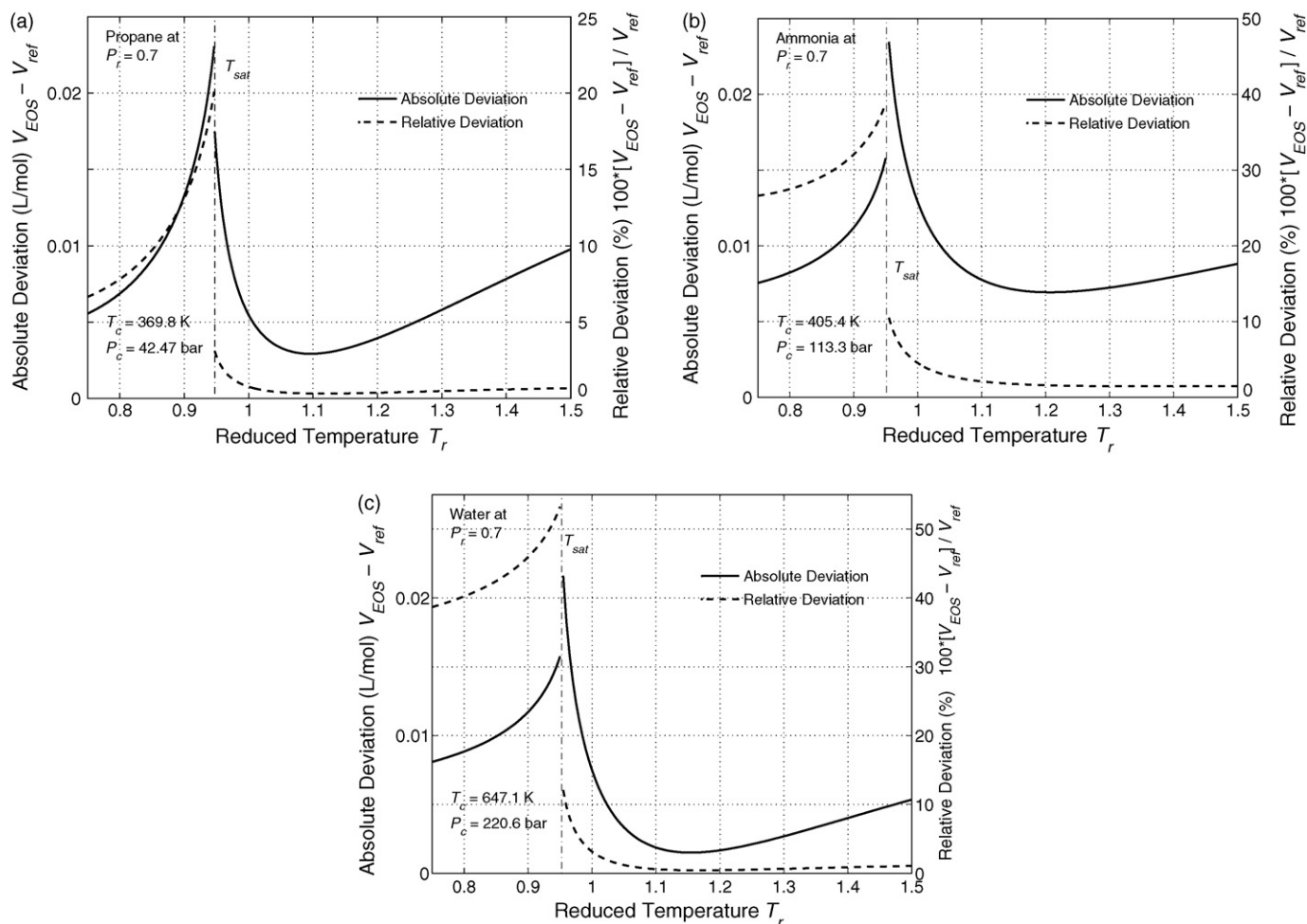


Fig. 3. The absolute and relative deviations between reference molar volumes for (a) propane, (b) ammonia, and (c) water and molar volumes predicted using the SRK EOS at  $P_r = 0.7$ .

peratures. The pattern of deviations exhibited by all other fluids listed in Table 1 is similar to the pattern observed for propane. For example, the absolute magnitude and relative intensity of deviations over the same range of conditions are presented for ammonia in Fig. 3b and for water in Fig. 3c. The deviations for water, ammonia, and propane are all comparable in absolute magnitude, although the relative intensity of the deviations for water and ammonia are much greater.

The molar volume residuals for supercritical isobars are similar to those for subcritical isobars and are not shown. The absolute deviations in molar volume predictions from the SRK EOS along supercritical isobars exhibit behavior that is the same as what is observed along the subcritical isobar, although without the discontinuity due to the phase change. Even though the absolute molar volume deviation begins to increase at high temperatures ( $T_r > 1.2$ ), the relative deviation does not increase because the molar volume is increasing more rapidly than the absolute magnitude of the volume residual.

### 2.5. Maxima in molar volume residuals

A general result for all fluids examined is that the relative deviations along an isobar attain a maximum, which for subcrit-

ical isobars ( $P < P_c$ ) occurs at the phase transition temperature and for supercritical isobars ( $P > P_c$ ) occurs at a temperature that corresponds roughly to the temperature at the pseudocritical point, defined as the temperature where the isobaric heat capacity attains a maximum.

At vapor–liquid equilibrium, the relationship between temperature and pressure can be expressed using a generalized Clapeyron relation shown in the following equation:

$$\left[ \frac{d \ln P}{d(1/T)} \right]_{L-V} = \frac{-\Delta H_{vap}}{R \Delta Z_{vap}} \quad (9)$$

The ratio  $(\Delta H_{vap}/\Delta Z_{vap})$  commonly has been observed to be a weak but nearly linear function of temperature for a large number of pure fluids [40]; the value of the ratio may also be approximated as a constant, in which case its value usually falls between 4.0 and 9.0 [7]. Many authors have taken advantage of this fact to create generalized vapor pressure charts in coordinates of inverse temperature and the logarithm of pressure by holding this ratio constant. As previously noted, the temperature of maximum relative molar volume deviation along an isobar where  $P < P_c$  occurs at the saturation temperature, which is correlated linearly in the coordinates of Eq. (9). Beyond the point where liquid and

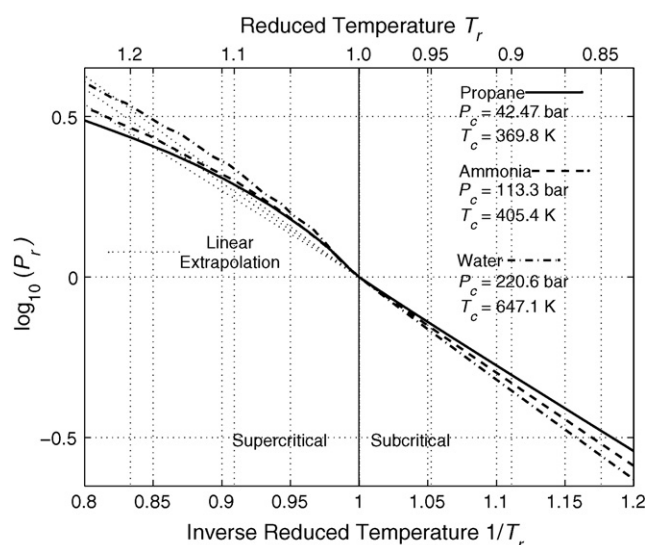


Fig. 4. The temperatures at which a maximum in relative molar volume deviation occurs along an isobar and the pressures of those isobars, as calculated for propane, ammonia, and water using the SRK EOS.

vapor can appear as distinct phases, the Clapeyron equation does not have physical meaning. In this supercritical region where  $P_r > 1$  and  $T_r > 1$ , however, the Clapeyron equation correlates the temperatures where the maximum relative molar volume deviations occur as a function of pressure along isobars  $P > P_c$ . The relationship between the temperatures where a maximum in relative molar volume deviations on an isobar occur and the pressures of those isobars is shown in Fig. 4.

The relation in Fig. 4 is calculated for propane, ammonia, and water using the SRK EOS; all other fluids listed in Table 1 exhibit similar behavior. The coexistence region ( $T_r < 1$ ) was calculated using highly accurate (uncertainty  $< 0.1\%$ ) values for the vapor pressure; the dotted lines are linear regressions of Eq. (9) to the subcritical region that were extrapolated into the supercritical region to serve as a guide for the eye. Temperatures of maximum molar volume deviation were calculated for isobars up to  $P_r = 10.0$ ; experimental data at higher pressures and temperatures were not used when creating the reference equations for propane and ammonia. These maxima remain close to the critical temperature ( $1.0 < T_r < 1.5$ ) even for very high pressures ( $P_r \geq 5.0$ ).

The correlation presented is useful for identifying the points of maximum deviation for cubic EOSs on supercritical isobars near  $P_c$ . Molar volume deviations that occur at temperatures above the point of maximum relative deviation rapidly decrease to insignificance as the fluid begins to behave in an ideal manner. However, molar volume residuals at temperatures below the point of maximum deviation remain significant; the residuals at these temperatures are large compared to the absolute molar volume and need to be corrected using volume translation. It is clear from this analysis that volume translation must extend into the supercritical region and should not be limited to subcritical temperatures.

## 2.6. Translation functions varying in temperature

The trends exhibited by the curves in Figs. 1 and 2 demonstrate that constant values of volume translation are unable to correct for the pattern of molar volume residuals that arise from cubic EOSs. Fig. 5a depicts the volume translation values required for propane at several different pressure conditions. Once again, propane is only used as a model fluid; the required volume translations for water and argon are shown in Fig. 5b and c, respectively. The volume translations required by the SRK EOS for all fluids are very similar in both shape and absolute magnitude.

Subcritical isobars are truncated at the saturation temperature and the vapor branch is not shown. Supercritical isobars are shown using solid lines up to the point where the correction required is at maximum; corrections at higher temperatures are shown using dotted lines to indicate that those values do not require correction because their relative intensities rapidly decrease to zero. The maxima are correlated as indicated by Eq. (9) and shown in Fig. 4.

The curves shown in Fig. 5a were calculated directly as the difference between the molar volumes predicted by the untranslated SRK equation, Eq. (6) with  $c = 0$ , and the pure component reference equation for propane [22]. Fitting a functional form for the parameter  $c$  to the data at one of the six pressure conditions shown would exactly correct the SRK equation for the selected pressure. However, the SRK equation would still have varying amounts of error when used at other pressure conditions.

Peneloux and Rauzy were able to show that phase equilibrium calculations are unaffected by temperature-dependent volume translation functions [8]. Subsequently, many authors have introduced volume translation functions that depend on temperature in order to further reduce the error of predicted molar volumes. Most temperature-dependent volume translations use saturated liquid volumes when formulating the translation function [41–43].

An alternative approach was used by Chou and Prausnitz [44] where the magnitude of volume correction was related to a dimensionless distance parameter based on the intrinsic stability (i.e.,  $(\partial P/\partial V)_T$ ). This volume translation was also constrained to be a function of only temperature and therefore retained the important property of being independent of the phase equilibrium. Ji and Lempe [11,12] also used the distance parameter approach, although they did not relate it to the intrinsic stability.

The common approach of using saturation data is only useful for isobars  $P_r < 0.5$ ; below this pressure the fluid can be approximated as incompressible to good accuracy. Isobars for  $P_r > 0.5$  begin to deviate from the saturation isobar and the volume translation overcorrects at temperatures below the saturation temperature. Many proposed translation functions are only applied at subcritical temperatures while volumetric behavior above the critical temperature is neglected. The deviations at supercritical temperatures need to be addressed when applying volume translation because they remain significant at least to the point where their absolute magnitude achieves a maximum.

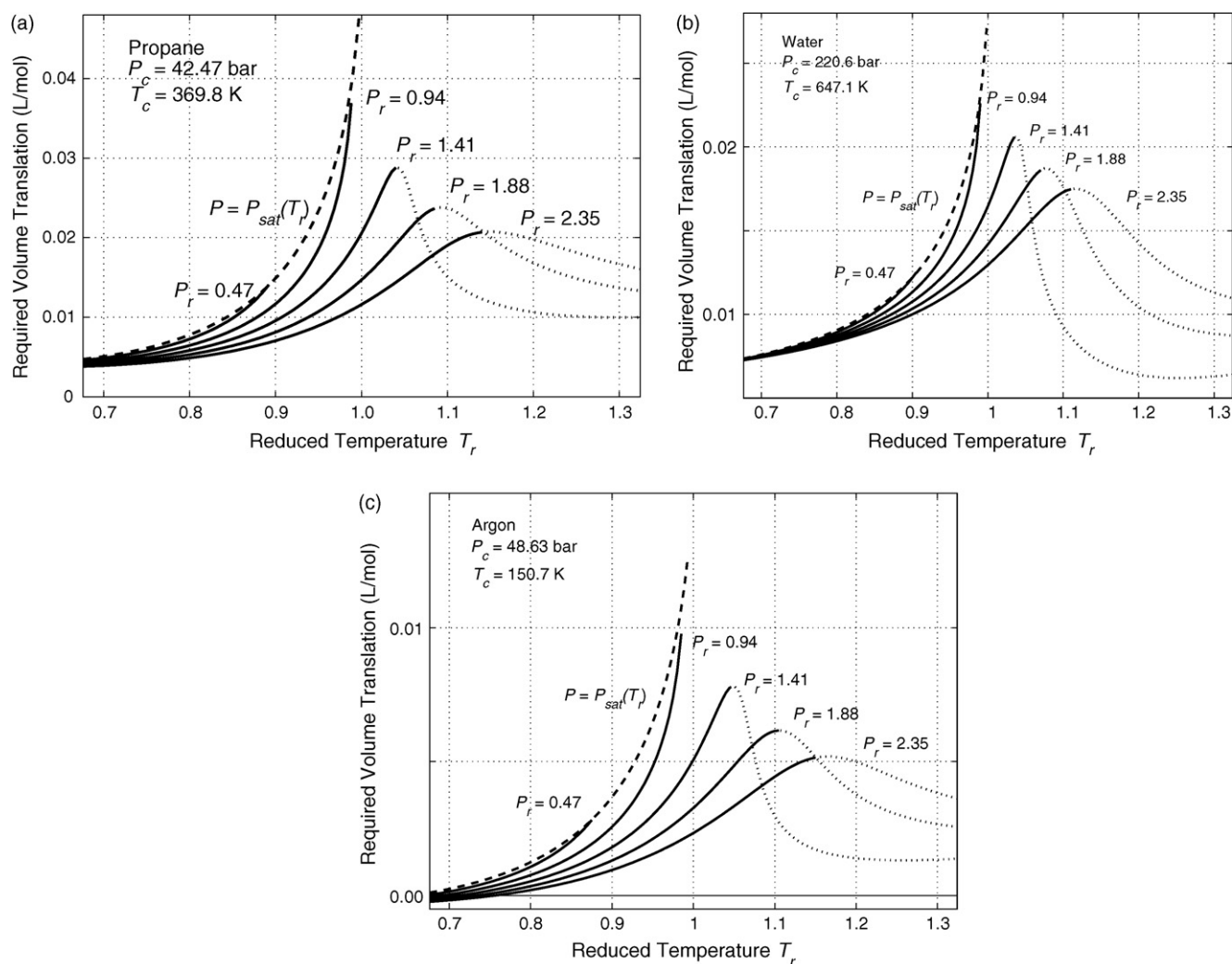


Fig. 5. (a) The required volume translation for propane as modeled by the SRK EOS. The required translation is evaluated at saturation, 20 bar, 40 bar, 60 bar, 80 bar, and 100 bar. (b) The required volume translation for water as modeled by the SRK EOS. The required translation is evaluated at saturation, 104 bar, 207 bar, 311 bar, 415 bar, and 518 bar. (c) The required volume translation for argon as modeled by the SRK EOS. The required translation is evaluated at saturation, 23 bar, 46 bar, 69 bar, 91 bar, and 114 bar.

All of these temperature-dependent approaches, however, can give rise to a crossover of isotherms described by Pfohl [16]. Isotherm crossover is a nonphysical result that occurs when  $P$ – $V$  isotherms at two different temperatures intersect. The intersection creates the situation where a pressure and molar volume coordinate has two possible temperature solutions, which violates a fundamental assumption of thermodynamics. This inconsistency is not limited to temperature-dependent volume translations and is relevant to temperature-dependent co-volumes,  $b$ , as well [45]. Any temperature dependence in either the co-volume or the volume translation can possibly give rise to isotherm crossover [46]. However, it has not been established that isotherm crossover occurs in regions physically relevant to the EOS model. Even the most robust EOS is still only relevant for fluid phase calculations in a limited region of  $PVT$  space. The pressures and temperatures at which isotherm crossover occurs may be outside this region.

## 2.7. Translation function regression

A review of volume translations at subcritical temperature [14] indicated that more robust volume translation is achieved by using high-pressure data to determine the appropriate volume translation. However, selection of any single correction value at a given temperature is insufficient. Using data from an isobar above the critical pressure simply results in a translation function that is more nearly linear. The high-pressure correction provides an incomplete correction near saturation, an accurate correction at the pressure selected, and shifts the isotherm crossover to even higher pressures.

The required translation value decreases from a maximum at saturation (or the corresponding point in the supercritical region determined by extrapolation of the saturation curve) and decreases with pressure. The variation of the required volume translation along selected isotherms is shown in Fig. 6.

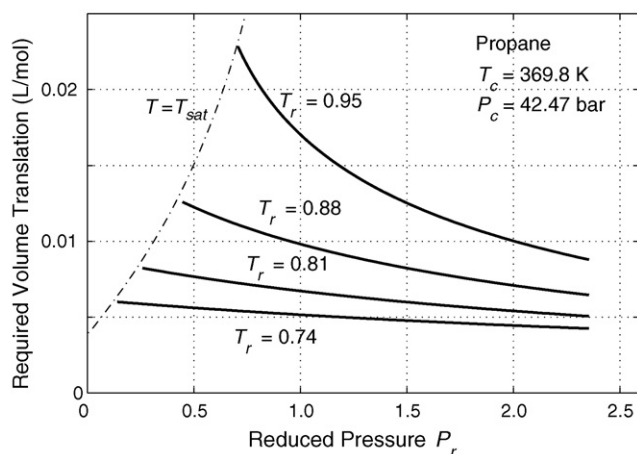


Fig. 6. The pressure dependence of the volume translation required to match reference values for propane as modeled by the SRK EOS. Isotherms of 275 K, 300 K, 325 K, and 350 K are shown.

The curves shown in Fig. 6 were calculated directly as the difference between the molar volumes predicted Eq. (6) with the volume translation term set to zero ( $c=0$ ), and the pure component reference equation for propane [22]. It is not possible to create a volume translation function that only depends on temperature and corrects the volumetric errors from cubic EOSs over a wide range of pressure conditions.

Many researchers argue that current methods of temperature-dependent volume translation are excessively empirical because isotherm crossover limits the range of applicability and the need for accurate experimental data in their regression is prohibitive [47]. Primary motivations for selecting a cubic formulation like the PR or SRK EOS are its validity in highly compressible regions and minimal data requirement for fitting parameters. In developing a group contribution approach, Ahlers and Gmehling [10] decided not to include temperature dependence into the volume translation parameter and instead used a constant volume translation in their EOS. Constant volume translation is able to minimize error arising from disagreement in the critical compressibility factor, but does not improve the overall performance of the equation.

Valderrama [48] discussed the limited use that volume translation has found thus far in process simulation. Aspen Plus [49] provides only one equation of state package (an EOS of the SRK form) that supports volume translation and even then defaults the translation to zero. Non-zero translation values must be manually regressed in the parameter region of interest and only serve to correct the molar volumes. A more robust method of volume translation would be to improve all derived thermodynamic properties by correcting the molar volume, not just correcting the predicted molar volumes independently.

### 3. Density- and temperature-dependent volume translation

The distance parameter approach used by Chou and Prausnitz [44] was originally attributed to Mathias et al. [27]. Their approach effectively created a volume translation that was

dependent on both temperature and density. There was a minor increase in complexity because the resulting equation was non-cubic, but a more important difficulty was identified by Kutney et al. [50]. Specifically, the untranslated phase equilibrium is not maintained under translations that vary in both temperature and density and as a result the alpha function must be re-regressed. The translation by Mathias et al. [27] could not easily be used to calculate fugacities and other derived thermodynamic properties because of numerical inconsistencies in the coexistence region. These numerical problems, such as being non-invertible, only occurred at conditions not physically relevant, such as negative absolute pressures or in mechanically unstable regions, but they prevented the use of the volume-translated equation in fugacity and phase equilibrium calculations that employ traditional isothermal integration methods. This limitation constrained the translation approach by Mathias et al. to be used only as a correction for volumes and not an improvement for other derived properties.

In order to affect a consistent improvement for all properties, there is a need for more than temperature dependency in the volume translations used to correct cubic EOSs. Mathias et al. [27] originally noted that the pattern of deviations in molar volumes for both polar and non-polar fluids was very similar. Fig. 7a–d depicts the pattern of deviations in molar volume predictions of the SRK EOS for a wide variety of polar and non-polar fluids at  $P_r = 0.50, 0.75, 2.5$ , and  $5.0$ , respectively. These curves have been truncated at their maximums as described in Section 2.5 in order to simplify their representation.

Reduced molar volume translations,  $c/V_c$ , for all fluids studied are roughly equivalent and show similar behavior with temperature at a specified pressure. With a constant, substance-dependent, translation value applied to each fluid, the volume translations required for the subcritical isobars can be nearly superimposed. The supercritical isobars cannot be superimposed by a constant translation although the similarity between curves still suggests a substantial improvement in accuracy is possible. A scaling factor other than the critical volume may be more suited at supercritical temperatures. This similarity is a remarkable finding when considering the wide range of fluids examined and it suggests that a corresponding states type behavior may be applicable.

Introducing density dependence into the volume translation parameter is functionally equivalent to creating a new EOS. A cubic EOS that has undergone density- and temperature-dependent volume translation, where the translation is designed to be used in fugacity and enthalpy calculations, no longer remains cubic in volume. However, appropriate volume translations can preserve many of the most important features of the cubic EOS. The limits of mechanical stability remain unchanged under a density-dependent volume translation as described in the following equation:

$$\frac{\partial P}{\partial V_T} = \frac{\partial P}{\partial (V_{UT} + c)} = \frac{\partial P}{\partial V_{UT}} \left( 1 + \frac{\partial c}{\partial V_{UT}} \right)^{-1} \quad (10)$$

The implication of Eq. (10) is that the mechanically unstable region of the untranslated cubic equation is the same as



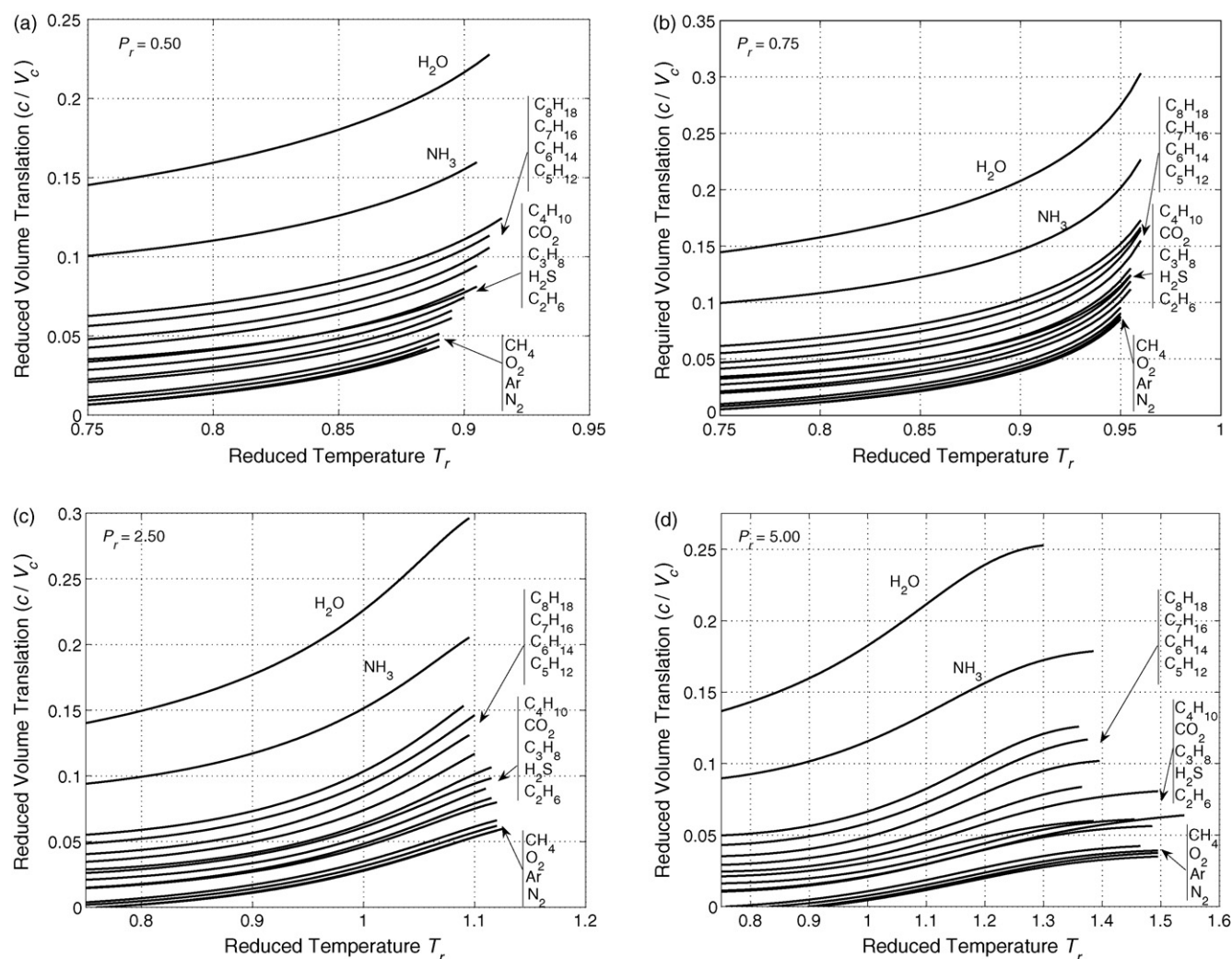


Fig. 7. The reduced volume translation, as modeled by the SRK EOS (Eq. (6)), required to match reference values at (a)  $P_r = 0.50$ , (b)  $P_r = 0.75$ , (c)  $P_r = 2.5$ , and (d)  $P_r = 5.0$  for water, ammonia, hydrogen sulfide, carbon dioxide, nitrogen, oxygen, argon, and the first eight normal paraffin alkanes.

that of the new translated equation. The spinodal locus of the original cubic equation (the limit of mechanical stability where  $(\partial P/\partial V_{UT})_T = 0$ ) is retained under a translation with the trivial restriction that the translation remains finite (i.e.,  $(\partial P/\partial V_{UT})_T \subset (\partial P/\partial V_T)_T$  if  $(\partial c/\partial V_{UT})_T$  is finite). In addition, enforcing the criterion that  $(\partial c/\partial V_{UT})_T \neq -1$  implies that the spinodal locus of the translated equation is exactly equal to that of the untranslated equation; no new or different mechanically stable regions are introduced by the translation. The translated equation will no longer be cubic in volume, but it will still retain the useful property of having only one real volume root when  $T_r > 1$  and three real volume roots when  $T_r < 1$ . All additional molar volume roots that arise from the volume translation will be complex valued and can be discarded. As a contrast to the traditional cubic formulation, it is useful to observe that all of the multiparameter equations cited in Table 1 can have five or more real roots when  $T_r < 1$  and involve auxiliary equations to enforce coexistence. Density-dependent volume translation can be a powerful tool for improving EOSs without adding unnecessary levels of complexity, as long as the translation is implemented while considering numerical consistency.

The similar functional dependence of translation values for these reference fluids suggests that there is a generalized and thermodynamically consistent approach to applying a temperature- and density-dependent volume translation that is relevant for all fluids. By using a density-dependent volume translation, it will be possible to improve the accuracy of all derived thermodynamic properties (i.e., enthalpies, entropies, fugacities, etc.) by unifying the correction of molar volumes.

#### 4. Conclusions

Volume translations that are only dependent on temperature are insufficient to correct cubic EOSs and only serve to change molar volumes without improving the accuracy of thermodynamic properties such as enthalpies and entropies. It is necessary to create a temperature- and density-dependent volume correction for robust and accurate predictions of derived thermodynamic properties. Linearly extrapolating the Clapeyron-based relation (Eq. (9)) of  $\ln(P_r) = f(1/T_r)$  into the supercritical region is a useful method of identifying the maximum relevant temperature along an isobar that a volume

translation function needs to represent. Errors above this maximum relevant temperature are not significant enough to warrant correction.

The functional form of the volume translations needed is the same for many different polar and non-polar fluids. Highly dissimilar fluids such as water, ammonia, argon, and many simple hydrocarbons require volume translations that are alike in both shape and magnitude. This similarity indicates that it is possible to formulate a common volume translation that can be used to not only improve the predicted molar volumes, but also the accuracy of enthalpies and other derived properties.

#### List of symbols

$a, b, c, u, w$  equation of state parameters

$N$  number of moles

$P$  pressure

$R$  gas constant

$t$  volume translation value

$T$  absolute temperature

$V$  molar volume

$\bar{V}$  extensive volume

$Z$  compressibility factor

#### Greek letters

$\alpha$  alpha function

$\Delta$  change in property

$\omega$  acentric factor

#### Subscripts

exp reference value from multiparameter equation

EOS estimated by an equation of state

$i$  index of a component in a mixture

L–V vapor–liquid coexistence property

c vapor–liquid critical point property

r property divided by its value at vapor–liquid critical point

sat evaluated at saturated conditions

T translated

UT untranslated

vap evaporation

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#### References

- [1] G. Soave, S. Sama, M. Oliveras, Fluid Phase Equilib. 156 (1999) 35–50.
- [2] R. Oakes, A. Clifford, C. Rayner, J. Chem. Soc. Perkin Trans. 1 (2001) 917.

- [3] M. Modell, Supercritical water oxidation, in: H. Freeman (Ed.), Standard Handbook of Hazardous Waste Treatment and Disposal, McGraw Hill, New York, 1989, pp. 8.153–8.168.
- [4] A. Danesh, PVT and Phase Behaviour of Petroleum Reservoir Fluids, Elsevier, Amsterdam, 1998.
- [5] G. Schmidt, H. Wenzel, Chem. Eng. Sci. 35 (1980) 1503–1512.
- [6] G. Soave, Chem. Eng. Sci. 27 (1972) 1197–1203.
- [7] J. Martin, Ind. Eng. Chem. 59 (1967) 35–54.
- [8] A. Peneloux, E. Rauzy, Fluid Phase Equilib. 8 (1982) 7–23.
- [9] G. Soave, A. Bertucco, M. Sponchiado, AIChE J. 41 (1995) 1964–1971.
- [10] J. Ahlers, J. Gmehling, Fluid Phase Equilib. 191 (2001) 177–188.
- [11] W. Ji, D. Lempe, Fluid Phase Equilib. 130 (1997) 49–63.
- [12] W. Ji, D. Lempe, Fluid Phase Equilib. 155 (1999) 339.
- [13] L. Wang, J. Gmehling, Chem. Eng. Sci. 54 (1999) 3885–3892.
- [14] H. de Sant'Ana, P. Ungerer, J. de Hemptinne, Fluid Phase Equilib. 154 (1999) 193–204.
- [15] H. Lin, Y. Duan, Fluid Phase Equilib. 233 (2005) 194–203.
- [16] O. Pföhl, Fluid Phase Equilib. 163 (1999) 157–159.
- [17] D. Peng, D. Robinson, Ind. Eng. Chem. Fundam. 15 (1976) 59–64.
- [18] P. Mathias, H. Klotz, Chem. Eng. Prog. 6 (1994) 67–75.
- [19] C. Twu, J. Coon, D. Bluck, Ind. Eng. Chem. Res. 37 (1998) 1580–1585.
- [20] J. Martin, Ind. Eng. Chem. Fundam. 18 (1979) 81–98.
- [21] C. Twu, J. Coon, J. Cunningham, Fluid Phase Equilib. 75 (1992) 65–79.
- [22] H. Miyamoto, K. Watanabe, Int. J. Thermophys. 21 (2000) 1045–1072.
- [23] P. Mathias, Ind. Eng. Chem. Proc. Des. Dev. 22 (1983) 385–391.
- [24] J. Boston, P. Mathias, Proceedings of the 2nd International Conference on Phase Equilibria, vols. 17–21, 1980, pp. 823–849.
- [25] J. Vidal, Fluid Phase Equilib. 13 (1983) 15–33.
- [26] J. Yu, B. Lu, Fluid Phase Equilib. 34 (1987) 1–19.
- [27] P. Mathias, T. Naheiri, E. Oh, Fluid Phase Equilib. 47 (1989) 77–87.
- [28] R. Span, Multiparameter equations of state, in: An Accurate Source of Thermodynamic Property Data, Springer-Verlag, Berlin, 2000.
- [29] U. Setzmann, W. Wagner, J. Phys. Chem. Ref. Data 20 (1991) 1061–1151.
- [30] D. Friend, H. Ingham, J. Ely, J. Phys. Chem. Ref. Data 20 (1991) 275–347.
- [31] R. Span, W. Wagner, Int. J. Thermophys. 24 (2003) 41–109.
- [32] R. Span, E. Lemmon, R. Jacobsen, W. Wagner, A. Yokozeki, J. Phys. Chem. Ref. Data 29 (2000) 1361–1433.
- [33] R. Schmidt, W. Wagner, Fluid Phase Equilib. 19 (1985) 175–200.
- [34] C. Tegeler, R. Span, W. Wagner, J. Phys. Chem. Ref. Data 28 (1999) 779–850.
- [35] R. Span, W. Wagner, J. Phys. Chem. Ref. Data 25 (1996) 1509–1596.
- [36] N. Sakoda, M. Uematsu, Int. J. Thermophys. 25 (2004) 709–737.
- [37] R. Tilner-Roth, F. Harms-Watzenberg, H. Baehr, DKV Con. Rep. 20 (1993) 167–181.
- [38] W. Wagner, A. Pruss, J. Phys. Chem. Ref. Data 31 (2002) 387–535.
- [39] E. Lemmon, R. Span, J. Chem. Eng. Data 51 (2006) 785–850.
- [40] J. Tester, M. Modell, Thermodynamics and its Application, Third ed., Prentice Hall, New Jersey, 1997.
- [41] H. Lin, Y. Duan, T. Zhang, Z. Huang, Ind. Eng. Chem. Res. 45 (2006) 1829–1839.
- [42] J. Tsai, Y. Chen, Fluid Phase Equilib. 145 (1998) 193–215.
- [43] K. Magoulas, D. Tassios, Fluid Phase Equilib. 56 (1990) 119–140.
- [44] G. Chou, J. Prausnitz, AIChE J. 35 (1989) 1487–1496.
- [45] L. Hnedkovsky, I. Cibulka, Fluid Phase Equilib. 60 (1990) 327–332.
- [46] P. Salim, M. Trebble, Fluid Phase Equilib. 65 (1991) 59–71.
- [47] J. Prausnitz, F. Tavares, AIChE J. 50 (2004) 739–761.
- [48] J. Valderrama, Ind. Eng. Chem. Res. 42 (2003) 1603–1618.
- [49] Aspen Plus, Aspen Technology Reference Manual, 2004, pp. 1–24.
- [50] M. Kutney, V. Dodd, K. Smith, H. Herzog, J. Tester, Fluid Phase Equilib. 128 (1997) 149–171.