Development of a Thermodynamically Consistent Volume Translation Method in Peng-Robinson Equation of State

By
Jialin Shi

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science

in

Petroleum Engineering

Department of Civil and Environmental Engineering

University of Alberta

ABSTRACT

Cubic equations of state (CEOS) are frequently used to predict the phase behavior and volumetric properties of pure compounds and mixtures encountered in the field of chemical and petroleum engineering. Volume translation is proposed to further improve the accuracy of density predictions by CEOS. Previous research shows that a temperature-dependent volume-translated EOS could result in crossing of pressure-volume isotherms for a pure compound, which leads to an anomalous behavior that the predicted molar volume for a pure component can be lower at a higher temperature at an isobaric condition. Such crossover phenomenon fails to consistently predict the thermodynamic properties of a pure compound, thus restricting the wide applications of the temperature-dependent volume translated EOS.

Aiming at addressing the above thermodynamic inconsistency in some volume-translated EOSs, a criterion is proposed to judge whether a volume-translated EOS will result in crossover issues, and if so, the extent of the temperature and pressure range over which the crossover phenomenon occurs. The criterion is developed based on a fundamental fact that the isobaric expansivity for a pure gas or liquid is positive. The recently proposed volume translations are evaluated on the basis of the developed criterion. For the various types of temperature-dependent volume translations, we obtain the specific temperature/pressure conditions over which there is certainly no crossover phenomenon. It can be concluded that there is thermodynamic inconsistency at a lower pressure for most nonlinear temperature-dependent volume translations, but no any crossover issues exist for the constant volume translations and linear temperature-dependent volume translations with a negative coefficient of temperature.

Next, a generalized temperature-dependent volume translation model is developed for the more accurate prediction of the liquid densities of pure components. On the basis of the criterion on thermodynamic consistency we have proposed, a mathematical constraint is introduced into the proposed model. The model parameters are determined based on the regression of the density data collected for16 pure compounds. The new volume-translated PR EOS can improve the liquid density prediction with an overall absolute average percentage deviation of 1.42%. Notably, the new volume translation model does not lead to the crossing of pressure-volume isotherms over a wide range of pressure and temperature (up to 100 MPa and 1000 K).

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisor, Dr. Huazhou Andy Li, for his supervision and support during my master program at the University of Alberta. He equipped me with brilliant ideas, critical thinking skills and professional skills that are helpful for my future academic endeavours. With Dr. Li's guidance and supervision, I also learn how to improve myself-management skills and how to prepare myself to become a good researcher. In addition, I want to thank my examination committee members, Dr. Zhehui Jin and Dr. Yuntong She for their critical and valuable comments.

I am grateful for the support from my family during my study at the University of Alberta. Thanks for the constant love and support from my Mom (Ju Zhang), Dad (Jianbing Shi), my girlfriend (Wanying Pang) and other family members.

I would also like to thank all my many friends in Edmonton; their friendship is invaluable to me. In addition, I always have the pleasure of working with the past and present group members (Lanxiao Hu, Bailu Teng, Yueliang Liu, Wanying Pang, Dashun Wang, Hanru Yu, Mian Qin, Gongjue Wei, Hao Sun, Sean Perkins, Chen Wang, Chao Wang, Jianyi Gao, Ruixue Li, Siyuan Yi, Chang Lu and Qianhui Zhao) in Dr. Li's research group. Thanks for their friendship and support!

Finally, I also greatly acknowledge the financial support provided by one Discovery Grant from the Natural Sciences and Engineering Research Council (NSERC) to Dr. Huazhou Andy Li (NSERC RGPIN 05394).

DEDICATION

This dissertation is dedicated to my dearest parents, Mrs. Ju Zhang and Mr. Jianbing Shi and to the memory of my friend, Chocho.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1 INTRODUCTION

1.1. Research Background

The relationship between the pressure, molar volume, and temperature (PVT) for pure fluids or mixtures is one of the most fundamental and significant aspects in the modeling of fluid phase behavior. A theoretical model is necessary to simulate the relationship of PVT for the real fluids in the chemical and petroleum engineering. For example, during CO_2 injection for enhanced oil recovery, reliable predictions of phase equilibria and volumetric properties of CO_2/oil mixtures are a prerequisite for achieving accurate compositional modeling of such a complicated process.

Since the publication of van der Waals equation [1] in 1873, cubic equations of state (CEOS) have been widely applied to model the compositional and volumetric phase behavior because of their simplicity and reliability. Thereafter,variousmodifications have been proposed to enhance the predictive capability of CEOS [2-4]. However, larger errors still exist for the two-parameter CEOSs because of the inaccurate representation of the critical compressibility factors for pure compounds.

1.2. Overview of CEOS

1.2.1. van der Waals EOS

Pressure, volume, and temperature determine the behavior of gas. The ideal gas law was first proposed by Émile Clapeyron [5 and 6]. The ideal gas law is given by,

$$P = \frac{RT}{V} \tag{1}$$

where P is pressure, T is absolute temperature, V is molar volume, and R is gas constant.

In 1873, van der Waals [1] first proposed a mathematical model to describe the behavior of real gases. It considers the volume occupied by molecules by adding the parameter b (co-volume) to the ideal gas law,

$$P = \frac{RT}{V - b} \tag{2}$$

It should be noted that when the pressure increases, the volume of the gas becomes small, and the attraction forces among molecules tend to reduce the observed pressure of the gas [6]. Considering this, van der Waals added another term to the pressure in Eq. (2). The complete expression of van der Waals EOS can be obtained,

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{3}$$

where a is a constant. In addition, the following two expressions should be satisfied at the critical point:

$$\begin{cases} \left(\dfrac{\partial P}{\partial V}\right)_{\mathrm{T=T_c,P=P_c}} = 0 \\ \left(\dfrac{\partial^2 P}{\partial V^2}\right)_{\mathrm{T=T_c,P=P_c}} = 0 \end{cases} \tag{4}$$

where T_c and P_c are the critical temperature and critical pressure, respectively. These two equations can be coupled to solve for the two constants a and b,

$$\begin{cases} a = \dfrac{27R^2T_c^2}{64P_c} \\ b = \dfrac{RT_c}{8P_c} \end{cases} \tag{5}$$

1.2.2. Redlich-Kwong EOS

In 1949, Redlich and Kwong [2] proposed the following CEOS,

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V\left(V+b\right)} \tag{6}$$

where *a* and *b* are different for various components. Their expression are given as follows,

$$\begin{cases} a = \dfrac{0.42748R^2T_c^{2.5}}{P_c} \\ b = \dfrac{0.08664RT_c}{P_c} \end{cases} \tag{7}$$

We can also rewrite the proposed EOS in terms of compressibility factor,

$$Z = 1 + BP - \frac{A^2P\left(Z-BP\right)}{Z\left(Z+BP\right)} \tag{8}$$

where Z is compressibility factor, and the two parameters A and B are given as below, respectively,

$$\begin{cases} A^2 = \dfrac{a}{R^2T^{5/2}} \\ B = \dfrac{b}{RT} \end{cases} \tag{9}$$

It should be noted that the critical compressibility factor, Z_c, is constant for all pure fluids, and its value is 0.33.

The proposed Redlich-Kwong EOS improves the accuracy in vapor pressure prediction. In addition, Redlich and Kwong replaced the term V^2 in van der Waals EOS with $V\left(V+b\right)$, leading to more accurate predictions of vapor-liquid equilibria (VLE) [2].

1.2.3. Soave-Redlich-Kwong EOS

Soave [3] further modified the Redlich-Kwong EOS with the introduction of a temperature/component-dependent parameter *a*, giving the famous SRK EOS. The so-called SRK EOS is given as [3],

$$P=\frac{RT}{V-b}-\frac{a\left(T\right)}{V\left(V+b\right)} \tag{10}$$

where

$$\begin{cases} a\left(T\right)=a_c\cdot\alpha\left(T\right) \\ a_c=\dfrac{0.42747R^2T_c^2}{P_c} \\ \alpha\left(T\right)=\left(1+m\left(1-\sqrt{\dfrac{T}{T_c}}\right)\right)^2 \\ m=0.480+1.574\omega-0.176\omega^2 \\ b=\dfrac{0.08664RT_c}{P_c} \end{cases} \tag{11}$$

where ω is acentric factor, and the so-called alpha function, $\alpha\left(T\right)$, becomes unity when the temperature is critical temperature. In addition, the parameter *m* is a function of acentric factor in the alpha function. The SRK EOS provides more accurate prediction of the vapor pressures for pure components. Similarly, the SRK EOS can be written in terms of compressibility factor as follows,

$$F = Z^3 - Z^2 + Z\left(A - B - B^2\right) - AB = 0 \tag{12}$$

where two parameters A and B are given as below,

$$\begin{cases} A = a\dfrac{P}{R^2T^2} = a_c\alpha\dfrac{P}{R^2T^2} \\ B = b\dfrac{P}{RT} \end{cases} \tag{13}$$

1.2.4. Peng-Robinson EOS

It is worth noting that a major deficiency of RK EOS and SRK EOS is that the predicted density values for the liquid phase are unreliable, albeit the calculated vapor densities are generally acceptable [4]. To overcome this drawback, Peng and Robinson [4] proposed a new two-parameter EOS with a modification in the attractive pressure term, namely, PR EOS,

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2} \tag{14}$$

where

$$\begin{cases} a(T) = a_c \cdot \alpha(T) \\ a_c = \dfrac{0.45724R^2T_c^2}{P_c} \\ \alpha(T) = \left(1 + m\left(1 - \sqrt{\dfrac{T}{T_c}}\right)\right)^2 \\ b = \dfrac{0.07780RT_c}{P_c} \end{cases} \tag{15}$$

The term m in the alpha function is a function of the acentric factor as shown below [7],

$$m = \begin{cases} 0.37464 + 1.54226\omega - 0.26992\omega^2, \omega < 0.49 \\ 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3, \omega > 0.49 \end{cases} \tag{16}$$

PR EOS can be also written as below,

$$F = Z^3 - \left(1 - B\right)Z^2 + \left(A - 2B - 3B^2\right)Z - \left(AB - B^2 - B^3\right) = 0 \tag{17}$$

1.2.5. Volume Translation Concept

The predicted liquid molar volume by these CEOSs could differ considerably from the experimental value, especially near the critical region. To address such limitation of two-parameter CEOS and improve the accuracy of predicted liquid density, Martin [8] in 1967 proposed the concept of volume translation concept for the first time. The essence of the volume translation concept is that it moves the liquid volume along the molar volume coordinate without altering the phase equilibrium calculations for pure components or mixtures. Later in 1982, Peneloux *et al.* [5] proposed a constant volume translation for SRK EOS, which became a milestone in the volume translation theory. The performance of this correlation is good in the low temperature range but tends to be compromised near the critical point. To accommodate the effect of temperature on the volume translation, many follow-up researches were carried out to develop temperature-dependent volume translations in CEOS.

1.3. Problem Statement

With an introduction of the volume translation concept, the prediction of liquid density can be improved without causing any change to the phase equilibrium calculations. However, for some nonlinear temperature-dependent volume translation techniques, the isotherms could cross each other in the pressure-volume (PV) diagram, leading to anomalous predictions of molar volume for a pure component at an isobaric condition. Such crossover phenomenon impairs the accuracy of predicted molar volume, causes thermodynamic inconsistency in the predicted thermodynamic properties, and restricts theapplication range of the temperature-dependent volume translated EOS. It is important that a volume-translated EOS should avoid the aforementioned crossover issue.

1.4. Objectives

The main objective of this research is to develop a thermodynamically consistent volume translation method in PR EOS. The detailed objectives include the following:

1) To develop a criterion to judge whether the crossover phenomenon exists with various volume translations;

2) To evaluate the specific temperature/pressure conditions over which there is certainly no crossover phenomenon for the recently published volume translation methods;

3) To present a mathematical constraint to make the new proposed volume translation capable of preventing the occurrence of crossover over a wide range of pressure and temperature; and

4) To develop a generalized consistent temperature-dependent volume translation model in PR EOS to improve the predicting accuracy of the liquid densities for pure components.

1.5. Thesis Structure

In this thesis, we first develop a criterion to judge whether a volume-translated EOS will result in crossover issues. Then, applying the proposed criterion, the recently published volume translations are evaluated and, the specific temperature/pressure conditions over which there is certainly no crossover phenomenon are obtained. Last, a generalized temperature-dependent volume translation model is developed by introducing a mathematical constraint to the proposed model, which ensures no crossing of pressure-volume isotherms occurs over a wide range of pressure/temperature and provides more accurate predictions of the liquid densities for pure components.

This thesis is a paper-based thesis, organized as follows:

In Chapter 1, the research background, a brief introduction of CEOS and volume translation concept as well as the problem statement are presented, followed by the objectives and the thesis structure.

Chapter 2 presents a criterion we have proposed to judge whether the crossover phenomenon exists for a given volume-translated EOS based on a fundamental rule that the isobaric expansivity for a pure gas or liquid is positive. This criterion can be used to judge whether the crossover issues occur over a temperature range of $[T_{\mathrm{tp}}, nT_{\mathrm{c}}]$ and a pressure range of $(0, nP_{\mathrm{c}}]$ for a given volume-translated EOS. The proposed criterion provides insights and guidance to develop a more reliable volume translation method presented in Chapter 3.

In Chapter 3, a generalized temperature-dependent volume translation model is developed in the PR EOS to enhance the accuracy of predicted molar volume. The new model consists of three acentric factor-dependent parameters. Based on the criterion of thermodynamic consistency, a constraint is introduced into the nonlinear regression, which ensures that there is no any crossing of isotherms at a wide range of pressure and temperature (up to 100 MPa and 1000K).

Chapter 4 summarizes the conclusions of this study as well as recommendations for future work.

References

[1] J.D. Waals, Over de continuiteit van den gas-en vloeistoftoestand, Sijthoff (1873).

[2] O. Redlich, J.N. Kwong, On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions, Chemical Reviews. 44 (1949) 233-244.

[3] G. Soave, Equilibrium constants from a modified Redlich–Kwong equation of state, Chem. Eng. Sci. 27 (1972) 1197-1203.

[4] D.Y. Peng, D.B. Robinson, A new two-constant equation of state, Ind. Eng. Chem. Fundam. 15 (1976) 59-64.

[5] É. Clapeyron, Mémoire sur la puissance motrice de la chaleur, J. Gabay (1834).

[6] T. Ahmed, Equations of state and PVT analysis, Elsevier (2013).

[7] D.B. Robinson, D.Y. Peng, The characterization of the heptanes and heavier fractions for the GPA Peng-Robinson programs, Gas Processors Association (1978).

[8] J.J. Martin, Equations of state-Applied thermodynamics symposium, Ind. Eng. Chem. 59 (1967) 34-52.

CHAPTER 2 CRITERION FOR DETERMINING CROSSOVER PHENOMENON IN VOLUME-TRANSLATED EQUATION OF STATES

A version of this chapter was presented at the 65th Canadian Chemical Engineering Conference held in Calgary, Alberta, Canada, 4-7 October 2015, and has been accepted for publication in *Fluid Phase Equilibria*, 430 (2016): 1-12.

Abstract

Volume translation is widely adopted in cubic equation of state (CEOS) to achieve more accurate density predictions for pure compounds and mixtures. Previous research reveals that a temperature-dependent volume-translated EOS could result in crossing of pressure-volume isotherms for a pure compound, which leads to an anomalous behavior that the predicted molar volume for a pure component can possibly be lower at a higher temperature at an isobaric condition. Such crossover phenomenon fails to consistently predict the thermodynamic properties of a pure compound, e.g., giving negative isobaric thermal expansivity. In this study, we develop a concise criterion to judge whether a volume-translated EOS will result in crossover issues, and if so, the extent of the temperature and pressure range over which the crossover phenomenon occurs. The recently proposed volume translations are evaluated on the basis of the developed criterion. For the various types of temperature-dependent volume translations, we obtain the specific temperature/pressure conditions over which there is certainly no crossover phenomenon.

Keywords: crossover phenomenon, volume translation, equation of state, thermodynamics, PVT relations

2.1. Introduction

Cubic equations of states (CEOS), such as the Peng-Robinson equation of state (PR EOS) [1] and Soave-Redlich-Kwong equation of state (SRK EOS) [2], are widely applied in chemical and petroleum industry for modeling compositional and volumetric phase behavior of pure compounds as well as mixtures. The generalized CEOS is given as [3],

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

where

$$a = a_{\mathrm{c}}\alpha \tag{2}$$

$$a_{\mathrm{c}} = \Omega_{\mathrm{a}}^{0} \frac{R^2 T_{\mathrm{c}}^2}{p_{\mathrm{c}}} \tag{3}$$

$$\alpha = \left[1 + m\left(1 - T_{\mathrm{r}}^{0.5}\right)\right]^2 \tag{4}$$

$$b = \Omega_{\mathrm{b}}^{0} \frac{RT_{\mathrm{c}}}{p_{\mathrm{c}}} \tag{5}$$

where P is pressure, T is temperature, T_{r} is reduced temperature, V is molar volume, a and b are EOS parameters, T_{c} and P_{c} are critical temperature and pressure, respectively, R is the universal gas constant, α refers to the so-called alpha function, u, w, Ω_{a}^{0}, Ω_{b}^{0} are constants, and m is a function of acentric factor. Table 1 shows the different values of the constants u, w, Ω_{a}^{0}, Ω_{b}^{0} and m for the PR EOS and SRK EOS, respectively.

The constant critical compressibility factor predicted by the PR EOS and SRK EOS, is larger than the experimental value. As a result, the predicted liquid molar volume by these CEOSs could differ considerably from the experimental value, especially near the critical region. To address such limitation of two-parameter CEOS and improve the prediction accuracy of liquid density, a volume translation concept was first proposed by Martin [4] in 1967. This method translates the predicted liquid volume along the volume coordinate without any changes in the phase equilibrium calculations for pure components or mixtures. In 1982, a constant volume translation for SRK EOS was proposed by Peneloux *et al.* [5]; this constant correction term significantly improves the predictions of liquid density in the low temperature range. However, its performance is compromised near the critical point.

In order to overcome the deficiency of the constant correction proposed by Peneloux *et al.* [5], many researchers have developed various types of temperature-dependent volume translations in two-parameter CEOS to accommodate the effect of temperature on the volume translation needed. To ensure that the introduced volume translation does not affect phase equilibrium calculations, it is constrained to be only a function of temperature. A general temperature-dependent volume translation for the CEOS can be represented as,

$$c(T) = V^{\mathrm{CEOS}} - V^{\mathrm{Corrected}} \tag{6}$$

where $c(T)$ is a temperature-dependent volume translation term, $V^{\mathrm{Corrected}}$ is the corrected molar volume, and V^{CEOS} is the original molar volume calculated by the CEOS model.

In 1989, Mathias *et al.* [6] proposed a distance correction, a dimensionless quantity related to the inverse of the isothermal compressibility, to improve density prediction near the critical region.

Based on the principle of distance correction, Chou and Prausnitz [7] presented a phenomenological correction to the SRK EOS for more accurate volumetric predictions; the volume translated SRK EOS provides absolute deviations of less than 3.1% in the calculated saturated liquid densities for 10 pure fluids. Furthermore, Ji and Lempe [8] proposed a new volume translation method with a modified distance function to the SRK EOS by introducing empirical parameters; using this volume translation method, the average relative deviation in the calculated saturated liquid densities has been reduced to 0.96% for 36 compounds. Aside from these distance corrections, some authors [9-12] proposed some other temperature-dependent volume translations. Magoulas and Tassios [9], for example, developed an exponential-type volume translation correction to the PR EOS and VDW EOS together with a modified α function for normal alkanes up to n-$C_{20}H_{42}$. De Sant'Ana *et al.* [10] proposed a volume translation that considers the temperature as well as the molecular weight of each compound. Although the above temperature-dependent volume translations improve the volume molar predictions in the saturated region, these methods do not perform equally well at high temperature/pressure conditions. To improve the prediction of molar volume at extreme conditions, Pedersen *et al.* [11] introduced a temperature-dependent volume translation in PR EOS and SRK EOS for paraffins, heavy aromatic fluids with a significant content of C_{81+}, and reservoir fluids. This new volume translation reduces the average deviation to less than 6.1% in the predicted densities for various reservoir fluids. Recently, Baled *et al.* [12] proposed a linear temperature-dependent volume translation for pure components at high temperature/pressure conditions, which is relevant to the phase-behavior modeling of ultradeep reservoir fluids. Applying this high-temperature/high-pressure volume translation implemented in both SRK EOS and PR EOS, they obtained mean absolute relative deviations of 1.47% and 2.01%, respectively, for 17 pure compounds.

2.2. Motivation

Most temperature-dependent volume translations can provide more accurate predictions of molar volume than the original CEOS; however, these methods may lead to the crossing of isotherms in the pressure-volume (PV) diagram because various degrees of volume shifts are required for the different isotherms along the molar volume coordinate [13]. Figs. 2.1 and 2.2 show the PV diagrams for CH_4 calculated by the original SRK EOS and those calculated by SRK EOS with the temperature-dependent volume translation proposed by Ji and Lempe [8], respectively. One can clearly observe the crossing of isotherms with this temperature-dependent volume translation, i.e., the predicted molar volume is lower at a higher temperature under isobaric conditions. Such so-called crossover phenomenon violates the basic physics of pure fluid: the molar volume of a pure fluid should be expanded when heated under an isobaric condition [13]. Moreover, it is noted that there are two different temperatures corresponding to a given molar volume or a given pressure due to the crossing of isotherms in the PV diagram, as shown in Fig.2.2. In particular, such thermodynamic inconsistency restricts the range of applications of the volume translated EOS, albeit these methods may improve the prediction accuracy of molar volumes under some conditions.

Some studies have been conducted to show the crossover phenomenon of PV isotherms calculated by a given volume-translated EOS. Salim and Trebble [14] pointed out that temperature-dependent co-volume could lead to crossover phenomenon. Yelash and Kraska [15] proposed an approach to analyze the crossover phenomenon in terms of virial coefficients and stated that a volume translation parameter that decreases with temperature does not cause isotherm crossing. Hoyos [16] proposed a method for evaluating whether volume translated EOS is consistent by drawing the partial derivative of pressure with respect to temperature at a constant volume. Recently, Frey *et al.* [17] pointed out that the region of PVT space related to fluid phase calculations is limited, and crossover phenomenon may be outside this region. But one must recognize that, very often, volume translations are also applied to fluid systems subjected to extreme conditions, such as the reservoir fluid contained in high temperature/pressure conditions. Baled *et al.* [12] demonstrated that their volume translation does not yield crossover phenomenon over wide ranges of temperature and pressure. In addition, for the temperature-dependent volume translation model proposed by Abudour *et al.* [18], the plots of liquid density versus pressure for CO_2 were used to demonstrate that their method does not lead to thermodynamic inconsistencies. To summarize, however, the aforementioned investigations on crossover issues are all conducted with limited scopes; for instance, a finite number of PV isotherms are often drawn to show there is no crossover issue. A conclusion that no crossover occurs over a wide range of temperature and pressure cannot be guaranteed. There is lacking of a methodology that can be used to judge whether crossover issue occurs or not. It is, thereby, highly necessary and meaningful to revisit the crossover issue, as well as develop a reliable and convenient criterion to evaluate the thermodynamic consistency of volume translation methods used in CEOS [12-18]. This will help researchers and engineers to choose the appropriate volume translation method that does not bear crossover issues and well suits specific application of interest.

In this work, we develop a criterion to judge whether a volume translation in CEOS can provide consistent prediction of PVT relations over a wide range of temperature and pressure. We apply this criterion to the popular volume translations used in CEOS and provide the application ranges over which there is certainly no crossover issue when using these volume translation methods.

2.3. Mathematical Formulation

The compressibility factor for a real fluid is given by,

$$Z = \frac{PV}{RT} \tag{7}$$

where Z is the compressibility factor which is a function of pressure and temperature, i.e., $Z = Z(P,T)$. Compressibility factor can be readily obtained by solving any CEOS such as PR EOS or SRK EOS.

If a volume translation is introduced in a two-parameter CEOS, the corrected molar volume can be obtained from Eq. (6),

$$V^{\text{Corrected}} = V^{\text{CEOS}} - c(T) \tag{8}$$

Based on theoretical examination of the nature of volume translation methods, Yelash and Kraska [15] concluded that crossing issue can be avoided if the pole-packing fraction decreases with an increasing temperature, leading to the following condition,

$$\frac{\partial\left[c(T)\right]}{\partial T} \leq 0 \tag{9}$$

Later, we will show that Eq. (9) is only a sufficient condition for a volume translation not to cause crossover phenomenon, but not a sufficient and necessary condition.

We next perform a graphical analysis regarding the crossover phenomenon. Fig. 2.3 shows two PV isotherms calculated with a volume translation method at T_1 and $T_1 + \Delta T$ (where ΔT is a positive temperature difference). As shown in Fig. 2.3, if crossing exists between these two isotherms in the PV diagram: at the intersection of the two isotherms corresponding to P_1, the difference in the corrected molar volumes corresponding to T_1 and $T_1 + \Delta T$ equals to 0, i.e., $V^{\text{Corrected}}\left(T_1 + \Delta T\right) - V^{\text{Corrected}}\left(T_1\right) = 0$, while the difference in molar volumes at the isobaric pressure P_2 is less than 0, i.e., $V^{\text{Corrected}}\left(T_1 + \Delta T\right) - V^{\text{Corrected}}\left(T_1\right) < 0$. This means that if there is no crossover between these two isotherms, the following relation holds,

$$\frac{V^{\text{Corrected}}\left(T_1 + \Delta T\right) - V^{\text{Corrected}}\left(T_1\right)}{\Delta T} > 0 \tag{10}$$

In a more general sense, if ΔT is infinitesimal, we will have,

$$\lim_{\Delta T \to 0}\left[\frac{V^{\text{Corrected}}\left(T_1 + \Delta T\right) - V^{\text{Corrected}}\left(T_1\right)}{\Delta T}\right]_{\mathrm{P}} = \left(\frac{\partial V^{\text{Corrected}}}{\partial T}\right)_{\mathrm{P}} > 0 \tag{11}$$

which ensures that there is no crossing of one isotherm with a neighbouring isotherm from a mathematical point of view. Thus, the following equation can be obtained,

$$\left(\frac{\partial V^{\text{Corrected}}}{\partial T}\right)_{\mathrm{P}} = \left[\frac{\partial\left(V^{\text{CEOS}} - c\left(T\right)\right)}{\partial T}\right]_{\mathrm{P}} = \left(\frac{\partial V^{\text{CEOS}}}{\partial T}\right)_{\mathrm{P}} - \frac{\partial\left[c\left(T\right)\right]}{\partial T} > 0 \tag{12}$$

where $\left(\frac{\partial V^{\mathrm{CEOS}}}{\partial T}\right)_{\mathrm{P}}$ can be evaluated as below based on Eq. (7),

$$\left(\frac{\partial V^{\mathrm{CEOS}}}{\partial T}\right)_{\mathrm{P}} = \left[\frac{\partial\left(\frac{ZRT}{P}\right)}{\partial T}\right]_{\mathrm{P}} = \frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{P}} + \frac{ZR}{P} \tag{13}$$

Because there is no crossover phenomenon for a two-parameter CEOS, the first derivative of the molar volume with respect to temperature calculated by a two-parameter CEOS is always positive,

$$\left(\frac{\partial V^{\mathrm{CEOS}}}{\partial T}\right)_{\mathrm{P}} = \frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{P}} + \frac{ZR}{P} > 0 \tag{14}$$

Substituting Eq. (13) into Inequality (12), the following inequality can be obtained,

$$D = \left(\frac{\partial V^{\mathrm{Corrected}}}{\partial T}\right)_{\mathrm{P}} = \frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{P}} + \frac{ZR}{P} - \frac{\partial\left[c(T)\right]}{\partial T} > 0 \tag{15}$$

where *D* is the first derivative of corrected molar volume with respect to temperature. Thereby, the condition for a volume translation without giving crossover phenomenon over a temperature range of $[T_{\mathrm{tp}}, nT_{\mathrm{c}}]$ and a pressure range of $(0, nP_{\mathrm{c}}]$ is obtained,

$$\frac{\partial\left[c(T)\right]}{\partial T} < \frac{RT}{nP_{\mathrm{c}}}\left(\frac{\partial Z}{\partial T}\right)_{nP_{\mathrm{c}}} + \frac{ZR}{nP_{\mathrm{c}}},\ \forall T \in \left[T_{\mathrm{tp}}, nT_{\mathrm{c}}\right] \tag{16}$$

where T_{tp} is triple point temperature; $\left(\frac{\partial Z}{\partial T}\right)_{nP_{\mathrm{c}}}$ and Z can be evaluated with Eq. (7) for PR EOS and SRK EOS, respectively, as shown by Appendix A; and the term $\frac{\partial\left[c(T)\right]}{\partial T}$ can be evaluated for different volume translations, as shown by Appendix B. It is noted that Inequality (16) needs only to be applied once at nP_{c} over the temperature range $[T_{\mathrm{tp}}, nT_{\mathrm{c}}]$, if one is interested in judging the existence of isotherm crossover over $[T_{\mathrm{tp}}, nT_{\mathrm{c}}]$ and $(0, nP_{\mathrm{c}}]$. It can be easily proven that the condition given by Inequality (16) is a necessary and sufficient condition for a volume translation without giving crossover issues over a given temperature range of $[T_{\mathrm{tp}}, nT_{\mathrm{c}}]$ and pressure range of $(0, nP_{\mathrm{c}}]$. In practice, nP_{c} and nT_{c} can be set as high values, for instance, $10P_{\mathrm{c}}$ and $10T_{\mathrm{c}}$, respectively, which brackets the range of pressure/temperature conditions relevant to most petroleum engineering and chemical engineering applications. In addition, comparison of Inequalities (9) and (16) shows that the condition given by Inequality (16) encloses the condition given by Inequality (9). Such criterion is also consistent with the physical principle that the volume of a pure fluid in gaseous state or liquid state should be expanded when heated under an isobaric condition, indicating the isobaric expansivity (β_{P}) for a pure fluid should be always positive,

$$\beta_{\mathrm{P}} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}} \tag{17}$$

Nevertheless, it should be noted that such statement is not always true for solid materials; some solid materials exhibit negative isobaric expansivity under specific conditions [23].

2.4. Results and Discussion

With the introduction of volume translation, the molar volume prediction for pure fluids is more accurate in comparison with the original two-parameter CEOS. Over the last 3 decades, various types of volume translation schemes have been proposed; most methods can be roughly grouped into the following categories: constant volume translations as proposed by Peneloux *et al.* [5], linear temperature-dependent volume translations, exponential-type temperature-dependent volume translations, and temperature-dependent volume translations based on distance functions. However, many volume translations were proposed at the expense of compromised thermodynamic consistency. The criterion developed in this study will be used to assess if these various types of volume translation methods lead to crossover phenomenon or not. Four pure compounds, CH_4, CO_2, *n*-C_5H_{12}, and *n*-$C_{10}H_{22}$, are used for demonstration purposes. Their basic physical properties are presented in Table 2.

2.4.1. Linear Temperature-Dependent Volume Translations

As for the constant volume translation corrections, a component-dependent term was first proposed by Peneloux *et al.* [5]. Pendersen *et al.* [11] introduced a temperature-dependent Peneloux parameter in the SRK and PR EOS to match the experimental data for simulating reservoir's phase behaviour; most notably, the correction remains constant for light component from CH_4 to *n*-C_6H_{14}. For constant volume translations, the derivative of constant volume translation with respect to temperature is always zero, indicating that the Inequality (16) is always satisfied and thus no crossover phenomenon occurs.

The molar volume prediction with the constant volume translation is generally not satisfactory especially when the critical point is approached. Such deficiency, to some extent, motivates the introduction of a linear temperature-dependent volume translation. Below is the generalized form of a linear temperature-dependent volume translation,

$$c(T) = AT + B \tag{17}$$

where A and B are constants that may vary for different compounds. As for such linear temperature-dependent volume translation, if its derivative with respect to temperature is negative, i.e.,

$$\frac{\partial\left[c(T)\right]}{\partial T} = A < 0 \tag{18}$$

the first derivative of corrected molar volume with respect to temperature (D) is always positive according to Inequality (15). This means that there is no crossover if the value of A in the linear temperature-dependent volume translation is negative. For instance, Baled *et al.* [12] proposed a linear temperature-dependent volume translation correction to SRK and PR EOS at extreme conditions; the two parameters A and B in the correction are a function of molecular weight and acentric factor. It was shown that all the optimized values of the parameter A in volume translation for different components are always negative, which ensures that no thermodynamic inconsistency exists with this method. As for the other linear temperature-dependent volume translation proposed by De Sant'Ana *et al.* [10], the two parameters A and B are related to molecular weight; the parameter A is given as,

$$\frac{\partial\left[c(T)\right]}{\partial T} = A = 0.023 - 0.00056MW \tag{19}$$

where MW is molecular weight. It can be seen that no crossover phenomenon exists if the molecular weight is larger than 41.07 g/mol because of a negative parameter A. Taking CO_2

(molecular weight is 44.01 g/mol) for example, the calculated value for A is negative (-0.00165), which ensures that there is no crossover phenomenon over a wide range of temperature and pressure for CO_2 based on Inequality (15). However, as for CH_4 (16.04 g/mol), the value of A is 0.01402, which is positive. Thus, further analysis is warranted. With the volume translation proposed by De Sant'Ana *et al.* [10], we can obtain the relationship between the first derivative of corrected molar volume with respect to temperature (D) versus the reduced temperature (T_r) for CH_4 at different constant pressure of $2P_c$, $5P_c$, $10P_c$ and $100P_c$, respectively. Fig. 2.4 shows the calculation results. No crossing of isotherms exists when the constant pressures are $2P_c$, $5P_c$ and $10P_c$, respectively, because the value of D is always positive. However, if the pressure increases to $100P_c$, we can encounter a range of temperature that yields a negative D. This implies that there is a crossing of any two isotherms from $0.476T_c$ to $0.524T_c$ at $100P_c$ in the PV diagram. Table 3 shows the detailed range of temperatures that yield negative D at different isobaric pressures for CH_4 for various volume translation methods. Also listed are the maximum pressures P_m^*, below which there is no crossover in the PV diagram over the temperature range of $[T_{tp}, 3T_c]$.

2.4.2. Exponential-Type Temperature-Dependent Volume Translations

In order to improve the molar volume prediction near or higher than the critical region, more complex volume translation methods, such as the exponential-type temperature-dependent volume translation, are proposed. In 1990, Magoulas and Tassios [9] developed an exponential temperature-dependent volume translation in PR EOS for the n-alkanes up to n-$C_{20}H_{42}$. The derivation of D based on the Magoulas and Tassios [9] method is given in Appendix B. To explore whether crossover phenomenon exists with this volume translation, Fig. 2.5 plots D as a function of reduced temperature (T_r) for CH_4 at different isobaric pressures. As can be seen from

Fig. 2.5, the value of D is always positive when the isobaric pressure is $2P_c$, which means there is no crossing of isotherms in the PV diagram over $[T_{tp}, 3T_c]$ and $(0, 2P_c]$. In comparison, D becomes negative over a temperature range of 0.869-0.999T_c at an isobaric pressure of $5P_c$. This indicates that the crossover phenomenon appears in this range of temperature of 0.869-0.999T_c for any two isotherms. In addition, at the isobaric pressure of $5P_c$, for isotherms corresponding to temperatures less than $0.869T_c$ or larger than $0.999T_c$, no crossover exists because of the positive value of D. However, it should be noted that one isotherm with a temperature falling between $0.869T_c$-$0.999T_c$ can possibly crossover with another isotherm with a temperature beyond the range of $0.869T_c$-$0.999T_c$. When the isobaric pressures are $10P_c$ and $100P_c$ respectively, we obtain wider ranges of temperatures that result in negative D, i.e., $0.814T_c$-$0.999T_c$ for $10P_c$ and $0.638T_c$-$0.999T_c$ for $100P_c$, respectively. For the other temperature-dependent volume translations with an exponential form proposed by Hong and Duan [19], similar conclusions can be made.

2.4.3. Temperature-Dependent Volume Translations Based on Distance Function

Several other researchers incorporated a density dependency, associated with the inverse of the isothermal compressibility, into the volume translation equation. Chou and Prausnitz [7] presented a phenomenological volume translation to the SRK EOS with a distance correction,

$$V^{\text{Corrected}} = V^{\text{CEOS}} - c - \frac{RT_c}{P_c}\left(\frac{1}{3} - Z_c\right)\left(\frac{0.35}{0.35 + d}\right) \tag{20}$$

where the distance function is given by,

$$d = \frac{1}{RT_c}\left(\frac{\partial P^{\mathrm{CEOS}}}{\partial \rho}\right)_T = \frac{1}{RT_c}\left(\frac{\partial P^{\mathrm{CEOS}}}{\partial\left(\frac{1}{V^{\mathrm{CEOS}}}\right)}\right)_T \tag{21}$$

where d is the distance function, c is the Peneloux volume translation [5], ρ is molar density, and Z_c is the experimental critical compressibility for a pure fluid.

We use the developed criterion to evaluate the crossover existence for the Chou and Prausnitz correlation [7]. With the Chou and Prausnitz correlation [7], Fig. 2.6 plots D as a function of T_r for CH_4 at different isobaric pressures. It can be observed that D is always positive over the temperature range of interest at different isobaric pressures, which indicates that no crossover phenomenon appears in the PV diagram over a wide range of temperatures and pressures, i.e., [T_{tp}, $3T_c$] and (0, $100P_c$]. Later, Ji and Lempe [8] proposed a new volume translation term with a modified distance function for the SRK EOS. Fig. 2.7 shows a 3D diagram that depicts the dependence of D on temperature and pressure with the volume translation proposed by Ji and Lempe [8]. Fig. 2.8 plots D as a function of T_r at different isobaric pressures, which are evaluated based on the Ji and Lempe [8] correlation. As shown in Fig. 2.8, at isobaric pressures up to $2P_c$, it is obviously observed that no crossover phenomenon occurs due to the positive values of D. Nonetheless, the crossover phenomenon appears in between $0.787T_c$-$0.983T_c$ for the pressure range of (0-$5P_c$]. When we continue to extend the range of pressures up to $10P_c$ and $100P_c$, respectively, the ranges of temperatures, over which crossing of any two isotherms occurs, are also expanded to $0.712T_c$-$0.993T_c$ and $0.476T_c$-$0.999T_c$, respectively.

On the basis of the proposed criterion, we have also examined other popular volume translation methods [18, 20]. Tables 3-6 list the detailed crossover analysis results on various volume translation methods for CH_4, CO_2, n-C_5H_{12} and n-$C_{10}H_{22}$, respectively. These tables include the maximum ranges of pressure $(0, P_m]$ over which there is certainly no crossing of two isotherms with temperatures falling between $[T_{tp}, 3T_c]$. It can be seen from these tables that some popular volume translation methods will cause crossover issues even at relatively low pressure/temperatures relevant to petroleum engineering or chemical engineering applications. For example, the Ji and Lempe [8] method begins to cause crossover of isotherms at a low pressure of $1.732P_c$ for CO_2, i.e., 12.777 MPa. Such relatively low pressure is frequently encountered in engineering applications, such as CO_2 enhanced oil recovery or CO_2 sequestration in depleted oil reservoirs. In addition, it is worthwhile noting that the crossover phenomenon could probably exist in the mixtures if there are isotherm crossings in the PV diagrams for the pure components.

2.5. Conclusions

In this work, we developed a criterion to judge whether the crossover phenomenon exists for a given volume-translated EOS based on a fundamental rule that the isobaric expansivity for a pure gas or liquid is positive. This criterion can be used to judge if one given volume-translated CEOS leads to crossover issues over a temperature range of $[T_{tp}, nT_c]$ and a pressure range of $(0, nP_c]$. We only need to apply the criterion once at nP_c over the temperature range of $[T_{tp}, nT_c]$ for such purpose. The criterion developed in this study can aid in developing more reliable volume translation methods that are guaranteed to not give rise to crossover issues, as well as avoid anomalous isobaric expansivity for pure compounds.

Based on this criterion, the widely used volume translation methods have been evaluated in terms of their thermodynamic consistency. It should be noted that not all temperature-dependent volume translation yields crossover phenomenon. For the most linear temperature-dependent volume translation corrections, there is no crossover phenomenon if the coefficient of temperature is negative. We find that there are crossover issues for most of the popular exponential-type volume translation methods [9, 19-20], and the crossover issue can appear at relatively low pressures. In comparison to the exponential-type volume translations, the volume translation methods based on the concept of distance correction, such as the methods proposed by Chou and Prausnitz [7] and Abudour *et al.* [18] tend to have wider temperature/pressure ranges over which no crossover issues appear.

References:

[1] D.Y. Peng, D.B. Robinson, A new two-constant equation of state, Ind. Eng. Chem. Fundam. 15 (1976) 59-64.

[2] G. Soave, Equilibrium constants from a modified Redlich–Kwong equation of state, Chem. Eng. Sci. 27 (1972) 1197-1203.

[3] G. Schmidt, H. Wenzel, A modified van der Waals type equation of state, Chem. Eng. Sci. 35 (1980) 1503-1512.

[4] J.J. Martin, Equations of state-Applied thermodynamics symposium, Ind. Eng. Chem. 59 (1967) 34-52.

[5] A. Peneloux, E. Rauzy, R. Freze, A consistent correction for Redlich–Kwong–Soave volumes, Fluid Phase Equilib. 8 (1982) 7-23.

[6] P.M. Mathias, T. Naheiri, E.M. Oh, A density correction for the Peng–Robinson equation of state, Fluid Phase Equilib. 47 (1989) 77-87.

[7] G.F. Chou, J.M. Prausnitz, A phenomenological correction to an equation of state for the critical region, AIChE J. 35 (1989) 1487-1496.

[8] W.R. Ji, D.A. Lempe, Density improvement of the SRK equation of state, Fluid Phase Equilib. 130 (1997) 49-63.

[9] K. Magoulas, D. Tassios, Thermophysical properties of n-alkanes from C1 to C20 and their prediction for higher ones, Fluid Phase Equilib. 56 (1990) 119-140.

[10] H.B. de Sant'Ana, P. Ungerer, J.C. de Hemptinne, Evaluation of an improved volume translation for the prediction of hydrocarbon volumetric properties, Fluid Phase Equilib. 154 (1999) 193-204.

[11] K.S. Pedersen, J. Milter, H. Sørensen, Cubic equations of state applied to HT/HP and highly aromatic fluids, SPE J. 9 (2004) 186-192.

[12] H. Baled, R.M. Enick, Y. Wu, M.A. McHugh, W. Burgess, D. Tapriyal, B.D. Morreale, Prediction of hydrocarbon densities at extreme conditions using volume-translated SRK and PR equations of state fit to high temperature, high pressure PVT data, Fluid Phase Equilib. 317 (2012) 65-76.

[13] O. Pfohl, Letter to the editor: "Evaluation of an improved volume translation for the prediction of hydrocarbon volumetric properties", Fluid Phase Equilib. 163 (1999) 157-159.

[14] P.H. Salim, M.A. Trebble, A modified Trebble-Bishnoi equation of state: thermodynamic consistency revisited, Fluid Phase Equilib. 65 (1991) 59-71.

[15] L.V. Yelash, T. Kraska, Volume-translated equations of state: Empirical approach and physical relevance, AIChE J. 49 (2003) 1569-1579.

[16] B. Hoyos, Generalized liquid volume shifts for the Peng-Robinson equation of state for C1 to C8 hydrocarbons, Latin Amer. Appl. Res. 34 (2004) 83-89.

[17] K. Frey, C. Augustine, R.P. Ciccolini, S. Paap, M. Modell, J. Tester, Volume translation in equations of state as a means of accurate property estimation, Fluid Phase Equilib. 260 (2007) 316-325.

[18] A.M. Abudour, S.A. Mohammad, R.L. Robinson, K.A.M. Gasem, Volume-translated Peng–Robinson equation of state for saturated and single-phase liquid densities, Fluid Phase Equilib. 335 (2012) 74-87.

[19] L. Hong, Y.Y. Duan, Empirical correction to the Peng–Robinson equation of state for the saturated region, Fluid Phase Equilib. 233 (2005) 194-203.

[20] M. Nazarzadeh, M. Moshfeghian, New volume translated PR equation of state for pure compounds and gas condensate systems, Fluid Phase Equilib. 337 (2013) 214-224.

[21] P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD, 20899, http://webbook.nist.gov.

[22] C.F. Spencer, R.P. Danner, Improved equation for prediction of saturated liquid density, J. Chem. Eng. Data. 17 (1972) 236-241.

[23] T.A. Mary, J.S.O. Evans, T. Vogt, A.W. Sleight, Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW2O8, Science. 272 (1996) 90.

Tables and Figures:

Table 2.1 Constants of the PR EOS and SRK EOS in Eq. (1)

EOS	u	w	Ω_a^0	Ω_b^0	m
PR[1]	2	-1	0.45724	0.07780	$0.37464+1.54226\omega-0.26992\omega^2$
SRK[2]	1	0	0.42748	0.08664	$0.480+1.574\omega-0.176\omega^2$

Table 2.2 Physical Properties of Pure Fluids Used in This Study

Compound	T_{tp} (K)	T_c (K)	P_c (MPa)	ω	z_c	z_{RA}	Reference
CH_4	90.71	190.56	4.5992	0.011	0.2863	0.2876	[21, 22]
CO_2	216.54	304.13	7.3773	0.22394	0.2746	0.2736	[21, 22]
n-C_5H_{12}	211.37	469.70	3.3700	0.251	0.2684	0.2685	[21, 22]
n-$C_{10}H_{22}$	339.74	617.70	2.1030	0.488	0.2501	0.2503	[21, 22]

Table 2.3 Range of Reduced Temperature over Which Crossover Occurs at Different Isobaric Pressures for CH_4

Reference	**Reduced Temperature**				P_m*
	$2P_c$	$5P_c$	$10P_c$	$100P_c$	
Peneloux *et al.* [5]	No	No	No	No	No
Chou and Prausnitz [7]	No	No	No	No	$2111.931P_c$
Ji and Lempe [8]	No	0.787-0.983	0.712- 0.993	0.476-0.999	$2.399P_c$
Magoulas and Tassios [9]	No	0.869-0.999	0.814-0.999	0.638-0.999	$2.077P_c$
De Sant'Ana *et al.* [10]	No	No	No	0.476-0.524	$98.166P_c$
Pedersen *et al.* [11]	No	No	No	No	No
Baled *et al.* [12]	No	No	No	No	No
Abudour *et al.* [18]	No	No	No	No	$2333.536P_c$
Hong and Duan [19]	0.987-0.999	0.879-0.999	0.831-0.999	0.676-0.999	$1.931P_c$
Nazarzadeh and Moshfeghian [20]	No	0.876-0.999	0.825-0.999	0.668-0.999	$2.012P_c$

*Note: P_m is the maximum pressure below which there is no crossover in the PV diagram over the temperature range of [T_{tp}, $3T_c$].

Table 2.4 Range of Reduced Temperature over Which Crossover Occurs at Different Isobaric Pressures for CO_2

Reference	Reduced Temperature				
	$2P_c$	$5P_c$	$10P_c$	$100P_c$	P_m^*
Peneloux *et al.* [5]	No	No	No	No	No
Chou and Prausnitz [7]	No	No	No	No	$3407.528P_c$
Ji and Lempe [8]	0.947-0.998	0.854-0.999	0.782- 0.999	0.712-0.999	$1.732P_c$
Magoulas and Tassios [9]	0.968-0.999	0.899-0.999	0.864-0.999	0.746-0.999	$1.722P_c$
De Sant'Ana *et al.* [10]	No	No	No	No	No
Pedersen *et al.* [11]	No	No	No	No	No
Baled *et al.* [12]	No	No	No	No	No
Abudour *et al.* [18]	No	No	No	No	$3774.546P_c$
Hong and Duan [19]	0.960-0.999	0.894-0.999	0.858-0.999	0.739-0.999	$1.682P_c$
Nazarzadeh and Moshfeghian [20]	0.964-0.999	0.886-0.999	0.847-0.999	0.723-0.999	$1.781P_c$

*Note: P_m is the maximum pressure below which there is no crossover in the PV diagram over the temperature range of [T_{tp}, $3T_c$].

Table 2.5 Range of Reduced Temperature over Which Crossover Occurs at Different Isobaric Pressures for *n*-C_5H_{12}

Reference	Reduced Temperature				
	$2P_c$	$5P_c$	$10P_c$	$100P_c$	P_m^*
Peneloux *et al.* [5]	No	No	No	No	No
Chou and Prausnitz [7]	No	No	No	No	$5297.625P_c$
Ji and Lempe [8]	No	No	No	0.450-0.999	$1.405P_c$
Magoulas and Tassios [9]	0.952-0.999	0.893-0.999	0.859-0.999	0.747-0.999	$1.592P_c$
De Sant'Ana *et al.* [10]	No	No	No	No	No
Pedersen *et al.* [11]	No	No	No	No	No
Baled *et al.* [12]	No	No	No	No	No
Abudour *et al.* [18]	No	No	No	No	$5873.90P_c$
Hong and Duan [19]	0.949-0.999	0.891-0.999	0.858-0.999	0.747-0.999	$1.560P_c$
Nazarzadeh and Moshfeghian [20]	0.953-0.999	0.887-0.999	0.852-0.999	0.738-0.999	$1.661P_c$

*Note: P_m is the maximum pressure below which there is no crossover in the PV diagram over the temperature range of [T_{tp}, $3T_c$].

Table 2.6 Range of Reduced Temperature over Which Crossover Occurs at Different Isobaric Pressures for *n*-$C_{10}H_{22}$

Reference	Reduced Temperature				P_m*
	$2P_c$	$5P_c$	$10P_c$	$100P_c$	
Peneloux *et al.* [5]	No	No	No	No	No
Chou and Prausnitz [7]	No	No	No	No	$6979.677P_c$
Ji and Lempe [8]	0.957-0.999	0.888-0.999	0.797-0.999	0.450-0.999	$1.100P_c$
Magoulas and Tassios [9]	0.942-0.999	0.904-0.999	0.881-0.999	0.797-0.999	$1.331P_c$
De Sant'Ana *et al.* [10]	No	No	No	No	No
Pedersen *et al.* [11]	No	No	No	No	No
Baled *et al.* [12]	No	No	No	No	No
Abudour *et al.* [18]	No	No	No	No	$7743.866P_c$
Hong and Duan [19]	0.940-0.999	0.901-0.999	0.876-0.999	0.789-0.999	$1.354P_c$
Nazarzadeh and Moshfeghian [20]	0.933-0.999	0.882-0.999	0.852-0.999	0.750-0.999	$1.502P_c$

*Note: P_m is the maximum pressure below which there is no crossover in the PV diagram over the temperature range of [T_{tp}, $3T_c$].

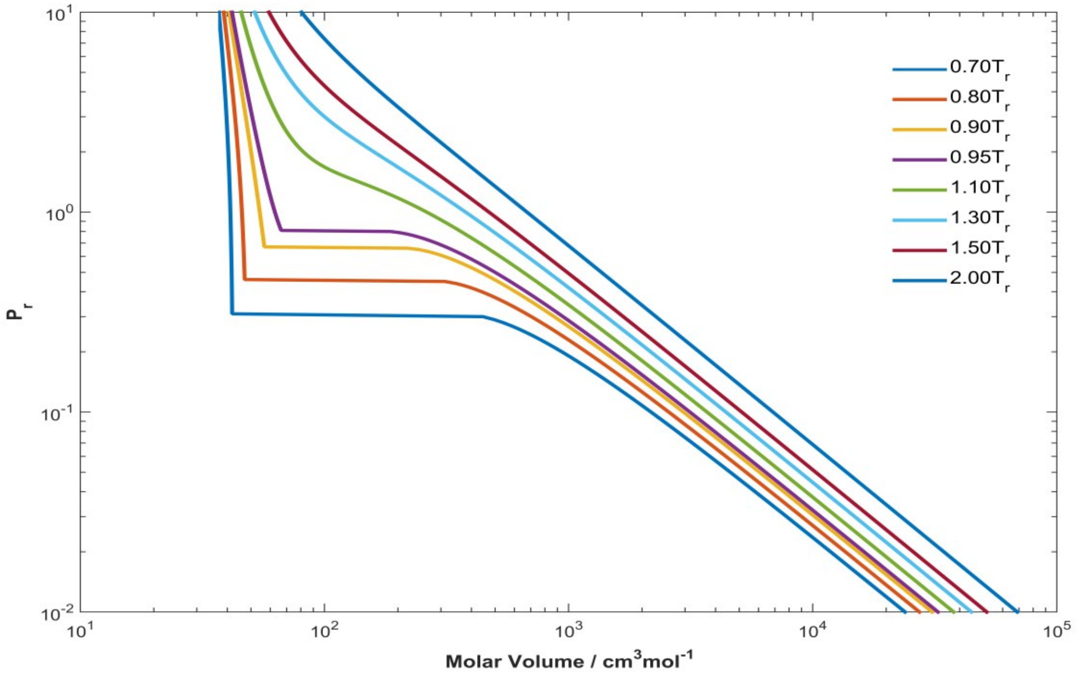


Fig.2.1 PV diagram for CH_4 calculated by SRK EOS

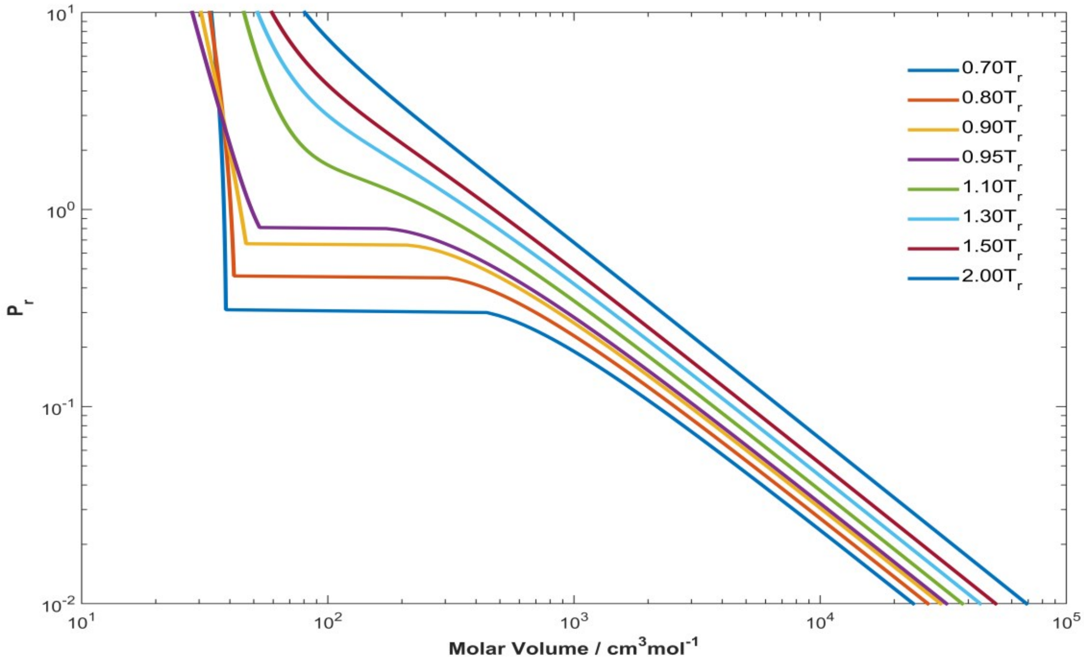


Fig.2.2 PV diagram for CH_4 calculated by SRK EOS with the temperature-dependent volume translation proposed by Ji and Lempe

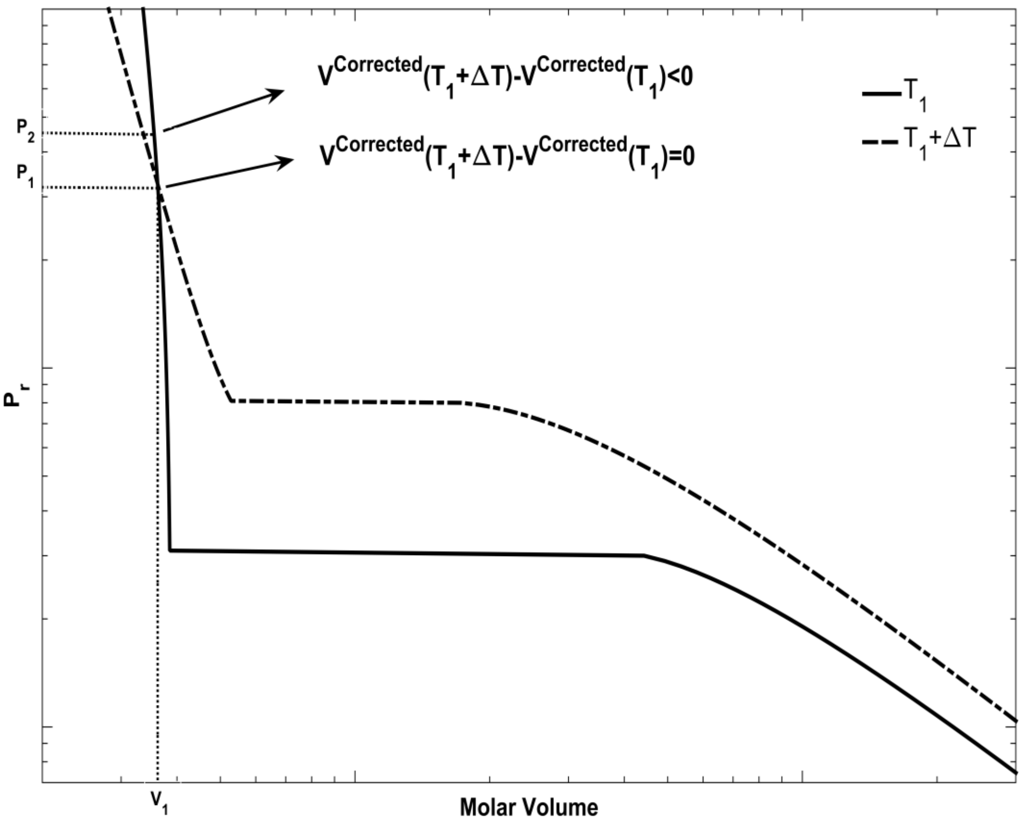
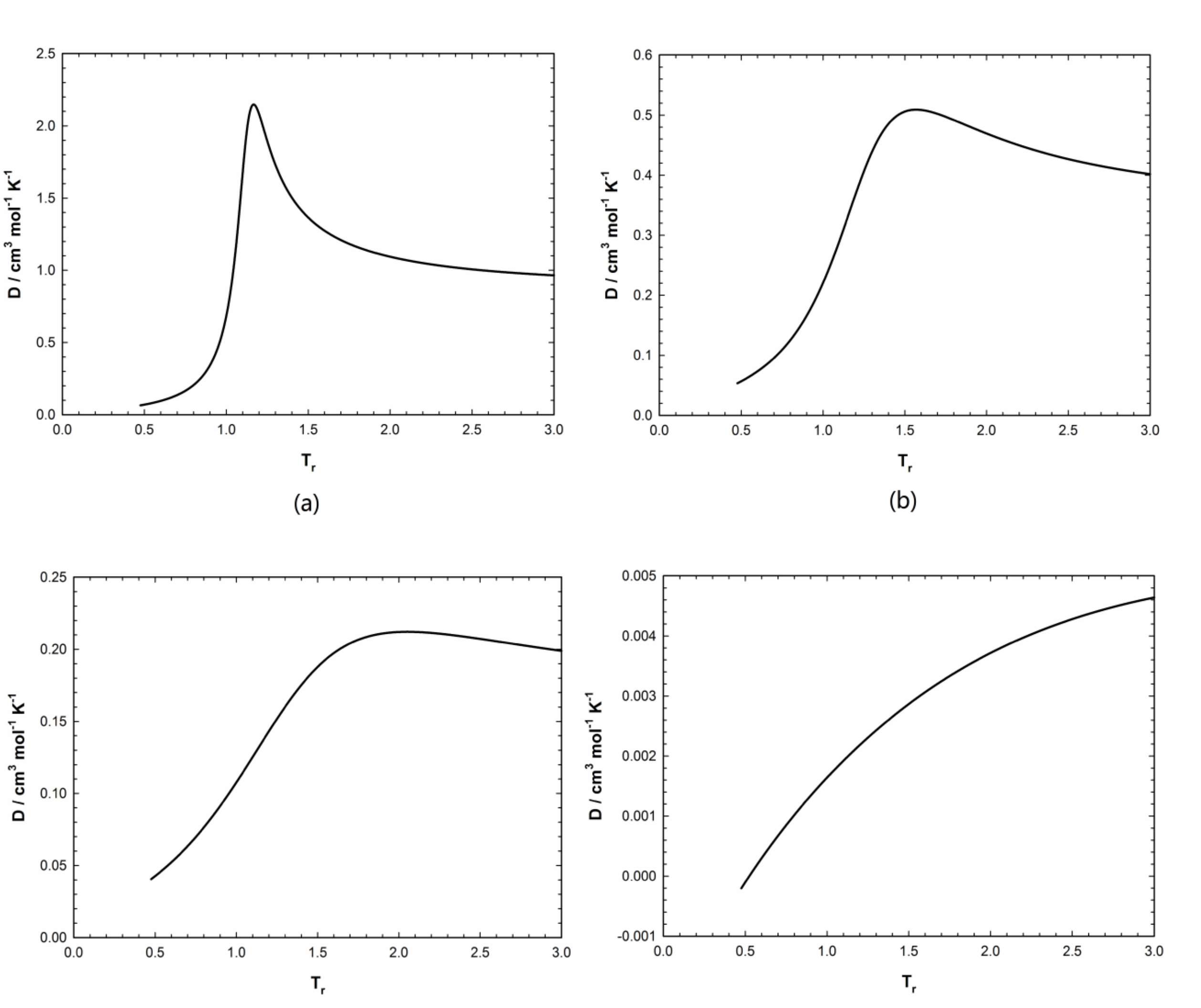
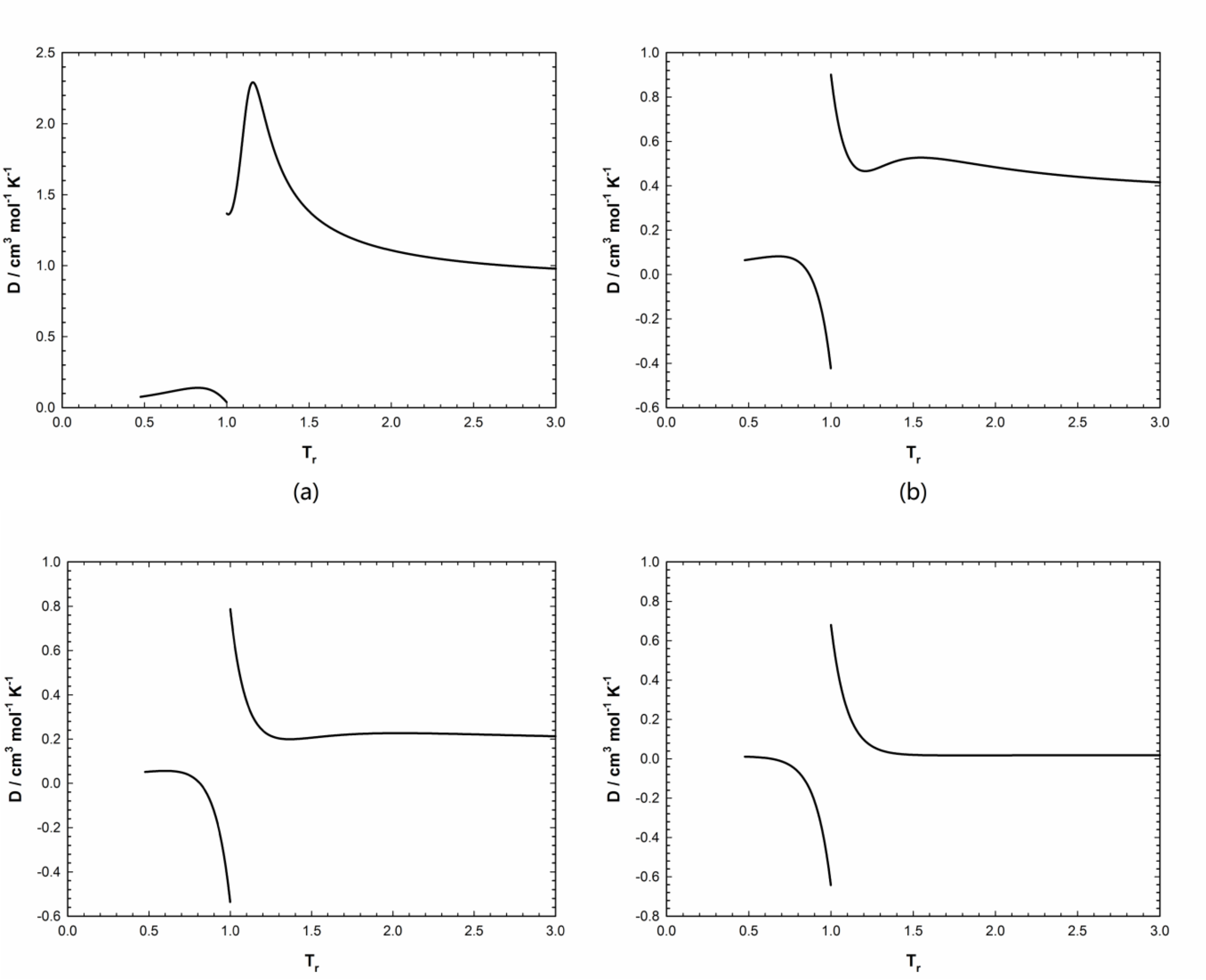


Fig.2.3 Schematic showing the nature of crossover of two neighboring isotherms



(a) (b) (c) (d)

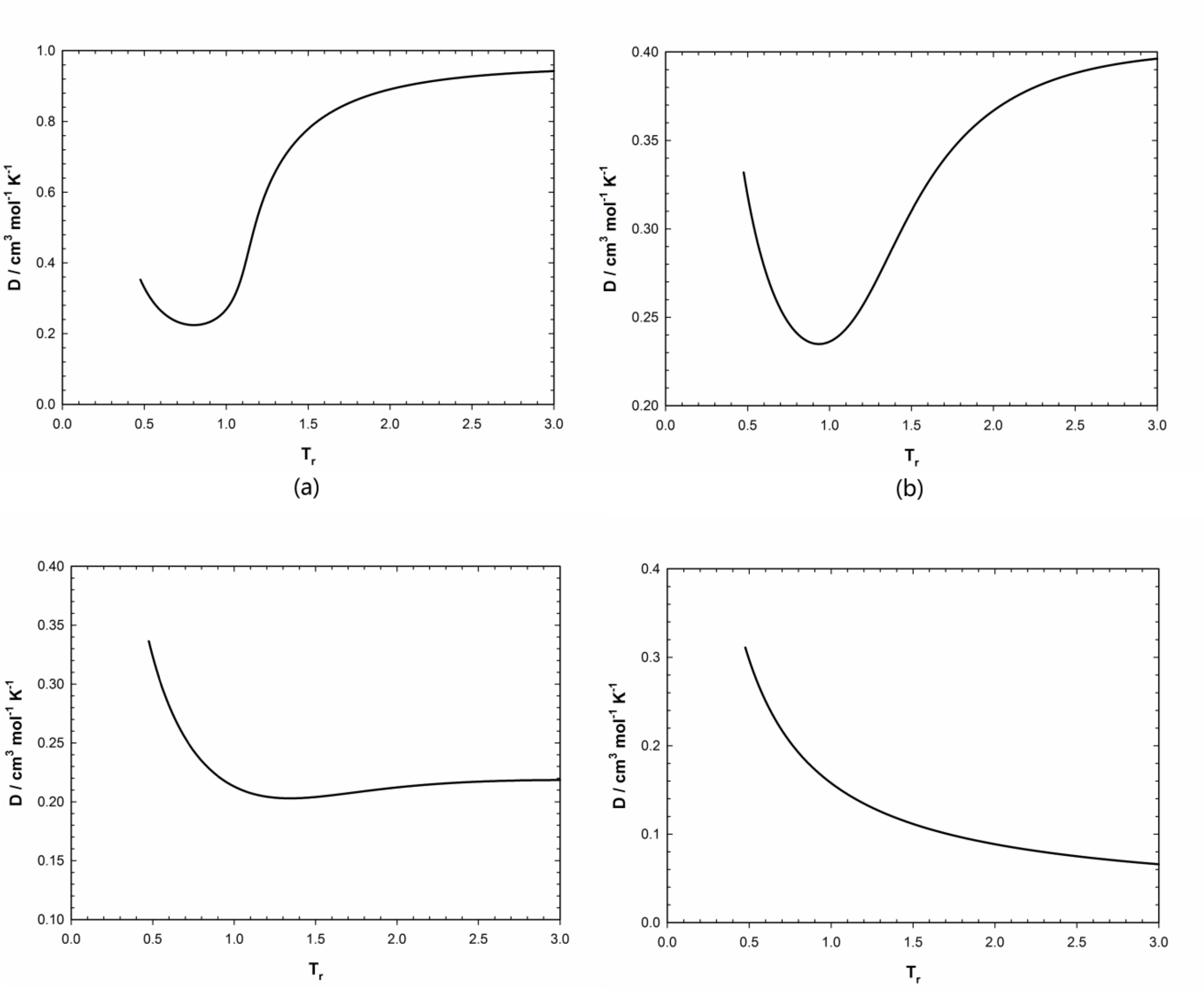
Fig.2.4 Relationship between the first derivative of corrected molar volume with respect to temperature (*D*) and reduced temperature (T_r) for the volume translation proposed by De Sant'Ana *et al.* [10] for CH_4 at different constant pressures of: (a) $2P_c$; (b) $5P_c$; (c) $10P_c$; and (d) $100P_c$



(a) (b)

(c) (d)

Fig.2.5 Relationship between the first derivative of corrected molar volume with respect to temperature (*D*) and reduced temperature (*T*r) for the volume translation proposed by Magoulas and Tassios [9] for CH4 at different constant pressures of: (a) 2*P*c; (b) 5*P*c; (c) 10*P*c; and (d) 100*P*c



(a) (b)

(c) (d)

Fig.2.6 Relationship between the first derivative of corrected molar volume with respect to temperature (*D*) and reduced temperature (T_r) for the volume translation proposed by Chou and Prausnitz [7] for CH_4 at different constant pressures of: (a) $2P_c$; (b) $5P_c$; (c) $10P_c$; and (d) $100P_c$

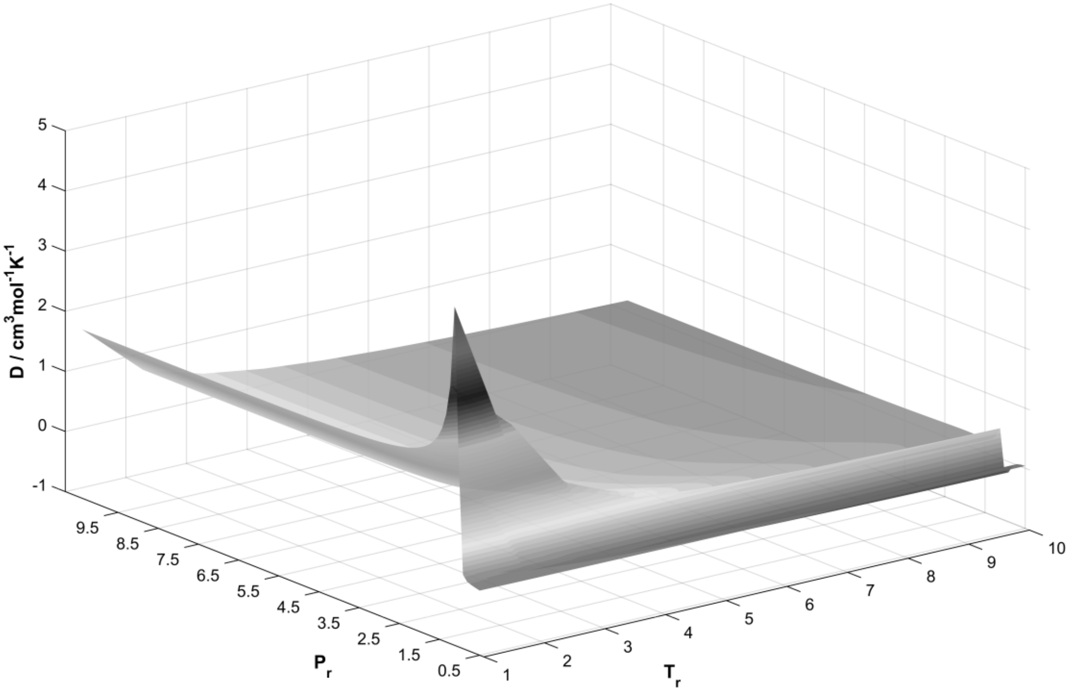
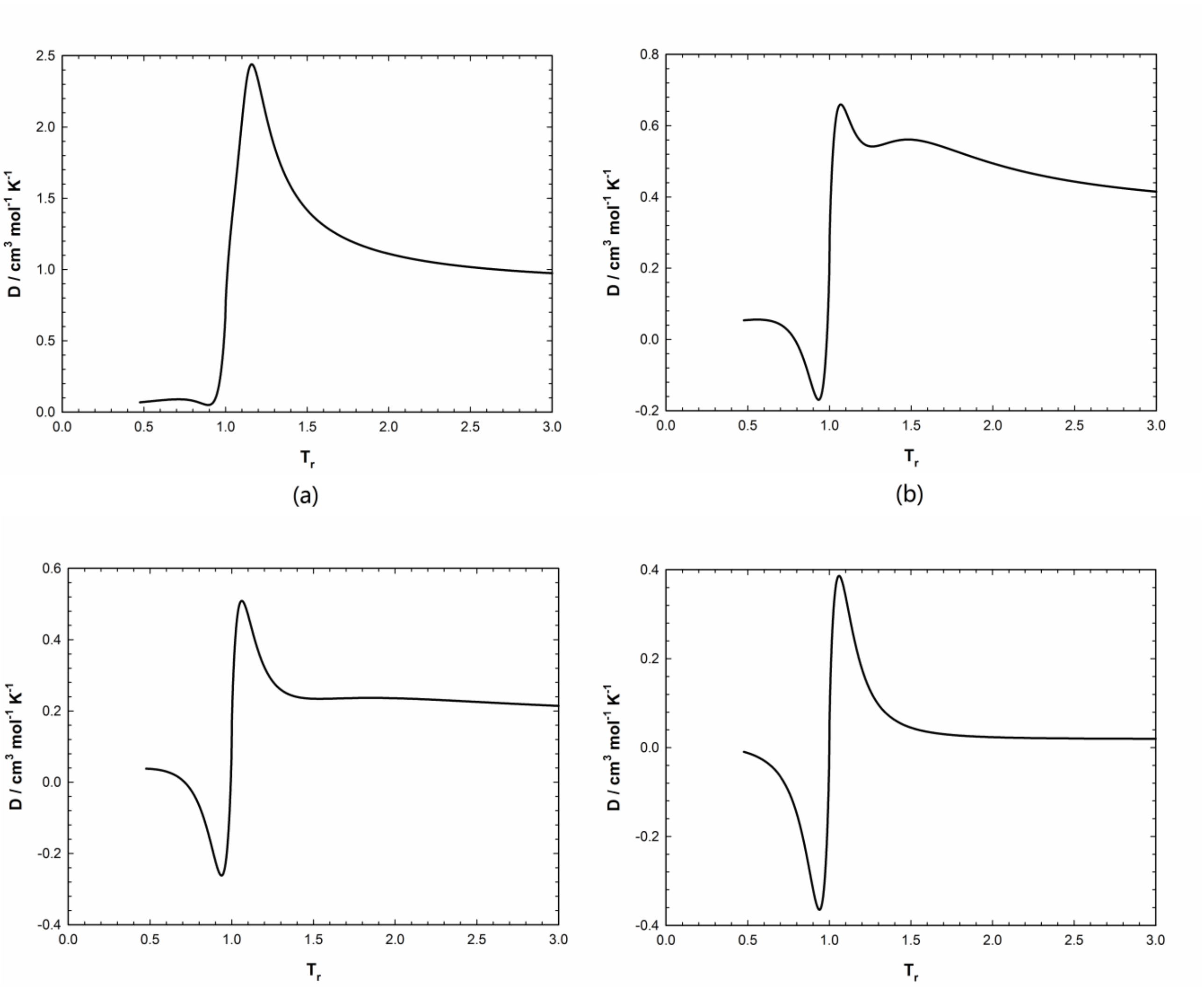


Fig.2.7 3D diagram showing the dependence of *D* on *T*$_r$ and *P*$_r$ for CH$_4$ with the volume translation proposed by Ji and Lempe [8]



(a) (b) (c) (d)

Fig.2.8 Relationship between the first derivative of corrected molar volume with respect to temperature (*D*) and reduced temperature (T_r) for the volume translation proposed by Ji and Lempe [8] for CH_4 at different constant pressures of: (a) $2P_c$; (b) $5P_c$; (c) $10P_c$; and (d) $100P_c$

Appendix A. Derivatives of Compressibility Factor With Respect to Temperature for SRK EOS and PR EOS

SRK equation of state is given by [2],

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + bV} \tag{A.1}$$

Letting,

$$V = \frac{ZRT}{P} \tag{A.2}$$

$$A = a\frac{P}{R^2T^2} = a_c\alpha\frac{P}{R^2T^2} \tag{A.3}$$

$$B = b\frac{P}{RT} \tag{A.4}$$

Eq.(A.1) can be written as,

$$F = Z^3 - Z^2 + Z\left(A - B - B^2\right) - AB = 0 \tag{A.5}$$

$$\frac{\partial F}{\partial Z} = 3Z^2 - 2Z + (A - B - B^2) \tag{A.6}$$

$$\frac{\partial F}{\partial A} = Z - B \tag{A.7}$$

$$\frac{\partial F}{\partial B} = -(1 + 2B)Z - A \tag{A.8}$$

Since pressure is constant, we can obtain the following equation,

$$\frac{\partial F}{\partial T}=\frac{\partial Z}{\partial T}\frac{\partial F}{\partial Z}+\frac{\partial F}{\partial A}\frac{\partial A}{\partial T}+\frac{\partial F}{\partial B}\frac{\partial B}{\partial T}=0 \tag{A.9}$$

Thus, the first derivative of compressibility factor with respect to temperature for SRK EOS can be obtained,

$$\frac{\partial Z}{\partial T}=-\frac{\frac{\partial F}{\partial A}\frac{\partial A}{\partial T}+\frac{\partial F}{\partial B}\frac{\partial B}{\partial T}}{\frac{\partial F}{\partial Z}} \tag{A.10}$$

Also,

$$\frac{\partial A}{\partial T}=\frac{\alpha'(T)\cdot R^2\cdot T^2-\alpha(T)\cdot R^2\cdot 2T}{R^4T^4}a_{\mathrm{c}}P \tag{A.11}$$

$$\frac{\partial B}{\partial T}=-b\frac{P}{RT^2} \tag{A.12}$$

Substituting the above equation into Eq. (A.10), we can obtain,

$$\frac{\partial Z}{\partial T}=-\frac{(Z-B)\frac{\alpha'(T)R^2T^2-\alpha(T)R^2 2T}{R^4T^4}a_{\mathrm{c}}P+\left(-Z-2BZ-A\right)\left(-\frac{bP}{RT^2}\right)}{3Z^2-2Z+A-B-B^2} \tag{A.13}$$

PR equation of state can be written as below [1],

$$F=Z^3-\left(1-B\right)Z^2+\left(A-2B-3B^2\right)Z-\left(AB-B^2-B^3\right)=0 \tag{A.14}$$

$$\frac{\partial F}{\partial Z}=3Z^2-2Z(1-B)+(A-3B^2-2B) \tag{A.15}$$

$$\frac{\partial F}{\partial A} = Z - B \tag{A.16}$$

$$\frac{\partial F}{\partial B} = Z^2 - 6BZ - 2Z - A + 2B + 3B^2 \tag{A.17}$$

$$\frac{\partial Z}{\partial T} = -\frac{\dfrac{\partial F}{\partial A}\dfrac{\partial A}{\partial T} + \dfrac{\partial F}{\partial B}\dfrac{\partial B}{\partial T}}{\dfrac{\partial F}{\partial Z}} \tag{A.18}$$

$$\frac{\partial A}{\partial T} = \frac{\alpha'\left(T\right)R^2T^2 - \alpha\left(T\right)R^2 2T}{R^4T^4} a_{\mathrm{c}}P \tag{A.19}$$

$$\frac{\partial B}{\partial T} = -b\frac{P}{RT^2} \tag{A.20}$$

The first derivative of compressibility factor with respect to temperature for PR EOS can be obtained,

$$\frac{\partial Z}{\partial T} = -\frac{(Z-B)\dfrac{\alpha'\left(T\right)R^2T^2 - \alpha\left(T\right)R^2 2T}{R^4T^4} a_{\mathrm{c}}P + \left(Z^2 - 6BZ - 2Z - A + 2B + 3B^2\right)\left(-\dfrac{bP}{RT^2}\right)}{3Z^2 - 2Z + 2ZB + A - 3B^2 - 2B}$$

(A.21)

Appendix B. Derivatives of the Corrected Molar Volume With Respect to Temperature (*D*)

Linear Temperature-Dependent Volume Translation. The volume translation with PR EOS proposed by Baled *et al.* [12] is given as,

$$c(T) = A + BT_\mathrm{r} \tag{B.1}$$

where *A* and *B*are functions of molecular weight, *M*, and acentric factor, ω, as shown below,

$$A,B = f(M,\omega) = k_0 + k_1 \exp\left(\frac{-1}{k_2 M\omega}\right) + k_3 \exp\left(\frac{-1}{k_4 M\omega}\right) + k_5 \exp\left(\frac{-1}{k_6 M\omega}\right) \tag{B.2}$$

wherek_0 through k_6 are constants. Thus, the first derivative of this volume translation with respect to temperaturecan be derived as,

$$\frac{\partial\left[c(T)\right]}{\partial T} = \frac{B}{T_\mathrm{c}} \tag{B.3}$$

Exponential-Type Volume Translation. The volume translation in PR EOS proposed by Magoulas and Tassios [9] is given as,

$$c(T) = c_0 + \left[\frac{RT_\mathrm{c}}{P_\mathrm{c}}(Z_\mathrm{c}^\mathrm{PR} - Z_\mathrm{c}) - c_0\right]\exp(\beta\left|1 - T_\mathrm{r}\right|) \tag{B.4}$$

where the expressions of c_0 and β are described by,

$$c_0 = \frac{RT_\mathrm{c}}{P_c}(k_0 + k_1\omega + k_2\omega^2 + k_3\omega^3 + k_4\omega^4) \tag{B.5}$$

$$\beta = l_0 + l_1\omega \tag{B.6}$$

where k_0 through k_4 as well as l_0 and l_1 are correction parameters for PR EOS respectively. In addition, the alpha function in Eq. (2) is given as,

$$\alpha = d_0 + d_1\omega + d_2\omega^2 + d_3\omega^3 + d_4\omega^4 \tag{B.7}$$

where d_0 through d_4 are constants.

Thus, the first derivative of this volume translation with respect to temperature can be written as follows,

when $T_\mathrm{r} \le 1$,

$$\frac{\partial\left[c(T)\right]}{\partial T} = -\frac{\beta}{T_\mathrm{c}}\left[\frac{RT_\mathrm{c}}{P_\mathrm{c}}(Z_\mathrm{c}^\mathrm{PR} - Z_\mathrm{c}) - c_0\right]\exp\left[\beta\left(1 - T_\mathrm{r}\right)\right] \tag{B.8}$$

when $T_\mathrm{r} > 1$,

$$\frac{\partial\left[c(T)\right]}{\partial T} = \frac{\beta}{T_\mathrm{c}}\left[\frac{RT_\mathrm{c}}{P_\mathrm{c}}(Z_\mathrm{c}^\mathrm{PR} - Z_\mathrm{c}) - c_0\right]\exp\left[\beta\left(T_\mathrm{r} - 1\right)\right] \tag{B.9}$$

Volume Translation with a Distance Function. The volume translation with PR EOS proposed by Abudour*et al.* [18] is given as,

$$c(T) = -\left(\frac{RT_\mathrm{c}}{P_\mathrm{c}}\right)\left[c_1 - \left(0.004 + c_1\right)\exp\left(-2d\right)\right] + \left(\frac{RT_\mathrm{c}}{P_\mathrm{c}}\right)\left(Z_\mathrm{c}^\mathrm{PR} - Z_\mathrm{c}\right)\left(\frac{0.35}{0.35 + d}\right) \tag{B.10}$$

where c_1 is a fluid-dependent parameter (e.g., c_1 has a value of 0.00652 for CO_2), $Z_{\mathrm{c}}^{\mathrm{PR}}$ is the critical compressibility factor given by PR EOS (0.3074), Z_c is the experimental critical compressibility factor and d is the dimensionless distance function described by,

$$d = \frac{1}{RT_{\mathrm{c}}}\left(\frac{\partial P^{\mathrm{PR}}}{\partial \rho}\right)_{\mathrm{T}} \tag{B.11}$$

It should be noted that the alpha function in Eq. (2) is calculated with the following expression [18],

$$\alpha = \exp\left[\left(A + BT_{\mathrm{r}}\right)\left(1 - T_{\mathrm{r}}^{\mathrm{C+D\omega+E\omega^2}}\right)\right] \tag{B.12}$$

where ω is the acentric factor, A through E are correction parameters. Thus, the first derivative of this volume translation with respect to temperature can be written as follows,

$$\frac{\partial\left[c(T)\right]}{\partial T} = -2\left(\frac{RT_{\mathrm{c}}}{P_{\mathrm{c}}}\right)\left(0.004 + c_1\right)\left(\frac{\partial d}{\partial T}\right)_{\mathrm{p}} \exp\left(-2d\right) - \left(\frac{RT_{\mathrm{c}}}{P_{\mathrm{c}}}\right)\left(Z_{\mathrm{c}}^{\mathrm{PR}} - Z_{\mathrm{c}}^{\mathrm{exp}}\right)\left[\frac{0.35}{\left(0.35 + d\right)^2}\right]\left(\frac{\partial d}{\partial T}\right)_{\mathrm{p}} \tag{B.13}$$

where the first derivative of d with respect to temperature can be obtained based on the derivation below. According to the real gas law, d can be written as follows,

$$d = \frac{-V^2}{RT_{\mathrm{c}}}\left[\frac{\partial P}{\partial\left(\frac{ZRT}{P}\right)}\right]_{\mathrm{T}} = -\frac{Z^2 T}{T_{\mathrm{c}}\left[P\left(\frac{\partial Z}{\partial P}\right)_{\mathrm{T}} - Z\right]} \tag{B.14}$$

Thus, the first derivative of d with respect to temperature can be obtained,

$$\left(\frac{\partial d}{\partial T}\right)_{\mathrm{P}} = -\frac{\left[2ZT\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{p}} + Z^2\right]\left[P\left(\frac{\partial Z}{\partial P}\right)_{\mathrm{T}} - Z\right] - Z^2T\left[P\frac{\partial\left[\left(\frac{\partial Z}{\partial P}\right)_{\mathrm{T}}\right]}{\partial T} - \frac{\partial Z}{\partial T}\right]}{T_{\mathrm{c}}\left[P\left(\frac{\partial Z}{\partial P}\right)_{\mathrm{T}} - Z\right]^2} \tag{B.15}$$

where the value of $\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{p}}$ can be assessed according to Eq. (A.21), while the terms of $\frac{\partial Z}{\partial P}$ and $\frac{\partial\left[\left(\frac{\partial Z}{\partial P}\right)_{\mathrm{T}}\right]}{\partial T}$ can be obtained based on the following derivations. According to Eq. (A.14), the first derivative of the compressibility factor with respect to pressure can be obtained as follows,

$$\left(\frac{\partial Z}{\partial P}\right)_{\mathrm{T}} = -\frac{a\left(Z-B\right) + bRT\left(Z^2 - 2Z - 6ZB - A + 2B + 3B^2\right)}{R^2T^2\left(3Z^2 - 2Z + 2ZB + A - 3B^2 - 2B\right)} \tag{B.16}$$

Subsequently, the first derivative of $\frac{\partial Z}{\partial P}$ with respect to temperature can be given as,

$$\frac{\partial\left[\left(\frac{\partial Z}{\partial P}\right)_{\mathrm{T}}\right]}{\partial T} = -\frac{aRT\left[\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{p}} - \frac{\partial B}{\partial T}\right] + \left(Z-B\right)a_{\mathrm{c}}\left[\alpha'\left(T\right)RT - 2\alpha\left(T\right)R\right]}{R^3T^3\left(3Z^2 - 2Z + 2ZB + A - 3B^2 - 2B\right)}$$

$$
-\frac{\left[bRT\left(2Z\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{p}}-2\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{p}}-6B\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{p}}-6Z\frac{\partial B}{\partial T}-\frac{\partial A}{\partial T}+2\frac{\partial B}{\partial T}+6B\frac{\partial B}{\partial T}\right)-bR\left(Z^2-2Z-6ZB-A+2B+3B^2\right)\right]}{R^2T^2\left(3Z^2-2Z+2ZB+A-3B^2-2B\right)}
$$

$$
+\frac{\left[a\left(Z-B\right)+bRT\left(Z^2-2Z-6ZB-A+2B+3B^2\right)\right]\left[\left(6Z-2+2B\right)\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{p}}+\left(2Z-2-6B\right)\frac{\partial B}{\partial T}+\frac{\partial A}{\partial T}\right]}{R^2T^2\left(3Z^2-2Z+2ZB+A-3B^2-2B\right)^2}
$$

(B.17)

where the first derivative of alpha function with respect to temperature is given by,

$$
\alpha'\left(T\right)=\left[\frac{B}{T_{\mathrm{c}}}-\frac{A\left(C+D\omega+E\omega^2\right)\left(T^{\mathrm{C+D\omega+E\omega^2\,-1}}\right)}{T_{\mathrm{c}}^{\mathrm{C+D\omega+E\omega^2}}}-\frac{B\left(1+C+D\omega+E\omega^2\right)\left(T^{\mathrm{C+D\omega+E\omega^2}}\right)}{T_{\mathrm{c}}^{\mathrm{1+C+D\omega+E\omega^2}}}\right]
$$

$$
\cdot\exp\left[\left(A+BT_{\mathrm{r}}\right)\left(1-T_{\mathrm{r}}^{\mathrm{C+D\omega+E\omega^2}}\right)\right] \qquad \text{(B.18)}
$$

CHAPTER 3 A GENERALIZED VOLUME TRANSLATION CORRELATION WITH THERMODYNAMIC CONSISTENCY FOR MORE ACCURATE LIQUID-DENSITY PREDICTION FOR PURE COMPONENTS

A version of this chapter will be submitted to *Fluid Phase Equilibria*.

Abstract

For the most nonlinear temperature-dependent volume translation techniques, there is a crossing of isotherms in the pressure-volume (PV) diagram, which leads to thermodynamic inconsistency and restricts the range of applications of the volume translated equation of state (EOS). In this work, a generalized consistent temperature-dependent volume translation model is developed to achieve more accurate prediction of the liquid densities of pure components. Based on a criterion we have derived in a prior work, a mathematical constraint is applied when the model parameters are being regressed to match the measured density data; by adopting this criterion, we ensure that that no any crossover phenomenon exists for the new volume translation model over a wide range of pressure and temperature (up to 100 MPa and 1000 K). The model parameters are determined based on the regression of the density data of 16 compounds. The new volume-translated PR EOS leads to improved liquid density prediction with an overall 1.42% absolute average percentage deviation.

Keywords: Volume translation, PR EOS, Thermodynamic consistency, Crossing of isotherms

3.1. Introduction

The relationship between the pressure, molar volume and temperature (PVT) for pure fluids or mixtures is one of most fundamental and important relationships that are used for phase behavior modeling and thermodynamic computations. Since the appearance of van der Waals equation in 1873, cubic equations of state (CEOS) such as Soave-Redlich-Kwong EOS (SRK EOS) [1] and Peng-Robinson EOS(PR EOS) [2] have been widely applied in the industry for modeling compositional and volumetric phase behavior over the past 100 years because of their simplicity and reliability. Taking methane as an example, however, the predicted molar volume by PR EOS differs considerably from the experimental value especially near the critical region, as presented in the Figs.3.1 and 3.2. Fig. 3.1 shows the molar volume residuals (defined as the difference between the measured molar volume and that calculated by PR EOS) for methane (P_c=4.599 MPa) when the pressure is 3.5 MPa, while Fig.3.2 presents the molar volume residuals for methane when the pressure is 5 MPa. It should be noted that the practically needed volume shift is not continuous because of the existence of the saturation pressure when the pressure is lower than the critical pressure. Likewise, Frey *et al.* [3] presented a similar overall tendency of molar volume residuals for propane. It is evident that the existing two-parameter EOSs such as SRK and PR EOS cannot accurately predict molar volumes, especially near the critical region.

One key reason for the above deficiency in CEOS is due to the inaccurate value of the critical compressibility factor used in the conventional two-parameter CEOS. It is noted that the critical compressibility factor $Z_{c,CEOS}$ is a constant for SRK EOS and PR EOS; the critical compressibility factors in SRK EOS and PR EOS are 0.3333 and 0.3074, respectively. One improvement in PR EOS is that it uses a slightly lower critical compressibility factor, which is closer to the experimental values for most hydrocarbons. In practice, however, the actual values of Z_c should vary from one component to another.

To address such limitation of two-parameter EOS, constant volume translations proposed by Peneloux *et al.* [4] and Jhaveri and Youngren [5] were introduced into the cubic EOS based on the justification that the needed correction for molar volume is nearly constant up to a reduced temperature of 0.75. Recently, Le Guennec *et al.* [6] presented a constant volume translation correlation that has been developed based on the experimental saturated-liquid density data at a reduced temperature of 0.8, which indeed improves the prediction of the volumetric, saturation and the other thermodynamic properties. However, as shown in Figs. 3.1 and 3.2, the performance of the constant volume translation models is compromised near the critical region. Some researchers focus on the development of the temperature-dependent volume translations to accommodate the effect of the temperature on the molar volume. Generally, for the most temperature-dependent models, there are three types of mathematical schemes: 1) linear temperature-dependent volume translations [9-11], 2) exponential-type temperature-dependent volume translations [12-18], and 3) temperature-dependent volume translations based on distance functions [17, 19-21]. In terms of the accuracy of density prediction, the exponential-type models and models with a distance function have a better performance than the linear temperature-dependent volume shift because these models can fit the overall tendency of the needed correction in molar volume. It should be noted that some temperature-dependent volume translation models [7, 8] are developed to improve the density prediction at subcritical conditions, and cannot be applied to the density prediction at supercritical conditions. Such deficiency limits the wide application of these models in the industry.

In volume translation techniques, however, apart from the prediction accuracy of thermodynamic properties, thermodynamic consistency is also an important factor to judge if the proposed model is reliable [22, 23]. For the constant volume translations or linear temperature-dependent volume translations with a negative coefficient of temperature, there is no any crossing of isotherms in the PV diagram [23]. Nonetheless, a crossover usually occurs between two isotherms (below than critical temperature) in the PV diagram at a relatively lower pressure (below than 2 P_c) for the most nonlinear temperature-dependent volume translations. The crossing of isotherms in the PV diagram means that the predicted molar volume is lower at a higher temperature under isobaric conditions, which violates a fundamental assumption of thermodynamics. In addition, such thermodynamically inconsistent phenomenon leads to negative values of several thermodynamic properties: isobaric thermal expansivity, speed of sound and heat capacity, which restricts the application range of the temperature-dependent volume translation models and makes the proposed models unreliable.

Recently, several authors presented some temperature/pressure-dependent volume translations to improve the prediction of molar volume considering that different levels of corrections are needed at different isobaric conditions [24, 25]. These volume translation methods may indeed provide more accurate density predictions than other constant and temperature-dependent volume translations. However, it should be noted that these pressure/temperature-dependent volume translations can lead to the alteration of vapor pressure and phase equilibrium, making them deviate much from the experimental data. The purpose of this work is to develop an improved volume translation model that cannot only achieve a higher accuracy in the density prediction but also avoid the crossing of isotherms over a wide range of temperature and pressure.

3.2. Concept of the Volume Translated EOS

To improve the prediction of liquid molar volumes, the following volume translation was introduced into the original PR EOS [4],

$$c(T) = V^{\text{CEOS}} - V^{\text{Corrected}} \tag{1}$$

where $c(T)$ is the volume translation, $V^{\text{Corrected}}$ is the corrected molar volume, and V^{CEOS} is the original molar volume calculated by the cubic EOS model. Fig.3.3 shows a sketch illustrating the impact of a constant or temperature-dependent volume translation on the calculated pressure/volume isotherms. As shown in Fig. 3.3, after the temperature-dependent volume translation has been applied, the predicted molar volume is translated along the molar volume coordinate without causing any changes in the phase equilibrium calculations for each isotherm.

Substituting V^{CEOS} with $V^{\text{Corrected}}$ in the original PR EOS, the following volume translated PR EOS can be obtained,

$$P = \frac{RT}{V+c-b} - \frac{a}{(V+c)(V+c+b)+b(V+c-b)} \tag{2}$$

where

$$a = a_{\text{c}}\alpha \tag{3}$$

$$a_{\text{c}} = \Omega_{\text{a}}^{0}\frac{R^2T_{\text{c}}^{2}}{p_{\text{c}}} \tag{4}$$

$$b = \Omega_{\text{b}}^{0}\frac{RT_{\text{c}}}{p_{\text{c}}} \tag{5}$$

where P is pressure, T is temperature, V is molar volume, T_c and P_c are critical temperature and pressure, respectively, R is the universal gas constant, α refers to the so-called alpha function, the constants of the a and b parameters of the above equations, Ω_a^0 and Ω_b^0, are 0.45724 and 0.07780, respectively.

3.3. Development of Thermodynamically Consistent Volume Translation Model

3.3.1. Choice of Alpha Function

Based on the van der Waal's theory, the parameter a is expected to decrease monotonically with temperature and approach zero at high temperatures [26]. However, for the Soave-type polynomial alpha function proposed by Peng and Robinson [2], the first derivative of the alpha function with respect to temperature is not always negative. Taking n-C_8H_{18}($\omega = 0.399552$) as an example, Fig.3.4 shows the variation of the alpha function as a function of temperature. It can be seen that the alpha function goes through a minimum value at $T_r = 4.223$ and then increases with temperature. To address such limitation of the Soave-type alpha function, some exponential alpha functions [27-30] are proposed by some researchers to ensure that the alpha values are always positive and decreasing over the entire temperature range.

In 2003, Coquelet *et al.* [27] argued that an alpha function must satisfy some basic requirements to have accurate representations of vapor pressures for pure compounds. Recently, Le Guennec *et al.* [26] proposed a theoretically-based guideline to derive an alpha function that could: 1) guarantee consistent calculations of residual molar enthalpy, 2) ensure that the first derivative of alpha function appears in the mathematical expression of the residual molar enthalpy and entropy, and 3) ensure that the second derivative of alpha appears in the mathematical expression of the residual heat capacity at a constant volume. Based on these constraints proposed by the above authors [26, 27], the following requirements should be satisfied for the alpha function: 1) the value of the alpha function should be equal to 1 at the critical point, 2) a list of mathematical constraints in terms of the thermodynamic properties should be applied at all temperatures:

$$\begin{cases} \alpha \geq 0 \text{ and } \alpha(T) \text{ continuous} \\ \dfrac{d\alpha}{dT_r} \leq 0 \text{ and } \dfrac{d\alpha}{dT_r} \text{ continuous} \\ \dfrac{d^2\alpha}{dT_r^2} \geq 0 \text{ and } \dfrac{d^2\alpha}{dT_r^2} \text{ continuous} \\ \dfrac{d^3\alpha}{dT_r^3} \leq 0 \end{cases} \tag{6}$$

where T_r is reduced temperature. In this work, based on the above sets of constraints, a consistent alpha function proposed by Le Guennec *et al.* [6] is chosen to more accurately predict the vapor pressure and the other thermodynamic properties for pure compounds. The generalized alpha function is presented as below [6],

$$\begin{cases} \alpha(T)_r = T_r^{2(M-1)} \exp\left[L\left(1 - T_r^{2M}\right)\right] \\ M(\omega) = 0.1760\omega^2 - 0.2600\omega + 0.8884 \\ L(\omega) = 0.1290\omega^2 + 0.6039\omega + 0.0877 \end{cases} \tag{7}$$

where ω is acentric factor, the parameters M and L are both acentric factor-dependent coefficients.

3.3.2. Development of a Consistent Volume Translation Model

3.3.2.1. Motivation of Developing a New Volume Translation

Various types of volume translation schemes have been proposed by researchers over the last three decades. Except constant volume translations and linear temperature-dependent volume translation with a negative coefficient of temperature, there are crossover phenomena for most of the other temperature-dependent volume translation methods under a lower isobaric condition [23].

In a prior work, we proposed a criterion to judge whether the crossover phenomenon exists for a given volume-translated EOS based on a fundamental rule that the isobaric expansivity for pure components is positive [23]. The mathematical inequality is shown as below,

$$D = \left(\frac{\partial V^{\text{Corrected}}}{\partial T}\right)_{\text{p}} = \frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_{\text{P}} + \frac{ZR}{P} - \frac{\partial\left[c(T)\right]}{\partial T} > 0 \tag{8}$$

where D is the first derivative of corrected molar volume with respect to temperature at a isobaric condition, and Z is the compressibility factor. This criterion can be used to judge if one given volume translated EOS leads to crossover issues over a temperature range of $[T_{\text{tp}}, nT_{\text{c}}]$ and a pressure range of $(0, nP_{\text{c}}]$,

$$\frac{\partial\left[c(T)\right]}{\partial T} < \frac{RT}{nP_{\text{c}}}\left(\frac{\partial Z}{\partial T}\right)_{nP_{\text{c}}} + \frac{ZR}{nP_{\text{c}}},\ \forall T \in \left[T_{\text{tp}}, nT_{\text{c}}\right] \tag{9}$$

where T_{tp} is triple point temperature; the derivation of $\left(\frac{\partial Z}{\partial T}\right)_{nP_{\text{c}}}$ and $\frac{\partial\left[c(T)\right]}{\partial T}$ are included in the previous work. If we are interested in judging the existence of isotherm crossover over $[T_{\text{tp}}, nT_{\text{c}}]$

and (0, nP_c], we only need to apply the inequality (9) once at nP_c over the temperature range of [T_{tp}, nT_c]. If the inequality (9) is violated, there will be crossover issue over [T_{tp}, nT_c] and (0, nP_c].

It can be clearly seen that the term D consists of two parts: part A is $\frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_P + \frac{ZR}{P}$ (denoted by $D1$) and part B is the first derivative of volume translation with respect to temperature. The term $D1$ is function of pressure and temperature, and Fig. 3.5 shows the relationship between the values of term $D1$ and reduced temperature for methane at three different isobaric conditions, i.e., 5 MPa, 10 MPa and 20 MPa, respectively. The value of the term $D1$ generally decreases with an increasing isobaric pressure, which means that the value of the first derivative of volume translation with respect to temperature should decrease at the same temperature as the isobaric pressure increases if the mathematical inequality needs to be satisfied. For the most of the proposed nonlinear temperature-dependent volume translations, there is a quite large value of the first derivative of volume translation with respect to temperature when the reduced temperature is less than 1 and especially close to 1.

In this work, thus, we developed a new generalized temperature-dependent volume translation model that can simultaneously satisfy the following requirements:

1) The new scheme should fit the overall trend of the needed volume shift and give a more accurate density prediction than the constant volume translation model;

2) The new scheme should ensure that there is no any crossing of isotherms at a wide range of pressure and temperature (up to 100 MPa and 1000 K).

3.3.2.2. Mathematical Formulation

In order to meet the above requirements, a generalized volume translation model based on the Gaussian function is proposed as below,

$$c\left(T_r\right)=V_c^{PR}\left\{A\exp\left[-\frac{\left(T_r-1\right)^2}{2B^2}\right]+C\right\} \tag{10}$$

where V_c^{PR} is the critical molar volume calculated by the PR EOS, and the parameters *A*, *B* and *C* are specific for each substance. This proposed model is slightly different from the one proposed by Monnery *et al.* [8] in that the proposed model is symmetric with respect to T_r=1, while the Monnery *et al.* model is symmetric with respect to a component-specific parameter. With a positive *A*, it exhibits a symmetric "bell" shape, which can match the overall tendency of the practically needed volume shift as shown in Figs. 3.1 and 3.2. The coefficients *A*, *B* and *C* appearing in Eq. (10) are component-dependent parameters, and the determination of these parameters will be shown later. Another feature of this function is that its first derivative with respect to temperature approaches zero when the reduced temperature increases close to 1, resulting in that it is easier for this function to satisfy the inequality (9) than the other nonlinear temperature-dependent models which normally shows a large and positive slope as the reduced temperature rises close to 1.

In order to ensure that there no crossover at the given temperature and pressure ranges, a mathematical constraint is applied,

$$\frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{P}}+\frac{ZR}{P}+V_c^{PR}A\left(\frac{T_r-1}{B^2T_c}\right)\exp\left(-\frac{\left(T_r-1\right)^2}{2B^2}\right)>0 \tag{11}$$

It is worthwhile noting that when $T_r > 1$, the value of the term $V_c^{PR} A\left(\frac{T_r - 1}{B^2 T_c}\right)\exp\left[-\frac{(T_r - 1)^2}{2B^2}\right]$ is negative with a positive A, which makes sure that the inequality is always positive and there is no crossover phenomenon. While if $T_r < 1$, the inequality only needs to be satisfied at the highest isobaric pressure to ensure that there is no any crossover between any two isotherms in the PV diagram.

To summarize, we propose a new volume translation model whose model parameters should be determined subject to a constraint as shown below,

$$\begin{cases} c(T_r) = V_c^{PR}\left\{A\exp\left[-\frac{(T_r - 1)^2}{2B^2}\right] + C\right\} \\ \frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_{\mathrm{P}} + \frac{ZR}{P} + V_c^{PR} A\left(\frac{T_r - 1}{B^2 T_c}\right)\exp\left[-\frac{(T_r - 1)^2}{2B^2}\right] > 0,\ P = 100\ \mathrm{MPa} \end{cases} \tag{12}$$

3.4. Results and Discussion

3.4.1. Determination of Model Parameters

Nonlinear regression should be applied to determine the model parameters shown in Eq. (10). Herein, we transform such nonlinear regression problem to a minimization problem in an attempt to easily accommodate the constraint shown in Inequality (11). The transformed objective function is defined as the summation of the squares of the difference between the calculated volume translation and the needed volume translation. The detailed objective function together with the constraint are given as below,

$$\begin{cases} \text{Min } F\left(x\right) = \displaystyle\sum_{j=1}^{N} \left(A e^{-\frac{\left(T_{rj}-1\right)^2}{2B^2}} + C - \frac{c_j}{V_c^{PR}} \right)^2 \\ \text{Subject to: } V_c^{PR} A \left(-\dfrac{T_{rj}-1}{B^2 T_c} \right) e^{-\frac{\left(T_{rj}-1\right)}{2B^2}} < D_j \end{cases} \tag{13}$$

where

$$\begin{cases} c_j = V_j^{\mathrm{PR}} - V_j^{\mathrm{Exp}} \\ D_j = \dfrac{RT_j}{P} \left(\dfrac{\partial Z}{\partial T} \right)_{\mathrm{P,j}} + \dfrac{Z_j R}{P},\ P\text{=100 MPa} \end{cases} \tag{14}$$

where *j* refers to the *j*th data point, and *N* is the number of data points considered for a given pure compound. The experimental density data are retrieved from the NIST database [31]. The sequential quadratic programming method (SQP) is used to determine the model parameters by solving the minimization problem. Table 1 shows the physical properties of the pure fluids considered in this study [31, 32], while Table 2 presents the values of *A*, *B* and *C* determined for each compound.

In addition, in order to provide a generalized volume translation model for compounds not included in the database, we attempt to correlate the three parameters *A*, *B* and *C* to the acentric factors of all the compounds considered. Fig.3.6 presents the comparison between the regressed and generalized values of *A*, *B* and *C* and it can be clearly seen from Fig.3.6 that a linear dependence on the acentric factor can be found for each model parameter. The three linear functions shown below can be used to describe such linear dependence,

$$\begin{cases} A = K_1\omega + K_2 \\ B = K_3\omega + K_4 \\ C = K_5\omega + K_6 \end{cases} \tag{15}$$

Table 3 shows the values of the parameters K_1through K_6 determined by regression.

3.4.2. Modeling Results for Pure Components

In order to demonstrate the prediction accuracy of the newly proposed volume translation scheme, we compare it against another four models that do not exhibit thermodynamic inconsistency: 1) the original PR EOS [2], 2) the Peneloux model for PR EOS [33], 3) the de Sant'Ana*et al.* model for PR EOS [9], 4) the Baled *et al.* model for PR EOS [11]. The average absolute percentage deviation (AAD%) is calculated to assess the performance of different models:

$$\mathrm{AAD\%} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{V_{\mathrm{cal}}^{i} - V_{\mathrm{cal}}^{i}}{V_{\mathrm{exp}}^{i}}\right| \tag{17}$$

where N is the number of data points considered, V_{cal}^{i} and V_{exp}^{i} are the calculated molar volume and experimental molar volume for the *i*th data point, respectively. Table 4 shows the comparative results. It can be seen from Table 4 that, overall, our generalized volume translation model provides the smallest AAD% of 1.42. In comparison, the original PR EOS model [2], the Peneloux *et al.* model [33], the de Sant'Ana *et al.* model [9] and the Baled *et al.* model [11] give higher values of the AAD%, i.e., 5.09%, 1.98%, 15.32% and 3.19%, respectively.

Figs.3.7 and 3.8 show a comparison between the needed volume shifts (black dots) at different constant pressures ($0.5P_c$, $0.6P_c$, $0.7P_c$, $0.8P_c$, $0.9P_c$, $1P_c$, $1.5P_c$ and $2P_c$) and the calculated volume shifts for n-butane and benzene, respectively. Compared with the other three models, it is clearly shown that the proposed model in this work provides a better match with the practically needed volume shift. The appendix presents the detailed comparisons for the other components. Figs.3.9 and 3.10 compare the original PR EOS and the PR EOS with the new volume translation model in terms of their accuracy in predicting the saturated-liquid molar volumes for n-butane and benzene, respectively. As seen from Figs. 3.9 and 3.10, it is evident that the proposed scheme can obviously provide an improved prediction of saturated-liquid molar volumes especially at subcritical temperatures. It is worthwhile mentioning that the performance of the proposed model can be even further augmented by removing the constraint applied during the regression, albeit such removal of the constraint will lead to the crossing of isotherms otherwise.

3.5. Conclusions

We develop a generalized temperature-dependent volume translation model for PR EOS in order to provide more accurate predictions of molar volumes for pure compounds. The new volume translation model has three parameters that are linearly dependent on the acentric factor of pure compounds. The proposed model can well capture the trend in the volume translations that are needed for the liquid-phase density. Notably, the new volume translation model does not bear crossover issues of the PV isotherms over a wide range of pressure and temperature (up to 100 MPa and 1000K). Compared with the other four models documented in the literature, the new model gives the smallest error.

References

[1] G. Soave, Equilibrium constants from a modified Redlich–Kwong equation of state, Chem. Eng. Sci. 27 (1972) 1197-1203.

[2] D.Y. Peng, D.B. Robinson, A new two-constant equation of state, Ind. Eng. Chem. Fundam. 15 (1976) 59-64.

[3] K. Frey, C. Augustine, R.P. Ciccolini, S. Paap, M. Modell, J. Tester, Volume translation in equations of state as a means of accurate property estimation, Fluid Phase Equilibr. 260 (2007) 316-325.

[4] A. Peneloux, E. Rauzy, R. Freze, A consistent correction for Redlich–Kwong–Soave volumes, Fluid Phase Equilibr. 8 (1982) 7-23.

[5] B.S. Jhaveri, G.K. Youngre, Three-parameter modification of the Peng-Robinson equation of state to improve volumetric prediction, in: 59th Annual Technical Conference and Exhibition, Houston, Sept. 16-19, SPE 13118, 1984.

[6] Y. Le Guennec, R. Privat, J.-N. Jaubert, Development of the translated-consistent tc-PR and tc-RK cubic equations of state for a safe and accurate prediction of volumetric, energetic and saturation properties of pure compounds in the sub- and supercritical domains, Fluid Phase Equilibr. 429 (2016) 301-312.

[7] B. Hoyos, Generalized liquid volume shifts for the Peng-Robinson equation of state for C1 to C8 hydrocarbons, Latin Amer. Appl. Res. 34 (2004) 83-89.

[8] W.D. Monnery, W.Y. Svrcek, M.A. Satyro, Gaussian-like volume shifts for the Peng-Robinson equation of state, Ind. Eng. Chem. Res.37 (1998) 1663–1672.

[9] H.B. de Sant'Ana, P. Ungerer, J.C. de Hemptinne, Evaluation of an improved volume translation for the prediction of hydrocarbon volumetric properties, Fluid Phase Equilibr. 154 (1999) 193-204.

[10] K.S. Pedersen, J. Milter, H. Sørensen, Cubic equations of state applied to HT/HP and highly aromatic fluids, SPE J. 9 (2004) 186-192.

[11] H. Baled, R.M. Enick, Y. Wu, M.A. McHugh, W. Burgess, D. Tapriyal, B.D. Morreale, Prediction of hydrocarbon densities at extreme conditions using volume-translated SRK and PR equations of state fit to high temperature, high pressure PVT data, Fluid Phase Equilibr. 317 (2012) 65-76.

[12] P. Watson, M. Cascella, D. May, S. Salerno, D. Tassios, Prediction of vapor pressures and saturated molar volumes with a simple cubic equation of state, 2. The Van der Waals-711 EOS, Fluid Phase Equilibr. 27 (1986) 35–52.

[13] I. Søreide, Improved phase behavior predictions of petroleum reservoir fluids from a cubic equation of state, Ph.D. thesis, Norwegian Institute of Technology, 1989.

[14] K. Magoulas, D. Tassios, Thermophysical properties of n-alkanes from C1 to C20 and their prediction for higher ones, Fluid Phase Equilibr. 56 (1990) 119-140.

[15] L. Hong, Y.Y. Duan, Empirical correction to the Peng–Robinson equation of state for the saturated region, Fluid Phase Equilibr. 233 (2005) 194-203.

[16] H. Lin, Y.Y. Duan, T. Zhang, Z.M. Huang, Volumetric property improvement for the Soave-Redlich-Kwong equation of state, Ind. Eng. Chem. Res. 45 (2006) 1829-1839.

[17] A.M. Abudour, S.A. Mohammad, R.L. Robinson, K.A.M. Gasem, Volume-translated Peng–Robinson equation of state for saturated and single-phase liquid densities, Fluid Phase Equilibr. 335 (2012) 74-87.

[18] M. Nazarzadeh, M. Moshfeghian, New volume translated PR equation of state for pure compounds and gas condensate systems, Fluid Phase Equilibr. 337 (2013) 214-224.

[19] P.M. Mathias, T. Naheiri, E.M. Oh, A density correction for the Peng–Robinson equation of state, Fluid Phase Equilibr. 47 (1989) 77-87.

[20] G.F. Chou, J.M. Prausnitz, A phenomenological correction to an equation of state for the critical region, AIChE J. 35 (1989) 1487-1496.

[21] W.R. Ji, D.A. Lempe, Density improvement of the SRK equation of state, Fluid Phase Equilibr. 130 (1997) 49-63.

[22] O. Pfohl, Letter to the editor: "Evaluation of an improved volume translation for the prediction of hydrocarbon volumetric properties", Fluid Phase Equilibr. 163 (1999) 157-159.

[23] J. Shi, H. Li, Criterion for determining crossover phenomenon in volume-translated equation of states, Fluid Phase Equilibr. 430 (2016) 1-12.

[24] J. Hekayati, A. Roosta, J. Javanmardi, Volumetric properties of supercritical carbon dioxide from volume-translated and modified Peng-Robinson equations of state, Korean J. Chem. Eng. 33.11 (2016) 3231-3244.

[25] K. Frey, M. Modell, J. Tester, Density-and-temperature-dependent volume translation for the SRK EOS: 1. Pure fluids, Fluid Phase Equilibr. 279 (2009) 56-63.

[26] Y. Le Guennec, S. Lasala, R. Privat, J.-N. Jaubert, A consistency test for alpha functions of cubic equations of state, Fluid Phase Equilibr. 427 (2016) 513-538.

[27] C. Coquelet, A. Chapoy, D. Richon, Development of a new alpha function for the Peng-Robinson equation of state: comparative study of alpha function models for pure gases (natural gas components) and water-gas systems, Int. J. Thermophys. 25 (2004) 133-158.

[28] M.A. Trebble, P.R. Bishnoi, Development of a new four-parameter cubic equation of state, Fluid Phase Equilibr. 35 (1987) 1-18.

[29] K.A.M. Gasem, W. Gao, Z. Pan, R.L. Robinson, A modified temperature dependence for the Peng-Robinson equation of state, Fluid Phase Equilibr. 181 (2001) 113-125.

[30] H. Li, D. Yang, Modified α function for the Peng-Robinson equation of state to improve the vapor pressure prediction of non-hydrocarbon and hydrocarbon compounds, Energy Fuels. 25 (2011) 215-223.

[31] P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD, 20899, http://webbook.nist.gov.

[32] C.F. Spencer, R.P. Danner, Improved equation for prediction of saturated liquid density, J. Chem. Eng. Data. 17 (1972) 236–241.

[33] J.-N. Jaubert, R. Privat, Y. Le Guennec, L. Coniglio, Note on the properties altered by application of a Peneloux-type volume translation to an equation of state, Fluid Phase Equilibr. 419 (2016) 88-95.

Tables and Figures:

Table 3.1 Physical Properties of Pure Fluids Used in This Study

Components	T_c (K)	P_c (MPa)	z_c	z_{RA}	ω	MW(g/mol)
Carbon dioxide	304.21	7.383	0.274	0.2736	0.223621	44.0095
Oxygen	154.58	5.043	0.2879	0.2909	0.0221798	31.9988
Methane	190.564	4.599	0.286	0.2876	0.0115478	16.0425
Ethane	305.32	4.872	0.279	0.2789	0.099493	30.069
Ethylene	282.34	5.041	0.281	0.281	0.0862484	28.0532
Propane	369.83	4.248	0.276	0.2763	0.152291	44.0956
n-Butane	425.12	3.796	0.274	0.2728	0.200164	58.1222
n-Pentane	469.7	3.37	0.27	0.2685	0.251506	72.1488
n-Hexane	507.6	3.025	0.266	0.2685	0.301261	86.1754
n-Heptane	540.2	2.74	0.261	0.2611	0.349469	100.202
n-Octane	568.7	2.49	0.256	0.2567	0.399552	114.229
n-Nonane	594.6	2.29	0.255	0.2547	0.44346	128.255
n-Decane	617.7	2.11	0.254	0.2503	0.492328	142.282
n-Dodecane	658	1.82	0.251	0.2466	0.576385	170.335
Toluene	591.75	4.108	0.264	0.2646	0.264012	92.1384
Benzene	562.05	4.895	0.268	0.2696	0.2103	78.1118

Table 3.2 Optimized Values of the Volume Translation Parameters *A*, *B* and *C* in Eq. (10)

Components	P (MPa) / T (K) range	*A*	*B*	*C*
Carbon dioxide	P=3.69, 4.43, 5.17, 5.91, 6.64, 7.38, 11.08, 14.77; $T \in [220,304]$	0.0399	0.0938	-0.0187
Oxygen	P=2.52, 3.02, 3.53, 4.03, 4.54, 5.04, 7.56, 10.09; $T \in [94.7,188]$	0.0209	0.1245	-0.0416
Methane	P=2.23, 2.86, 3.22, 3.68, 4.14, 6.90, 9.20; $T \in [94.7,188]$	0.0208	0.1158	-0.0418
Ethane	P=2.44, 2.92, 3.41, 3.90, 4.38, 4.87, 7.31, 9.74; $T \in [123,305]$	0.0309	0.1135	-0.0290
Ethylene	P=2.52, 3.02, 3.53, 4.03, 4.54, 5.04, 7.56, 10.08; $T \in [113,281]$	0.0293	0.1094	-0.0292
Propane	P=2.12, 2.55, 2.97, 3.40, 3.82, 4.25, 6.37, 8.50; $T \in [148,368]$	0.0301	0.1114	-0.0227
n-Butane	P=1.90, 2.28, 2.66, 3.04, 3.42, 3.80, 5.69, 7.59; $T \in [180,420]$	0.0299	0.1150	-0.0178
n-Pentane	P=1.69, 2.02, 2.36, 2.70, 3.03, 3.37, 5.06, 6.74; $T \in [188,463]$	0.0283	0.1176	-0.0093
n-Hexane	P=1.51, 1.82, 2.12, 2.42, 2.72, 3.03, 4.54, 6.05; $T \in [215,503]$	0.0281	0.1277	-0.0023
n-Heptane	P=1.37, 1.64, 1.92, 2.19, 2.47, 2.74, 4.11, 5.48; $T \in [228,540]$	0.0267	0.1305	0.0039
n-Octane	P=1.25, 1.49, 1.74, 2.00, 2.24, 2.49, 3.74, 4.98; $T \in [228,566]$	0.0254	0.1331	0.0118
n-Nonane	P=1.15, 1.37, 1.60, 1.83, 2.06, 2.29, 3.44, 4.58; $T \in [238,574]$	0.0233	0.1322	0.0161
n-Decane	P=1.06, 1.27, 1.48, 1.69, 1.90, 2.11, 3.17, 4.22; $T \in [248,612]$	0.0220	0.1340	0.0216
n-Dodecane	P=0.91, 1.09, 1.27, 1.46, 1.64, 1.82, 2.73, 3.64; $T \in [279,654]$	0.0188	0.1321	0.0310
Toluene	P=2.05, 2.46, 2.88, 3.29, 3.70, 4.11, 6.16, 8.22; $T \in [237,587]$	0.0352	0.1144	-0.0007
Benzene	P=2.45, 2.94, 3.43, 3.92, 4.41, 4.90, 7.34, 9.79; $T \in [292,556]$	0.0375	0.1042	-0.0124

Table 3.3 Values of the Parameters Shown in Eq. (15)

Parameters	Value
K_1	-0.0086
K_2	0.0297
K_3	0.0421
K_4	0.1093
K_5	0.1341
K_6	-0.0439

Table 3.4 Average Absolute Percentage Deviations (%AAD) in Liquid Density Predictions Provided by the New Volume Translation Model and Other Volume Translation Models

Components	**%AAD in liquid density**				
	PR EOS[2]	Peneloux for PR EOS [33]	De Sant'An *et al.* [9]	Baled *et al.* [11]	This work
Carbon dioxide	3.22	2.68	31.98	10.58	2.03
Oxygen	9.43	1.48	54.07	5.07	0.92
Methane	8.95	1.52	51.10	1.60	0.64
Ethane	6.57	1.54	26.58	1.59	1.05
Ethylene	6.62	1.47	31.84	2.04	1.08
Propane	5.24	1.57	13.38	1.64	1.15
n-Butane	4.19	1.57	6.66	2.49	1.24
n-Pentane	2.59	1.72	3.80	2.84	1.24
n-Hexane	1.93	3.51	2.68	2.95	1.45
n-Heptane	2.29	2.03	2.47	2.88	1.35
n-Octane	4.22	2.11	2.67	2.87	1.53
n-Nonane	5.38	2.16	2.52	2.69	1.63
n-Decane	6.84	2.11	2.94	3.01	1.95
n-Dodecane	9.27	2.18	4.52	3.33	2.35
Toluene	1.82	2.34	3.26	2.91	2.25
Benzene	2.95	1.76	4.67	2.73	1.19
Overall	5.09	1.98	15.32	3.19	1.42

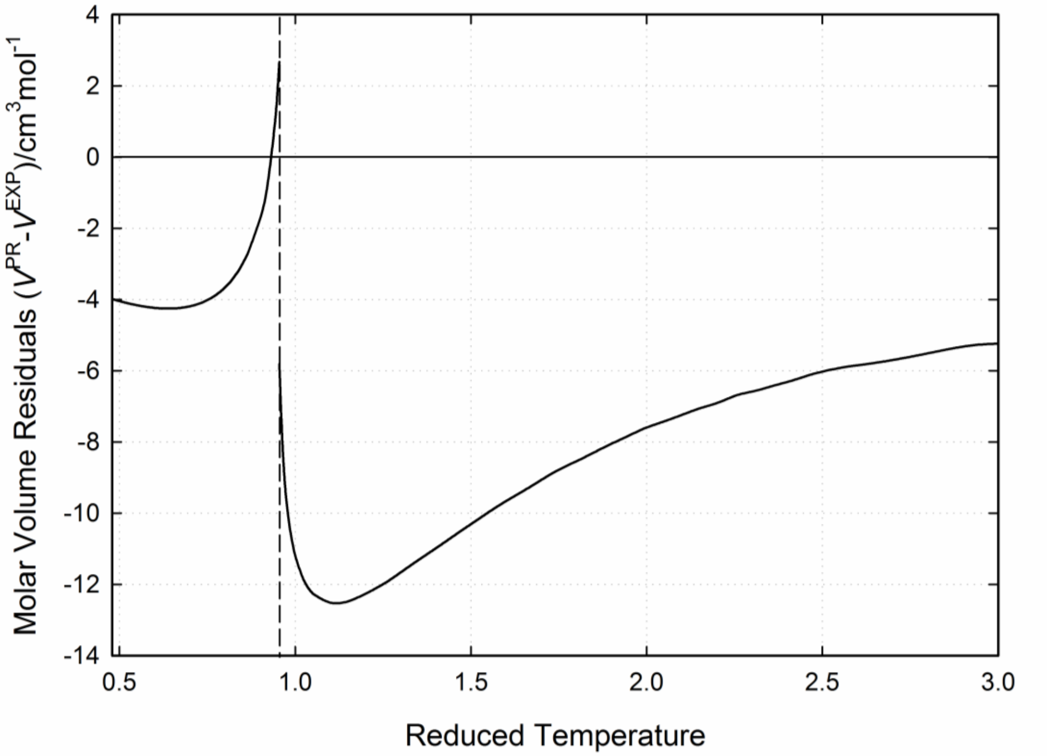


Fig.3.1 The needed volume shift in PR EOS for methane at *P*=3.5 MPa

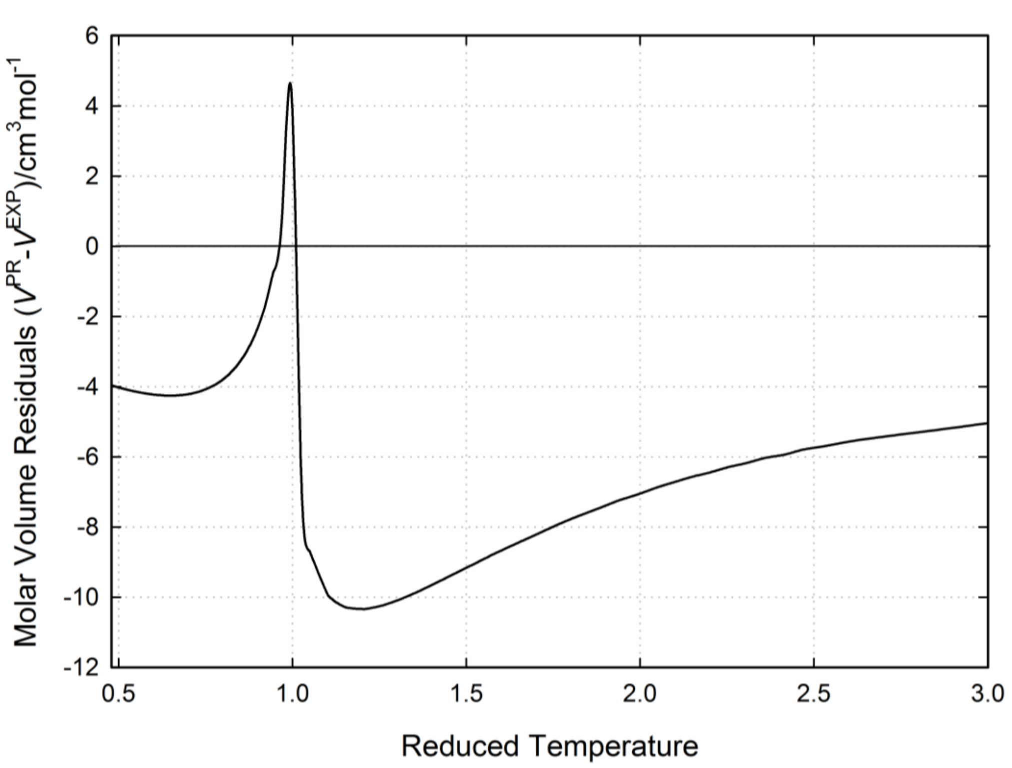


Fig.3.2 The needed volume shift by PR EOS for methane at *P*=5 MPa

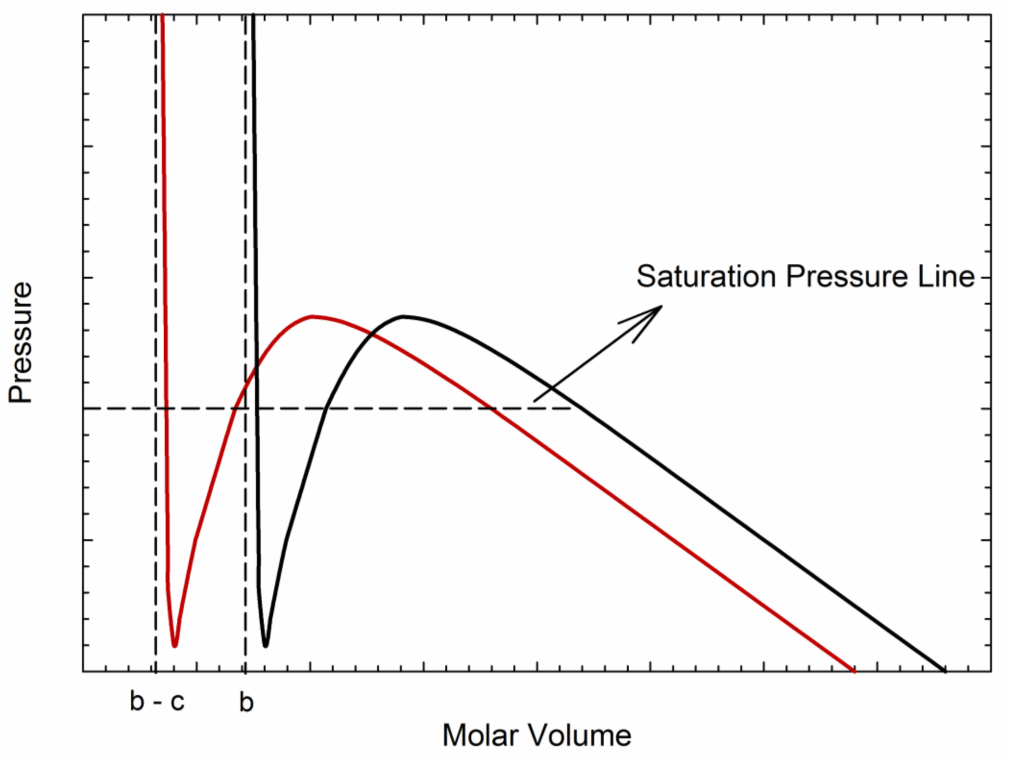


Fig.3.3 A sketch illustrating the impact of a constant or temperature-dependent volume translation on the calculated pressure/volume isotherms

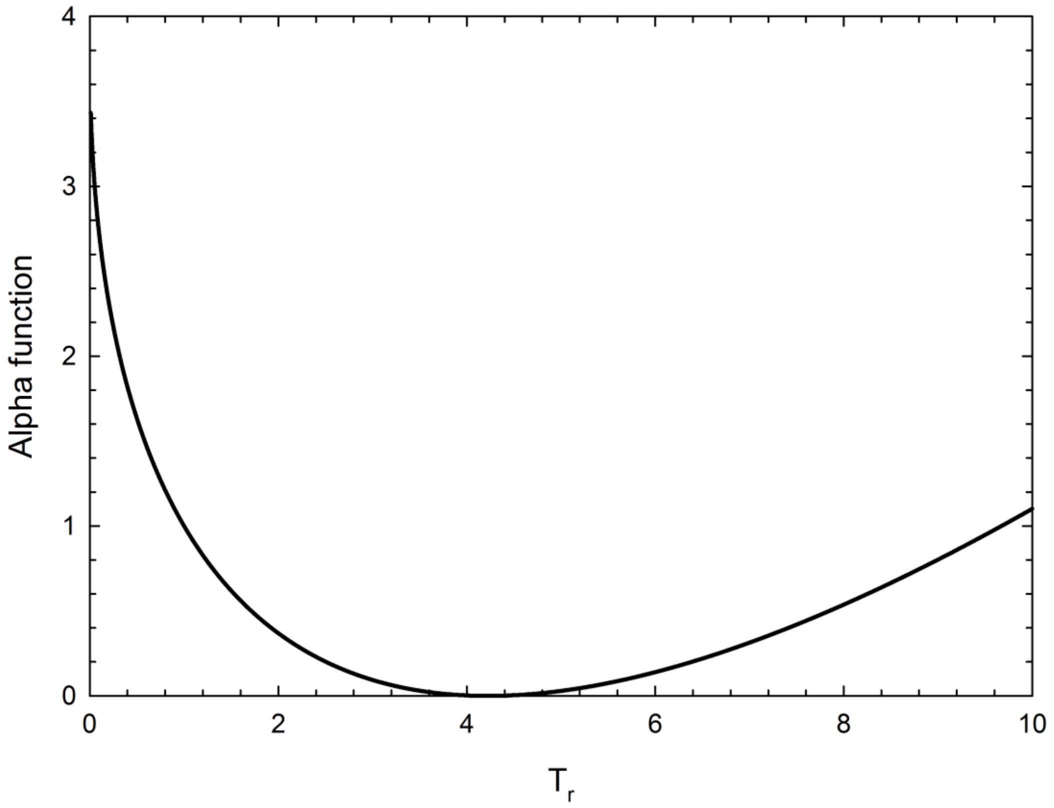


Fig.3.4 The relationship between the soave alpha function [2] and reduced temperature

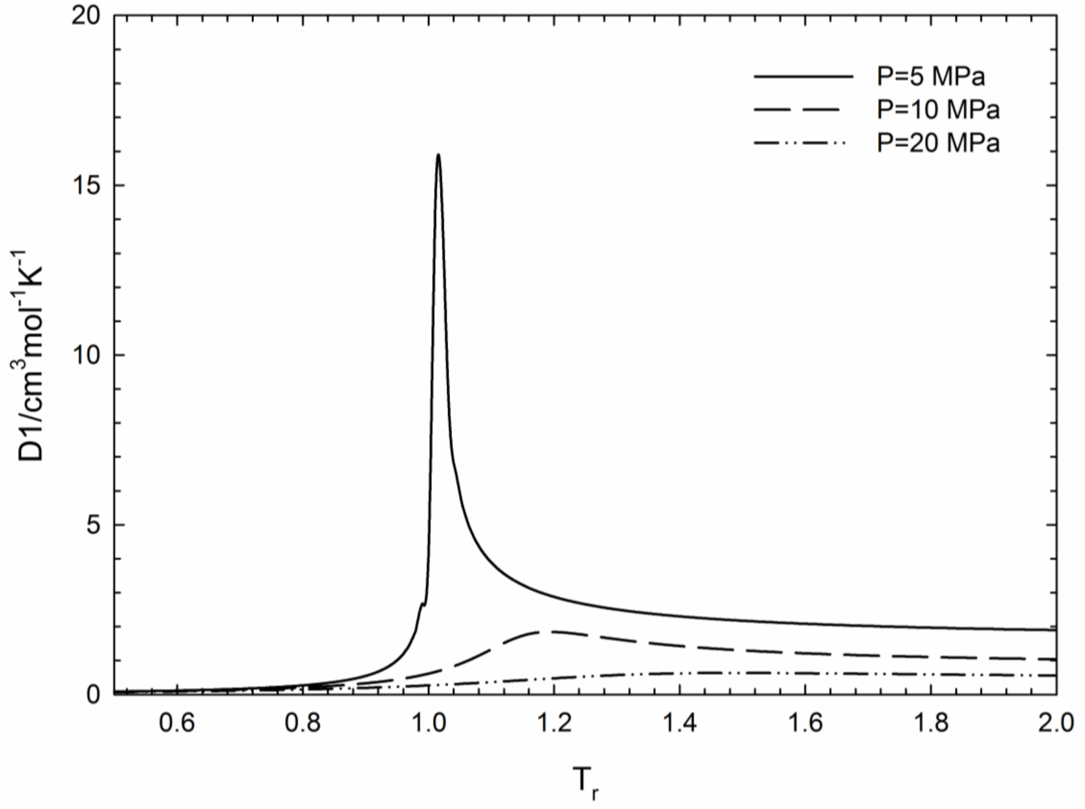


Fig.3.5 The relationship between the value of *D_1* and reduced temperature at three different constant pressures (5 MPa, 10 MPa and 20 MPa)

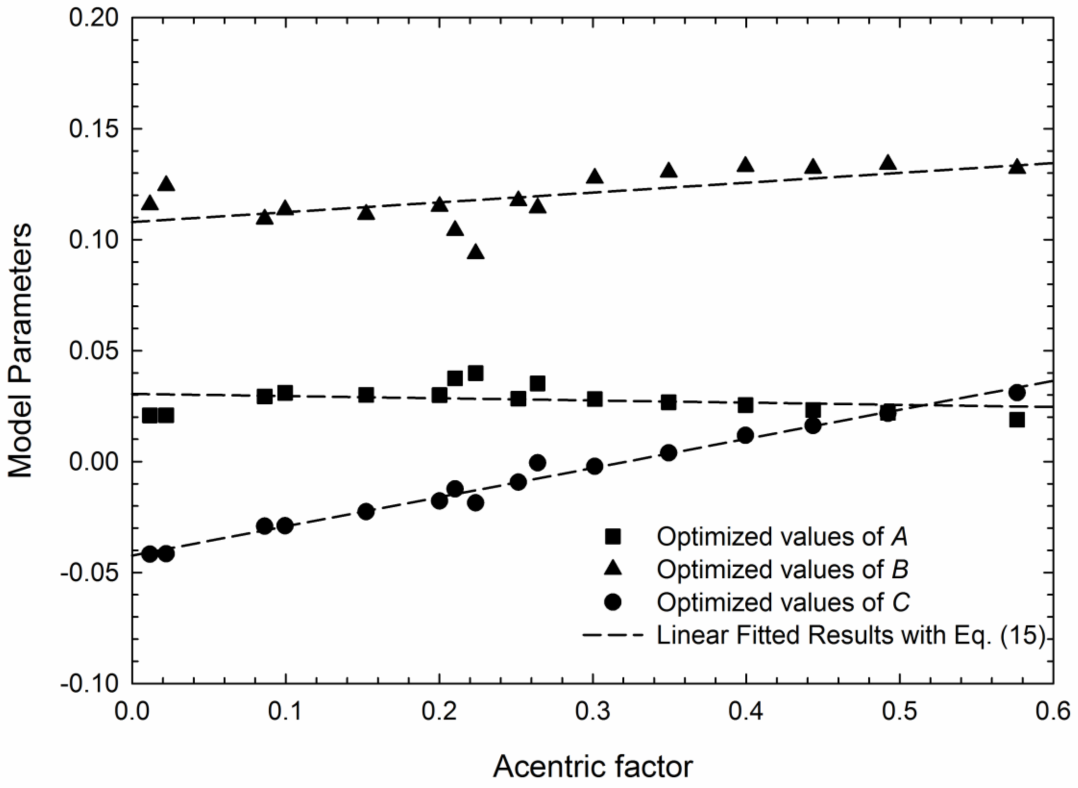


Fig.3.6 Plots of model parameters *A*, *B* and *C* in Eq. (10) vs. the acentric factor

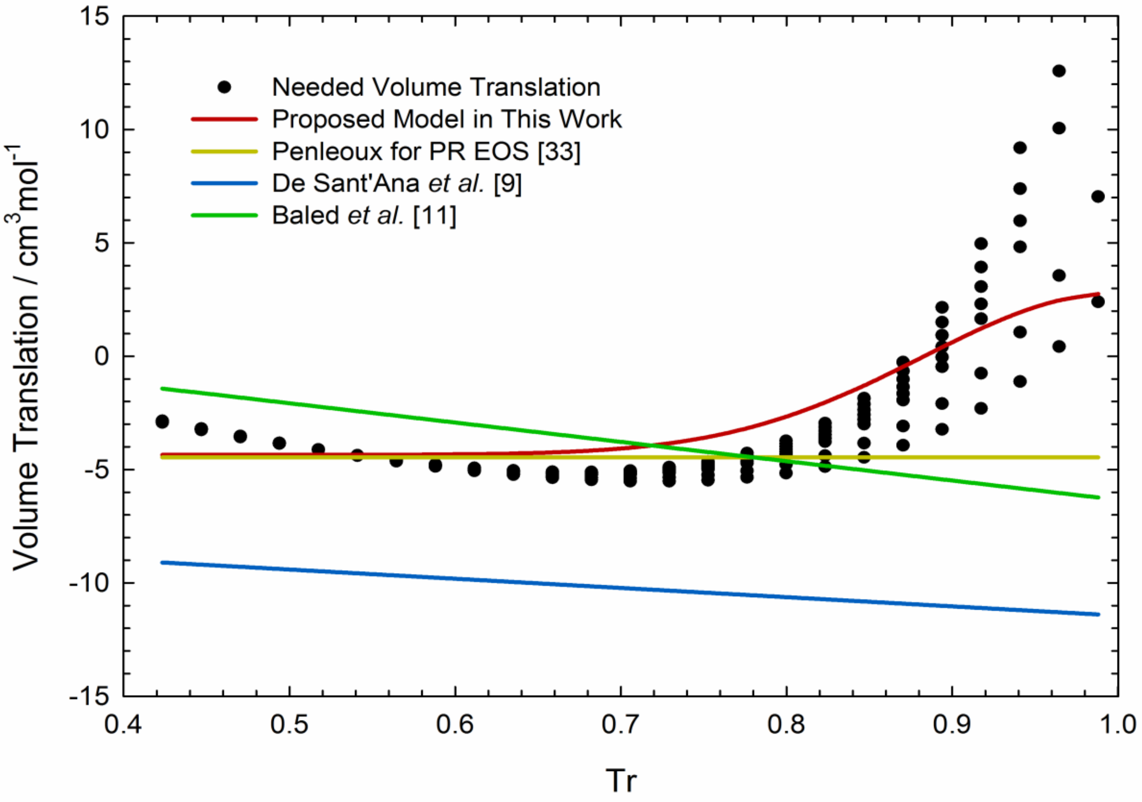


Fig.3.7 Comparison between the needed volume shift (black dots) for n-butane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

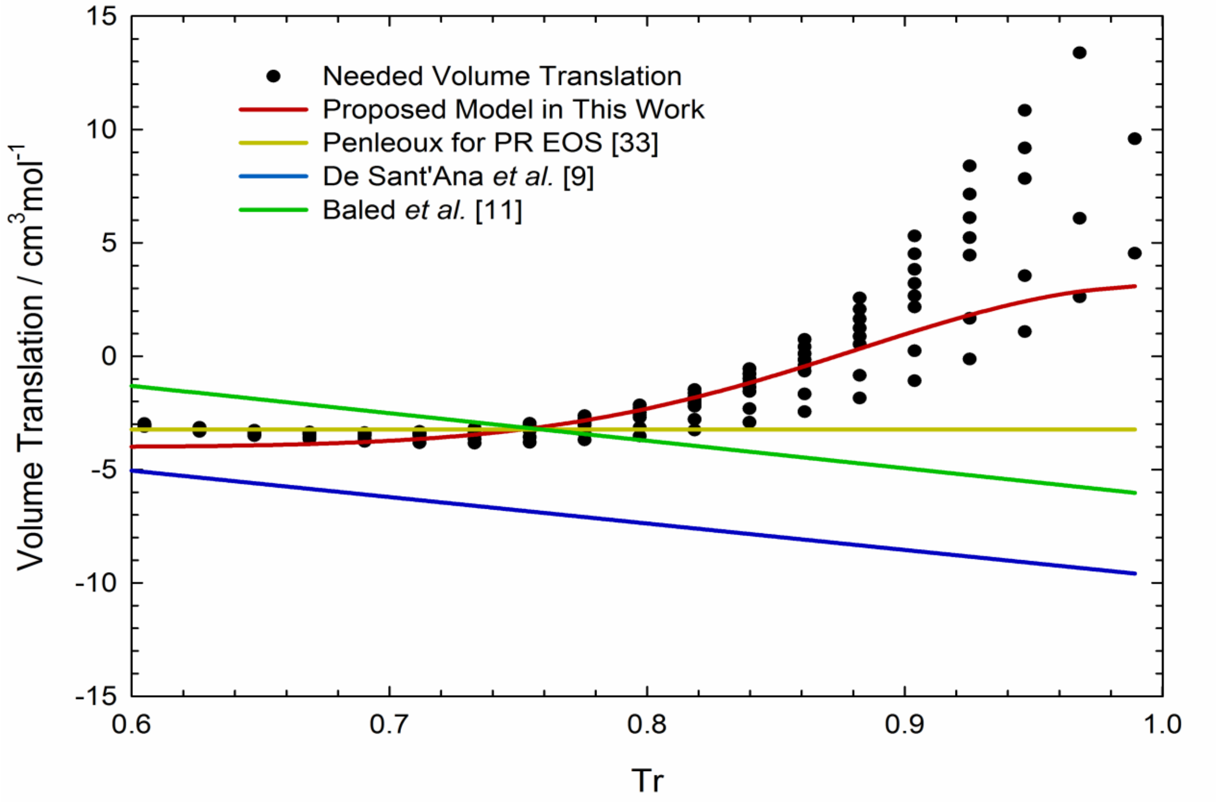


Fig.3.8 Comparison between the needed volume shift (black dots) for benzene (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

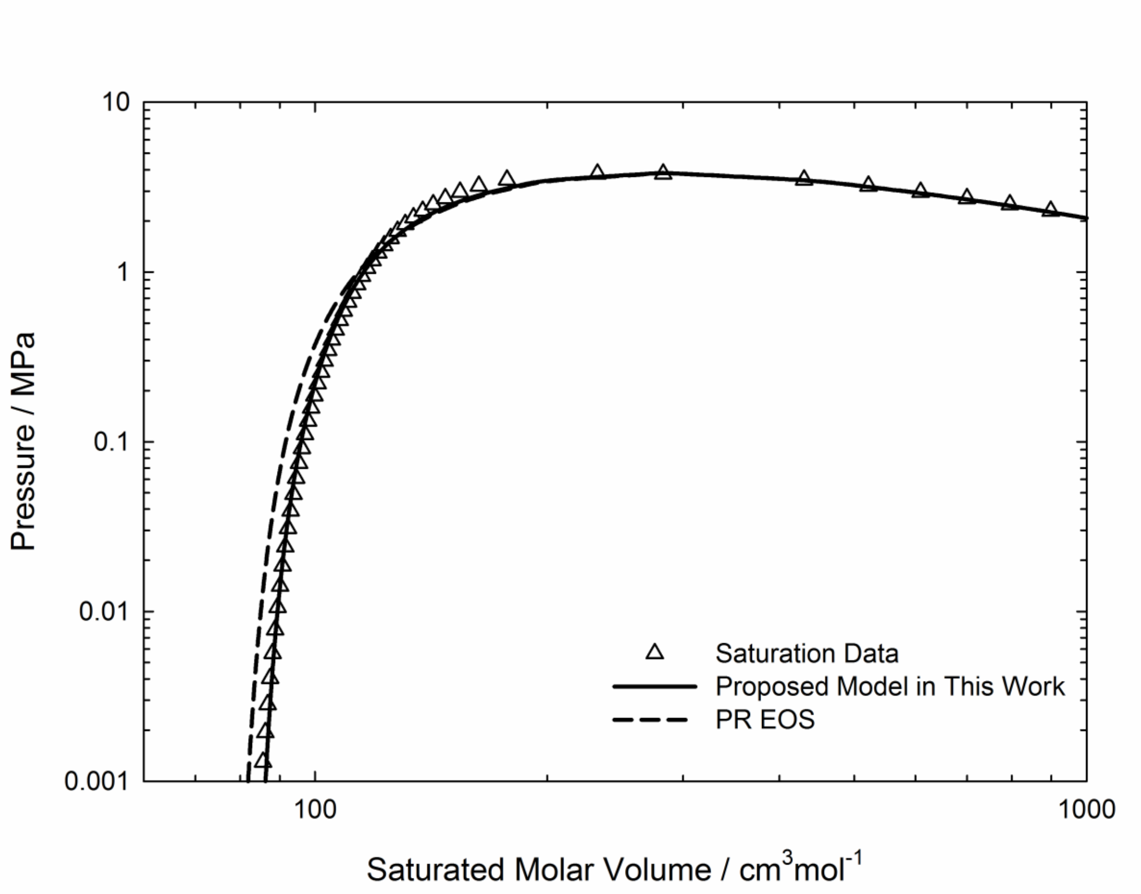


Fig.3.9 Comparison of the measured saturated molar volumes [31] for n-butane and calculated ones with different models

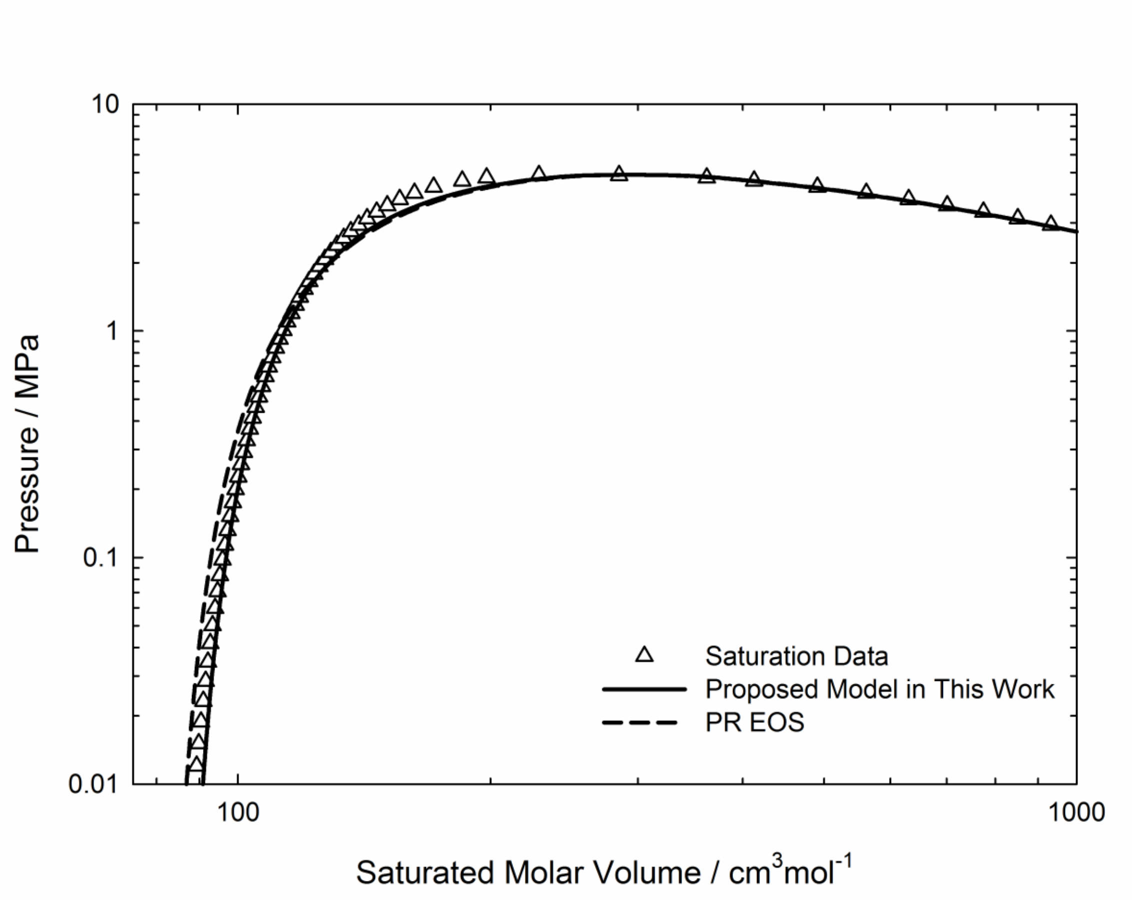


Fig.3.10 Comparison of the measured saturated molar volumes [31] for benzene and calculated ones with different models

Appendix A:

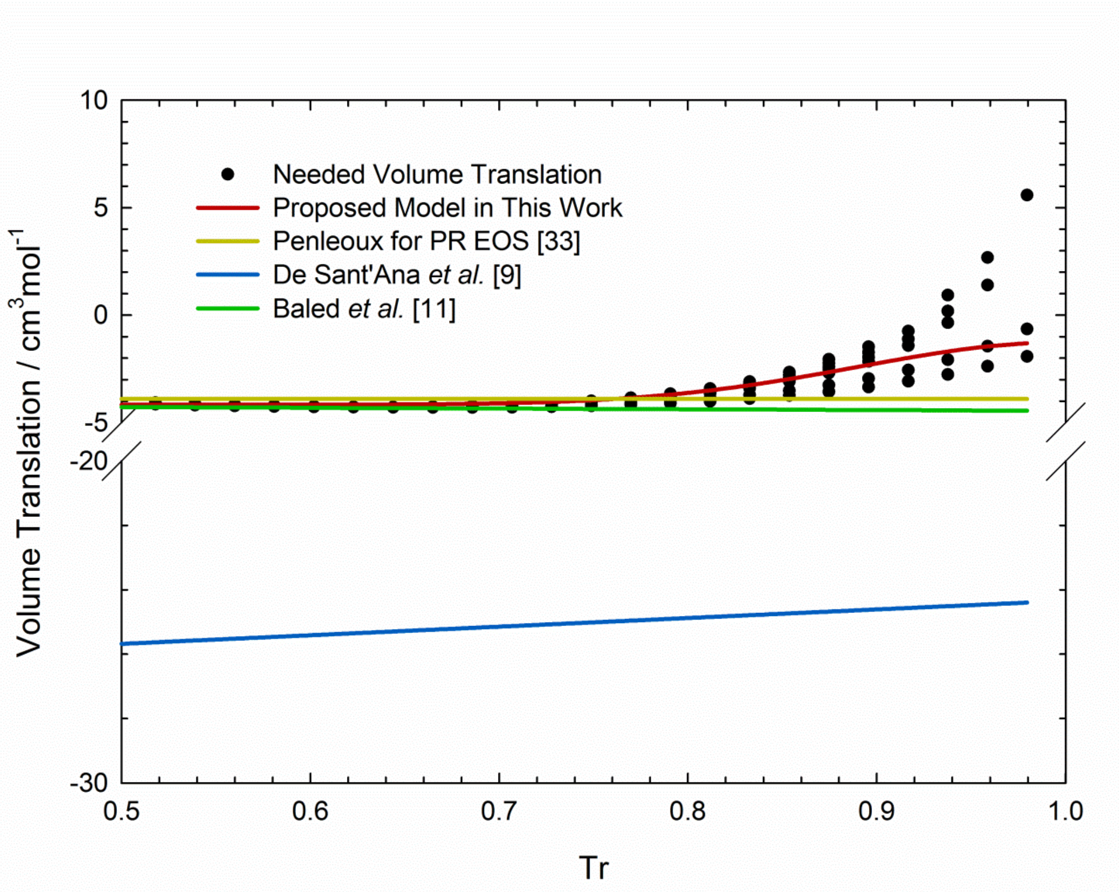


Fig.3.11 Comparison between the needed volume shift (black dots) for methane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

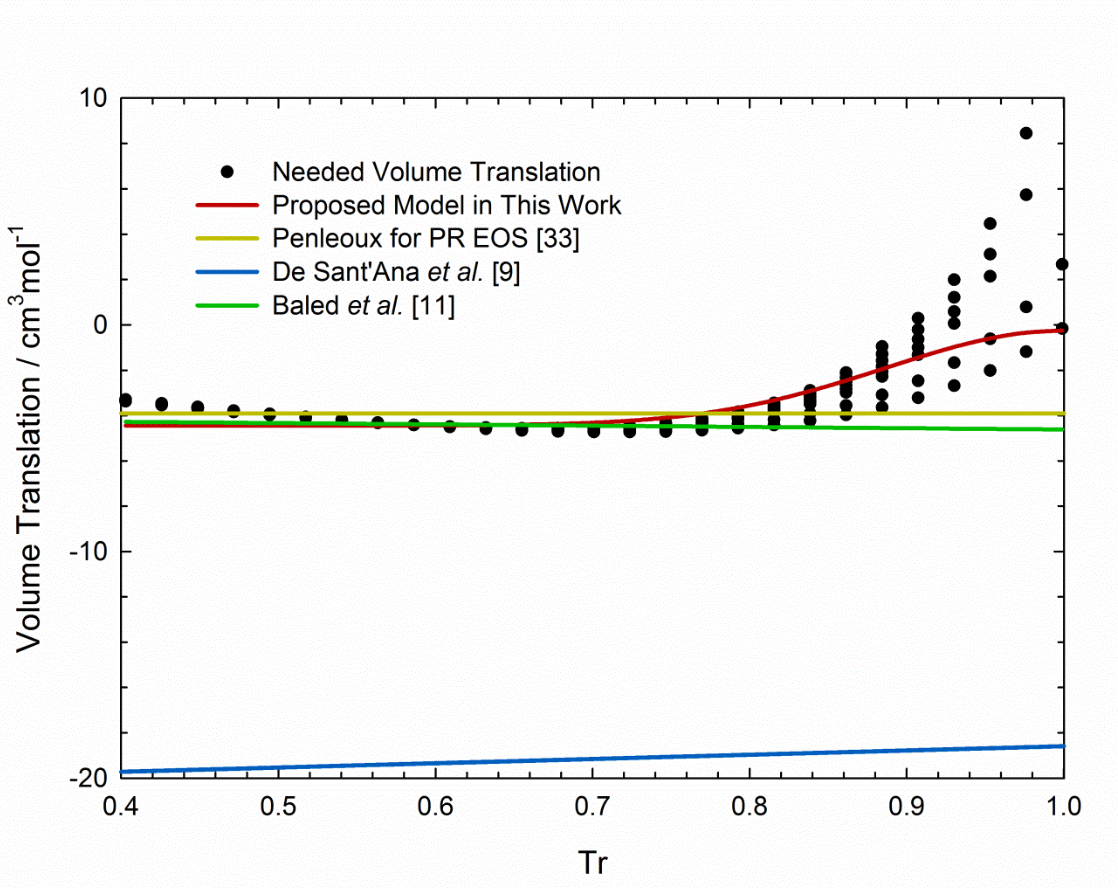


Fig.3.12 Comparison between the needed volume shift (black dots) for ethane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

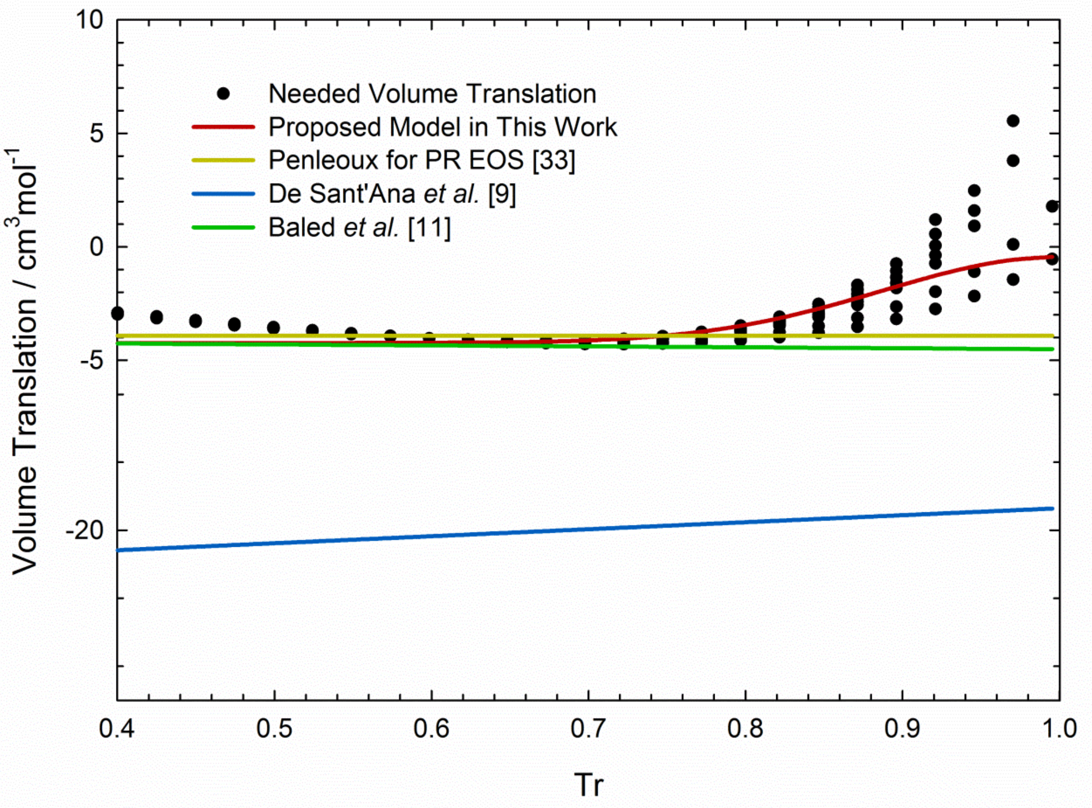


Fig.3.13 Comparison between the needed volume shift (black dots) for ethylene (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

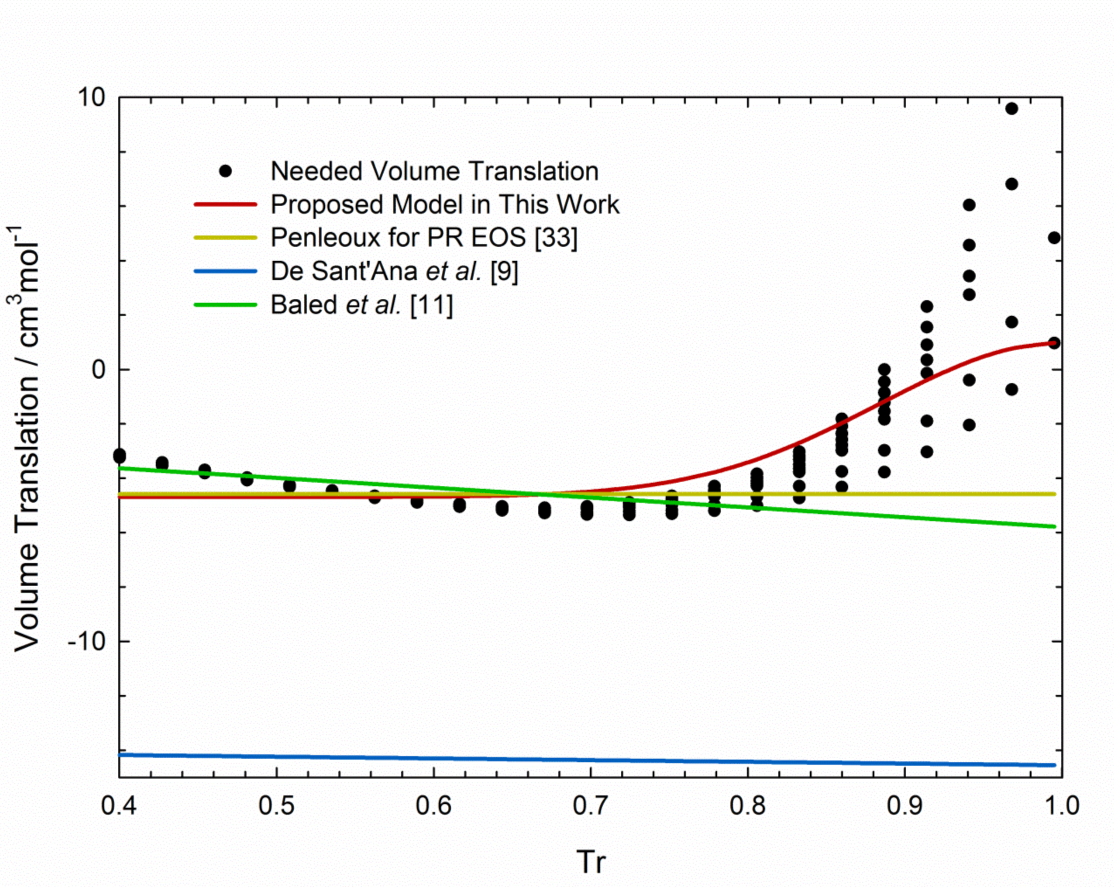


Fig.3.14 Comparison between the needed volume shift (black dots) for propane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

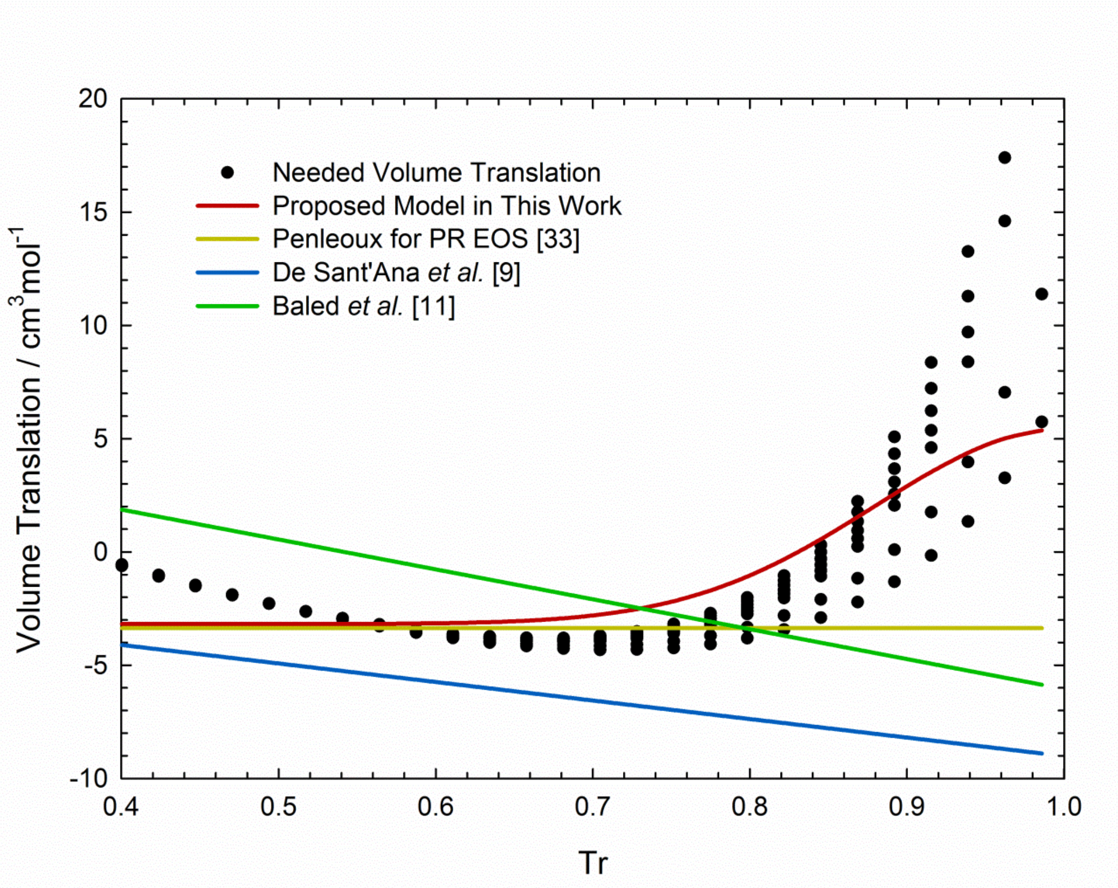


Fig.3.15 Comparison between the needed volume shift (black dots) for n-pentane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

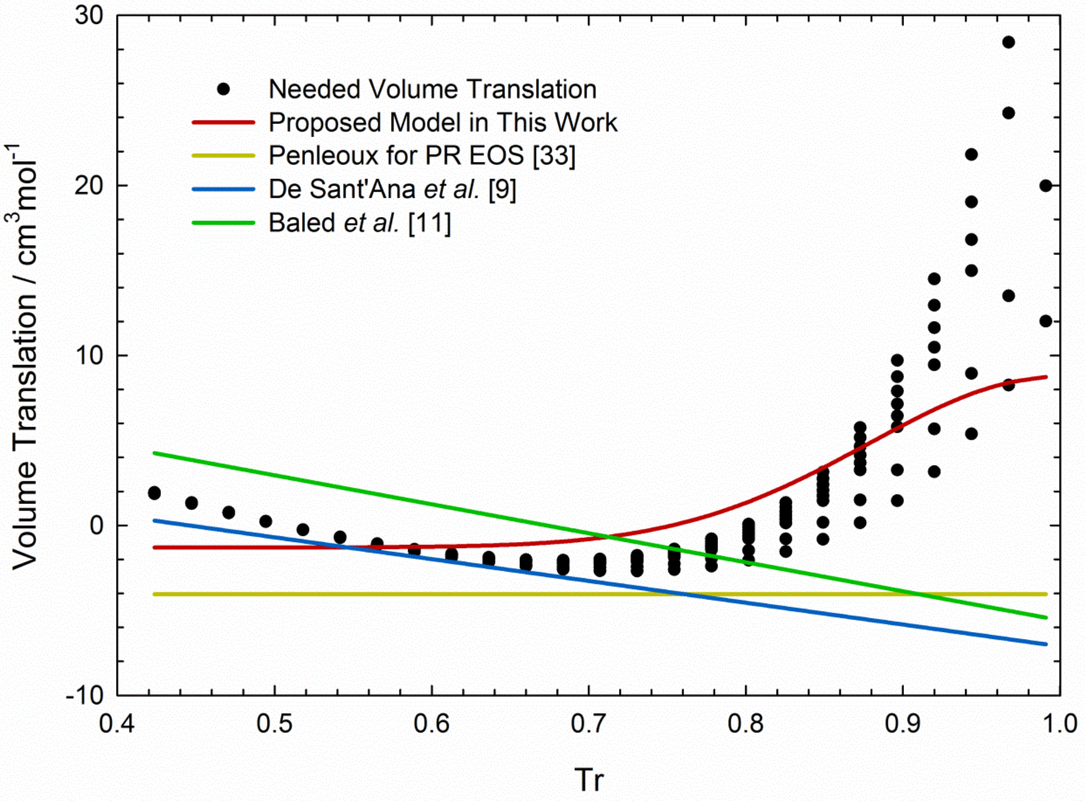


Fig.3.16 Comparison between the needed volume shift (black dots) for n-hexane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

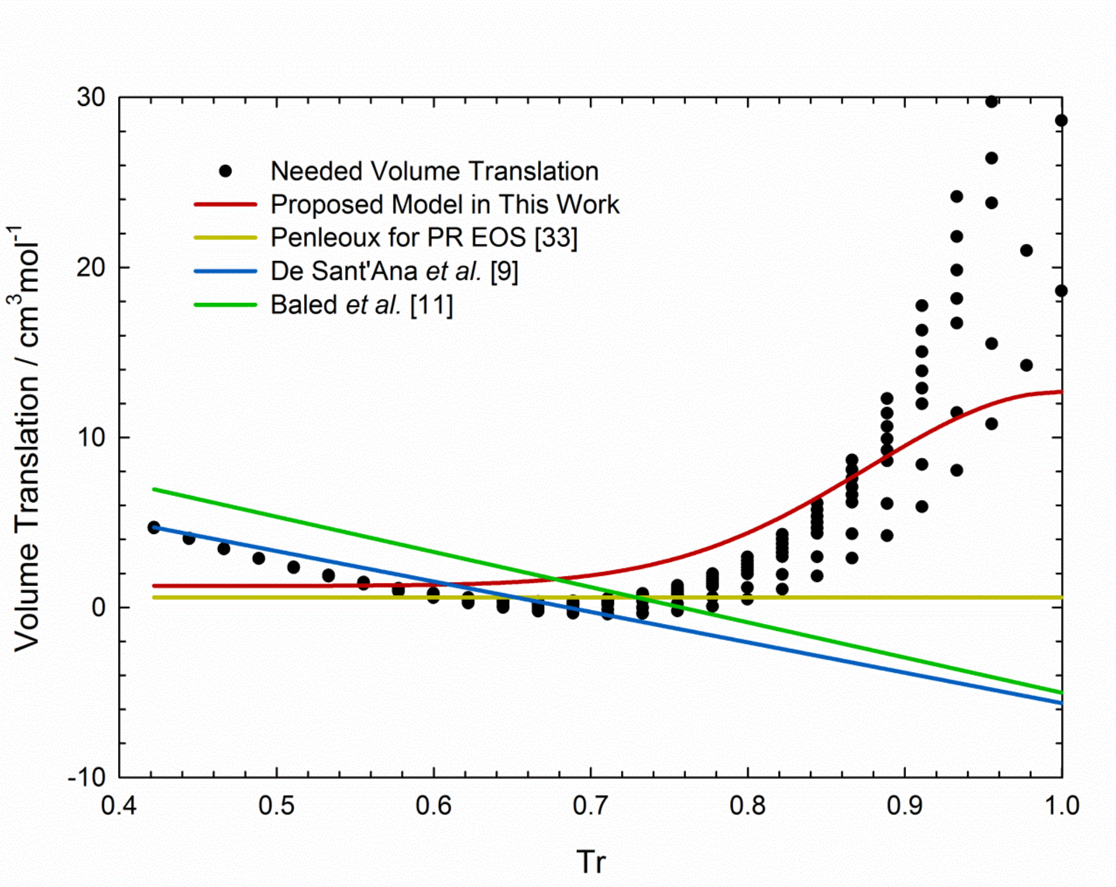


Fig.3.17 Comparison between the needed volume shift (black dots) for n-heptane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

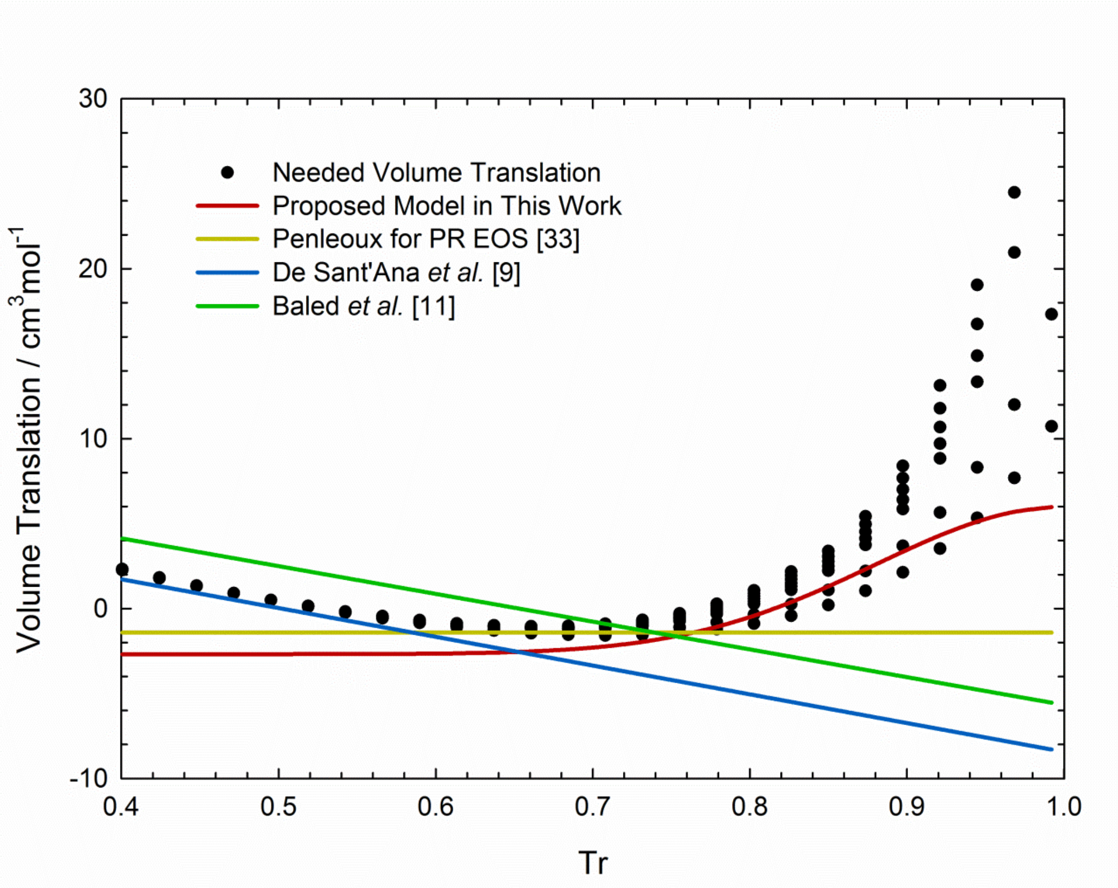


Fig.3.18 Comparison between the needed volume shift (black dots) for toluene (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

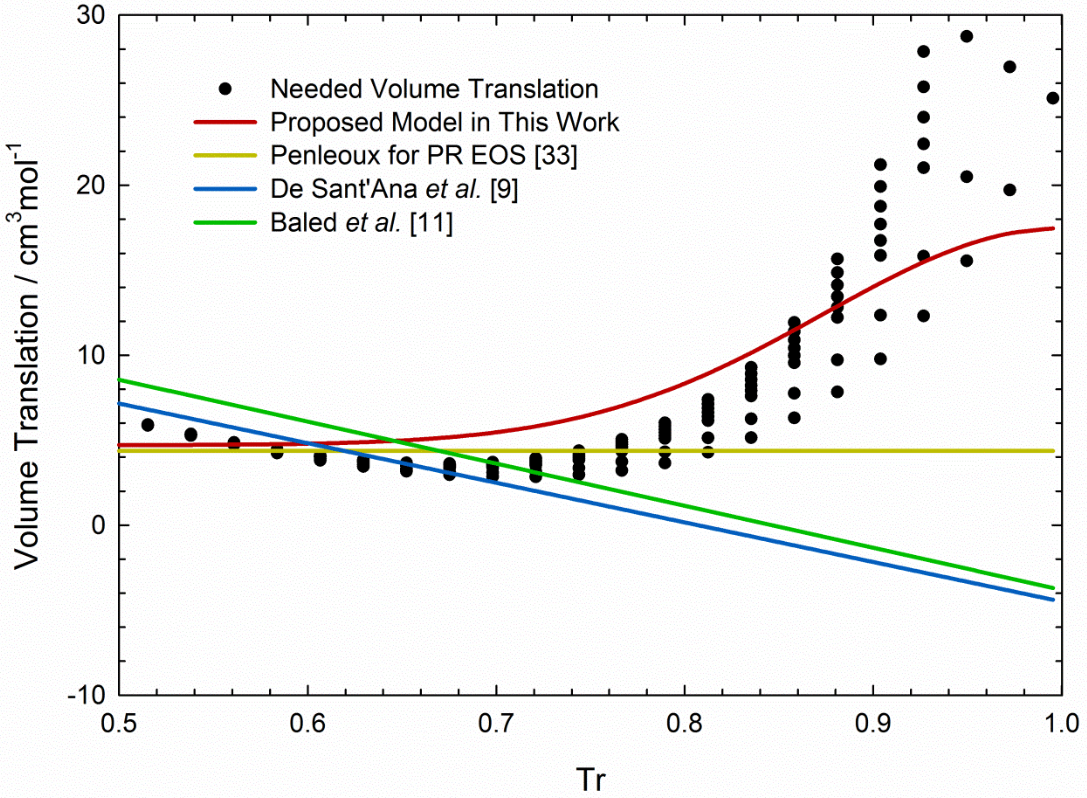


Fig.3.19 Comparison between the needed volume shift (black dots) for n-octane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

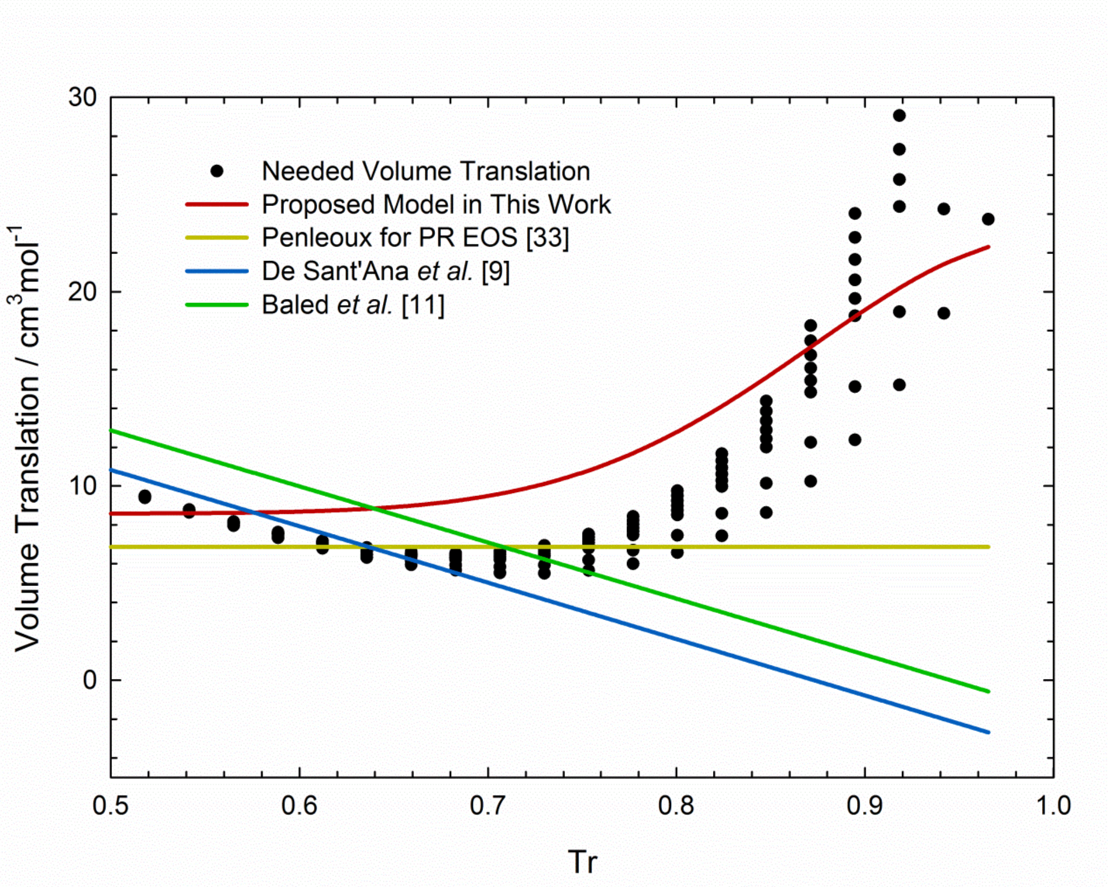


Fig.3.20 Comparison between the needed volume shift (black dots) for n-nonane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

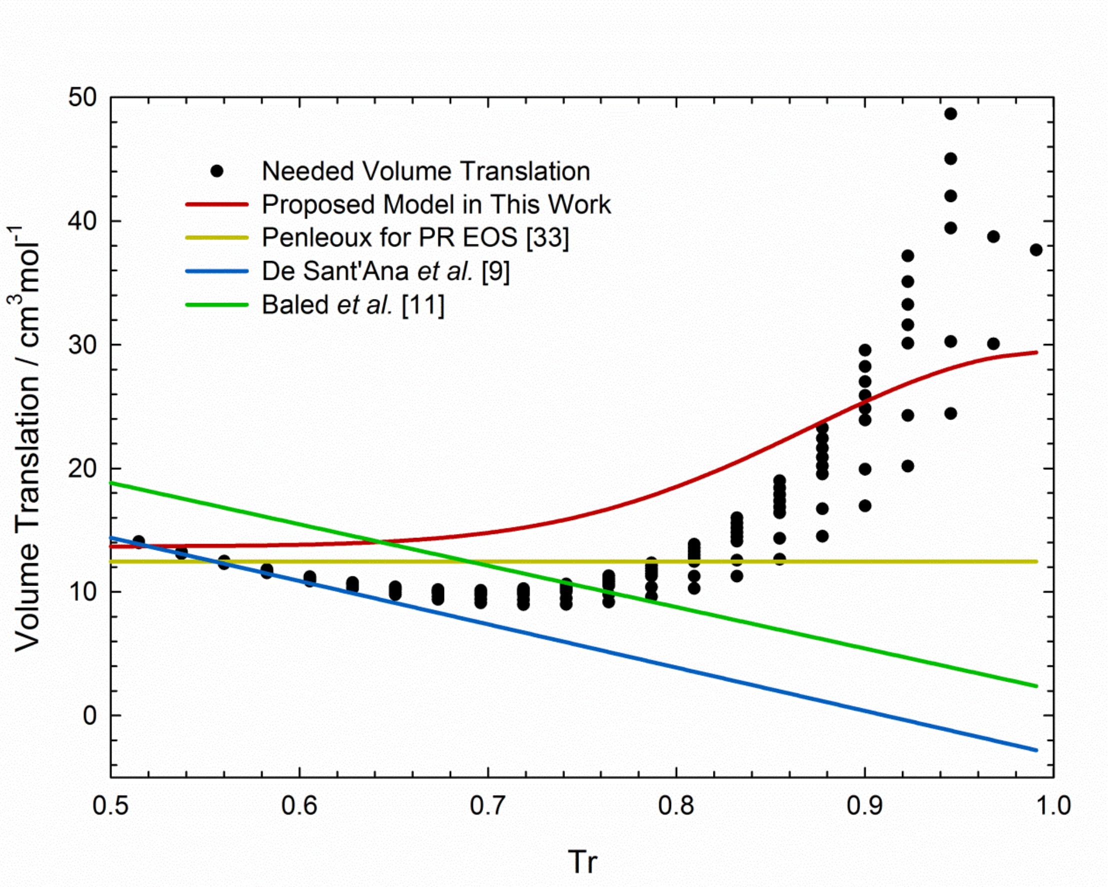


Fig.3.21 Comparison between the needed volume shift (black dots) for n-decane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

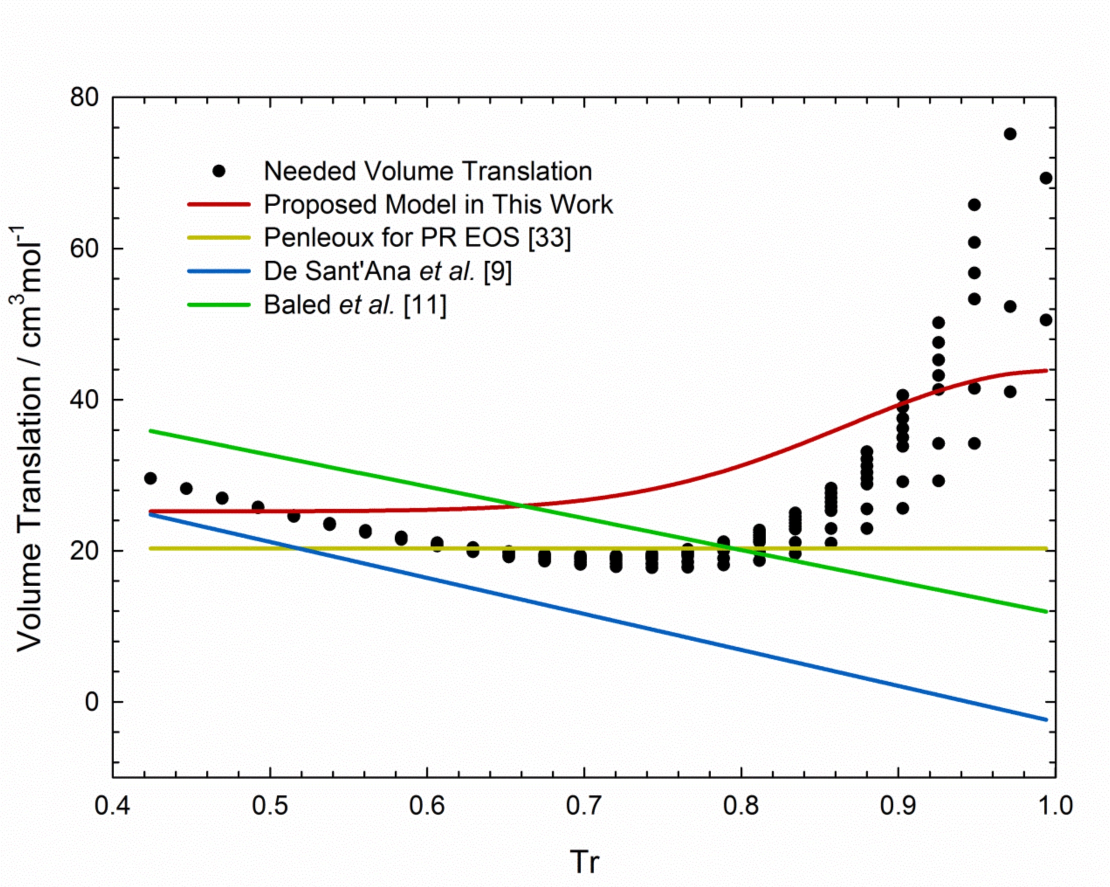


Fig.3.22 Comparison between the needed volume shift (black dots) for n-dodecane (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

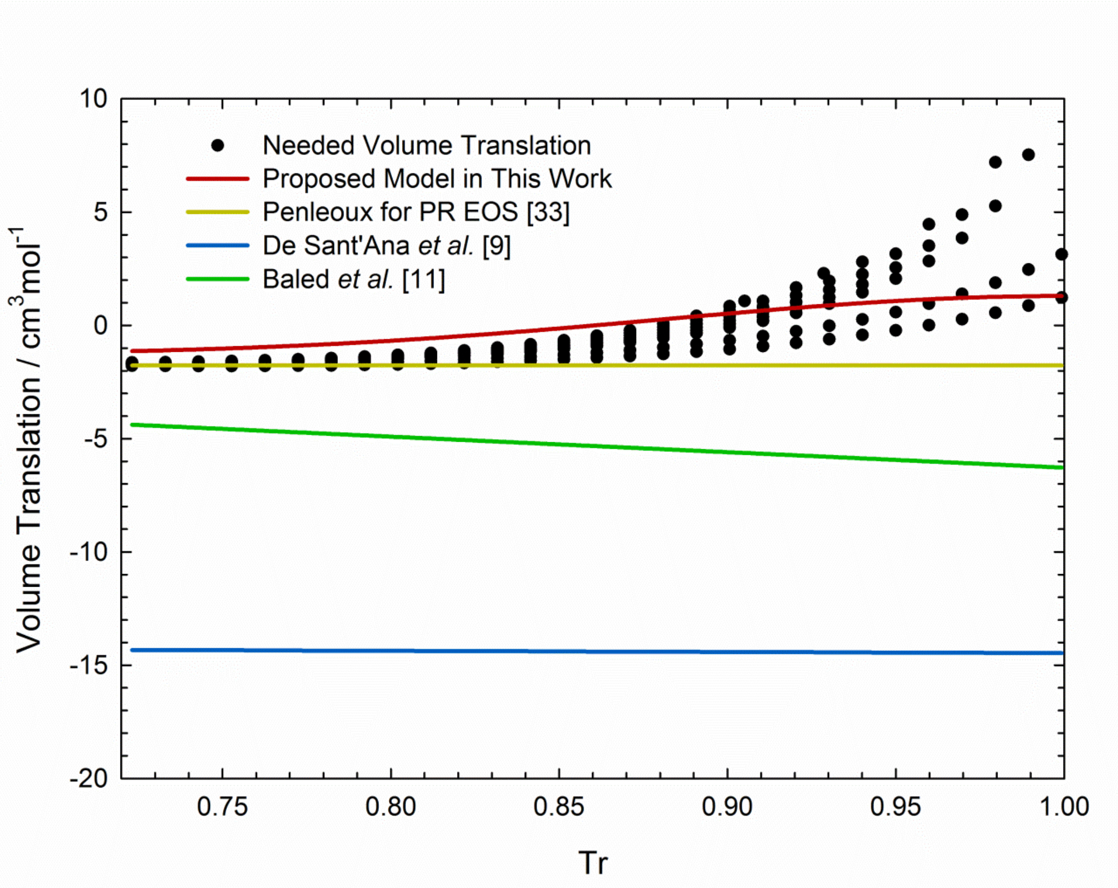


Fig.3.23 Comparison between the needed volume shift (black dots) for carbon dioxide (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

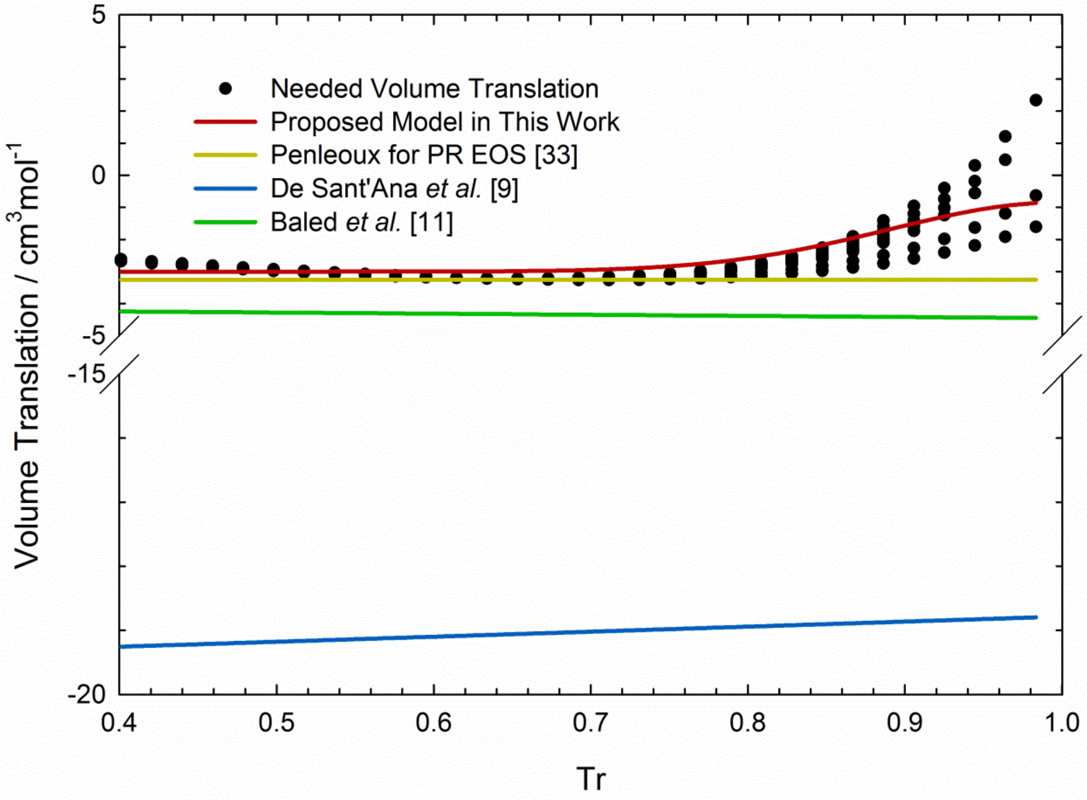


Fig.3.24 Comparison between the needed volume shift (black dots) for oxygen (P=0.5P_c, 0.6P_c, 0.7P_c, 0.8P_c, 0.9P_c, 1P_c, 1.5P_c and 2P_c) and those calculated by the other four different volume translation models

CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

In this study, crossover phenomenon with thermodynamic inconsistency is analyzed based on the PV diagram for pure component. A criterion is proposed to judge if the crossover phenomenon exists in various volume translations, and if so, the extent of the temperature and pressure range over which the crossover phenomenon occurs. The recently proposed volume translations are evaluated on the basis of the developed criterion. It can be concluded that there is thermodynamic inconsistency at a lower pressure for most nonlinear temperature-dependent volume translations, but no any crossover issues exist for the constant volume translations and linear temperature-dependent volume translations with a negative coefficient of temperature.

In addition, a generalized temperature-dependent volume translation model is proposed for the PR EOS for the more accurate prediction of molar volume. The method consists of three acentric factor dependent parameters. On the basis of the criterion of thermodynamic consistency we have proposed, a constraint is introduced into the nonlinear regression combined with the proposed volume translation model. The model parameters are determined based on the regression of the density data of 16 pure compounds. The new volume-translated PR EOS leads to an improved liquid density prediction with an overall absolute average percentage deviation of 1.42%. Notably, the new volume translation model does not lead to the crossing of pressure-volume isotherms over a wide range of pressure and temperature (up to 100 MPa and 1000 K).

4.2. Recommendations

With the introduction of a mathematical constraint on the basis of the criterion on thermodynamic consistency, no crossing appears in the PV isotherms calculated by our volume-translated PR EOS over a wide range of temperature and pressure. However, for the more complicated mixtures, future work is needed to check if the thermodynamic consistency in terms of the PVT relations remains valid for mixtures.

Liquid density prediction for pure components is improved by using a generalized volume translation technique developed in this study. In the future, in combination with the use of proper mixing rules, the newly proposed volume translated EOS can be extended to the phase behavior modeling for mixtures, e.g., heavy oil/solvent mixtures, for achieving more accurate density predictions.

BIBLIOGRAPHY

A. Peneloux, E. Rauzy, R. Freze, A consistent correction for Redlich–Kwong–Soave volumes, Fluid Phase Equilib. 8 (1982) 7-23.

A.M. Abudour, S.A. Mohammad, R.L. Robinson, K.A.M. Gasem, Volume-translated Peng–Robinson equation of state for saturated and single-phase liquid densities, Fluid Phase Equilib. 335 (2012) 74-87.

B. Hoyos, Generalized liquid volume shifts for the Peng-Robinson equation of state for C1 to C8 hydrocarbons, Latin Amer. Appl. Res. 34 (2004) 83-89.

B.S. Jhaveri, G.K. Youngre, Three-parameter modification of the Peng-Robinson equation of state to improve volumetric prediction, in: 59th Annual Technical Conference and Exhibition, Houston, Sept. 16-19, SPE 13118, 1984.

C. Coquelet, A. Chapoy, D. Richon, Development of a new alpha function for the Peng-Robinson equation of state: comparative study of alpha function models for pure gases (natural gas components) and water-gas systems, Int. J. Thermophys. 25 (2004) 133-158.

C.F. Spencer, R.P. Danner, Improved equation for prediction of saturated liquid density, J. Chem. Eng. Data. 17 (1972) 236–241.

D.B. Robinson, D.Y. Peng, The characterization of the heptanes and heavier fractions for the GPA Peng-Robinson programs, Gas Processors Association (1978).

D.Y. Peng, D.B. Robinson, A new two-constant equation of state, Ind. Eng. Chem. Fundam. 15 (1976) 59-64.

É. Clapeyron, Mémoire sur la puissance motrice de la chaleur, J. Gabay (1834).

G. Schmidt, H. Wenzel, A modified van der Waals type equation of state, Chem. Eng. Sci. 35 (1980) 1503-1512.

G. Soave, Equilibrium constants from a modified Redlich–Kwong equation of state, Chem. Eng. Sci. 27 (1972) 1197-1203.

G.F. Chou, J.M. Prausnitz, A phenomenological correction to an equation of state for the critical region, AIChE J. 35 (1989) 1487-1496.

H. Baled, R.M. Enick, Y. Wu, M.A. McHugh, W. Burgess, D. Tapriyal, B.D. Morreale, Prediction of hydrocarbon densities at extreme conditions using volume-translated SRK and PR equations of state fit to high temperature, high pressure PVT data, Fluid Phase Equilib. 317 (2012) 65-76.

H. Li, D. Yang, Modified α function for the Peng-Robinson equation of state to improve the vapor pressure prediction of non-hydrocarbon and hydrocarbon compounds, Energy Fuels. 25 (2011) 215-223.

H. Lin, Y.Y. Duan, T. Zhang, Z.M. Huang, Volumetric property improvement for the Soave-Redlich-Kwong equation of state, Ind. Eng. Chem. Res. 45 (2006) 1829-1839.

H.B. de Sant'Ana, P. Ungerer, J.C. de Hemptinne, Evaluation of an improved volume translation for the prediction of hydrocarbon volumetric properties, Fluid Phase Equilib. 154 (1999) 193-204.

I. Søreide, Improved phase behavior predictions of petroleum reservoir fluids from a cubic equation of state, Ph.D. thesis, Norwegian Institute of Technology, 1989.

J.D. Waals, Over de continuiteit van den gas-en vloeistoftoestand, Sijthoff (1873).

J. Hekayati, A. Roosta, J. Javanmardi, Volumetric properties of supercritical carbon dioxide from volume-translated and modified Peng-Robinson equations of state, Korean J. Chem. Eng. 33.11 (2016) 3231-3244.

J. Shi, H. Li, Criterion for determining crossover phenomenon in volume-translated equation of states, Fluid Phase Equilibr. 430 (2016) 1-12.

J.J. Martin, Equations of state-Applied thermodynamics symposium, Ind. Eng. Chem. 59 (1967) 34-52.

J.-N. Jaubert, R. Privat, Y. Le Guennec, L. Coniglio, Note on the properties altered by application of a Peneloux-type volume translation to an equation of state, Fluid Phase Equilibr. 419 (2016) 88-95.

K. Frey, C. Augustine, R.P. Ciccolini, S. Paap, M. Modell, J. Tester, Volume translation in equations of state as a means of accurate property estimation, Fluid Phase Equilib. 260 (2007) 316-325.

K. Frey, M. Modell, J. Tester, Density-and-temperature-dependent volume translation for the SRK EOS: 1. Pure fluids, Fluid Phase Equilibr. 279 (2009) 56-63.

K. Magoulas, D. Tassios, Thermophysical properties of n-alkanes from C1 to C20 and their prediction for higher ones, Fluid Phase Equilib. 56 (1990) 119-140.

K.A.M. Gasem, W. Gao, Z. Pan, R.L. Robinson, A modified temperature dependence for the Peng-Robinson equation of state, Fluid Phase Equilibr. 181 (2001) 113-125.

K.S. Pedersen, J. Milter, H. Sørensen, Cubic equations of state applied to HT/HP and highly aromatic fluids, SPE J. 9 (2004) 186-192.

L. Hong, Y.Y. Duan, Empirical correction to the Peng–Robinson equation of state for the saturated region, Fluid Phase Equilib. 233 (2005) 194-203.

L.V. Yelash, T. Kraska, Volume-translated equations of state: Empirical approach and physical relevance, AIChE J. 49 (2003) 1569-1579.

M. Nazarzadeh, M. Moshfeghian, New volume translated PR equation of state for pure compounds and gas condensate systems, Fluid Phase Equilibr. 337 (2013) 214-224.

M.A. Trebble, P.R. Bishnoi, Development of a new four-parameter cubic equation of state, Fluid Phase Equilibr. 35 (1987) 1-18.

O. Pfohl, Letter to the editor: "Evaluation of an improved volume translation for the prediction of hydrocarbon volumetric properties", Fluid Phase Equilib. 163 (1999) 157-159.

O. Redlich, J.N. Kwong, On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions, Chemical Reviews. 44 (1949) 233-244.

P. Watson, M. Cascella, D. May, S. Salerno, D. Tassios, Prediction of vapor pressures and saturated molar volumes with a simple cubic equation of state, 2. The Van der Waals-711 EOS, Fluid Phase Equilibr. 27 (1986) 35–52.

P.H. Salim, M.A. Trebble, A modified Trebble-Bishnoi equation of state: thermodynamic consistency revisited, Fluid Phase Equilib. 65 (1991) 59-71.

P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD, 20899, http://webbook.nist.gov.

P.M. Mathias, T. Naheiri, E.M. Oh, A density correction for the Peng–Robinson equation of state, Fluid Phase Equilib. 47 (1989) 77-87.

T. Ahmed, Equations of state and PVT analysis, Elsevier (2013).

T.A. Mary, J.S.O. Evans, T. Vogt, A.W. Sleight, Negative thermal expansion from 0.3 to 1050 Kelvin in ZrW2O8, Science. 272 (1996) 90.

W.D. Monnery, W.Y. Svrcek, M.A. Satyro, Gaussian-like volume shifts for the Peng-Robinson equation of state, Ind. Eng. Chem. Res.37 (1998) 1663–1672.

W.R. Ji, D.A. Lempe, Density improvement of the SRK equation of state, Fluid Phase Equilib. 130 (1997) 49-63.

Y. Le Guennec, R. Privat, J.-N. Jaubert, Development of the translated-consistent tc-PR and tc-RK cubic equations of state for a safe and accurate prediction of volumetric, energetic and saturation properties of pure compounds in the sub- and supercritical domains, Fluid Phase Equilibr. 429 (2016) 301-312.

Y. Le Guennec, S. Lasala, R. Privat, J.-N. Jaubert, A consistency test for alpha functions of cubic equations of state, Fluid Phase Equilibr. 427 (2016) 513-538.