

**BIFURCATION ANALYSIS OF MULTI-PARAMETER
EQUATIONS OF STATE**

BY

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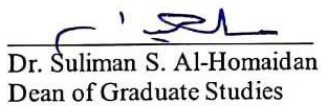
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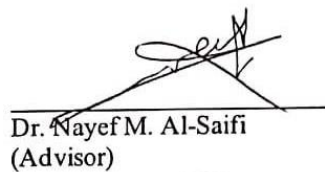
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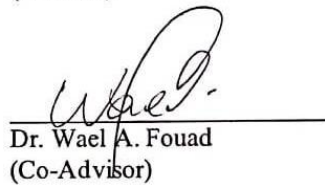

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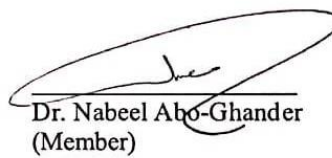
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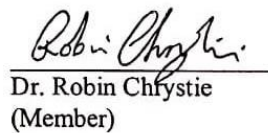
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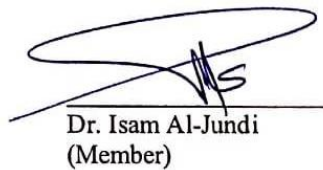



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*To my loving parents,
dear family,
precious friends, and every
person who supported me in this
journey*

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LIST OF ABBREVIATIONS

CEOSs	:	Cubic Equations of State
BWR	:	Benedict-Webb-Rubin
EOSs	:	Equations of State
LJ	:	Lennard Jones
mBWR	:	modified Benedict-Webb-Rubin
MP EOSs	:	Multi-Parameter Equations of State
P/P_c	:	Reduced Pressure
PVT	:	Pressure-Volume-Temperature
P-V	:	Pressure-Volume
SAFT	:	Statistical Associating Fluid Theory
T/T_c	:	Reduced Temperature
V-T	:	Volume-Temperature
V/V_c	:	Reduced Volume

ABSTRACT

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Bifurcation analysis is utilized to identify erroneous behaviors in accurate reference multi-parameter equations of state (MP EOSs). The bifurcation diagrams are constructed by tracking the volume roots curve as temperature changes at constant pressure. The study covers twenty one fundamental MP EOSs, which are classified into seven categories based on their functional forms. Their bifurcation diagrams are studied to show how the functional form influences the physical behavior. The bifurcation analysis is conducted for each EOS at subcritical, critical and supercritical isobars.

The study reveals that the MP EOSs experience multiplicity in volume roots, nonphysical branches, nonphysical stability limits, erroneous pressure-volume-temperature curves, and spurious two-phase coexistence regions. The study investigates the reasons behind non-physical behaviors. The generated bifurcation diagrams illustrate the regions where the MP EOSs are not safe to use. Although the MP EOSs for mixtures are not explored in this study, the results can be used as guidelines for proposing an appropriate functional form for mixtures since it is still a serious problem for developers.

ملخص الرسالة

الاسم الكامل	:	طارق علي عبد القادر لباييدي سلمه جي
عنوان الرسالة	:	تحليل التشعب لمعادلات الحالة ذات العوامل المتغيرة المتعددة
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في هذا العمل تم استخدام تحليل التشعب لتحديد السلوكيات الخاطئة في معادلات حالة المادة عديدة العوامل المتغيرة ذات النتائج الدقيقة و المرجعية. يتم إنشاء مخططات التشعب من خلال تتبع منحنيات حلول المعادلة لحجم المادة مع تغير عامل الحرارة عند قيمة ضغط ثابتة. تغطي الدراسة واحدا و عشرين معادلة أساسية عديدة العوامل المتغيرة لوصف حالة المادة، والتي تم تصنيفها في سبعة فئات مختلفة حسب أشكال الدوال الرياضية المكونة لها. تمت دراسة مخططات التشعب الخاصة بهم لإظهار كيف تؤثر أشكال الدوال الرياضية على سلوك المعادلة الفيزيائي. و قد استخدم تحليل التشعب لكل معادلة عند قيم ضغط تحت النقطة الحرجة، و عندها، و فوقها.

الدراسة تظهر أن معادلات حالة المادة عديدة العوامل المتغيرة تعاني من تعدد جذور المعادلة لقيم الحجم، و الفروع غير المادية في مخططات التشعب، و الحدود غير المادية لمنطقة استقرار المادة، و سلوك خاطئ لمنحنيات الضغط-الحرارة-الحجم، و مناطق زائفة لتعدد حالة المادة. الدراسة تحقق في الأسباب الكامنة وراء السلوكيات غير الواقعية. مخططات التشعب التي تم إنشاؤها توضح المناطق التي يكون استخدام معادلات حالة المادة عديدة العوامل المتغيرة غير آمن فيها. و على الرغم من أن معادلات حالة المادة عديدة العوامل المتغيرة للمخاليط لم يتم استكشافها في هذه الدراسة، إلا أن النتائج يمكن استخدامها كمبادئ توجيهية لاقتراح شكل دالة رياضية مناسبة للمخاليط نظرا لأنها لا تزال تمثل مشكلة جادة للمطورين.

CHAPTER 1

INTRODUCTION

For more than a century, significant progress has been made in the determination of thermodynamic properties of fluids using equations of state (EOSs). The progress started with simple empirical expressions and dramatically improved to advanced theoretical EOSs. The extensive effort has led to the development of useful types of equations of state, such as cubic equations of state (CEOSs) (van der Waals, 1873; Redlich and Kwong, 1949; Soave, 1972; Peng and Robinson, 1976; Valderrama, 2003) and statistical associating fluid theory (SAFT) (Chapman *et al.*, 1989, 1990; Huang and Radosz, 1990; Müller and Gubbins, 1995, 2001; Banaszak, Chen and Radosz, 1996; Kraska and Gubbins, 1996; Blas and Vega, 1997, 1998; Gil-Villegas *et al.*, 1997; MacDowell and Vega, 1998; Pfohl and Brunner, 1998; Kiselev and Ely, 1999; Gross and Sadowski, 2001; Tan, Adidharma and Radosz, 2008).

Although these equations of state are useful in practical applications, they still have some limitations and drawbacks. For instance, CEOSs are generally not applicable for polar and hydrogen-bonded molecules (Valderrama, 2003; Li and Yan, 2009; Kontogeorgis and Economou, 2010). The SAFT EOSs also experience various types of erroneous behaviors such as multiplicity of volume roots and spurious two-phase separation regions (Yelash *et al.*, 2005b; Polishuk, 2010; Privat *et al.*, 2012; Alsaifi *et al.*, 2017, 2019; Wilhelmssen *et al.*, 2017). Regardless of these limitations, the main concern is commonly focused on the accuracy of these EOSs. The accuracy

is still a subject of concern for all available EOSs. For instance, the SAFT EOSs still need improvement to obtain more accurate thermodynamic properties such as heat capacities, speed of sound and mixing properties. The need of accurate thermodynamic data is not only driven by the determination of common thermodynamic properties but also motivated by a large number of industrial applications. Table 1 gives a few examples of these applications.

Despite the importance of these industrial applications, the development of a highly accurate equation of state that is applicable for various types of molecules has remained a longstanding problem. To overcome this inherent challenge, attention has been paid to empirically-developed alternatives designated by multi-parameter equations of state (MP EOSs) (Span, 2000; Span *et al.*, 2001; Thol *et al.*, 2016). This type of equations accurately reproduces experimental data with the aid of a large number of adjustable parameters. Early MP EOSs were typically made by modifying the truncated virial expansion via adding simple mathematical functional forms. The growing interest in accurate MP EOSs has contributed to the development of more complex mathematical expressions including power series, exponential terms, Gaussian bell-shaped terms, and non-analytic terms (Jacobsen *et al.*, 2000; Bell *et al.*, 2014).

The success of MP EOSs relies on several factors such as the proper choice of the mathematical expressions, the availability of thermodynamic data over a broad range of temperatures and pressures, the use of a robust optimization technique for parameter estimation, numerical stability, and the capability of extrapolation. Moreover, the fact that a certain MP EOS is usually intended for only a single substance gives greater opportunity for its success and reliability. In principle, MP EOSs would expectedly represent thermodynamic properties within the experimental uncertainty, as a function of temperature and pressure (Span *et al.*, 2001).

Table 1: Examples of industrial applications requiring highly accurate thermodynamic data.

Application	Source
Calculating wave-propagation velocity (speed of sound) to model CO ₂ flow in pipelines with natural gas. This is to avoid phase-change (due to its high triple point) causing cracks in pipes during depressurization, start-up, or shut-down.	Aursand <i>et al.</i> , 2013
Prediction of maximum water content allowable in natural gas transport, and the compositions in multiphase-forming systems like hydrates.	Wilhelmsen <i>et al.</i> , 2017
Choosing the crystallization method in the drug industry by determining correct solubility data, whether used for particle formation or purification.	M.A. Reus <i>et al.</i> , 2016
Intricate modeling of interfacial phenomena, required for the use of surfactants in petroleum production, polymerization and catalysis.	Myers, 2005
Finding polymer-systems viscosity, surface tension and solid-liquid-liquid equilibria at high-pressure conditions needed in their manufacturing.	Gupta and Olsont, 2003
Evaluating safe operation conditions.	
Detecting adsorption and ion exchange equilibria for purification processes.	
Obtaining electrolyte mixtures properties necessary in wastewater treatment.	
Reliable calculation of heat capacities, heat transfer rate constants, and pressure drops in heat exchanger modeling.	Skaugen <i>et al.</i> , 2013

Indeed, the results generated using MP EOSs have commonly been used with confidence as a substitute or replacement for experimental data in handbooks (Perry and Green, 2013; Bell *et al.*, 2014). For that reason, they are known as fundamental or reference EOSs as well. Therefore, due to MP EOSs high capability, they were implemented in many applications to provide accurate thermodynamic data for industrial and scientific purposes (Span, 2000; Lemmon and Span, 2006).

Currently, the literature offers numerous examples of successful MP EOSs developed for hydrogen (Leachman *et al.*, 2009), argon (Tegeler, Span and Wagner, 1999), nitrogen (Jacobsen and Stewart, 1973; Jacobsen, Stewart and Myers, 1973; Jacobsen, Stewart and Jahangiri, 1986; Span *et al.*, 1998), oxygen (Jacobsen, Stewart and Myers, 1973; Schmidt and Wagner, 1985), water (Kiselev and Friend, 1999; Wagner and Pruß, 2002), carbon dioxide (Chung *et al.*, 1985; Sterner and Pitzer, 1994; Span and Wagner, 1996; Sun, Kiselev and Ely, 2005), hydrocarbons (McCarty, 1974; Jahangiri *et al.*, 1986; Setzmann and Wagner, 1991; Smukala, Span and Wagner, 2000; Span and Wagner, 2003a, 2003b, 2003c; Bücker and Wagner, 2006a, 2006b; Lemmon, McLinden and Wagner, 2009; Tho, Lemmon and Span, 2012; Alexandrov, Gerasimov and Grigor'ev, 2013; Zhou *et al.*, 2014; Gedanitz, Davila and Lemmon, 2015; Grigor'ev, Alexandrov and Gerasimov, 2016), and refrigerants (Tillner-Roth, 1993; Tillner Roth and Baehr, 1994; Lemmon and Jacobsen, 2005; Lemmon and Span, 2006, 2015; Pan *et al.*, 2012; Wu and Zhou, 2012; Rui, Pan and Wang, 2013; Akasaka, Zhou and Lemmon, 2015; Zhou and Lemmon, 2016).

The great success of MP EOSs does not imply that these equations are not without drawbacks. For instance, the presence of multiple Maxwell loops is a common problem in MP EOSs for pure compounds. Such a problem can be numerically overcome for phase equilibrium

calculations of pure compounds. However, that is not the case for mixtures, as stability testing is sensitive to the presence of multiple Maxwell loops (Span *et al.*, 2001; WilhelmSEN *et al.*, 2017). This is why it is impractical to extend reference MP EOSs into mixture calculations. The only way to overcome that challenge is to develop MP EOSs for specific mixtures. There have been a few examples of establishing such mixture relations (Tillner-Roth, 1993; Tillner-Roth and Friend, 1998; Lemmon and Tillner-Roth, 1999; Lemmon and Jacobsen, 1999, 2004; Lemmon *et al.*, 2000; Duan and Zhang, 2006; Kunz and Wagner, 2012; Atalay and Coban, 2015; Hernández-Gómez *et al.*, 2016, 2017; Hernández-Gómez, Tuma, Lozano-Martín, *et al.*, 2018; Hernández-Gómez, Tuma, Pérez, *et al.*, 2018; Beckmüller *et al.*, 2021). But such a process requires a tremendous effort to establish a MP EOS for just one mixture, so it is not a definitive solution.

The presence of a second Maxwell loop predicted by MP EOSs also creates an artificial pseudo-stable phase, which makes using the equation with the density functional theory to model interfacial phenomena impractical (WilhelmSEN *et al.*, 2017). In an attempt to eliminate the nonphysical Maxwell loops, some researchers introduced a modified MP EOS functional form and imposed additional constraints in the fitting of their models (Lemmon and Jacobsen, 2005; Lemmon, McLinden and Wagner, 2009). These modifications only reduced the magnitude of the second Maxwell loop but could not eliminate it completely.

Another drawback of the MP EOSs is that they are not always reliable for extrapolation beyond the range of experimental data that have been used in their development. However, because of the lack of experimental data, some authors were forced to use them for extrapolation. For example, to minimize the power requirements for compressors, Lettieri *et al.* (2018) proposed to run supercritical carbon dioxide compressors near saturation. To do so, they used the Span and Wagner MP EOS (Span and Wagner, 1996) to obtain metastable properties and calculate spinodal

lines. The use of MP EOSs for such purposes may not be safe in the presence of multiple Maxwell loops and nonphysical spinodal lines.

The roots of these problems can be traced back to the empirical nature of the original functional forms used for pure compounds. Although some evaluation techniques have been used to identify nonphysical issues, it may not be sufficient to find all nonphysical behavior. The current methods depend on either comparison with experimental data or studying the physical behaviors of thermodynamic properties as temperature, pressure and density change (Klimeck, Span and Wagner, 1996; Kilner and Craven, 1997; Koak, De Loos and Heidemann, 1999; Span, 2000b; Yelash *et al.*, 2005a, 2005b; Polishuk, 2010, 2011; Privat, Gani and Jaubert, 2010). These methods are random and may miss erroneous behaviors. Furthermore, it is not clear how the mathematical expressions proposed for a certain MP EOS contribute to the nonphysical behaviors.

A new powerful methodology was recently established by Alsaifi *et al.* (Alsaifi *et al.*, 2017, 2019; Alsaifi, 2020) to identify nonphysical behaviors in thermodynamic models using bifurcation analysis. The numerical pseudo arc-length continuation method (Binous and Shaikh, 2015; Al-Mubaiyedh and Binous, 2018) is implemented to construct isobaric volume-temperature bifurcation diagrams. By varying the temperature and tracking all volume roots, several defects can be discovered including: multiplicity of volume-roots, spurious two-phase separation regions, fictitious critical points, nonphysical roots at equilibrium, and nonphysical stability limits. A guide on how to generate and interpret bifurcation diagrams is presented in **Chapter 2**.

In this thesis, we apply the bifurcation analysis to evaluate the most popular MP EOSs. The ultimate objective is to determine all types of nonphysical behaviors in these MP EOSs and study the role of mathematical expressions in creating erroneous behaviors. The conclusions will

hopefully guide developers to propose alternative functional forms and utilize existing ones to create more accurate and less problematic MP EOSs for pure compounds and mixtures. We investigate twenty one MP EOSs designated by their respective developers as: Jacobsen, Stewart and Myers (1973), Jacobsen and Stewart (1973), McCarty (1974), Schmidt & Wagner (1985), Chung *et al.* (1985), Jahangiri *et al.* (1986), Setzmann and Wagner (1991), Tillner Roth and Baehr (1994), Sterner and Pitzer (1994), Span and Wagner (1996), Span *et al.* (1998), Tegeler, Span and Wagner (1999), Smukala, Span and Wagner (2000), Wagner and Pruß (2002), Span and Wagner (2003a, 2003b, 2003c), Lemmon and Jacobsen (2005), Bückner and Wagner (2006a), Bückner and Wagner (2006b), Lemmon and Span (2006), Lemmon, McLinden and Wagner (2009), and Zhou and Lemmon (2016).

Thesis objectives:

The main objectives of this thesis are:

1. To generate volume-temperature bifurcation diagrams for different fundamental MP EOSs at subcritical, critical and supercritical isobars.
2. To analyze the bifurcation diagrams and determine the nonphysical behavior exhibited by different fundamental MP EOSs.
3. To compare the effects of different functional forms on the physical behavior of empirical MP EOSs.
4. To propose guidelines to reduce the nonphysical behavior exhibited by empirical MP EOSs.

The rest of this thesis is presented as follows: **Chapter 2** illustrates the bifurcation analysis and how it can be used to detect nonphysical behaviors. **Chapter 3** categorizes the mathematical functional forms of the MP EOSs found in the literature. **Chapter 4** shows the results of the generated bifurcation diagrams for the equations in this study. **Chapter 5** analyzes those results, and discusses the effects of different functional forms on MP EOSs behavior. The last chapter highlights the conclusions and some recommendations for future work.

CHAPTER 2

BIFURCATION ANALYSIS

2.1 Evaluation of Thermodynamic Models

The literature offers several methods of evaluating the accuracy and physical behavior of thermodynamic EOSs. The most common method is to reproduce experimental or molecular simulation data within the equation's validity region. The comparison with other proposed EOSs in the literature is also a typical method to check the validity of the proposed EOS. Another evaluative procedure is to study the physical behaviors of different thermodynamic properties over a wide range of temperatures, pressures and densities (Klimeck, Span and Wagner, 1996; Kilner and Craven, 1997; Span, 2000). The test of the equation's capability of extrapolation and representation in the critical and metastable regions is also an important method for evaluation (Wagner and Pruß, 2002). Some authors also apply constraints on certain parameters such as predicting partial derivatives of thermal or caloric properties, and phase identification parameters (Venkatarathnam and Oellrich, 2011; Jayanti and Venkatarathnam, 2016).

Although these methods are useful for developing a new EOS, they only test thermodynamic properties at random temperature and pressure values. The random selection of temperatures and pressures can miss some erroneous behaviors in the MP EOSs. Moreover, they do not easily detect hidden mathematical artifacts caused by the used functional forms in developing MP EOSs. The literature is rich with studies showing that some EOSs predict nonphysical behaviors as a result of mathematical artifacts (Koak, De Loos and Heidemann, 1999;

Jacobsen *et al.*, 2000; Span, 2000; Yelash *et al.*, 2005a, 2005b; Polishuk, 2010; Privat, Gani and Jaubert, 2010). The evaluation of these studies shows that the success of finding problems in a certain equation is based on studying thermodynamic properties at random temperatures and pressures. A more thorough and efficient approach is required to identify hidden defects in a more reliable and trustworthy way.

Recently, Alsaifi et al. (2017, 2019, 2020) proposed a reliable procedure to analyze thermodynamic EOSs. The procedure utilizes the bifurcation theory, which is a numerical method that has been used before in other fields of science (Mangold and Gilles, 1996; Mei, 2000; Aslam and Sunol, 2006). The bifurcation analysis can generally determine all possible solutions for a system of equations as one parameter changes (Seydel, 2009). Alsaifi et al. (2017, 2019, 2020) exploited the power of bifurcation diagrams to analyze several widely-used thermodynamic EOSs. From just one bifurcation diagram, it was possible to show different types of nonphysical behaviors such as multiple nonphysical volume roots, spurious two-phase separation regions, and erroneous PVT behavior. Table 2 provides a list of the EOSs that have been examined by bifurcation analysis so far.

Table 2: A list of thermodynamic EOSs previously studied using bifurcation analysis.

Equation of State	Source
The Poole et al. modified van der Waals	(Alsaifi <i>et al.</i> , 2019)
Original SAFT	
CK-SAFT	
Soft-SAFT	
SAFT-VR-Mie	
PC-SAFT	(Alsaifi <i>et al.</i> , 2017, 2019)
Thol et al. LJ MP EOS	(Alsaifi, 2020)
May and Mausbach LJ MP EOS	
Nicolas et al. LJ MP EOS	
Johnson et al. LJ MP EOS	
Mecke et al. LJ MP EOS	
Kolafa and Nezbeda LJ MP EOS	

2.2 Constructing the Bifurcation Diagrams

To study a nonlinear algebraic EOS using the bifurcation analysis, one variable is designated as the bifurcation parameter and one is specified as the state variable. At a fixed isobar, temperature is selected as the bifurcation parameter while molar or specific volume is chosen as the state variable. It is not always feasible to obtain an analytical solution for complex mathematical models. Several numerical techniques can be used to generate the bifurcation diagrams instead.

One of the most common techniques used is the arc-length continuation method (Keller, 1977, 1979). Basically, this method transforms the nonlinear algebraic equation of state [$f(T, V, P) = 0$] into a differential algebraic equation. That is attained by relating the variables to an arc-length segment (s) using the Pythagorean rule as follows:

$$f(T(s), V(s); P \text{ is fixed}) = 0 \quad (1)$$

and

$$\left(\frac{\partial V}{\partial s}\right)^2 + \left(\frac{\partial T}{\partial s}\right)^2 = 1 \quad (2)$$

To solve this system of differential algebraic equations, an arbitrary initial condition [$T(s = 0), V(s = 0)$] is required. One volume root at a selected temperature and pressure is provided as an initial guess. The reader can refer to previous work for a more detailed numerical analysis of the method (Binous and Shaikh, 2015; Alsaifi et al., 2017; Al-Mubaiyedh and Binous, 2018).

The set of all solutions for this system of equations is used to construct a plot of temperature (abscissa) vs volume (ordinate). Each independent continuous curve in the plot is called a branch. The diagram may have a single branch or multiple branches. Different initial conditions might be needed to find all the branches at a single isobar. Figure 1 shows a simple bifurcation diagram representing the change of volume with temperature at a subcritical isobar generated from a cubic EOS for a pure fluid.

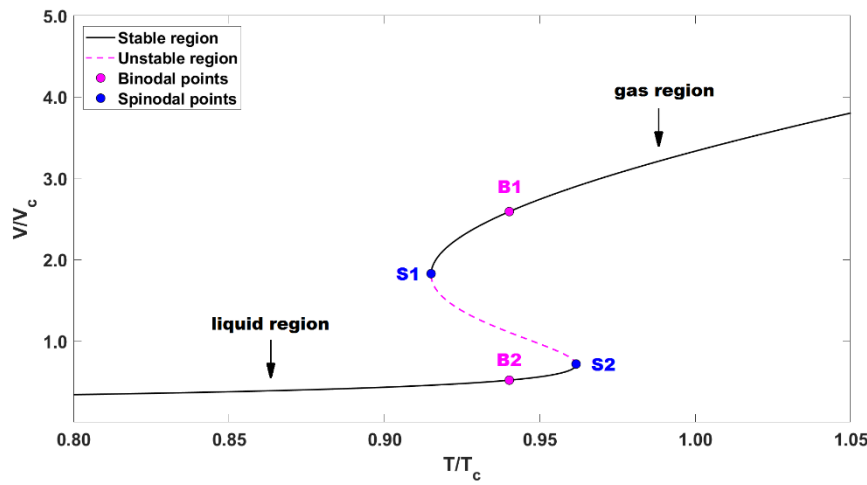


Figure 1: A V-T bifurcation diagram of a single S-shaped subcritical isobar. The dashed part between the turning points is the unstable region. Binodal points (B1 and B2) and spinodal points (S1 and S2) are identified.

2.3 Interpretation of the Bifurcation Diagram

It is important to know how to interpret the bifurcation diagrams to identify the erroneous behaviors of an EOS. Figure 2 shows a typical example of a volume-temperature (V-T) bifurcation diagram for a pure fluid at subcritical, critical, and supercritical isobars. At subcritical conditions, the isobar appears as an S-shaped curve with only two turning points, as displayed in Figure 1.

The two turning points where the branch changes direction are designated by the spinodal points **S1** and **S2**, and they represent the stability limits of vapor and liquid. The binodal points **B1** and **B2** represent the values where the vapor and liquid coexist at equilibrium. In other words, that the chemical potential at **B1** in the vapor region equals that at point **B2** in the liquid region.

As the pressure increases and reaches the critical value, the two turning points join at the critical point as shown in Figure 2. Therefore, at the critical point, there is only one turning point representing the critical condition. At supercritical conditions, no turning points exist and the fluid has only one phase. To get more insight into the turning points, Figure 3 shows the typical pressure-volume (P-V) phase diagram with the corresponding binodal (equilibrium) points and spinodal (stability limit) points.

For pure fluids, the S-shaped behavior with two turning points at subcritical conditions shown in Figure 1 is designated in this thesis as the correct physical behavior since it represents the experimental PVT behavior and the stability limits. However, most empirical and semi-empirical EOSs do not display this S-shaped behavior as a result of nonphysical behaviors. For example, Figure 4 shows a bifurcation diagram of a very accurate Lennard-Jones fluid based EOS (Alsaifi *et al.*, 2017, 2019; Alsaifi, 2020).

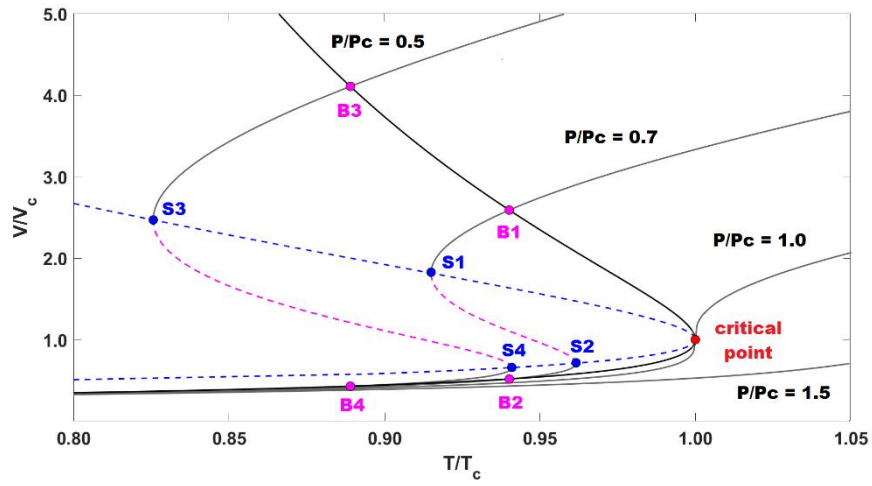


Figure 2: A V-T bifurcation diagram of a pure fluid. Four isobars are shown (at reduced pressure values of 0.5, 0.7, 1.0 and 1.5). The binodal curve connects the equilibrium points and the dashed spinodal curve connects the turning points (stability limits).

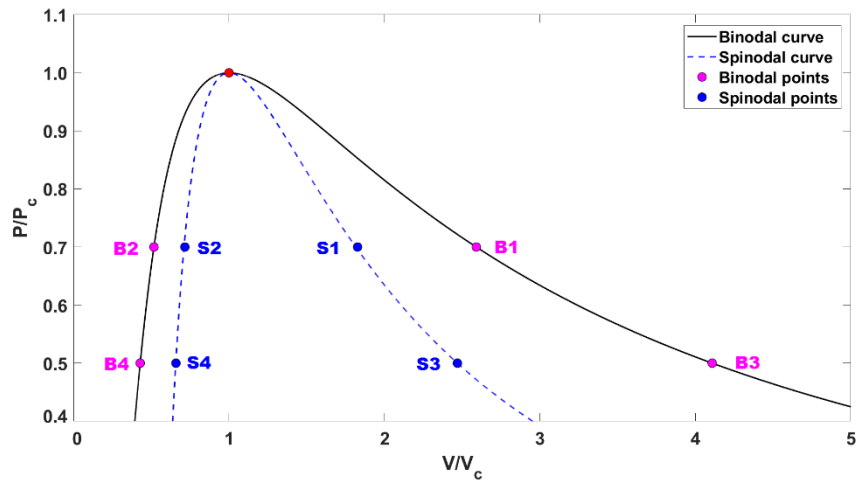


Figure 3: A P-V phase diagram of a pure fluid. The binodal (phase coexistence) curve and spinodal (stability limit) curve are shown. The binodal points (B1, B2, B3 and B4) and spinodal points (S1, S2, S3 and S4) correspond to the same ones in the V-T phase diagram.

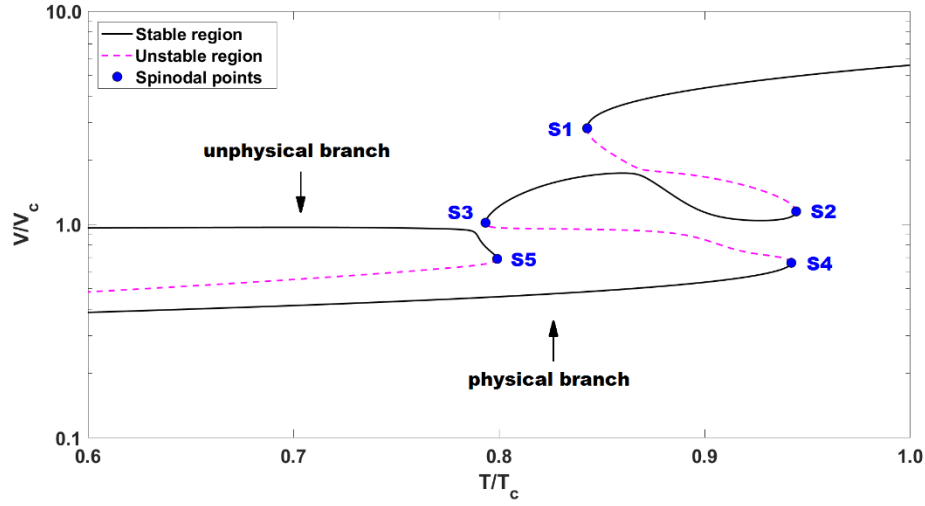


Figure 4: A V-T bifurcation diagram for Argon at a reduced pressure value of 0.5, using a reference MP EOS by Tegeler, Span and Wagner (1999). The solid lines are mechanically stable and the dashed parts are unstable.

Bifurcation diagrams offer a useful way to inspect the behavior of the physical branch. Figure 4 shows a bifurcation diagram displaying a zig-zag behavior instead of the S-shape. The diagram reveals the multiplicity of volume roots exhibited by the EOS. For example, Figure 4 shows five volume roots instead of three for reduced temperatures between around 0.8 and 0.95. The diagram also reveals the existence of fictitious turning points predicted by the EOS. This creates mechanically stable segments in the unstable region and leads to the equation predicting spurious phase-separation regions. Furthermore, the bifurcation diagram illustrates the presence of the nonphysical branches which can result in more erroneous behaviors.

CHAPTER 3

MULTI-PARAMETER EQUATIONS OF STATE

In this chapter, we shall give a summary of the MP EOSs that will be studied by bifurcation analysis. The MP EOSs are purely empirical formulations. Although their origins can be traced back to the virial series, their adjustable parameters do not represent physical meaning like those in the virial EOS. Early MP EOSs, such as the Benedict-Webb-Rubin (BWR) type, Bender type or modified BWR (mBWR) type EOSs (Jacobsen *et al.*, 2000), were pressure-explicit equations in terms of density (ρ) and temperature (T). More recent MP EOSs are expressed in terms of reduced residual Helmholtz free energy (φ^{res}) as a function of reduced density (δ) and inverse reduced temperature (τ). The purpose of the recent Helmholtz free energy forms is to simplify the derivation of other thermodynamic properties since Helmholtz free energy is a generating function.

Each MP EOS consists of a series of mathematical terms formed by power polynomial, exponential, Gaussian, and nonanalytic terms. Table 3 describes these different categories. All MP EOSs contain polynomial and exponential terms. Some of them utilize Gaussian and nonanalytic terms to improve the accuracy in the critical region. The literature is rich with many MP EOSs constructed by these functional forms. In this thesis, we study widely used MP EOSs. Table 4 summarizes these MP EOSs. In the table, the range of validity is given in terms of temperature and pressure. One can also notice that each MP EOS was designed for a certain compound. The table also lists the number of terms of a certain functional form that is used in the MP EOS. The reader can refer to their original sources for the detailed expressions, adjustable parameters and analysis of the equations.

Table 3: The types of functional forms for the MP EOS models (Bell *et al.*, 2014).

Type	Description	Functional form ^a
I	Power polynomial	$\sum_i n_i \delta^{d_i} \tau^{t_i}$
II	Exponential in density	$\sum_i n_i \delta^{d_i} \tau^{t_i} \exp[-\sigma^{c_i}]$
III	Exponential in density and temperature	$\sum_i n_i \delta^{d_i} \tau^{t_i} \exp[-\sigma^{c_i}] \exp[-\tau^{m_i}]$
IV	Ratio of polynomials	$\frac{\sum_i n_i \delta^{d_i} \tau^{t_i}}{\sum_k n_k \delta^{d_k} \tau^{t_k}}$
V	Gaussian	$\sum_i n_i \delta^{d_i} \tau^{t_i} \exp[-\alpha_i (\delta - \epsilon_i)^2 - \beta_i (\tau - \gamma_i)^2]$
VI	Nonanalytic ^b	$\sum_i n_i \Delta^{b_i} \delta \exp[-C_i (\delta - 1)^2 - D_i (\tau - 1)^2]$ Where: $\Delta = \left\{ (1 - \tau) + A_i [(\delta - 1)^2]^{\frac{1}{2\beta_i}} \right\}^2 + B_i [(\delta - 1)^2]^{a_i}$

^a The corresponding forms for MP EOSs expressed in terms of pressure as a function of density and temperature can be obtained by derivation.

^b Some MP EOSs have different expressions for the nonanalytic functional form.

Table 4: A list of the reference MP EOSs studied in this work.

Authors	Year	Substance	Range of Validity		Number of terms from different functional forms					
			T (K)	P (bar)	I	II	III	IV	V	VI
Jacobsen, Stewart and Myers	1973	Oxygen	56-323	≤ 363	19	13	0	0	0	0
Jacobsen and Stewart	1973	Nitrogen	63-2000	≤ 10000	19	13	0	0	0	0
McCarty	1974	Methane	91-398	≤ 3500	19	13	0	0	0	0
Schmidt and Wagner	1985	Oxygen	54 – 300	≤ 818	13	19	0	0	0	0
Chung <i>et al.</i>	1985	Carbon Dioxide	216 – 423	≤ 3103	6	2	0	0	0	3
Jahangiri <i>et al.</i>	1986	Ethylene	104 – 450	≤ 2600	15	26	0	0	0	0
Setzmann and Wagner	1991	Methane	90 – 620	≤ 10000	13	23	0	0	4	0
Tillner Roth and Baehr	1994	HFC-134a	170 – 455	≤ 700	8	13	0	0	0	0
Sterner and Pitzer	1994	Carbon Dioxide	215 – 2000	≤ 100000	6	12	0	36	0	0
Span and Wagner	1996	Carbon Dioxide	216 – 1100	≤ 8000	7	27	0	0	5	3

Table 4: A list of the reference MP EOSs studied in this work. (Cont.)

Authors	Year	Substance	Range of Validity		Number of terms from different functional forms					
			T (K)	P (bar)	I	II	III	IV	V	VI
Span <i>et al.</i>	1998	Nitrogen	63.151 – 5000	≤ 250000	6	26	0	0	4	0
Tegeler, Span and Wagner	1999	Argon	84 – 700	≤ 10000	12	25	0	0	4	0
Smukala, Span and Wagner	2000	Ethylene	104 – 450	≤ 3000	6	24	0	0	5	0
Wagner and Pruß	2002	Water	251.2 – 1273	≤ 10000	7	44	0	0	3	2
Span and Wagner	2003	27 different substances (studied for Argon)	84 – 520	≤ 1000	6	6	0	0	0	0
Lemmon and Jacobsen	2005	HFC-125	172.52 – 500	≤ 600	5	10	3	0	0	0
Bücker and Wagner	2006	Ethane	90.368 – 675	≤ 9000	5	34	0	0	5	0

Table 4: A list of the reference MP EOSs studied in this work. (Cont.)

Authors	Year	Substance	Range of Validity		Number of terms from different functional forms					
			T (K)	P (bar)	I	II	III	IV	V	VI
Bücker and Wagner	2006	n-butane and isobutane	134.895 – 575 (for n-butane), 113.730 – 575 (for isobutane)	≤ 690 (for n-butane), ≤ 350 (for isobutane)	7	16	0	0	2	0
Lemmon and Span	2006	20 different substances (studied for R-245fa)	171.05 – 440	≤ 2000	5	7	0	0	0	0
Lemmon, McLinden and Wagner	2009	Propane	82.525 – 650	≤ 10000	5	6	0	0	7	0
Zhou and Lemmon	2016	R-245ca	196 – 450	≤ 100	5	5	0	0	4	0

These MP EOSs are the most accurate thermodynamic EOSs available. They can predict any thermodynamic property with an accuracy that rivals experimental data (Span, 2000). Unlike theory-based EOSs, they can accurately reproduce the physical behavior of thermodynamic properties such as isochoric heat capacity and speed of sound. Figure 5 illustrates how the IAPWS-95 MP EOS predicts a sharp increase in isochoric heat capacity as it approaches the critical point, even within a very small temperature difference (Wagner and Pruß, 2002). Figure 6 compares the isochoric heat capacity results of the IAPWS-95 MP EOS to experimental values for water (Abdulagatov, Dvoryanchikov and Kamalov, 1998). The plots are made at density values close to the critical density where an abundance of experimental data is available.

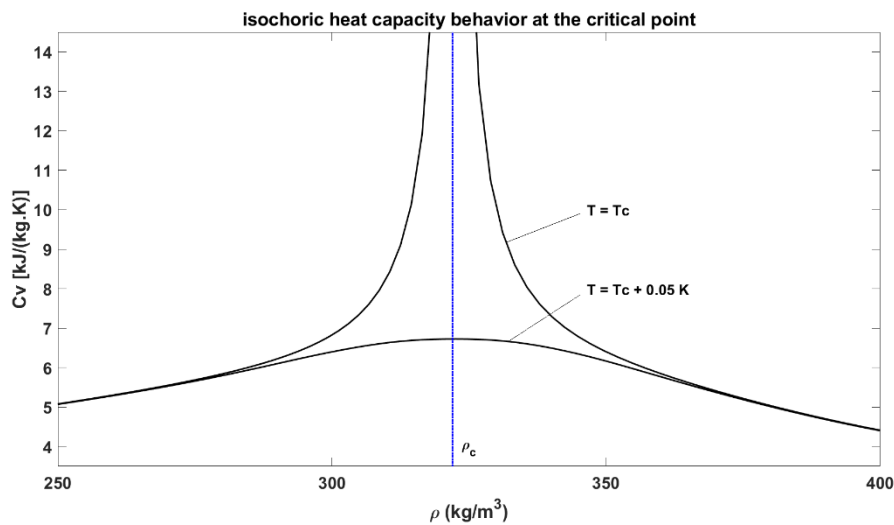


Figure 5: Isochoric heat capacity vs specific density for water using the Wagner and Pruß (2002) IAPWS-95 MP EOS.

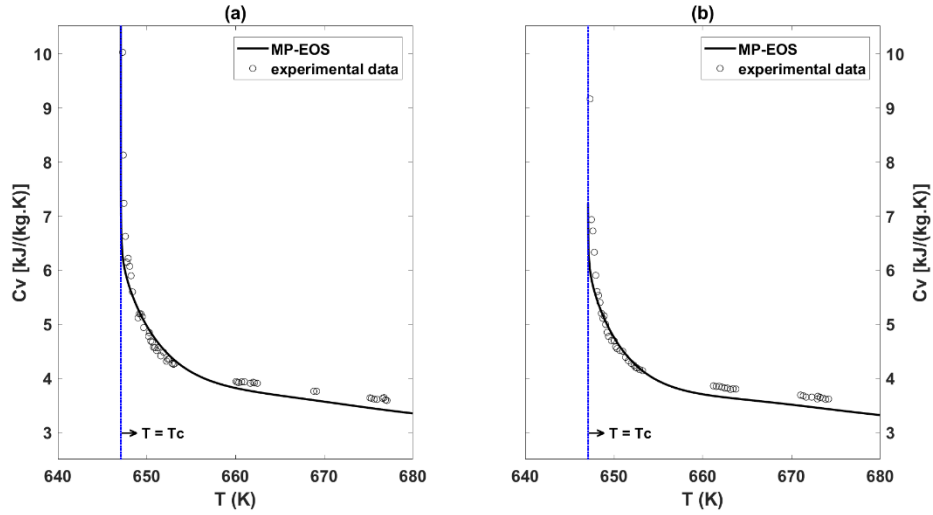


Figure 6: Isochoric heat capacity vs temperature for water using the Wagner and Pruß (2002) IAPWS-95 MP EOS at (a) $\rho = 0.98 \rho_c = 316.84 \text{ kg/m}^3$ and (b) $\rho = 1.07 \rho_c = 344.828 \text{ kg/m}^3$. The experimental data points are from Abdulagatov, Dvoryanchikov and Kamalov (1998).

The MP EOSs also display powerful extrapolation capability outside of their range of validity. Although it is not safe to extrapolate outside the validity region, it is claimed that the MP EOSs are accurate outside the fitting range. The reason to claim the accuracy of MP EOSs outside the validity region arises from the common extrapolation tests used in their developments. Among these tests are the so-called ideal curves or the comparison of shock-wave measurements with the Hugoniot curve (Wagner and Pruß, 2002). As will be shown later, the bifurcation analysis proves that these tests are not sufficient to detect erroneous behaviors outside the validity region.

Figure 7 shows several Hugoniot curves plotted for carbon dioxide and nitrogen. The plots display the extrapolation capability of the Span and Wagner (1996) MP EOS for carbon dioxide and the Span *et al.* (1998) MP EOS for nitrogen at high pressure and density values. Figure 8 compares the extrapolation behavior of isotherms plotted using the IAPWS-95 MP EOS and a common water EOS by Hill (1990). The equation by Hill shows the isotherms intersecting each

other and displaying mechanical instability at high pressure and density values. On the other hand, the IAPWS-95 MP EOS creates conforming isotherms free of such nonphysical behavior.

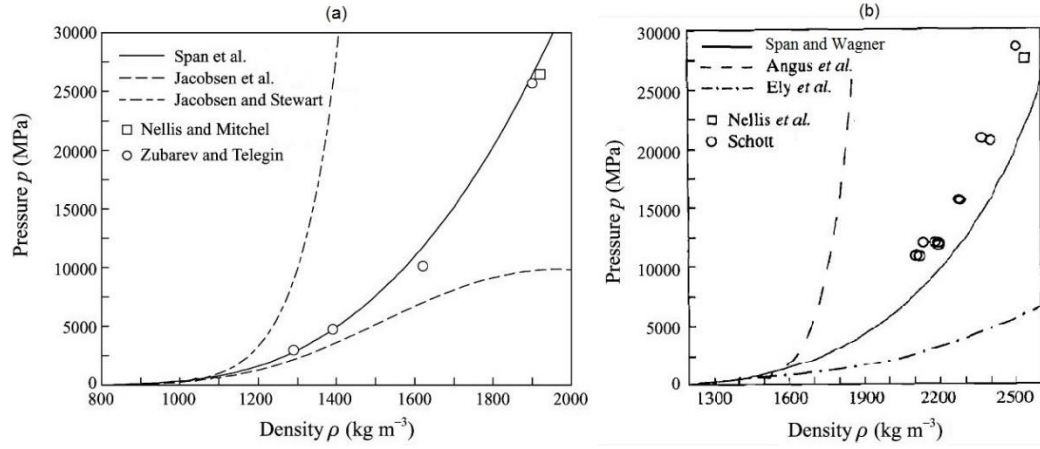


Figure 7: The Hugoniot curves for (a) Nitrogen. The figure is taken from an article by Span *et al.* (2001). (b) Carbon Dioxide. The figure is taken from an article by Span and Wagner (1996).

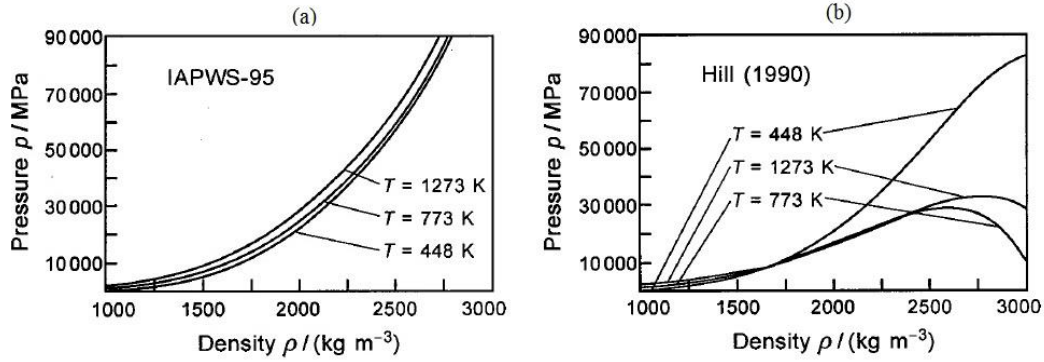


Figure 8: Isotherms extrapolation behavior at extremely high pressure. The comparison is made for water using (a) the IAPWS-95 MP EOS. (b) the Hill (1990) EOS. The figures are taken from an article by Wagner and Pruß (2002).

CHAPTER 4

BIFURCATION DIAGRAMS AND RESULTS

This chapter shows examples of bifurcation diagrams generated for the studied MP EOSs. The bifurcation diagrams reveal erroneous behaviors such as multiplicity of volume roots, spurious two-phase separation regions and nonphysical metastability limits. Modern MP EOSs are usually established for one specific substance. They have different functional forms and a different number of terms for different substances. Thus, comparing MP EOSs for different substances is not a straightforward task. For this reason, we categorize the MP EOSs into seven main categories based on the type of functional forms used in their development. The chapter is divided into seven sections analyzing each of these categories:

1. Modified Benedict-Webb-Rubin (mBWR).
2. Power polynomial plus exponential terms in density.
3. Power polynomial plus exponential terms in density plus Gaussian bell-shaped terms.
4. Power polynomial plus exponential terms in density plus Gaussian bell-shaped terms plus nonanalytic terms.
5. Power polynomial plus exponential terms in both density and temperature.
6. Power polynomial plus exponential terms in density plus nonanalytic terms.
7. Power polynomial plus ratio of polynomial terms plus exponential terms in density.

4.1 Category I: modified Benedict-Webb-Rubin MP EOS

One of the most common empirical thermodynamic models is the modified Benedict-Webb-Rubin (mBWR) model (Jacobsen and Stewart, 1973; Jacobsen, Stewart and Myers, 1973; McCarty, 1974; Nicolas *et al.*, 1979; Johnson, Zollweg and Gubbins, 1993; Sun and Teja, 1996; Jacobsen *et al.*, 2000; Span *et al.*, 2001; May and Mausbach, 2012). The mBWR type EOS contains a series of power polynomial and exponential terms. It is given by the following pressure-explicit function of density and temperature:

$$P = \sum_{n=1}^9 a_n \rho^n + \sum_{n=10}^{15} a_n \rho^{2n-17} \exp(-\gamma \rho^2) \quad (3)$$

where a_n are temperature-dependent polynomials. They include a total of 32 adjustable parameters to be fitted for any molecule. The final adjustable parameter γ is approximated by $\gamma = 1/\rho_c^2$, where ρ_c is the critical density.

We analyze three MP EOSs of the mBWR type using V-T bifurcation diagrams. Namely: Jacobsen, Stewart and Myers (1973) MP EOS for oxygen, Jacobsen and Stewart (1973) MP EOS for nitrogen, and McCarty (1974) MP EOS for methane. For simplicity, we designate the three equations of state by JSM, JS and McCarty; respectively. This enables us to examine the effect of different adjustable parameters on the same functional form and number of terms. Figure 9, Figure 10 and Figure 11 show the bifurcation diagrams for the three MP EOSs at reduced subcritical and critical pressures (P/P_c) of 0.5 and 1.0.

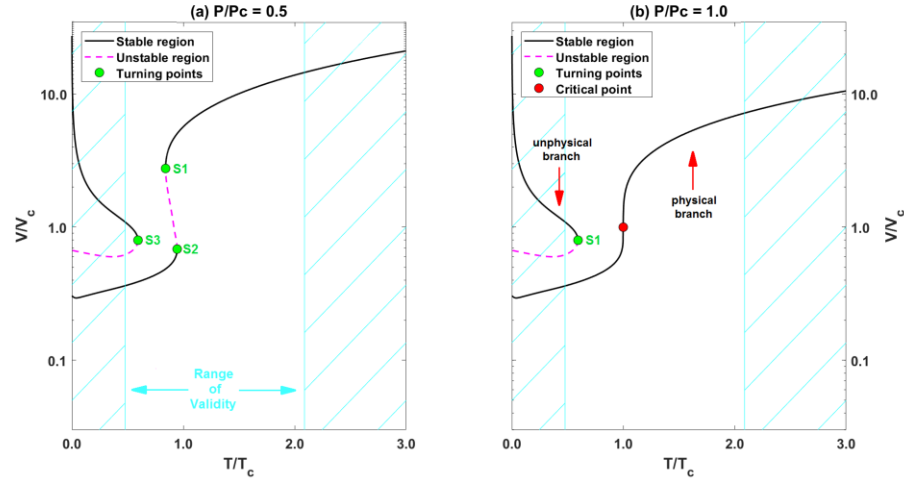


Figure 9: The V-T bifurcation diagram of methane using the McCarty (1974) MP EOS at (a) $P/P_c = 0.5$ and (b) $P/P_c = 1.0$. The solid lines represent mechanically stable curves, the dashed lines are mechanically unstable, and the dot points denote the turning points. The shaded area is outside of the reported range of validity of the EOS.

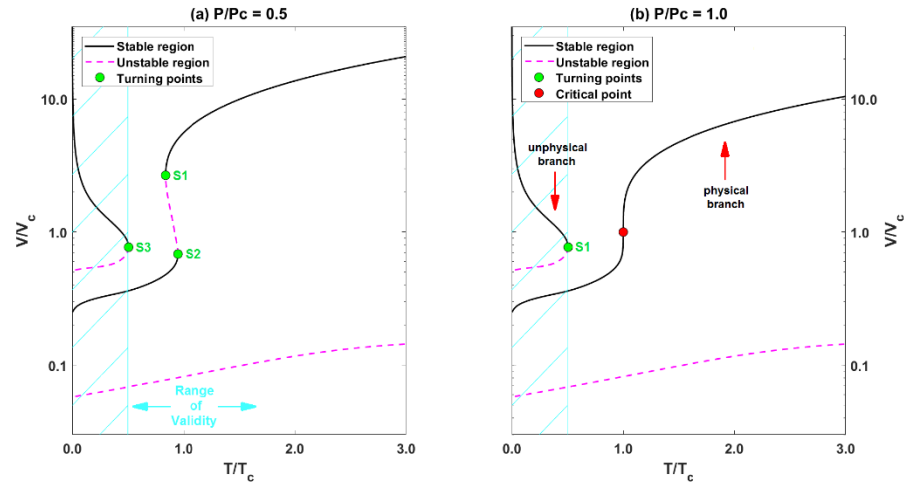


Figure 10: The V-T bifurcation diagram of nitrogen using the Jacobsen and Stewart (1973) MP EOS at (a) $P/P_c = 0.5$ and (b) $P/P_c = 1.0$. The solid lines represent mechanically stable curves, dashed lines are mechanically unstable, and the dot points denote the turning points. The shaded area is outside of the stated range of validity of the EOS.

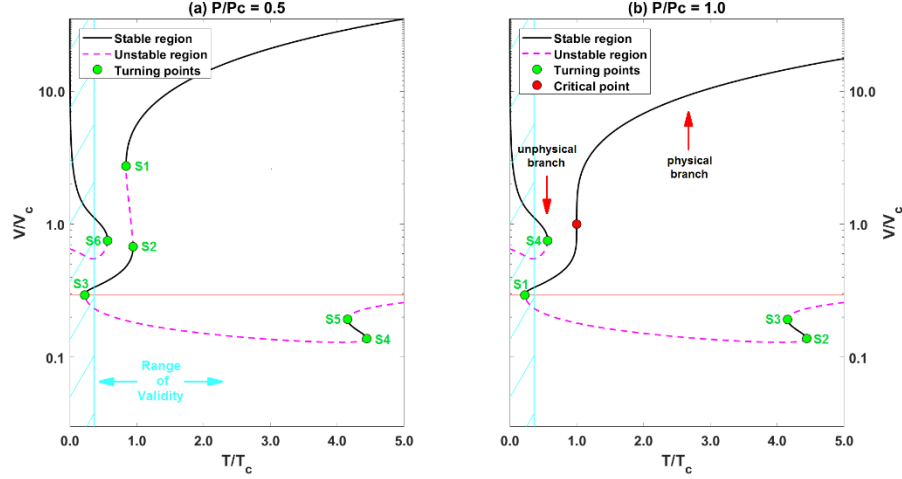


Figure 11: The V-T bifurcation diagram of oxygen using the Jacobsen, Stewart and Myers (1973) MP EOS at (a) $P/P_c = 0.5$ and (b) $P/P_c = 1.0$. The solid lines represent mechanically stable curves, dashed lines are mechanically unstable, and the dot points denote the turning points. The shaded area is outside of the range of validity of the EOS. The horizontal red line represents the reduced molar volume value of ($V/V_c = 0.21$).

Although the three MP EOSs possess the same analytical expression, their behavior is not exactly the same. The physical branches of McCarty EOS shown in Figure 9 and of JS EOS shown in Figure 10 give the correct S-shaped behavior. Each one of them has a maximum of three volume roots, and only two turning points representing the physical spinodal points. On the other hand, the physical branch of JSM EOS shown in Figure 11 has five turning points. However, it has the correct S-shape in the range above the reduced molar volume (V/V_c) value of 0.21, as illustrated above the horizontal red line. The extension of the physical branch below the horizontal red line is nonphysical but it is found to be a weak function of pressure, and does not cause any spurious two phase regions.

In all three figures, the turning points, which are designated by 1 and 2 at reduced pressure of 0.5, represent the physical spinodal points. Those turning points disappear at the critical isobar. All three MP EOSs also form a nonphysical branch with one turning point at low temperatures.

Yet these nonphysical branches exist outside the range of validity, and are not a strong function of pressure. So their significance is negligible, even though they still cause multiplicity of volume roots at low temperatures and pressures. The bifurcation diagram of the JS EOS shows another nonphysical branch, as seen in Figure 10. However, its effect is also negligible because it is not a strong function of pressure, and does not contribute to any erroneous behavior.

4.2 Category II: Power Polynomial + Exponential Series MP EOSs

While the mBWR type model generally uses a constant number of power polynomial and exponential terms, modern MP EOSs are more flexible to the number of terms. This allows for a less rigid specification of the number of terms of different functional forms. The general analytical expression used by modern MP EOSs is in terms of reduced residual Helmholtz free energy. It consists of different combinations of a series of power polynomial, exponential, Gaussian and nonanalytic terms. The general analytical expression is given by:

$$\begin{aligned}
\varphi^{\text{res}}(\delta, \tau) &= \varphi(\delta, \tau) - \varphi^{\text{ideal}}(\delta, \tau) \\
&= \sum_i n_i \delta^{d_i} \tau^{t_i} + \sum_i n_i \delta^{d_i} \tau^{t_i} \exp[-\sigma^{c_i}] \\
&\quad + \sum_i n_i \delta^{d_i} \tau^{t_i} \exp[-\alpha_i (\delta - \epsilon_i)^2 - \beta_i (\tau - \gamma_i)^2] \\
&\quad + \sum_i n_i \Delta^{b_i} \delta \exp[-C_i (\delta - 1)^2 - D_i (\tau - 1)^2]
\end{aligned} \tag{4}$$

$$\text{with} \quad \Delta = \left\{ (1 - \tau) + A_i [(\delta - 1)^2]^{\frac{1}{2\beta_i}} \right\}^2 + B_i [(\delta - 1)^2]^{a_i} \tag{5}$$

where $\varphi^{res} = A^{res}/RT$ is the reduced residual Helmholtz free energy, $\delta = \rho/\rho_c$ is the reduced density and $\tau = T_c/T$ is the inverse reduced temperature. The adjustable parameters, which are $n_i, d_i, t_i, c_i, \alpha_i, \beta_i, \varepsilon_i, \gamma_i, A_i, B_i, C_i, D_i$, and a_i are fitted using experimental data.

In this section, we analyze a reference MP EOS for oxygen proposed by Schmidt and Wagner (1985). This MP EOS is classified in the second category as it consists of thirteen power polynomial terms and nineteen exponential terms. The bifurcation diagrams can be compared with the ones for the mBWR type MP EOS for oxygen analyzed in **Section 4.1**. This will provide an insight on how a different number of terms of certain functional forms change the apparent physical behavior of the same molecule.

Figure 12 shows the V-T bifurcation diagrams at reduced pressure ($\mathbf{P/P_c}$) of 0.5, 0.7 and 1.0. It has three separate branches at reduced pressure of 0.5 as shown in Figure 12 (a). The first branch has an S-shape with only two turning points, the second is a closed loop with two more turning points, and the third branch is a continuous curve. Although the S-shaped branch gives the impression of being the physical branch, only the vapor part of it represents the actual physical roots. The physical liquid roots exist in the closed loop branch. The binodal points (denoted by open dots on the figure) represent the vapor and liquid roots in equilibrium for this isobar. The existence of multiple branches inside the range of validity gives rise to multiplicity of volume roots, which can lead to spurious phase separation regions.

An interesting phenomena occurs at reduced pressure of 0.7. Two branches combine and form one branch with four turning points, as displayed in Figure 12 (b). This branch features some nonphysical parts that are mechanically stable. Also, some of its sections display negative volume

expansivity. At the critical isobar in Figure 12 (c), the two physical turning points disappear. Two nonphysical turning points and one nonphysical branch remain unaffected by pressure change.

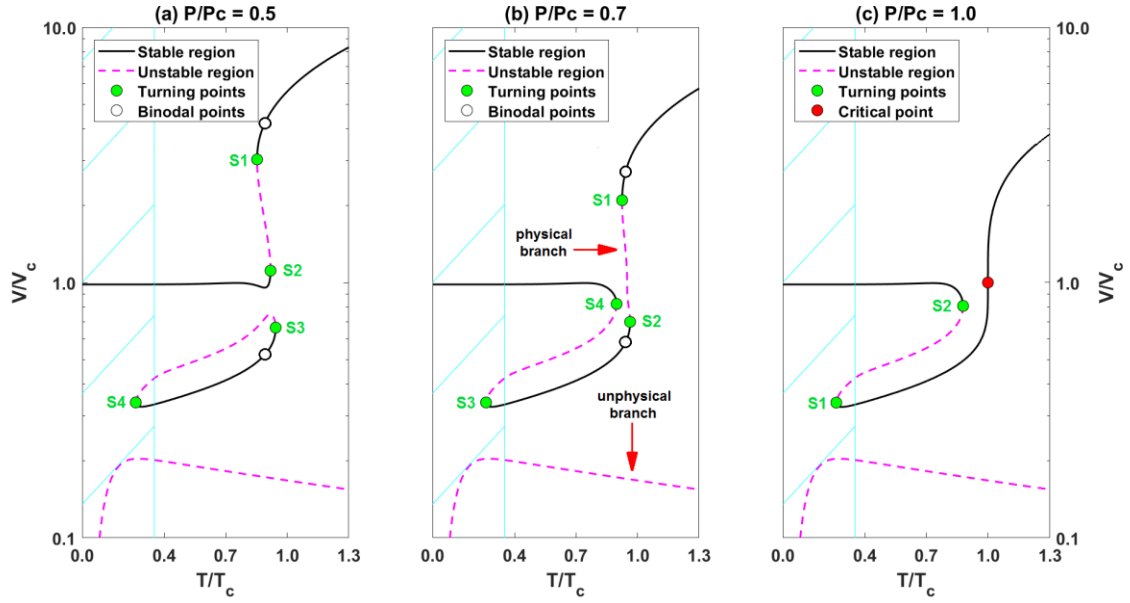


Figure 12: The V-T bifurcation diagram for oxygen using the Schmidt and Wagner (1985) MP EOS at (a) $P = 0.5 P_c$, (b) $P = 0.7 P_c$, and (c) $P = 1.0 P_c$. The solid lines represent mechanically stable curves, dashed lines are mechanically unstable, the green points denote the turning points, and the open dots denote the binodal points. The shaded area is outside of the range of validity of the EOS.

Further investigation of this MP EOS reveals several spurious two-phase separation regions other than the conventional gas-liquid phase separation region. This problem can be described by examining Figure 13, showing the bifurcation diagram at reduced pressure of 0.65. Figure 13 focuses on the zigzag part of the physical branch, divided into seven segments designated as **Line 1** to **Line 7**. The four turning points signify the limits of metastability. Point **A** on **Line 1** and point **B** on **Line 5** represent the physical coexistence vapor and liquid roots in equilibrium at that pressure. Their equivalent positions are shown on the physical binodal curve in the P-V phase diagram in Figure 14 (a), along with the turning points **1** and **4** on the spinodal curve.

The zigzag behavior of the branch can result in other line segments forming additional two-phase separation regions, similar to **Line 1** and **Line 5**. For this model, several other pairs of points at different isobars are found to satisfy the conditions of equal chemical potential. For example, at reduced pressure of 0.65, point **C** on **Line 2** and point **D** on **Line 4**, and point **E** on **Line 7** with point **F** on **Line 5**, are nonphysical binodal points. Each one of these pairs constitutes one of the spurious two-phase separation regions. Six nonphysical vapor-liquid coexistence curves, aside from the physical one, can be obtained from these combinations. This is further explored in **Section 5.3**.

Figure 14 (b) shows one of those spurious two-phase envelopes predicting an nonphysical critical point. The nonphysical critical point is found around the ($V = 0.9722 V_c$, $P = 0.6923 P_c$) point, located at the ($T = 0.9478 T_c$) isotherm. It is worth noting that some of the binodal lines are mechanically unstable. For example, referring back to Figure 13, **Line 2** with point **C** on it and **Line 4** with point **D** on it are unstable. Accordingly, the spurious binodal curve in Figure 14 (b) is mechanically unstable.

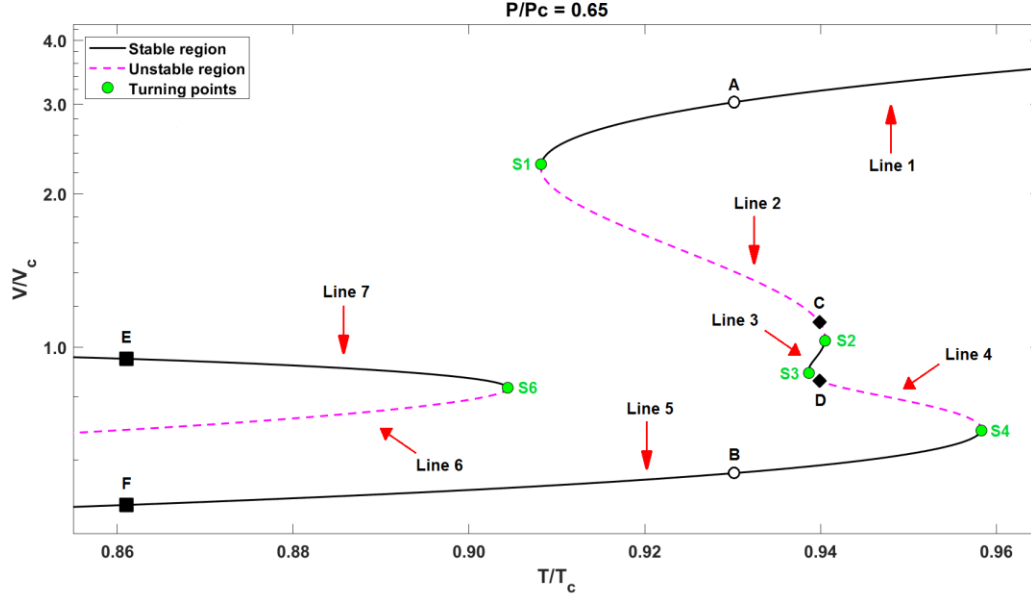


Figure 13: V-T bifurcation diagram for oxygen using the Schmidt and Wagner (1985) MP EOS at $P = 0.65 P_c$. The close up shows the zigzag behavior in the physical branch. The solid lines represent mechanically stable segments, dashed lines are mechanically unstable segments, and the green turning points denote the spinodal limits. The open dots (A-B) denote the physical vapor and liquid binodal points in equilibrium. The closed dots (C-D and E-F) are nonphysical binodal points, where the first letter refers to the vapor root and the second letter refers to the liquid root.

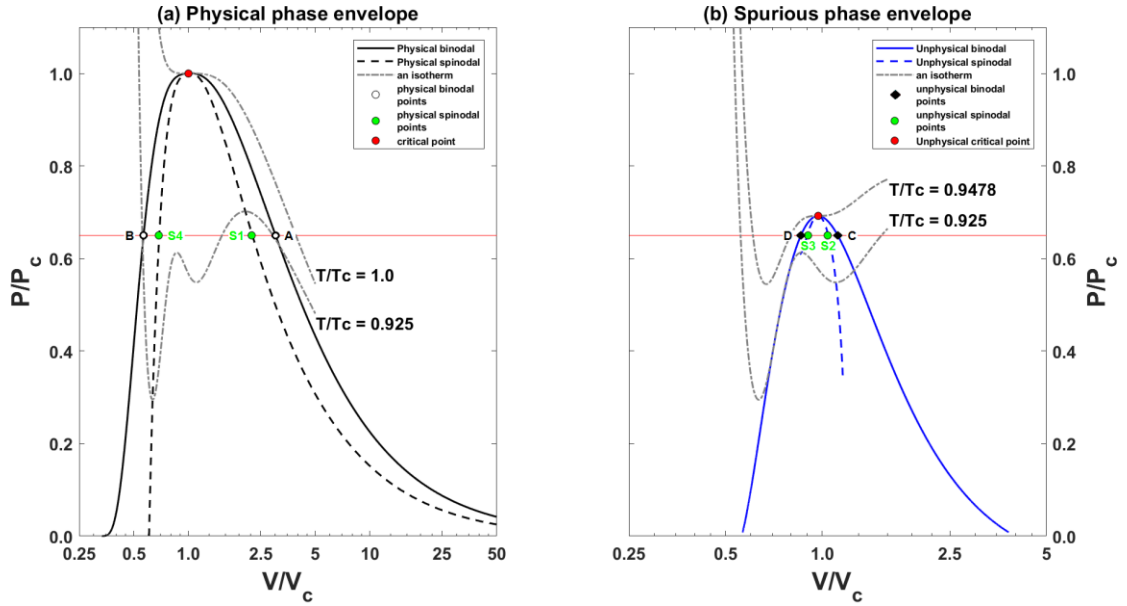


Figure 14: P-V phase diagrams for oxygen using the Schmidt and Wagner (1985) MP EOS. (a) The traditional gas-liquid binodal and spinodal curves with two isotherms. (b) A spurious phase diagram with two isotherms.

4.3 Category III: Power Polynomial + Exponential + Gaussian Series MP EOSs

The Gaussian type functional form is utilized in MP EOSs to improve the accuracy of the results. This complex form enables the MP EOS to better represent thermodynamic properties near the critical region specifically. The enhanced accuracy comes at a trade off with increased nonphysical behavior. We analyze the nitrogen reference MP EOS by Span *et al.* (1998) which employs this functional form. The results can be compared with the mBWR type MP EOS for nitrogen analyzed in **Section 4.1**. This will elucidate the effect of different analytical expressions on fundamental MP EOSs modeling the same substance. The following figures show the Span *et al.* MP EOS bifurcation diagrams at the normal point isobar and reduced pressure of 0.65, 0.85 and 10.0.

At the normal point pressure, Figure 15 (a) shows two branches; one resembles the S-shape with two turning points, and one is a closed loop with four turning points. The S-shaped branch is not exactly the physical branch. It only contains the physical vapor roots, while the physical liquid roots are in the other branch. The binodal points (denoted by open dots on the figure) designate the physical vapor and liquid roots in equilibrium at this isobar. As pressure increases, the two turning points in the S-shaped branch disappear and two other turning points appear in the closed loop branch, as shown at reduced pressure of 0.65 in Figure 15 (b). Additionally, the top branch exhibits a peak in the middle and has a segment with negative volume expansivity.

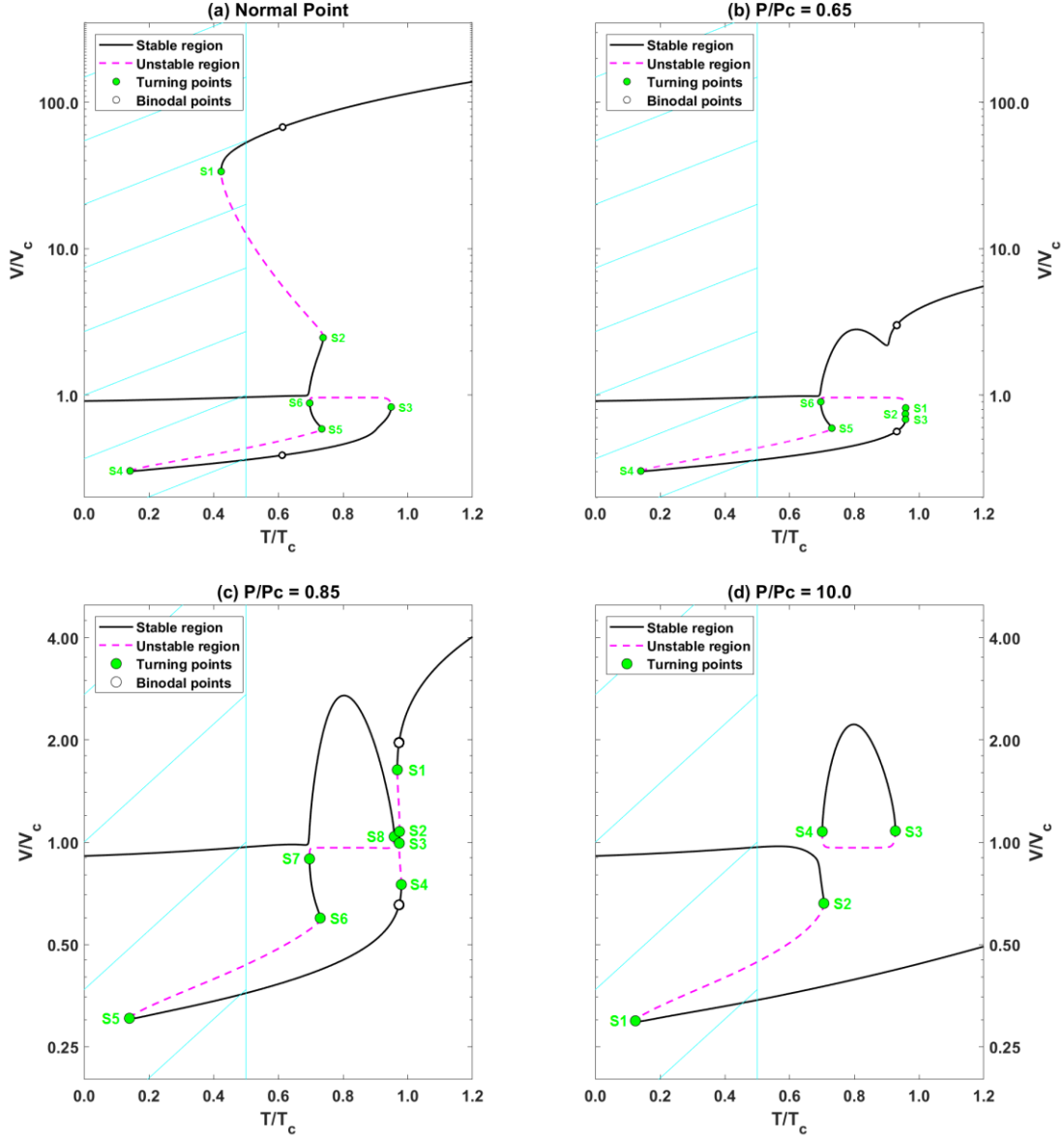


Figure 15: V-T bifurcation diagram for nitrogen using the Span *et al.* (1998) MP EOS at (a) Normal point ($P = 101.325$ kPa), (b) $P = 0.65 P_c$, (c) $P = 0.85 P_c$, and (d) $P = 10.0 P_c$. The solid lines represent mechanically stable curves, dashed lines are mechanically unstable, the green points denote the turning points, and the open dots denote the binodal points. The shaded area is outside of the range of validity of the EOS.

As the pressure further increases, the two branches combine to form one branch containing a total of eight turning points, as shown at reduced pressure of 0.85 in Figure 15 (c). This branch has nonphysical segments that are mechanically stable and display negative volume expansivity.

Spinodal points S1-S4 disappear at the critical isobar, leaving the branch with four nonphysical turning points. At high supercritical pressure as seen in Figure 15 (d), the branch separates into two; one includes the physical roots with two turning points, and the second one is a nonphysical closed loop with two turning points.

This irregular behavior of the branches causes the MP EOS to exhibit various nonphysical phenomena. Moreover, it shows its incapability of predicting the limits of stability. Figure 16 demonstrates the MP EOS's prediction of the spinodal curves. It maps out the variation in the number of turning points in bifurcation diagrams across different pressure ranges. It also shows that this MP EOS cannot fully predict the physical spinodal curve. This is further explored in **Section 5.2**.

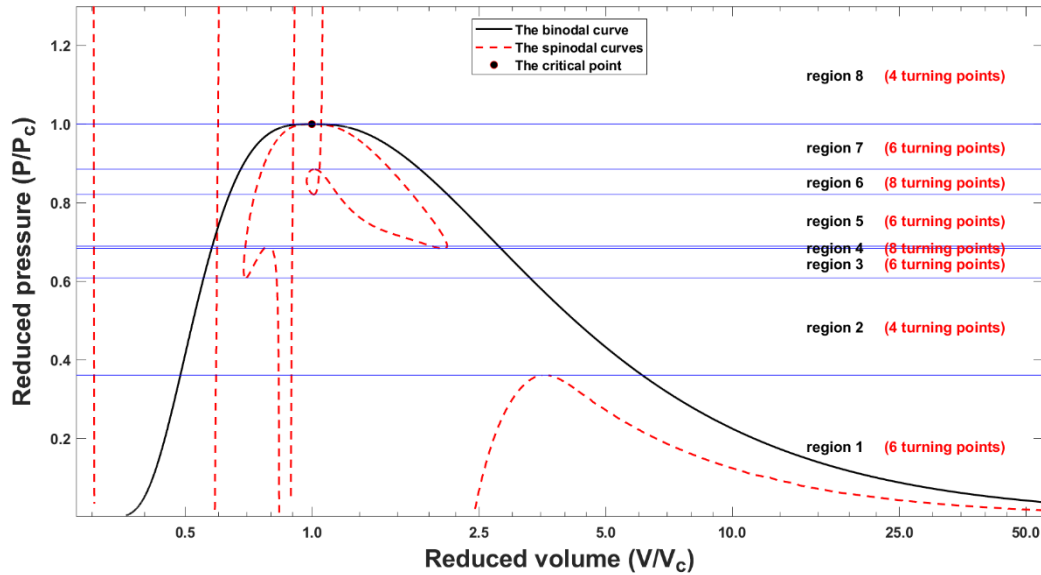


Figure 16: The spinodal limits predicted by the Span *et al.* (1998) nitrogen reference MP EOS. The solid curve is the physical P-V phase envelope. The dashed lines are the spinodal lines. The horizontal lines mark the pressure values where the number of turning points change.

4.4 Category IV: Power Polynomial + Exponential + Gaussian + Nonanalytic Series MP EOSs

The Wagner and Pruß (2002) IAPWS (International Association for Properties of Water and Steam) reference MP EOS uses both Gaussian and non-analytic functional forms to improve the accuracy and representation in the critical-region. Figure 17 presents V-T bifurcation diagrams generated for the MP EOS at the triple point isobar and reduced pressure of 0.9, 1.0 and 50.0.

Three separate branches are observed at the triple point, displayed in Figure 17 (a). The first branch has an S-shape with two turning points, the second is a closed loop with two turning points, and the third curve located at low temperatures has three turning points. While the S-shaped branch appears to be the physical branch, it only contains the physical vapor roots. The physical liquid roots are located in a separate closed loop branch. This can be verified by the determination of the binodal vapor and liquid points demonstrated by open dots on the figure. Figure 17 (b) displays the behavior at reduced pressure of 0.9, showing that two branches combined to form the physical branch. Some segments of the new branch are mechanically stable but they are nonphysical. The new branch exhibits zigzag behavior, having a total of six turning points. The existence of more than two turning points leads to spurious phase separation regions. Even at the critical isobar in Figure 17 (c), the physical branch still possesses two nonphysical turning points.

Finally, Figure 17 (d) shows the supercritical reduced pressure of 50.0, which is around the maximum pressure in the MP EOS's reported range of validity. It demonstrates how the physical branch and the nonphysical branch combine and separate again to form a new configuration. The new physical branch at this supercritical isobar resembles an S-shape. It shows two nonphysical

turning points located at low temperatures below the region of validity. The other branch which is nonphysical contains five turning points. Most of them exist outside the validity range too.

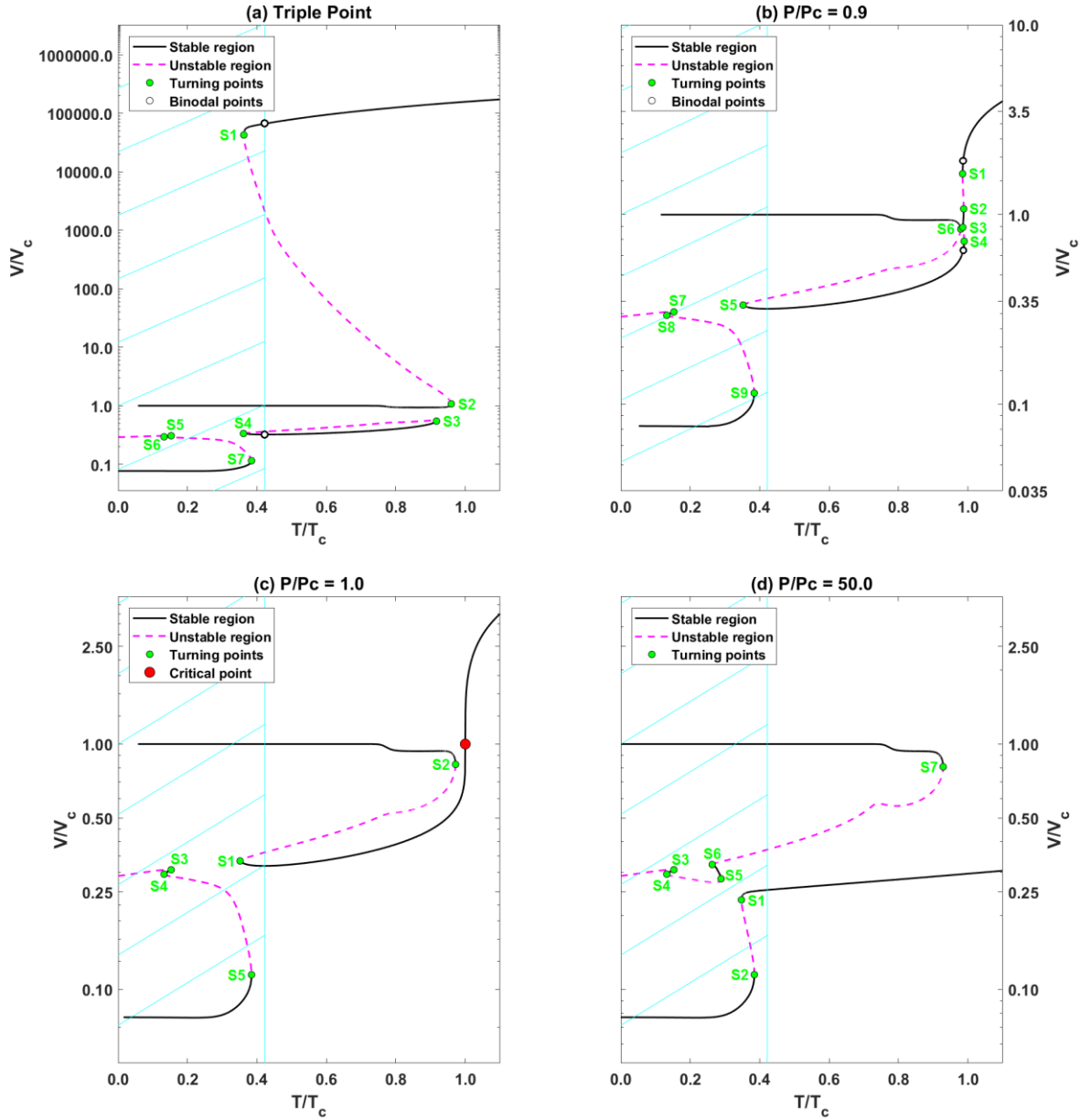


Figure 17: Bifurcation diagram of V - T using the Wagner and Prüss (2002) MP EOS for water at (a) Triple point ($P = 0.61173$ kPa), (b) $P = 0.9 P_c$, (c) $P = 1.0 P_c$, and (d) $P = 50.0 P_c$. The solid lines represent mechanically stable curves, dashed lines are mechanically unstable, the green points denote the turning points, and the open dots denote the binodal points. The shaded area is outside of the range of validity of the MP EOS.

4.5 Category V: Power Polynomial + Exponential Series in Both Density and Temperature MP EOSs

The Lemmon and Jacobsen (2005) equation for the coolant pentafluoroethane (also known as HFC-125) possesses a unique functional form. It has terms with an exponential function both in density and in temperature, as opposed to density only like other MP EOSs. We generate V-T bifurcation diagrams at the triple point isobar and reduced pressure of 0.5 and 1.0.

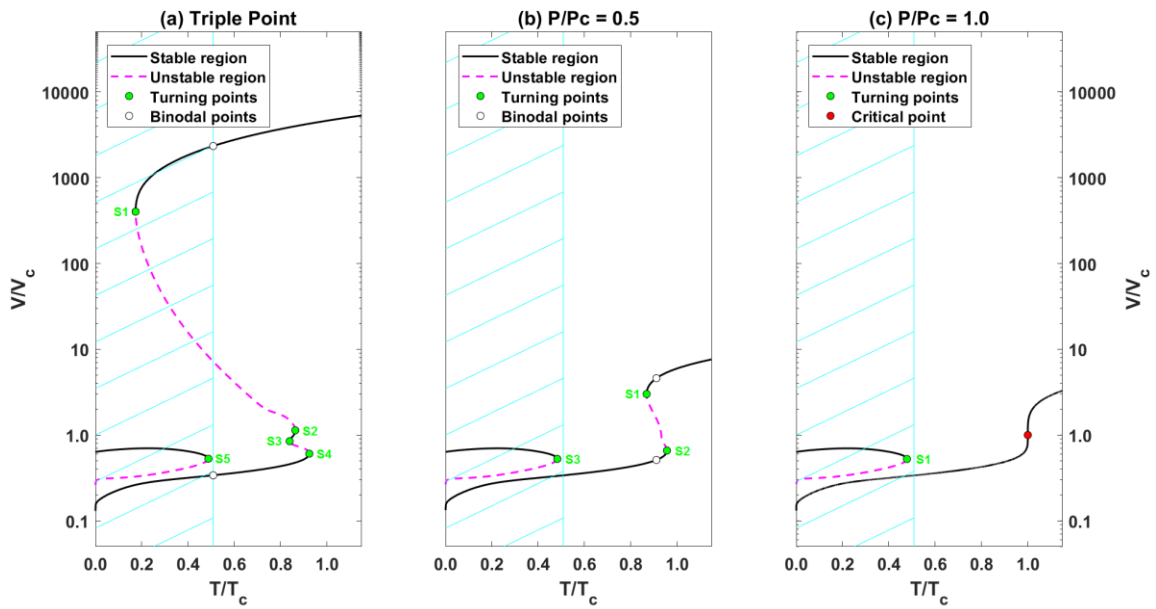


Figure 18: V-T bifurcation diagram using the Lemmon and Jacobsen (2005) MP EOS for HFC-125 at (a) Triple point ($P = 2.914$ kPa), (b) $P = 0.5 P_c$, and (c) $P = 1.0 P_c$. The solid lines represent mechanically stable curves, dashed lines are mechanically unstable, the green points denote the turning points, and the open dots denote the binodal points. The shaded area is outside of the range of validity of the EOS.

Figure 18 (a) shows two branches at the triple point; the physical branch shows zigzag behavior with four turning points and a nonphysical branch with one turning point. The nonphysical branch is independent of pressure and exists outside the range of validity. The binodal points are denoted by open dots on the figure. At reduced pressure of 0.5 as seen in Figure 18 (b),

the two nonphysical turning points have disappeared from the physical branch and the MP EOS gives the correct S-shaped behavior. Figure 18 (c) shows the critical isobar, where the physical branch has no turning points.

This MP EOS seems to show the correct behavior inside its reported range of validity for most of the pressure range. However, the physical branch exhibiting zigzag behavior indicates the presence of nonphysical issues. This gets explored further in **Section 5.3**.

4.6 Category VI: Power Polynomial + Exponential + Nonanalytic Series MP EOSs

The Chung *et al.* (1985) MP EOS for carbon dioxide combines a series of power polynomial and exponential terms with unique nonanalytic terms. The MP EOS is given by the following compressibility-explicit expression:

$$\begin{aligned}
 Z = \frac{P}{\rho RT} = & 1 + b_2 \rho' + b_3 \rho'^2 + b_4 \rho'^3 + b_5 \rho'^4 + b_6 \rho'^5 \\
 & + b_7 \rho'^2 \exp[-c_{21} \rho'^2] + b_8 \rho'^4 \exp[-c_{21} \rho'^2] \\
 & + c_{22} \rho' \exp[-c_{27} (\Delta T)^2] \\
 & + c_{23} \Delta \rho / \rho' \exp[-c_{25} (\Delta \rho)^2 - c_{27} (\Delta T)^2] \\
 & + c_{24} \Delta \rho / \rho' \exp[-c_{26} (\Delta \rho)^2 - c_{27} (\Delta T)^2]
 \end{aligned} \tag{6}$$

where the reduced density and temperature expressions are defined by $\rho' = \rho/\rho_c$, $T' = T/T_c$, $\Delta \rho = 1 - 1/\rho'$, and $\Delta T = 1 - 1/T'$. The parameters b_n are 8 temperature-dependent polynomials. They include 20 adjustable coefficients (c_n) to be fitted along with 7 more (c_n) in the equation itself for a total of 27 adjustable parameters.

It is important to note that carbon dioxide possesses a triple point temperature higher than that of the normal boiling point. The liquid phase does not form below the triple point, and solid carbon dioxide undergoes sublimation in these conditions. The MP EOS's scope of validity does not cover the range below the triple point and is only valid for the fluid phase. But exploring that range and comparing it to experimental data is beneficial for determining the MP EOS's extrapolation capability.

Figure 19 shows the V-T bifurcation diagrams at the normal boiling point, triple point, and critical point. An interesting behavior is observed when comparing the diagram at the normal point to the one at triple point. The two branches combine and separate again to form different configurations. As seen in Figure 19 (a), two branches are observed at the normal point; one with three turning points containing the liquid roots and another one containing the vapor roots. The physical vapor and liquid roots in equilibrium are denoted by open dots on the branches. Two branches are observed at the triple point too, as shown in Figure 19 (b); the physical branch contains four turning points and a nonphysical branch at very low temperatures with one turning point.

The physical branch's behavior resembles the S-shaped behavior inside the reported range of validity. The nonphysical branch and nonphysical turning points fall below the triple point temperature, which is outside of the MP EOS's range of validity. Up to five volume roots can be found at certain temperatures. Some of them are mechanically stable, and some sections of the curves display negative volume expansivity. The nonphysical branch and nonphysical turning points located at low temperature are weak functions of pressure. Nevertheless, it presents a problem when extrapolating below the specified temperature range of validity.

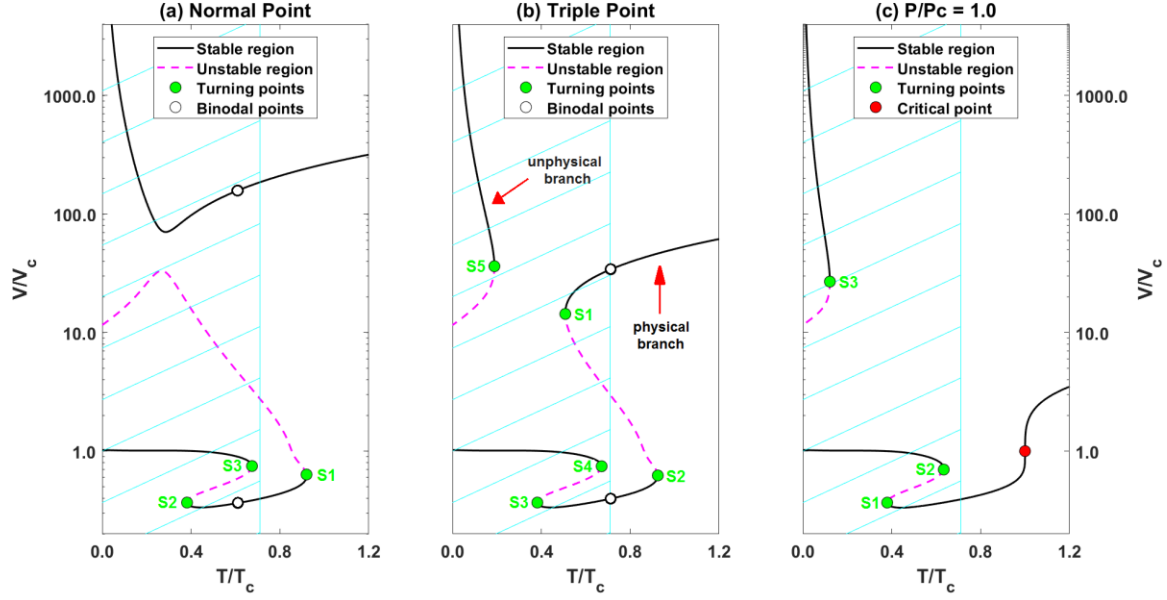


Figure 19: V-T bifurcation diagram for carbon dioxide using the Chung *et al.* (1985) MP EOS at (a) $P = 101.325$ kPa (normal point), (b) $P = 516.757$ kPa (triple point), and (c) $P/P_c = 1.0$. The solid curves represent mechanically stable lines, dashed curves are mechanically unstable, and the green dots denote the turning points. The shaded area is outside of the MP EOS range of validity.

4.7 Category VII: Power Polynomial + Ratio of Polynomials + Exponential Series MP EOSs

Another MP EOS that uses a unique functional form is the Sterner and Pitzer (1994) MP EOS. This equation uses rational functions (a ratio between polynomials) to model carbon dioxide properties. The equation is given by the following expression:

$$\begin{aligned} \varphi^{res}(\delta, \tau) = a_1 \rho + \left(\frac{1}{a_2 + a_3 \rho + a_4 \rho^2 + a_5 \rho^3 + a_6 \rho^4} - \frac{1}{a_2} \right) \\ - \left(\frac{a_7}{a_8} \right) [\exp(-a_8 \rho) - 1] - \left(\frac{a_9}{a_{10}} \right) [\exp(-a_{10} \rho) - 1] \end{aligned} \quad (6)$$

$$\text{with} \quad a_i = c_{i,1} T^{-4} + c_{i,2} T^{-2} + c_{i,3} T^{-1} + c_{i,4} + c_{i,5} T + c_{i,6} T^2 \quad (7)$$

Figure 20 displays the V-T bifurcation diagrams for the MP EOS at the triple point isobar and the critical isobar. The physical branch shows the correct S-shape at subcritical conditions and displays no nonphysical turning points at the critical isobar. Only one nonphysical branch with one turning point is predicted by this MP EOS. But it is a weak function of pressure and it is located at extremely low temperature outside of the equation's validity region. The MP EOS was found to be free from spurious phase separation regions. It is also able to predict the correct limits of stability. The equation's absence of abnormal behavior shows the potential of its functional forms.

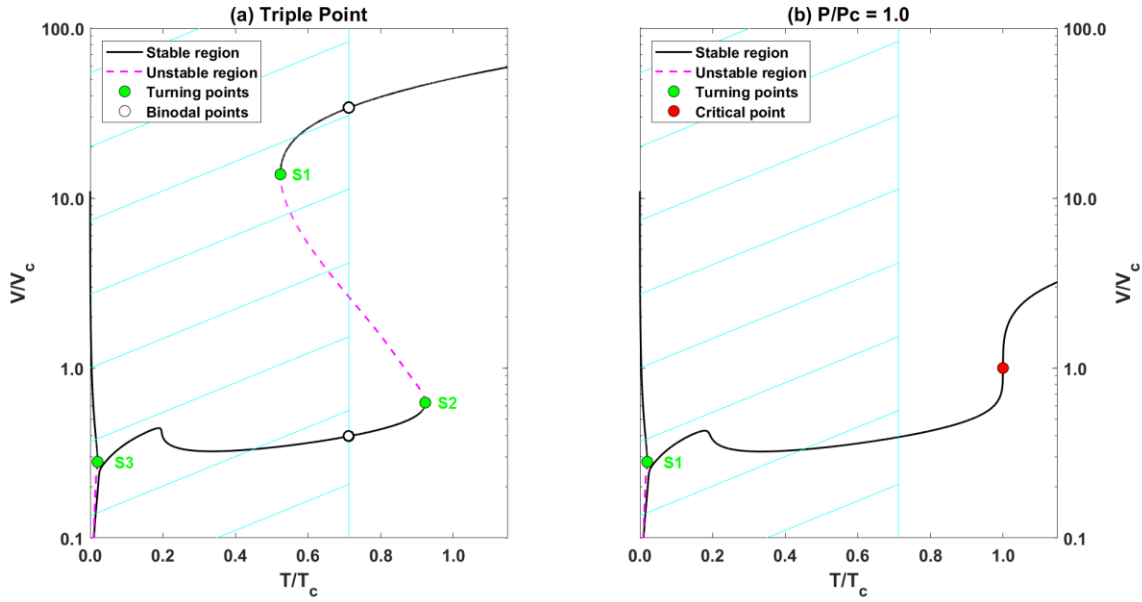


Figure 20: A V-T bifurcation diagram using the Sterner and Pitzer (1994) MP EOS for carbon dioxide at (a) Triple point ($P = 5.16757$ kbar), and (b) $P = 1.0 P_c$ ($P = 73.748$ kbar). The solid lines represent mechanically stable curves, and dashed lines are mechanically unstable. The green points denote the turning points, and the open dots denote the binodal points. The shaded area is outside of the range of validity of the EOS.

CHAPTER 5

DISCUSSION OF THE RESULTS

5.1 A Summary of Bifurcation Diagram Analysis

We generated V-T bifurcation diagrams for twenty one different MP EOSs. Their behavior was mapped over subcritical, critical and supercritical conditions. The results of the bifurcation analysis showed that all the MP EOSs exhibited erroneous behaviors but the degree of severity was not the same. The two main types of artifacts are: nonphysical behavior in the physical branch, and the existence of nonphysical branches. These two types lead to several issues. A summary of the main issues found with the studied MP EOSs is presented in Table 5. The table specifies the category of each equation. We also add a column entitled “the physical model” to illustrate the correct and expected physical behavior from the equation of state.

The regions of validity for the MP EOSs are provided in the table as reported in their respective references. Irregular and nonphysical behavior outside the region of validity is only reported when it is very close to the limits. This is because it can affect the MP EOS behavior at different conditions and cause issues inside of the region of validity.

Table 5: A summary of nonphysical problems associated with reference MP EOSs.

Reference MP EOS	The physical model	Jacobsen, Stewart and Myers	Jacobsen and Stewart	McCarty	Schmidt and Wagner	Jahangiri et al.	Tillner Roth and Baehr
Category	-	I	I	I	II	II	II
Valid temperature region (K)	-	56-323	63-2000	91-398	54-300	104-450	170-455
Max No. of subcritical volume roots (inside the range of validity)	3	6	4	5	6	5	5
Max No. of supercritical volume roots (inside the range of validity)	1	4	2	3	4	3	3
Max No. of Subcritical nonphysical branches	0	1	2	1	2	1	1
Max No. of Supercritical nonphysical branches	0	1	2	1	1	0	1
Max No. of Subcritical turning points	2	6	3	3	4	6	5
Max No. of Supercritical turning points	0	4	1	1	2	2	1
No. of Spurious phase envelopes	0	0	0	0	6	3	6
Type of spurious phase envelopes	-	-	-	-	Gas-liquid, solid-liquid	Gas-liquid	Gas-liquid, solid-liquid

Table 5: A summary of nonphysical problems associated with reference MP EOSs. (Cont.)

Reference MP EOS	The physical model	Span and Wagner (Argon)	Lemmon and Span (R-245fa)	Setzmann and Wagner	Span et al.	Tegeler, Span and Wagner
Category	-	II	II	III	III	III
Valid temperature region (K)	-	84 – 520	171.05 – 440	90 – 620	63.2 – 5000	84 – 700
Max No. of subcritical volume roots (inside the range of validity)	3	5	5	5	7	7
Max No. of supercritical volume roots (inside the range of validity)	1	3	3	3	5	5
Max No. of Subcritical nonphysical branches	0	1	1	1	1	2
Max No. of Supercritical nonphysical branches	0	0	0	1	1	2
Max No. of Subcritical turning points	2	6	6	5	8	9
Max No. of Supercritical turning points	0	2	2	1	4	3
No. of Spurious phase envelopes	0	4	4	8	11	21
Type of spurious phase envelopes	-	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid

Table 5: A summary of nonphysical problems associated with reference MP EOSs. (Cont.)

Reference MP EOS	The physical model	Smukala, Span and Wagner	Bücker and Wagner (ethane)	Bücker and Wagner (n-butane)	Lemmon, McLinden and Wagner	Zhou and Lemmon
Category	-	III	III	III	III	III
Valid temperature region (K)	-	104 – 450	90.37 – 675	134.9 – 575	82.53 – 650	196 – 450
Max No. of subcritical volume roots (inside the range of validity)	3	5	7	5	5	5
Max No. of supercritical volume roots (inside the range of validity)	1	3	5	3	3	3
Max No. of Subcritical nonphysical branches	0	1	2	1	2	2
Max No. of Supercritical nonphysical branches	0	1	2	1	2	2
Max No. of Subcritical turning points	2	6	7	5	7	7
Max No. of Supercritical turning points	0	4	3	1	3	3
No. of Spurious phase envelopes	0	6	13	4	7	5
Type of spurious phase envelopes	-	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid

Table 5: A summary of nonphysical problems associated with reference MP EOSs. (Cont.)

Reference MP EOS	The physical model	Span and Wagner (CO ₂)	Wagner and Pruß	Lemmon and Jacobsen	Chung et al.	Sterner and Pitzer
Category	-	IV	IV	V	VI	VII
Valid temperature region (K)	-	216 – 1100	251.2 – 1273	172.52 – 500	216-423	215 – 2000
Max No. of subcritical volume roots (inside the range of validity)	3	5	5	5	3	3
Max No. of supercritical volume roots (inside the range of validity)	1	3	3	1	1	1
Max No. of Subcritical nonphysical branches	0	1	1	0	1	0
Max No. of Supercritical nonphysical branches	0	1	1	0	1	0
Max No. of Subcritical turning points	2	5	6	4	5	2
Max No. of Supercritical turning points	0	3	2	0	3	0
No. of Spurious phase envelopes	0	6	6	1	0	0
Type of spurious phase envelopes	-	Gas-liquid, solid-liquid	Gas-liquid, solid-liquid	Gas-liquid	-	-

One of the main objectives of bifurcation diagrams is to demonstrate the number of volume roots at any temperature for a given isobar. Table 5 gives the maximum number of volume roots found at subcritical and supercritical isobars, inside the validity region, for each equation. The results vary between three and up to seven volume roots. The majority of MP EOSs have five volume roots inside their validity region. Although the physical volume roots can usually be determined by testing mechanical stability, many of the studied MP EOSs have nonphysical roots that are mechanically stable.

The only MP EOSs that displayed the correct number of volume roots at subcritical isobars -which is three- are the Chung *et al.* (1985) and the Sterner and Pitzer (1994) MP EOSs. However, the Chung *et al.* equation can give five volume roots at low temperatures, below its region of validity (see Figure 19).

Table 5 also provides the maximum number of nonphysical branches found at subcritical and supercritical isobars. The results show that most MP EOSs display at least one nonphysical branch. Some MP EOSs can have more nonphysical branches below their valid temperature region. The significance of these nonphysical branches is determined by examining whether they affect the physical branch at different isobars or not. If the nonphysical branches at low temperature are not sensitive to change in pressure, they are not reported in the tables. The results reveal that only the Lemmon and Jacobsen (2005) and the Sterner and Pitzer (1994) MP EOSs possessed no nonphysical branches inside their regions of validity (see Figure 18 and 19). The only nonphysical branches these MP EOSs had were outside their regions of validity at low temperatures. These nonphysical branches existence is negligible because they are largely independent of pressure and they do not affect the physical branches.

Other MP EOSs such as Jacobsen, Stewart and Myers (1973), Jacobsen and Stewart (1973), McCarty (1974), Chung *et al.* (1985), Bückner and Wagner (2006) for n-butane, and Zhou and Lemmon (2016) have nonphysical branches that are not a strong function of pressure and do not affect the physical branch. However, a part of them is contained inside the temperature validity region. To determine the significance of their impact, we study the spinodal and binodal behaviors in the next two sections and find if they form spurious two-phase regions or not.

5.2 Modeling the Limits of Stability

Another feature of bifurcation diagrams is to locate the turning points of the branches. Turning points represent the mechanical stability limits. Those turning points form the spinodal curves in phase diagrams. The presence of nonphysical turning points means that isotherms may exhibit multiple Maxwell loop. This is a problem because a second Maxwell loop implies the existence of a homogeneous pseudo-stable phase inside the unstable region. This phenomenon does not reflect the physical behavior where the fluid breaks up into vapor and liquid naturally. Furthermore, the pseudo-stable phase can possess lower Gibbs energy than superheated vapor, supercooled liquid or even saturated fluid, making it appear as the most stable state.

This nonphysical behavior represented by artificial Maxwell loops is purely a result of mathematical artifacts. Nevertheless, the inability of the MP EOSs to represent accurate metastable and unstable regions leads to several issues. For instance, it makes the extension of MP EOSs to mixtures very complicated. Also, it makes MP EOSs unreliable in equilibrium calculations, as the pseudo-stable phase can act as a second liquid phase. And finally, the homogeneous pseudo-stable

phase contradicts the formation of a vapor-liquid interface. This makes MP EOSs unable to model interfacial phenomena using density functional theory. In order to safely use the MP EOSs in these applications, we must carefully examine the turning points in bifurcation diagrams.

The number of turning points may vary throughout different pressure ranges. Bifurcation diagrams of different MP EOSs showcased how branches can combine or separate, and turning points can generate or disappear at certain isobars. Table 5 gives the maximum number of turning points found at subcritical and supercritical isobars for each MP EOS studied. The results vary between three and up to nine turning points. In fact, more turning points can be found in certain cases at low temperature outside the validity region.

An example of mapping turning points across different pressure ranges was presented in **Section 4.3** in Figure 16 for the Span *et al.* MP EOS. It demonstrated that the MP EOS is not able to fully predict the physical spinodal curves. It also showed that the equation predicts various nonphysical spinodal curves. Other MP EOSs in the same category as the Span *et al.* equation were found to possess the largest number of turning points. That category uses a combination of power polynomial, exponential, and Gaussian terms. Figure 21 maps out the turning points at different pressure ranges for two such MP EOSs. Namely the Tegeler, Span and Wagner (1999) argon reference EOS and the Bucker and Wagner (2006) ethane reference EOS. Both equations also exhibit zigzag behavior in their physical branch. This leads them to form nonphysical phase coexistence regions and predict nonphysical critical points.

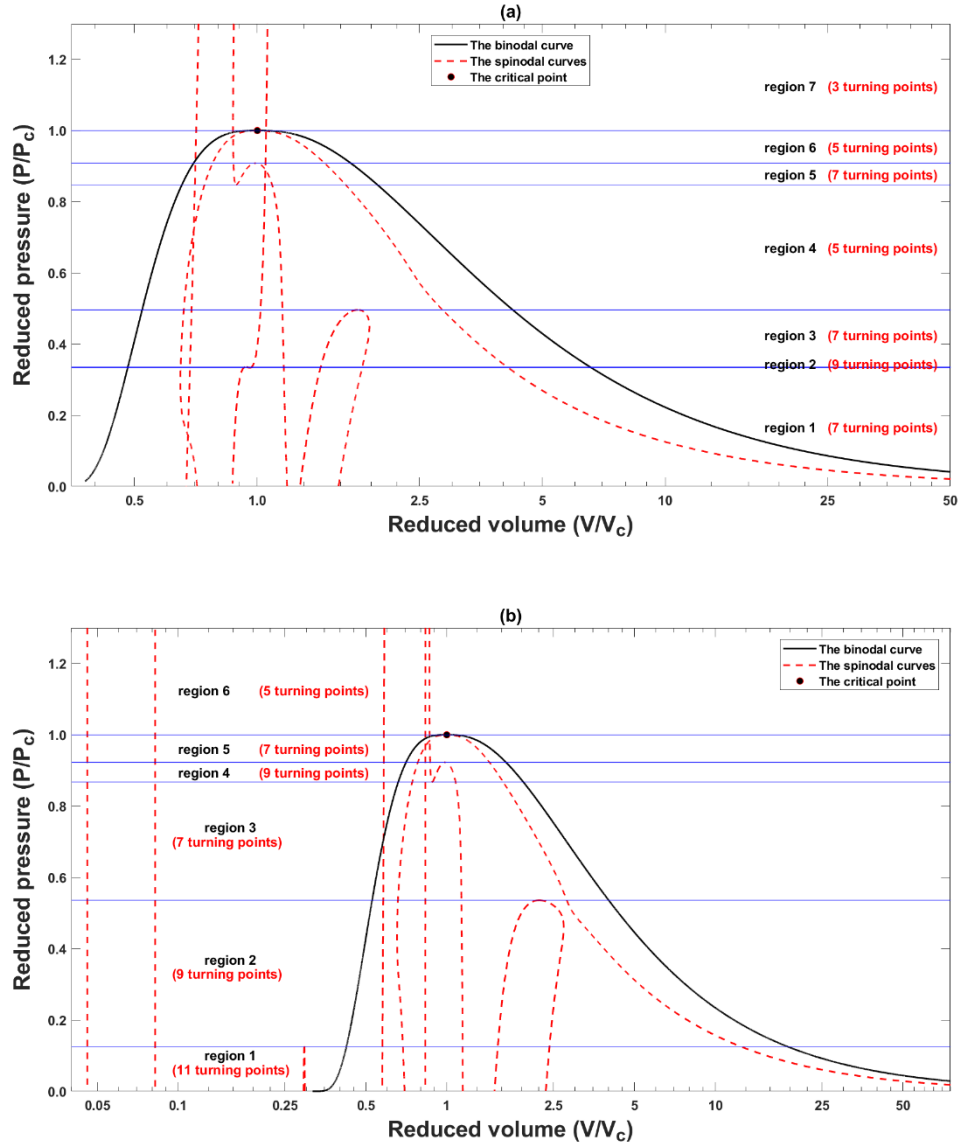


Figure 21: The spinodal curves predicted by (a) the Tegeler, Span and Wagner (1999) argon reference MP EOS and (b) the Bücker and Wagner (2006) ethane reference MP EOS. The solid curve is the physical P-V phase envelope. The dashed lines are the spinodal lines. The horizontal lines mark the pressure values where the number of turning points change.

5.3 Spurious Phase Coexistence Regions

An elegant feature of bifurcation diagrams is its power to reveal spurious coexistence curves without the need of conducting equilibrium calculations. By noting the presence of zig-zag behavior or the existence of nonphysical branches, we can predict that the equation forms spurious coexistence regions. This was briefly discussed in **Section 4.2** with regards to the Schmidt and Wagner (1985) oxygen MP EOS. Figure 13 and Figure 14 showed how nonphysical behaviors in the branches indicate that the equation forms spurious two-phase separation regions. Six spurious two-phase regions were found for the Schmidt and Wagner oxygen MP EOS. Figure 22 (a) shows all six spurious coexistence curves plotted along the physical curve on a P-V plane. Figure 22 (b) demonstrates the corresponding vapor pressure curves on a P-T plane.

Some of the spurious curves meet at their end points. This reflects the behavior of the branches in the bifurcation diagrams as they combine or separate at certain isobars. That change leads to nonphysical segments of the branches being created or dismantled, causing multiplicity of volume roots and the formation of spurious curves. Most of the spurious P-V phase diagrams were found to be located inside the physical phase envelope, with the exception of one spurious curve that deviates outside of its bounds. Finally, some of the nonphysical binodal lines are found to be mechanically stable.

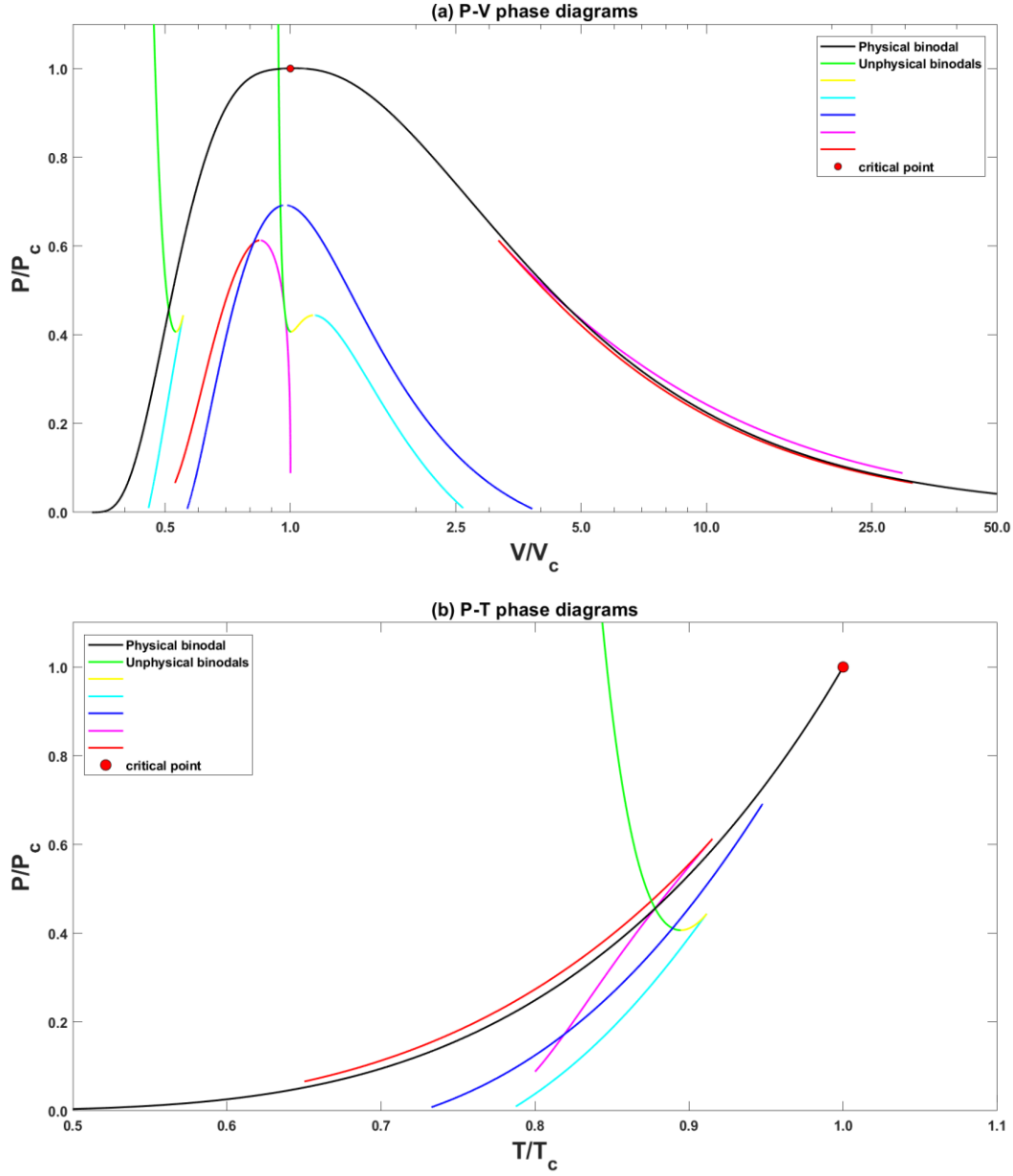


Figure 22: (a) A P-V phase diagram of the Schmidt and Wagner (1985) oxygen MP EOS's physical and nonphysical coexistence curves. (b) The corresponding vapor pressure curves in a P-T plane.

Table 5 gives the number of spurious phase envelopes predicted by each MP EOS. Aside from the three mBWR-type MP EOSs, the Chung *et al.* MP EOS, and the Sterner and Pitzer MP EOS, all other MP EOSs formed artificial two-phase separation regions. Table 5 categorizes the spurious phase envelopes as either gas-liquid-like or solid-liquid-like coexistence curves. It is

important to keep in mind that the MP EOSs are designed to predict fluid region properties only. So the solid-liquid-like nonphysical curves are not related to any physical values.

All MP EOSs that formed spurious phase diagrams had both gas-liquid and solid-liquid type coexistence regions. The only exceptions are the Jahangiri *et al.* (1986) and Lemmon and Jacobsen (2005) MP EOSs which only formed gas-liquid coexistence regions. Besides the MP EOSs that formed no spurious curves, these two equations were the ones that formed the least spurious phase diagrams. The Jahangiri *et al.* MP EOS showed only three spurious curves and Lemmon and Jacobsen MP EOS showed only one spurious curve.

Figure 23 displays the bifurcation diagram for the Jahangiri *et al.* MP EOS at reduced pressure of 0.4. It shows that the main branch exhibits zigzag behavior at this isobar, with a total of six turning points. Points A and B represent the physical coexisting vapor and liquid roots in equilibrium at that pressure, respectively. The other pairs (C-D, E-F, and G-H) signify spurious two-phase separation regions.

Figure 24 displays the phase diagrams formed by the Jahangiri *et al.* MP EOS in both the P-V and P-T planes. The three nonphysical phase-separation curves all exist within the bounds of the physical gas-liquid coexistence envelope. However, it is worth noting that some of the binodal lines are mechanically unstable. Referring to Figure 23 again, points C, D and H lie on unstable segments of the branches. Accordingly, the binodal lines these roots lie on such as the blue spurious coexistence curve in Figure 24 are mechanically unstable. In addition, one of the spurious curves shows a nonphysical critical point predicted by this MP EOS. It occurs at $V = 0.97 V_c$ and $P = 0.495 P_c$. It is also located at $T = 0.91875 T_c$.

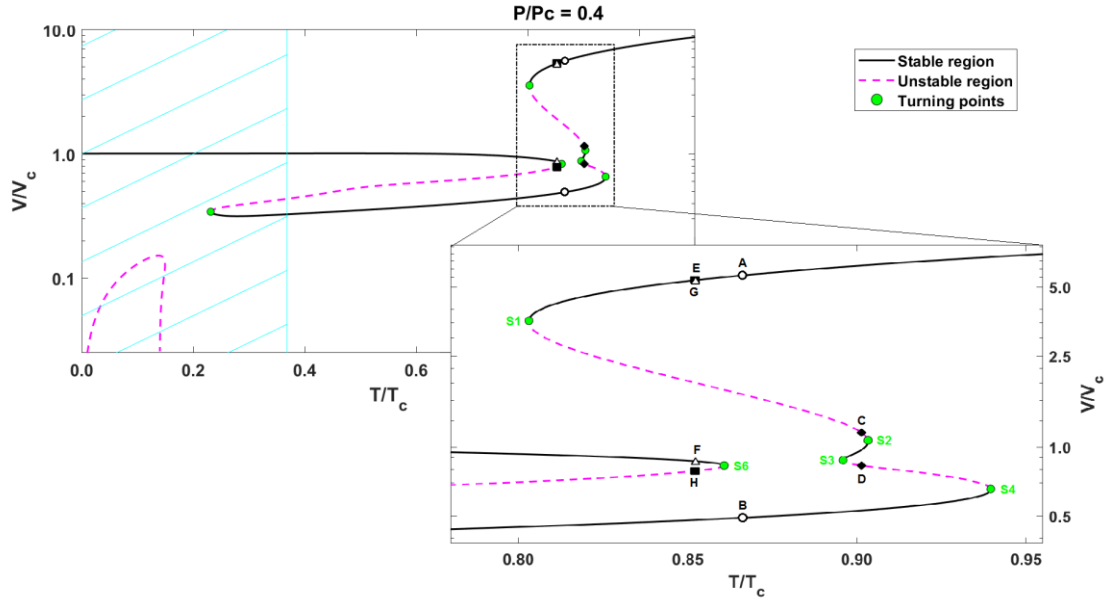


Figure 23: A V-T bifurcation diagram for ethylene using the Jahangiri *et al.* (1986) MP EOS at $P = 0.4 P_c$. The close up shows the zigzag behavior in the physical branch. The solid lines represent mechanically stable segments, dashed lines are mechanically unstable segments, and the green turning points denote the spinodal limits. The open dots (A-B) denote the physical vapor and liquid binodal points in equilibrium. The closed dots (C-D, E-F and G-H) are nonphysical binodal points, where the first letter refers to the vapor root and the second letter refers to the liquid root.

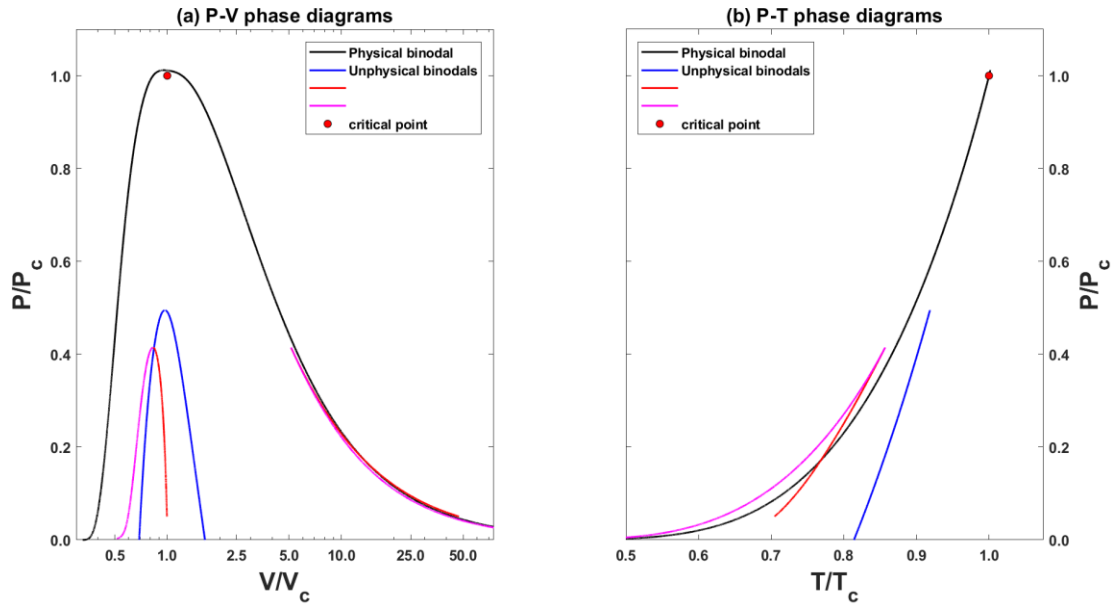


Figure 24: (a) A P-V phase diagram of the Jahangiri *et al.* (1986) ethylene MP EOS's physical and nonphysical coexistence curves. (b) The corresponding vapor pressure curves in a P-T plane.

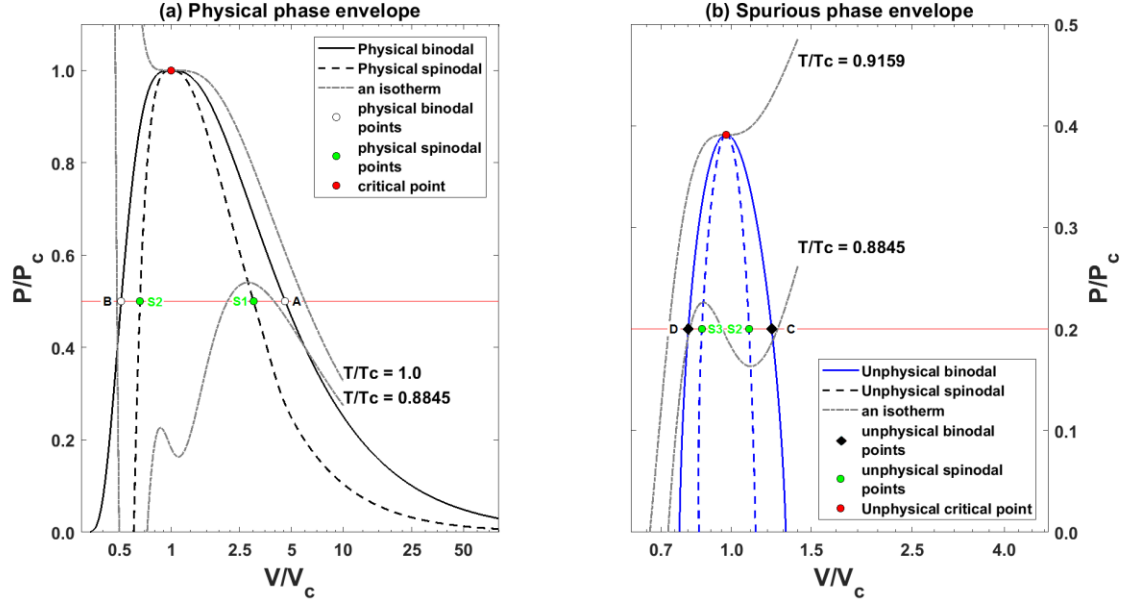


Figure 25: A P-V phase diagrams for the Lemmon and Jacobsen (2005) HFC-125 MP EOS. (a) The traditional gas-liquid binodal and spinodal curves with two isotherms. (b) A spurious phase diagram with two isotherms.

Figure 25 displays the physical P-V phase diagram for the Lemmon and Jacobsen (2005) MP EOS, along with the one nonphysical phase diagram the equation forms. The nonphysical phase-separation curve is located inside the bounds of the physical gas-liquid coexistence envelope. The pairs of points **A-B** and **C-D** are the physical and the nonphysical roots with equal chemical potential, respectively. The first letter refers to the vapor root and the second letter refers to the liquid root. The nonphysical curve is found to be mechanically unstable. Its roots fall on the unstable segments of the physical branch in Figure 18. Figure 25 (b) also shows a nonphysical critical point predicted by this MP EOS. Its location is at $V = 0.974 V_c$ and $P = 0.391 P_c$. It is also located at $T = 0.9159 T_c$.

We also performed equilibrium calculations for the Wagner and Pruß (2002) water reference EOS analyzed in **Section 4.4**. It revealed seven pairs of points satisfying the conditions of equal chemical potential. Figure 26 shows the zigzag part of the bifurcation diagram at reduced

pressure of 0.9. The physical coexisting vapor and liquid roots at this isobar are designated by the points **A** and **B**, respectively. Their equivalent positions are shown on the physical binodal curve in the P-V phase diagram in Figure 27 (a), along with turning points **1** and **4** on the spinodal curve. The other pairs (**C-D**, **E-F**, **G-H**, **I-J**, **K-L**, and **M-N**) form six spurious two-phase regions. Figure 27 (b) displays one of those spurious envelopes. It reveals a nonphysical critical point predicted by the MP EOS at $V = 0.96 V_c$ and $P = 0.958 P_c$. It is also located at $T = 0.995 T_c$.

Some of the binodal lines found for the Wagner and Pruß equation are mechanically unstable. This can be concluded by looking at Figure 26. Points **C**, **D**, **F**, and **I** lie on unstable segments of the branch. Consequently, the binodal lines these roots lie on such as the spurious coexistence curve in Figure 27 (b) are unstable. This means that the physical volume roots can be in equilibrium with nonphysical and mechanically unstable roots.

Figure 28 shows all the spurious P-V coexistence curves plotted together. Some of them meet each other at their ends. This is due to segments disappearing or forming when the branches in the bifurcation diagrams combine or separate. Figure 29 plots the corresponding vapor pressure curves on a P-T plane. It is observed that as the temperature increases, the spurious vapor pressure curves get closer to the physical one. Consequently, as it decreases, the spurious curves move away from the physical curve.

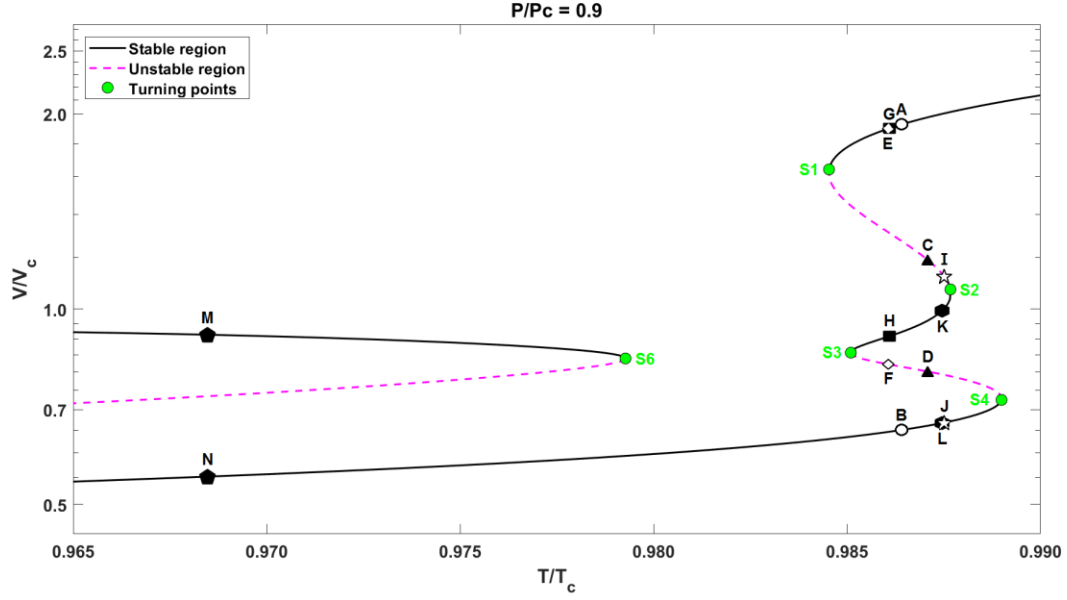


Figure 26: A V-T bifurcation diagram using the Wagner and Pruß (2002) MP EOS for water at $P = 0.9 P_c$. The figure displays the zigzag behavior in the physical branch. The solid lines represent mechanically stable segments, and the dashed lines are mechanically unstable segments. The green turning points denote the spinodal limits. The open dots (A-B) denote the physical vapor and liquid binodal points in equilibrium. The other pairs of dots (C-D, E-F, G-H, I-J, K-L and M-N) are nonphysical binodal points, where the first letter refers to the vapor root and the second letter refers to the liquid root.

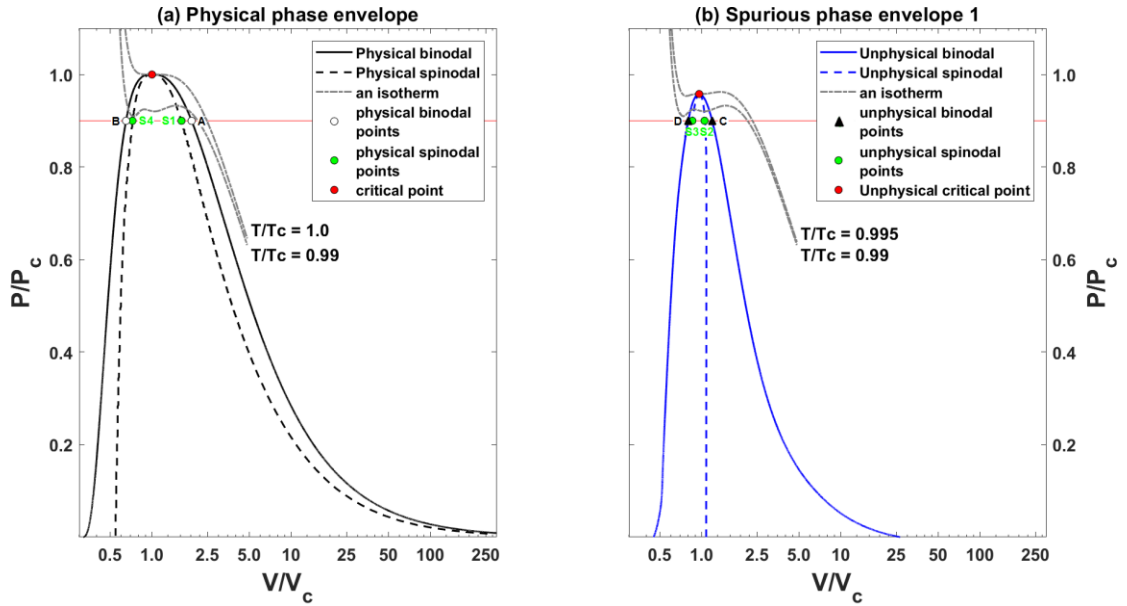


Figure 27: A P-V phase diagrams for the Wagner and Pruß (2002) water MP EOS (a) The physical gas-liquid binodal and spinodal curves, with two isotherms. (b) Nonphysical binodal and spinodal curves, with two isotherms.

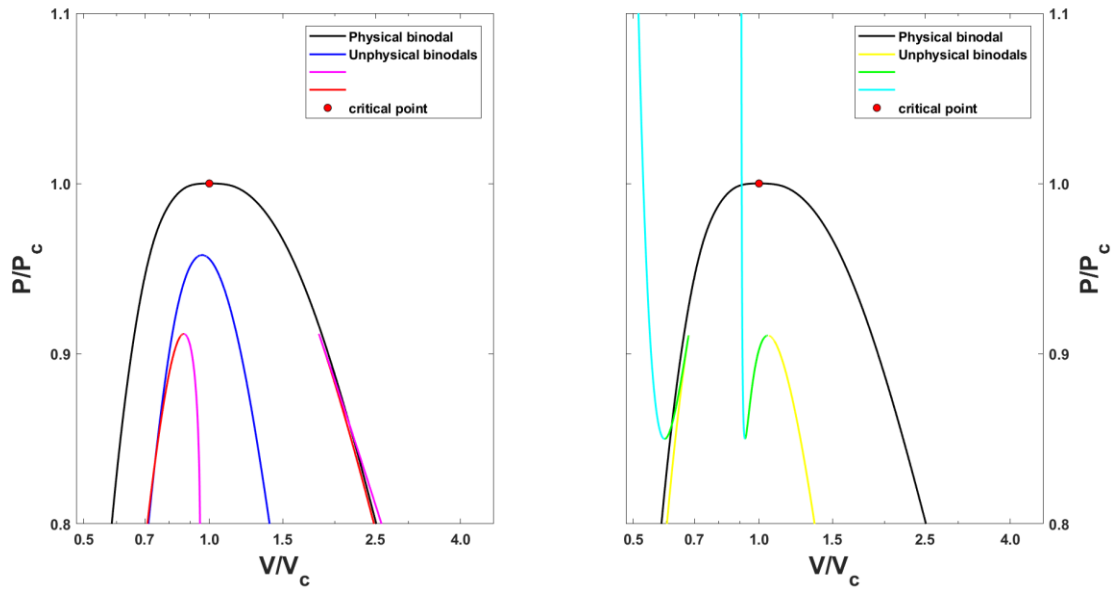


Figure 28: A P-V phase diagrams of the Wagner and Pruß (2002) water MP EOS's physical and nonphysical coexistence curves.

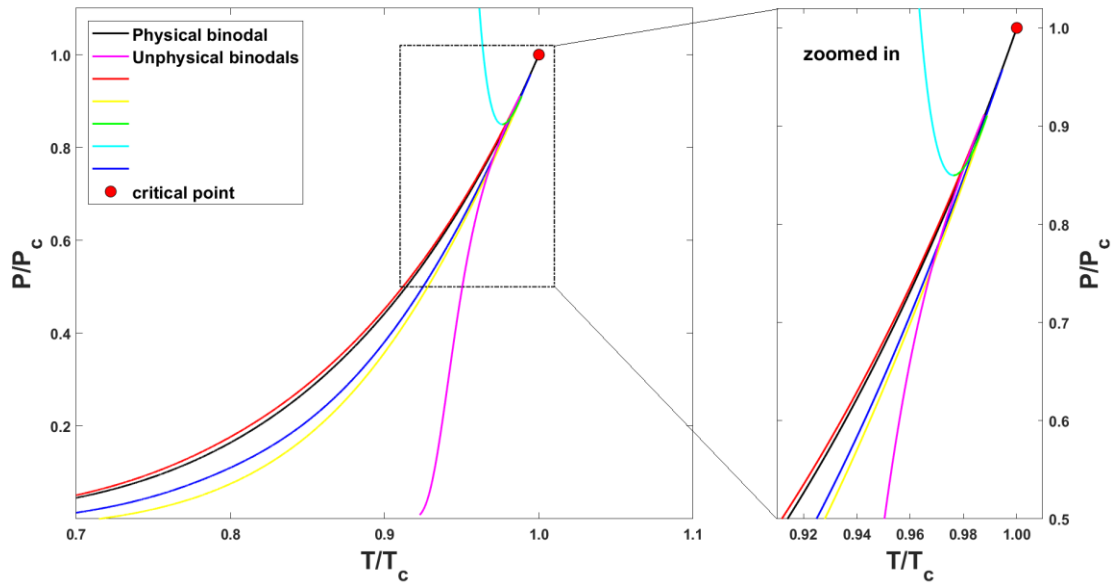


Figure 29: Physical and nonphysical P-T vapor pressure curves of the Wagner and Pruß (2002) water MP EOS.

On the other hand, the MP EOSs that displayed the largest number of volume roots and turning points also formed the most spurious phase diagrams. With the Span *et al.* nitrogen MP EOS showing eleven spurious curves, the B cker and Wagner ethane MP EOS showing thirteen, and the Tegeler, Span and Wagner argon MP EOS showing twenty one. All three equations share the same functional forms, consisting of power polynomials, exponential, and Gaussian terms.

Figure 30 plots the eleven spurious coexistence curves found for the Span *et al.* nitrogen MP EOS, along with the physical envelope. The nonphysical curves display an unusual shape, and several of them can be seen connected at their ends. This follows from the change in the segments of the branches in the bifurcation diagrams. Furthermore, several nonphysical binodal lines are mechanically stable. And some nonphysical volume roots that are unstable are found to be in equilibrium with the physical roots.

Some spurious phase-separation curves suggest the existence of multiple critical points. Figure 31 singles out the physical P-V vapor-liquid curve and two nonphysical phase coexistence curves that show nonphysical critical points. The first nonphysical critical point is at $V = 1.013 V_c$ and $P = 0.885 P_c$, also located at $T = 0.981 T_c$. The second nonphysical critical point is at $V = 3.593 V_c$ and $P = 0.361 P_c$, also located at $T = 0.775 T_c$.

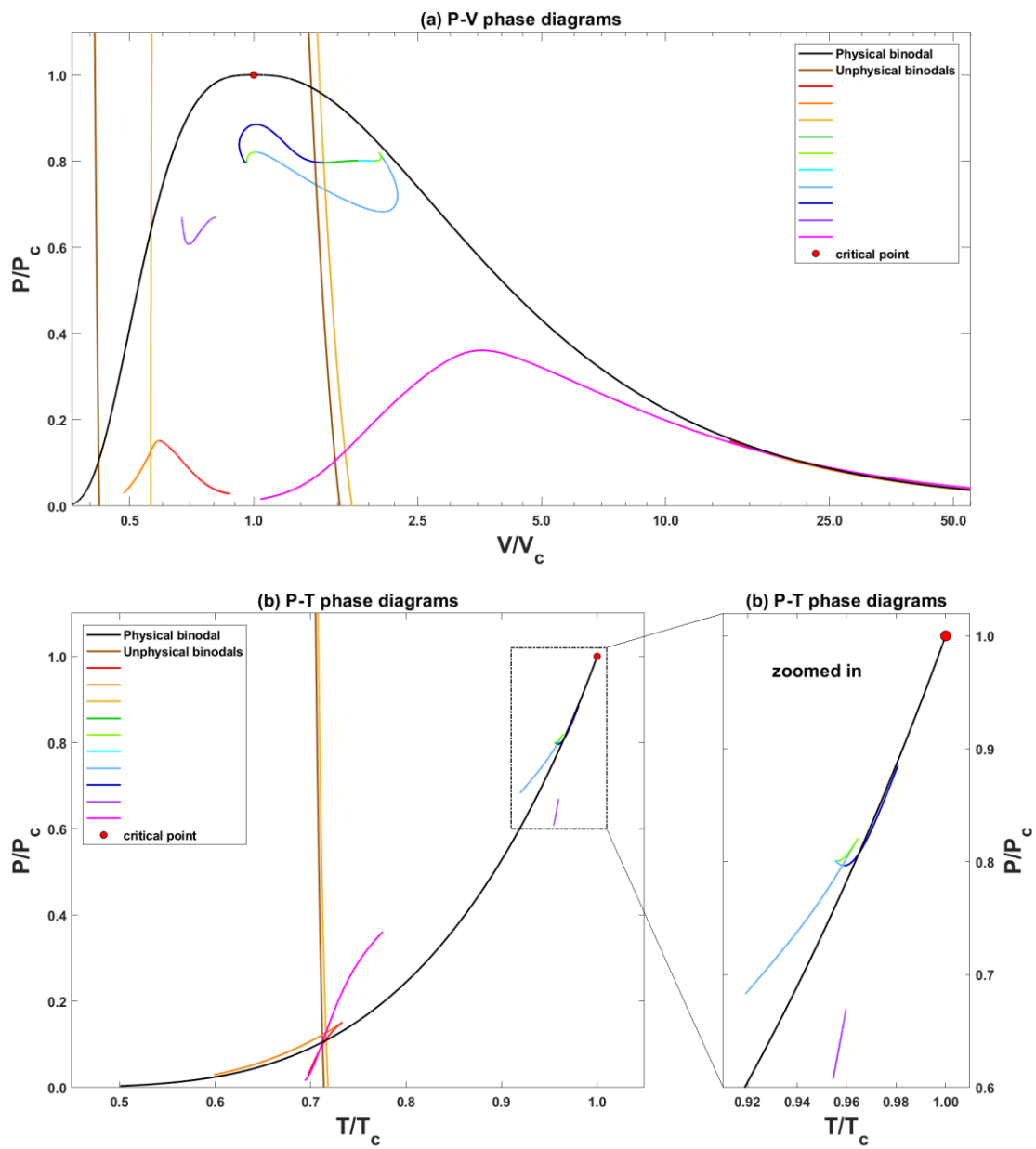


Figure 30: (a) A P-V phase diagram of all the Span *et al.* (1998) nitrogen MP EOS's physical and nonphysical coexistence curves.

(b) The corresponding vapor pressure curves in a P-T plane.

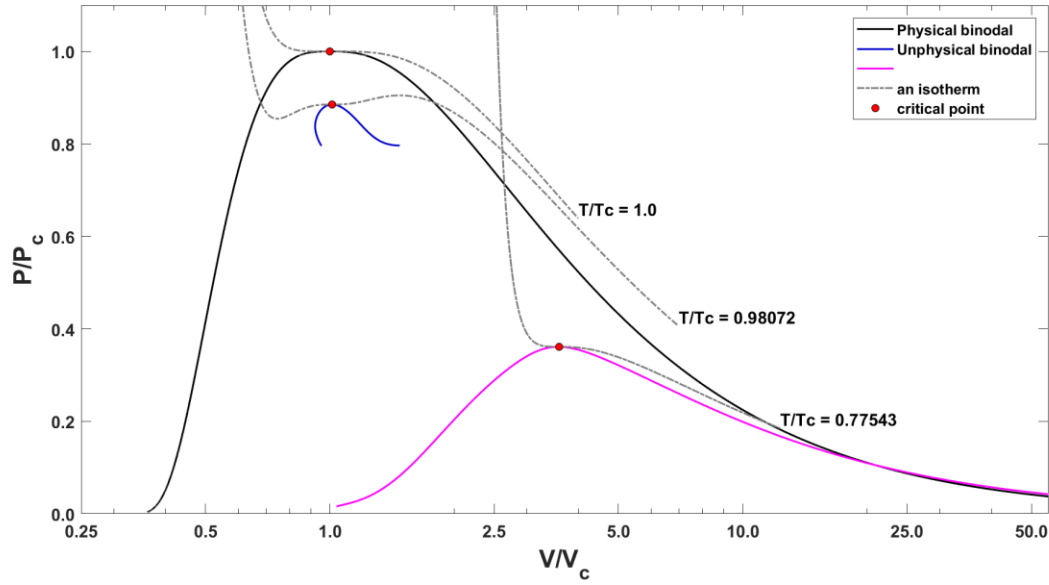


Figure 31: A P-V phase diagram for the Span *et al.* (1998) nitrogen MP EOS. The black curve is the physical gas-liquid binodal curve, and the blue and pink curves are nonphysical binodal curves with nonphysical critical points. The gray dotted lines are isotherms showcasing the Maxwell loops inside the phase diagram.

Figure 32 (a) shows the thirteen spurious phase separation regions the Tegeler, Span and Wagner (1999) argon reference EOS forms, and Figure 32 (b) shows the twenty one spurious phase separation regions the Bückner and Wagner (2006) ethane reference EOS forms. Some of those fictitious phase diagrams form due to the physical branch combining with a nonphysical branch. Some of them exist in very narrow PVT ranges. However, the spurious curves formed due to zig-zag behavior in the physical branch display nonphysical critical points. Also, some of the spurious binodal lines were found to be mechanically stable and others were mechanically unstable. Some were also observed to have negative volume expansivity, even though the substance does not undergo that phenomenon in reality. Such issues make it crucial to find out the reason certain MP EOSs exhibit nonphysical behavior more severely than others.

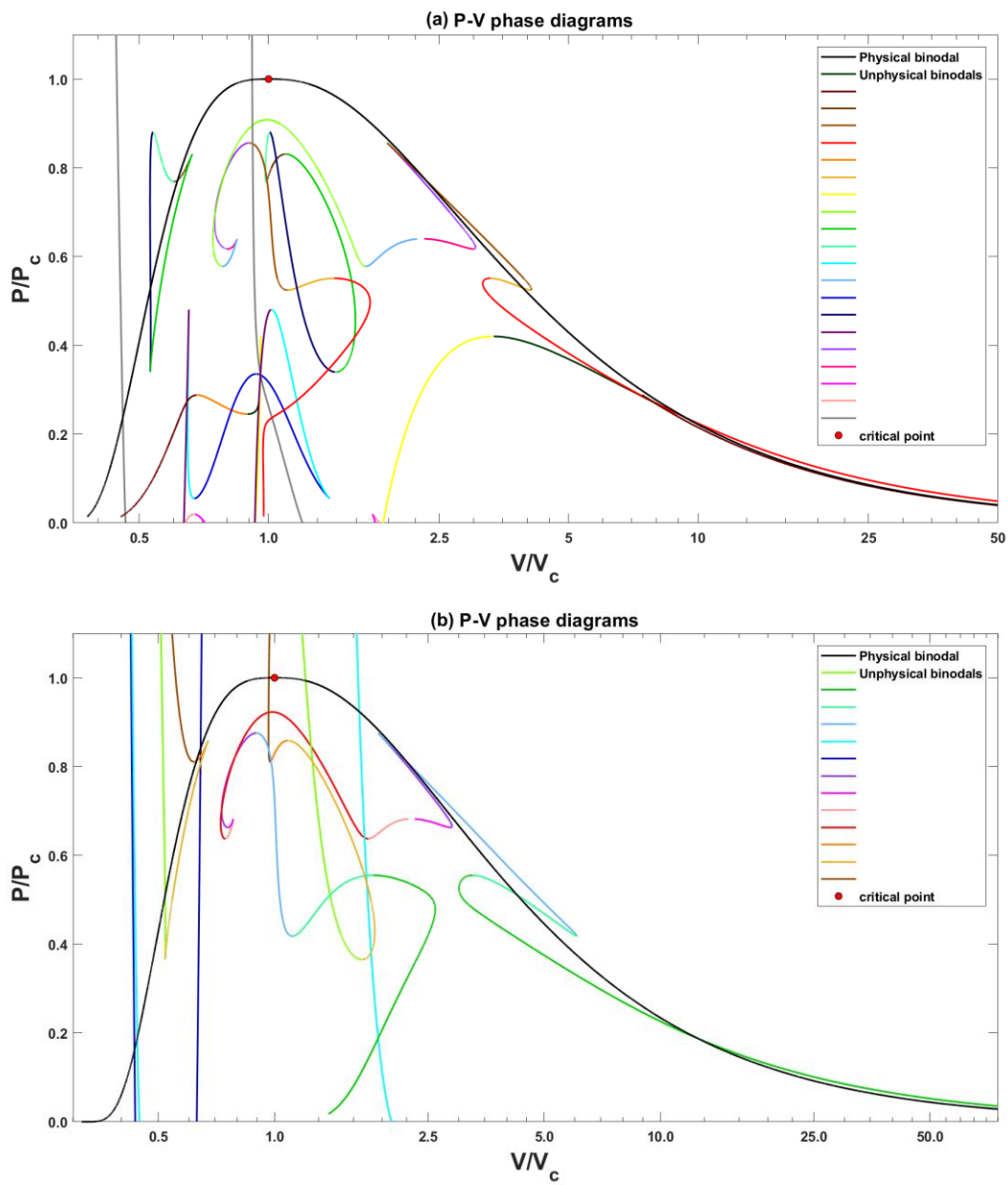


Figure 32: (a) A P-V phase diagram of all the Tegeler, Span and Wagner (1999) argon MP EOS's coexistence curves. (b) A P-V phase diagram of all the Bucker and Wagner (2006) ethane MP EOS's coexistence curves.

5.4 Sensitivity Analysis of the Different Functional Forms

The nature of the MP EOSs semi-empirical and empirical functional forms is the main factor behind their nonphysical behavior. This formulation cannot be avoided when constructing those reference EOSs as it provides the most accurate results. In a previous article, Alsaifi (2020) compared three EOSs for the LJ-fluid with the same analytical expression. The study suggested that the set of adjustable parameters can cause a difference in the equation's behavior. Although comparing the results of the three mBWR type MP EOSs in this study shows a few differences, their significance is negligible. The rest of the obtained results suggest that possessing certain types of functional forms is what amplifies nonphysical behavior.

Span and Wagner (1997) proposed that the extrapolation behavior of a MP EOS is affected by having a larger number of polynomial terms than exponential terms. Following that approach, we study the effect of the number of polynomial and exponential terms on the MP EOSs. Table 6 lists several MP EOSs chosen to compare ones with more polynomial than exponential terms versus ones with fewer polynomial than exponential terms. Table 7 lists some more MP EOSs chosen for the analysis that include Gaussian bell-shaped, nonanalytic and exponential in temperature terms. We analyze the contribution of polynomial terms to the total residual Helmholtz free energy at different pressures and temperatures.

The reduced residual Helmholtz free energy (φ^{res}) was calculated using the data of the physical branch from bifurcation diagrams. The analysis was conducted at subcritical, critical and supercritical isobars. The contribution of polynomial terms to the total φ^{res} was compared between low temperatures and large densities (typically liquid phase values), high temperatures and low densities (typically vapor phase values), and in the two-phase region or near the critical region.

Table 6: MP EOSs analyzed in this section that contain only type I and II functional forms.

Source	Substance	Numbers of terms from different functional form types					
		I	II	III	IV	V	VI
Jacobsen, Stewart and Myers (1973)	Oxygen	19	13	0	0	0	0
Jacobsen and Stewart (1973)	Nitrogen	19	13	0	0	0	0
McCarty (1974)	Methane	19	13	0	0	0	0
Schmidt and Wagner (1985)	Oxygen	13	19	0	0	0	0
Jahangiri <i>et al.</i> (1986)	Ethylene	15	26	0	0	0	0
Tillner Roth and Baehr (1994)	HFC-134a	8	13	0	0	0	0
Ihmels, Lemmon and Gmehling (2003)	Sulfur Dioxide	5	7	0	0	0	0
Span and Wagner (2003)	27 different substances (studied for Argon)	6	6	0	0	0	0
Sun and Ely (2004)	22 different substances (studied for Nitrogen)	6	8	0	0	0	0
Lemmon and Span (2006)	20 different substances (studied for R-245fa)	5	7	0	0	0	0
Ihmels and Lemmon (2007)	Dimethyl Ether	4	6	0	0	0	0

Table 7: MP EOSs analyzed in this section that contain type III, IV, V or VI functional forms.

Source	Substance	Numbers of terms from different functional form types					
		I	II	III	IV	V	VI
Chung <i>et al.</i> (1985)	Carbon Dioxide	6	2	0	0	0	3
Setzmann and Wagner (1991)	Methane	13	23	0	0	4	0
Span and Wagner (1996)	Carbon Dioxide	7	27	0	0	5	3
Span <i>et al.</i> (1998)	Nitrogen	6	26	0	0	4	0
Lemmon and Jacobsen (2005)	HFC-125	5	10	3	0	0	0

Figure 33 shows an example of the contribution of the polynomial and exponential terms to the total φ^{res} . The figure plots φ^{res} vs temperature for the physical branch of the McCarty (1974) methane MP EOS at a reduced pressure of 0.5. We see that both polynomial and exponential terms contribute to some degree at low temperature (in the liquid phase) and near the critical region (in the two-phase region). However, the close up shows that the total contribution to φ^{res} at high temperature (in the vapor phase) is dominated by the polynomial terms only. The contribution of exponential terms approaches zero as temperature increases.

This is shown more clearly by plotting the percentage contribution of polynomial terms to the total φ^{res} as in Figure 34. The cutoff lines around 10% and 90% were chosen arbitrarily simply to show if either functional form was dominating in a certain temperature region.

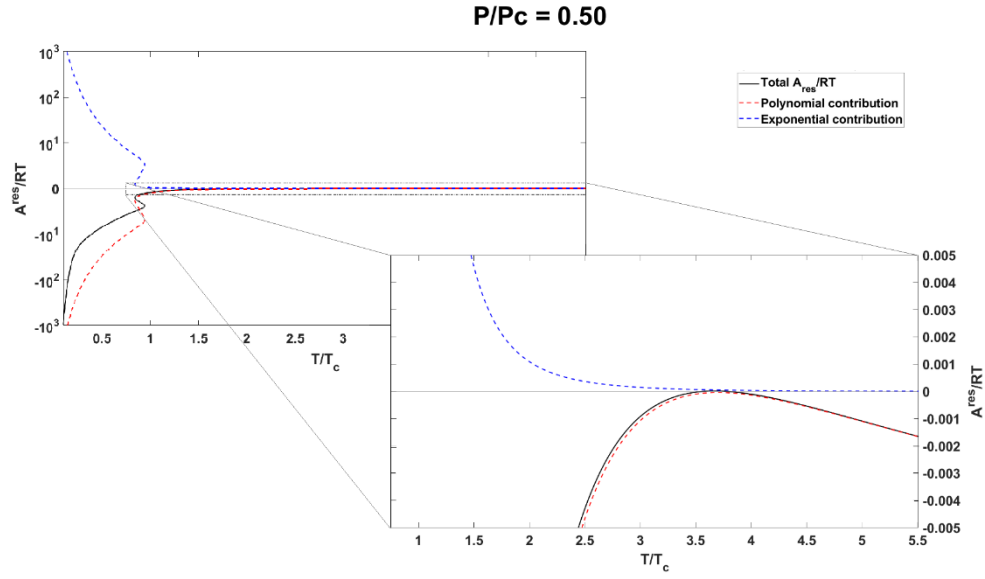


Figure 33: Contribution of the polynomial and exponential terms in the McCarty (1974) methane MP EOS to the total residual Helmholtz free energy (A^{res}/RT). The values match the data of the physical branch at $P = 0.5 P_c$. The red dashed curve represents the contribution of polynomial terms. The blue dashed curve represents the contribution of exponential terms. The black solid curve represents the total A^{res}/RT . The close up shows that the contribution of exponential terms approaches zero at high temperature.

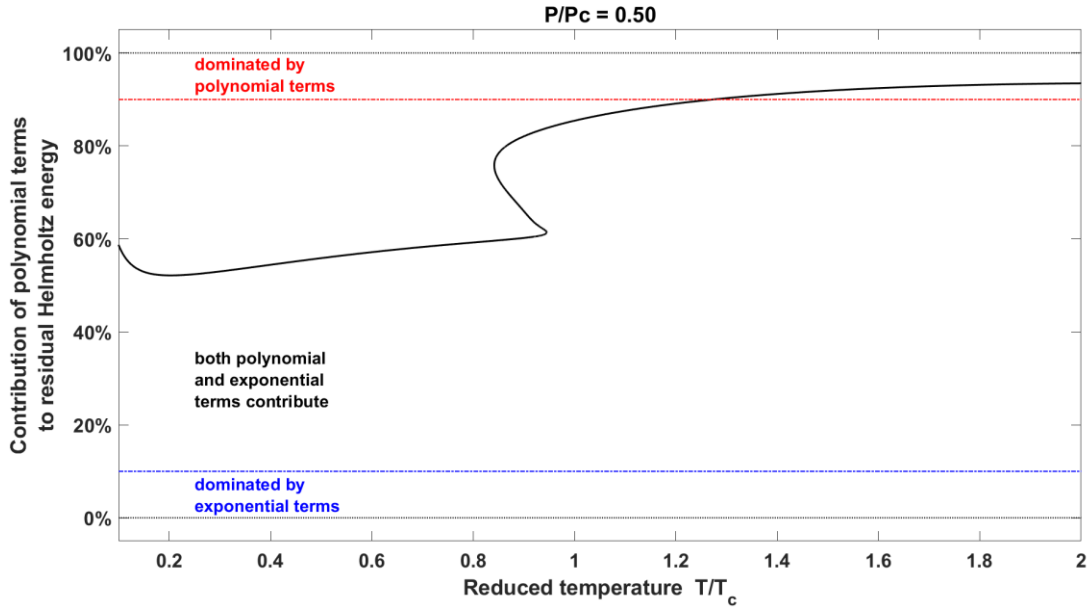


Figure 34: The percentage of the contribution of polynomial terms in the McCarty (1974) methane MP EOS to the total residual Helmholtz free energy (A^{res}/RT).

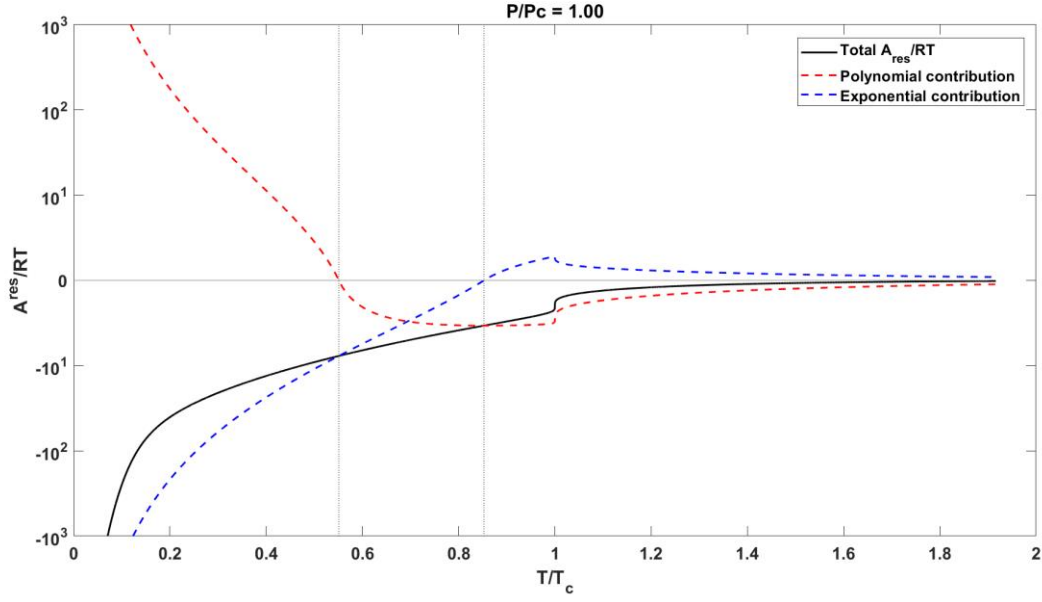


Figure 35: Contribution of the polynomial and exponential terms in the Lemmon and Jacobsen (2004) HFC-125 MP EOS to the total residual Helmholtz free energy (A^{res}/RT). The values match the data of the physical branch at the critical pressure. The red dashed curve represents the contribution of polynomial terms. The blue dashed curve represents the contribution of exponential terms. The black solid curve represents the total A^{res}/RT .

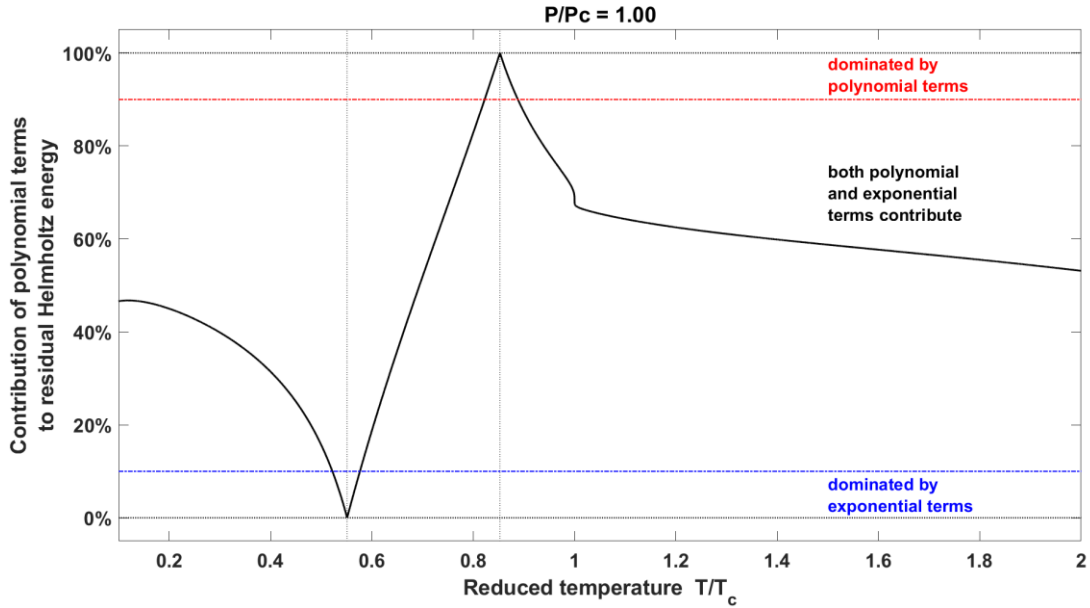


Figure 36: The percentage contribution of the polynomial terms in the Lemmon and Jacobsen (2004) HFC-125 MP EOS to the total residual Helmholtz free energy (A^{res}/RT).

Another example showing the contribution of the polynomial and exponential terms to the total φ^{res} is seen in Figure 35. The figure plots φ^{res} vs temperature for the physical branch of the Lemmon and Jacobsen (2004) HFC-125 MP EOS at the critical pressure. Figure 36 displays the corresponding percentage contribution of polynomial terms to the total φ^{res} . We see that both polynomial and exponential terms contribute to some degree throughout the temperature range. The only exceptions are around the two points marked with a vertical line, at around $T/T_c = 0.55$ and $T/T_c = 0.87$. As the φ^{res} of the polynomial terms or the exponential terms changes signs at those points, their contribution approaches zero. However, there is no clear trend of either type of functional forms dominating in a certain temperature range.

The analysis of the MP EOSs containing fewer polynomial than exponential terms versus ones with more polynomial than exponential terms did not show a general trend for all equations. However, three separate cases were noticed:

1. For the first six equations in Table 6, which have more than twenty terms in total: when the number of polynomial terms is larger than the exponential terms (i.e. the three mBWR MP EOSs), both types of functional forms contribute to some degree at lower temperature and near the critical region. The polynomial terms dominate at higher temperature. And when the number of polynomial terms is lower than the exponential terms, then the polynomial terms dominate throughout the whole temperature range, except in the two-phase region at low pressure.

2. For the last five equations in Table 6, which have less than fifteen terms in total: no uniform trend can be distinguished. But overall, both types of functional forms contribute to some degree at lower temperature and in the two-phase region. The polynomial terms dominate in the critical and supercritical temperature and pressure regions. The one exception is the Sun and Ely

(2004) MP EOS studied for nitrogen, where the polynomial terms dominate throughout the whole temperature range except in the two-phase region at low pressure. The one common trend between all equations in Table 6 is that the exponential terms contribution approaches zero and polynomial terms dominate at high temperature.

3. For the five equations in Table 7, which contain more complex exponential functional forms: The overall behavior is that both polynomial terms and exponential terms contribute evenly. The main exception is the Chung *et al.* (1985) carbon dioxide MP EOS, where polynomial terms dominate at lower temperature (liquid phase region). And their contribution at higher temperature (the two-phase and vapor phase regions) increased as pressure increased, until they dominated the whole range at supercritical pressures.

The analysis did not reveal a clear relation between the number of terms from certain functional forms and the effect on nonphysical behaviors exhibited by MP EOSs. However, it showed that more complex functional forms can overcome the proportional contribution of the simpler terms, which usually leads to erroneous behavior.

CHAPTER 6

CONCLUSIONS

In this study, the method of bifurcation diagrams was utilized to analyze the performance of fundamental multi-parameter equations of state. The method provided a framework to uncover nonphysical phenomena exhibited by these state-of-the-art equations of state. The technique uses pseudo arc-length continuation method in order to generate volume-temperature bifurcation diagrams at subcritical and supercritical isobars. This technique was used to evaluate the behavior of twenty one reference equations of state from literature. The study revealed several defects displayed by the different multi-parameter equations of state, such as predicting multiple nonphysical volume roots, nonphysical turning points, nonphysical branches, spurious phase coexistence regions, fictitious critical points, and incorrect PVT behavior.

The results showed that MP EOSs that included complex critical-region terms or had more exponential than polynomial terms had the most severe nonphysical behaviors. Most notably, the nitrogen MP EOS by Span et al., the ethane MP EOS by Bücker and Wagner, and the argon MP EOS by Tegeler, Span and Wagner formed the most spurious coexistence curves, nonphysical branches, nonphysical turning points and most volume roots, as well as exhibiting erroneous PVT behavior. However, we observed that MP EOSs employing both non-analytic and Gaussian bell-shaped terms had a decreased severity of nonphysical issues in comparison with ones containing Gaussian bell-shaped terms only.

The MP EOSs that were closest to replicating the correct physical behavior are: the three modified Benedict-Webb-Rubin MP EOSs (JSM, JS and McCarty), the Chung et al. MP EOS that uses special nonanalytic terms, and the Sterner and Pitzer MP EOS that uses rational function terms. It is also notable that these five equations use fewer exponential terms than polynomial terms. These MP EOSs did not form any spurious phase coexistence curves inside their reported validity regions. Also, their physical branches displayed the correct S-shape, with the exception of the JSM EOS below a certain volume.

Another notable MP EOS that only had minor nonphysical behaviors is the Lemmon and Jacobsen MP EOS. It contained exponential terms in both temperature and density, instead of density alone. Although this equation developed zig-zag behavior and one artificial phase separation region, this was confined to a small range at low pressure. The equation displayed the correct physical behavior for most of its validity region.

An analysis of the contribution of different functional forms to the total residual Helmholtz free energy was conducted at different pressures and temperatures. The analysis focused on comparing the contribution of polynomial terms and the contribution of exponential terms to the physical branch in the bifurcation diagrams. We found that MP EOSs with critical-region terms had a more equivalent contribution between complex exponential terms and the simpler polynomial terms. This observation corresponds with the severe erroneous behavior exhibited by these equations. A more rigorous analysis that includes nonphysical branches and zig-zag segments, and isolates the effect of every term of the equation, might help identify the exact part contributing to every nonphysical behavior.

We recommend using the following functional forms in the development of future MP EOSs: rational functions (or fractions of polynomials) such as the ones used by Sterner and Pitzer, the special nonanalytic form used by Chung et al., and exponential in both temperature and density such as the one used by Lemmon and Jacobsen. These special mathematical forms might help decrease or eliminate nonphysical behaviors in empirical and semi-empirical MP EOSs. Furthermore, accurate MP EOSs can be substituted for the hard-sphere term in advanced EOSs like the SAFT models in order to improve their accuracy. Finding a suitable MP EOS with a mathematical expression that limits nonphysical behavior is beneficial for developing more accurate thermodynamic models in the future.

Nevertheless, the use of complex functional forms provides a more accurate prediction of thermodynamic properties. In order to avoid the nonphysical problems associated with these functional forms, a thorough evaluation must be conducted for every set of functional forms and adjustable parameters used for the equation under development. This study demonstrates that bifurcation diagrams are the most effective method to start that procedure. The method reveals useful information by simply studying temperature, pressure and volume behavior, without necessarily resorting to thermodynamic potentials or partial derivatives. The generation of one V-T bifurcation diagram is usually enough to clarify if the MP EOS under development shows flawed behavior or not.

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