Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

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To my parents, Berta Marín and Oscar Cañas for their unconditional love. To my daughter Stephanie because she represents the maximum achievement in my life. To my brother Leonardo and my sister Orfa Nelly. My brother Oscar Emilio died in the 90’s, but I know he would be happy with this thesis if he still lived.
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Resumen

Desarrollo de una ecuación de estado fundamentada en teoría de perturbación termodinámica (TPT) para mezclas propensas a la precipitación de asfaltenos.

En esta tesis usamos la teoría molecular de los líquidos para revisar la Ecuación de Estado de la Teoría de Fluidos de Asociación Estadística de Cadena Perturbada (PC-SAFT EoS) y formulamos nuevos términos dispersivos y repulsivos para este modelo. Como es bien sabido en la literatura, la PC-SAFT original normalmente predice curvas de presión de inicio de precipitación de asfaltenos (AOP) en fluidos de yacimientos de petróleo, así como puntos de nube (CP) en sistemas poliméricos, muy aceleradas a bajas temperaturas. Este fenómeno se estudió en esta tesis con la ayuda de las teorías de perturbación termodinámica (TPT) y la teoría de ecuaciones integrales (IET). Al combinar estas teorías, formulamos varias expresiones de diámetro efectivo que dependen de la temperatura y la densidad, con el objetivo de reemplazar el diámetro efectivo original de PC-SAFT, que sólo es función de la temperatura. Además, se introdujo en PC-SAFT una modificación para el término de dispersión de segundo orden de Barker y Henderson, la cual está basada en un concepto de capas correlacionadas de fluido, estududiándose su efecto especialmente a bajas temperaturas. Los nuevos diámetros efectivos formulados y el término de dispersión de segundo orden modificado producen curvas AOP y CPs menos aceleradas a bajas temperaturas. De igual manera, las constantes universales originales (denominadas aquí como GSUC) en la parte atractiva of PC-SAFT también se analizaron en este trabajo. La conclusión principal es que las GSUCs no deben usarse, y en su lugar es preferible utilizar el conjunto de estas constantes presentado por Liang y Kontogeorgies (LKUC). De hecho, estas últimas no sólo corrigen el defecto de PC-SAFT de predecir múltiples raíces de densidad a temperaturas bajas, sino que reducen la tendencia de PC-SAFT de predecir curvas AOP y CP aceleradas a tales condiciones. También se estudian las predicciones de PC-SAFT de hiper presiones de inicio de precipitación de asfaltenos (HAOPs), reportándose nuevos diagramas de fase a bajas temperaturas para fluidos de yacimiento propensos a la precipitación de asfaltenos. Las HAOPs se desplazan a temperaturas muy bajas cuando se usa la versión modificada del término de dispersión de segundo orden de Barker y Henderson o cuando los LKUC se combinan...
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**Palabras clave:** PC-SAFT, teoría de perturbaciones termodinámicas, teoría de ecuaciones integrales, potencial intermolecular, diámetro efectivo, presión de inicio de asfaltenos.
Abstract

Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation.

We use the molecular theory of liquids to review the Perturbed Chain-Statistical Association Fluid Theory Equation of State (PC-SAFT EoS) and formulate new dispersive and repulsive terms for this model. As a well-known fact in the literature, the original PC-SAFT normally predicts accelerated asphaltene onset pressures (AOPs) in petroleum reservoir fluids and cloud points (CPs) in polymeric systems at low temperatures. This phenomenon was studied in this thesis. Thermodynamic perturbation theories (TPTs) and integral equation theory (IET) are central. By combining these theories, we formulate several effective diameter expressions dependent upon temperature and density to replace the original effective diameter of PC-SAFT, which depends on temperature only. Barker and Henderson’s second-order dispersion term based upon a concept of correlated shells of fluids was introduced into PC-SAFT and its effect was studied, especially at low temperatures. Both the new effective diameters formulated, and the modified second-order dispersion term produce less accelerated AOPs and CPs curves at low temperatures. The original universal constants (called here as GSUCs) in the attractive part PC-SAFT were also analyzed in this work. The main conclusion is that GSUCs should not be used at all, and the set of these constants presented by Liang and Kontogeorgies (LKUCs) are preferred instead. In fact, LKUCs not only correct the defect of PC-SAFT of predicting multiple density roots at low temperatures but also reduces the tendency of PC-SAFT of predicting accelerated AOP and CP curves at low temperatures. The PC-SAFT predictions of HAOP loci at very high pressures were also studied. New phase diagrams at low temperatures are presented in this work. HAOPs are displaced at very low temperatures when the modified second-order dispersion term is used or when the LKUCs are combined with the temperature- and density-dependent effective diameters presented in this thesis. Unfortunately, these HAOPs are not possible of being experimentally tested. Nonetheless, the high densities at which these HAOPs are predicted
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to precipitate asphaltenes by the original PC-SAFT represent non-isotropic conditions. Under those conditions, the TPTs for fluids lose validity. The combination of the LKUCs and the temperature-and density-dependent effective diameters presented in this thesis substantially increases the isotropic range, allowing a most robust use of the TPTs, and then of PC-SAFT. The failure of the original PC-SAFT to predict coherent Amagat curves is also amply studied. As a result, the failure was found to be directly related to the soft-core repulsion included in PC-SAFT by the effective diameter. Intermolecular potentials as the square well square shoulder (SWSS) are not “soft” enough to correctly predict these curves. Then, we demonstrate in this dissertation that intermolecular potentials soft enough, like Lennard-Jones one, need to be introduced.

**Keywords:** PC-SAFT, thermodynamic perturbation theory, integral equation theory, intermolecular potential, effective diameter, asphaltene onset pressure, soft repulsion.
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Introduction

Perturbed-chain statistical associating fluid theory (PC-SAFT EoS) represents one of the most important equations of state (EoS) developed in the last 20 years. This EoS has been used to model the thermodynamic behavior and physical properties of simple and complex mixtures, such as the petroleum ones. At present, literally, thousands of papers have been published in the literature showing diverse advantages of using this molecular-based EoS, instead of the classical cubic EoS models. However, as will be discussed later in this dissertation, PC-SAFT has also been criticized for issues such as its well-known numerical pitfalls, the possibility of predicting unreal phase equilibria at low temperatures or high pressures. This model also presents problems to represent derivative properties such as speeds of sound, and characteristic curves wherein the effective diameter in PC-SAFT has a predominant effect, e.g., Amagat curves. Then, the approaches have been focused on introducing some modifications to PC-SAFT with the aim of correcting some of its deficiencies. Nevertheless, those modifications are mainly phenomenological. The main focuses have been to refit the so-called “universal constants” of the perturbative contribution or include corrections into the repulsive part of this EoS to eliminate both the prediction of multiple liquid roots at low temperatures and the prediction of multiple critical points for a pure component.

The focus in this thesis is different because the goal was to review the theoretical bases of PC-SAFT and propose some theoretical-based modifications to this EoS. To do that, Barker and Henderson's thermodynamic perturbation theory (TPT), wherein PC-SAFT is rooted, was reviewed.

The first proposed modification was to remove the restriction of “uncorrelated fluid shells” of this molecular theory. In fact, PC-SAFT adopted this concept implicitly, and it is not possible to understand its implications by simply analyzing the mathematics of this EoS. Another important point tried in this dissertation is the concept of effective diameter. As a well-recognized issue in the literature related to the theory of liquids, the effective diameter concept is central to TPTs like Barker and Henderson's one. But the effective diameter expression adopted by PC-SAFT from that TPT is a simplification, and it is theoretically incorrect. Then, we focus this work on theoretically deducing temperature-and density-dependent effective diameter expressions from Barker and Henderson's
TPT, including the effect of introducing different “soft-core” expressions by using different intermolecular potential expressions. Moreover, effective diameters from Rowlinson’s TPT were also deduced.

It was necessary to resort to the integral equation theory (IET) to find all effective diameter expressions here presented.

This thesis is outlined as follows:

Chapter 1, “Theoretical context”, presents all the practical and theoretical fundamentals required to understand the work and results obtained in this project. We review concepts such as the liquid state, intermolecular forces, thermodynamic perturbation theory, hard-core reference, effective diameter, equations of state, and asphaltene precipitation and modeling.

Chapter 2, “Main theoretical developments from this thesis”, contains all the subsections with all the theoretical developments obtained in this thesis. These findings have already been published in the literature by the author, and this is duly referenced at the beginning of each subsection. Each subsection has its respective results and discussion, and it finishes with some conclusions.

Chapter 3, “Conclusions and Recommendations”, summarizes the main conclusions of this doctoral project and presents some recommendations for future developments.
1. Theoretical context

1.1 Problems of the liquid state and the definition of a reference state

The most common aggregation states of matter are solid, liquid, and gas, but of these states, the most difficult to describe theoretically and to predict their thermodynamic and dynamic behavior is the liquid state.

In the case of a solid, it is feasible to define an ideal solid as the one in which its atoms are located in nodes of a perfect crystalline network, and the atoms can only oscillate around their positions of equilibrium without overlapping among them. Now, if all the atoms oscillate with the same frequency, it is considered then as an ideal crystalline solid, and it is described by Einstein's model. Hence, this ideal crystalline solid is a candidate to be taken as a reference to introduce corrections like the multi-frequency oscillations or vibration modes of the oscillators, which leads to obtaining the Debye model and other models even more advanced. Also, alternatively, it is possible in certain cases to use the perfect solid as a reference but at the limit of high densities (packing), and then to introduce successive corrections in incremental volume powers.

For a diluted real gas, it is feasible to use the ideal gas model as a reference system and then to carry out corrections to define the equation of state (EoS) for that real gas. In fact, this approach is used in the development of the virial equation of state for a real gas, which consists in introducing successive corrections of density to the ideal gas EoS. Alternatively, one can take van der Waals’ approach [1], who theoretically introduced corrections to the ideal gas EoS with the purpose of accounting for the finite size of the molecules and the existence of attractive and repulsive intermolecular forces between them; being these last forces the main responsible for the structure of the fluid and the first ones are intimately responsible for the liquid-vapor phase transitions predicted by this EoS.
The main challenge is to define a reference model for the "liquid" state and the real dense gases. Moreover, even at present, there are very interesting discussions about what exactly the liquid state represents and how to define this state unambiguously [2]-[4]. For instance, is a liquid a kind of compressed "gas"? or could it be considered as a solid that has lost its order to different degrees of magnitude? In fact, the definition of "liquid" loses its meaning even more in certain regions of the phase space, such as the supercritical region, in which the term "fluid" is commonly used instead. A supercritical fluid is then either a compressed (dense) "gas" or an expanded "liquid". Precisely to avoid that ambiguity, it is simply called "fluid," although nowadays even this term "fluid" generates discussion [2].

In principle, one could choose to extend the virial EoS, valid only for low densities, to obtain an expression for the thermodynamic description of dense gases or liquids. This is done by considering enough terms in such a virial expansion. However, the main problem with this approach is that such an expansion leads to slow convergence of the series, and, additionally, it is not feasible to obtain more than about five to eight terms, that is insufficient to achieve a model with enough flexibility and range of application. For the problem of convergence of the virial series, acceleration methods have been developed, such as Padé approximants [5], and the development of the rescaled virial [6], but these methods fail for dense fluids due to the abrupt variations that suffer the virial coefficients at low temperatures. Similarly, another way would be to use a crystalline solid as a reference and then apply corrections to consider the lower order of the molecules. Such an approach even seems less promising than the previous one, and, in fact, attempts have been made in that direction, but the results obtained are not sufficiently satisfactory [7].

The problem is that a liquid, for example, can be isotropic like a gas but also dense like a disordered solid. Therefore, this wide range of changes leads to a delicate competition between enthalpy forces that permit, for instance, the condensation phenomenon, and entropic forces opposite, for example, to the crystallization. Such a play of forces complicates to define a reference from which to build a robust molecular-based theory for the description of the thermodynamic and phase behavior of liquids and dense gases.
1.2 Intermolecular forces and their role in the description of the dense gas and liquid state

One of the first difficulties in defining a reference system for liquids and real gases is the description of intermolecular forces and how these forces contribute to the structure and thermodynamics of a liquid or gas. Historically, at the beginning of the nineteenth century, Young [8] and Laplace [9] were convinced that it was necessary to consider both attractive and repulsive forces between particles to be able to explain the phenomena of cohesion and capillarity observed in fluids, but it took a long time to be able to specify how these interactions were. Mossoti [10] was among the first in developing an explicit potential for attractive interactions in terms of electrostatic forces for dense and electrically neutral fluids, expressing this potential as a damped version of Coulombic interactions. This form is now commonly known as the Yukawa potential [11]. After Mossoti, Clausius [12] expressed that molecules repel each other at relatively short distances and that they attract each other at moderate distances. Such an idea then awakened in the scientists an incessant search to find the mathematical forms of both types of interaction, among them James Clerk Maxwell [13], who extended his earlier work on perfectly elastic hard spheres to particles interacting through an additive-pair type repulsive force; mathematically expressing the latter as inversely proportional to the fourth power of the distance of separation between them, i.e., like the attractive form of Newton's law of gravity. However, he noted that his mathematical expression for hard spheres was not able to describe the phenomenon of gas diffusion. Boltzmann [14] concluded that a completely different law of intermolecular force should be used to reproduce data such as gas viscosities. The above ideas and developments allowed van der Waals [1] to deduce his famous EoS for fluids, which, for the first time, made it possible to describe the liquid-vapor equilibrium. In his model, van der Waals represented the molecules as perfect spherical hard nuclei (repulsive) that allowed to describe the low compressibility of dense fluids, plus long-range attractions needed for predicting phenomena such as condensation (i.e., vapor-liquid transition). Such attractive interactions were included with the help of an integrated energy term (medium field), which allowed him to avoid the use of the precise and explicit algebraic form of such interactions as a function of the separation distance. Sutherland [15]-[17] followed van der Waals’ ideas and coupled a model of hard spheres with pair-attractive forces, which, according to him, would vary with the fourth inverse power of the separation (i.e., giving a pair potential that varies with the inverse of the third power of the separation of the centers of mass of two particles). With this fourth power formulation, he was able to reconcile to a large extent the available experimental information of thermodynamic properties, such as gas viscosities [17], liquid-vapor interfacial stresses [16], and the equation of state [15]. On the other
hand, one of the great later advances to reveal the empirical form of repulsive interactions between particles was given by Mie [18], who represented the repulsive pair potential as the inverse of a generic power, $n$, of the separation between the centers of mass of two particles; that is $u(r) \propto 1/r^n$, where $n$ is the exponent that characterizes the range of repulsion; Mie in turn introduced the attractive forces implicitly using the approach developed by van der Waals [1]. This combination gives Mie's approach great versatility to describe different scenarios and contrasts between "softness" and "hardness" for the repulsive term, and the attractive interactions of different ranges are made available by manipulating van der Waals' constant in the attractive term of Mie's potential.

Keesom [19] focused on the mathematical form of the attractive potential and examined the second virial coefficient of molecules considered as hard and rigid spheres with attractive Newton-type interactions. He found within the range of $n = 3$ and $n = 5$ insensitivities to the temperature dependence of that virial coefficient. Lennard-Jones [20]-[22], for his part, has the credit of having expressed in an explicit and condensed manner the full intermolecular potential as $u(r) = A/r^n - B/r^m$; with $A$ and $B$ representing the respective repulsive and attractive constants. In 1931 already Lennard-Jones had established the values of $n = 12$ and $m = 6$.

With the emergence of quantum mechanics in the 1920s, a more rigorous and detailed treatment of electrostatic interactions between particles became possible. Wherein Pauli's exclusion principle gave meaning to repulsive interactions such as those due to the repulsion between electronic clouds; although the precise dependence on the separation between the particles was still difficult to describe. Here, a compact exponential mathematical expression of the form $\exp(-r/\sigma_0)$ could be used, being $\sigma_0$ a parameter related to the Bohr radius, to represent the repulsive potential resulting from the overlap of the electronic density of orbitals $s$, but only applicable to single atoms [23]-[24]. On the other hand, Wang [25] had shown at the end of the twenties of the last century that the attractive interactions of the dispersive type between atoms were the result of fluctuating electric dipoles, which at the quantum level gave rise to a contribution proportional to $1/r^6$; which was later corroborated by Eisenschitz and London [26], which is now known as London scattering interactions. The fluctuations of the electrons in larger molecules lead to the presence of quadrupole and superior multipoles, which then results in a sum of contributions due to electronic fluctuations that scale in powers of $n = 6, 8, 10$, etc. Therefore, for a simple but rigorous representation based on quantum mechanics, it would be necessary to combine an exponential dependence in $r$ for
repulsive interactions with a series of powers in $r$, and of different orders, to take into consideration
the attractive contributions. It is very interesting to note that the simple square well potential (SW)
model, widely used in the development of equations of state, also has its roots in the wave mechanics
of Schrödinger, Fermi, Dirac, and others. In quantum mechanics, this potential model is analogous
to the "particle in the box". In fact, for example, the SW model allows exact and simpler calculations
based on statistical mechanics for the mathematical evaluation of the first virial coefficients [27]-
[28].

In summary, by the 1950s the nature of the pair intermolecular potential and the sensitivity of the
thermophysical properties to the mathematical form of this potential were already understood [29].
With the advent of special experimental techniques, it was also possible to directly determine the
pair interactions, confirming the exponential form of the repulsion at short distances and the London
type form of the interactions at moderate distances. But it was also recognized that it was complicated
to achieve a universal form of pair potential, for example, with their respective fixed exponents and
applicable to all pairs of molecules. Therefore, one cannot expect potentials like Lennard-Jones to
be universal but rather applicable to the interaction between certain types of molecules [30]. The fact
that potentials such as Lennard-Jones or SW potentials are still used in the 21st century for the
development of fluid theories and in molecular simulation calculations is partly due to their relative
simplicity in comparison with more generic potential models such as Mie's. Now, deficiencies in the
use of simple potentials such as SW, SWSS (square well square shoulder), Lennard-Jones (LJ), etc.,
are to some degree "smoothed out" or "corrected" by adjusting the resulting models as EoS models
to experimental information, which then have their parameters adjusted to experimental information
from real substances. Nevertheless, this practice, although valid and necessary, for example, from
an engineering viewpoint, takes away the predictive capacity of the model and inclines the EoS more
to a correlative model. It also makes the EoS more difficult for its parameters to be interpreted from
a molecular perspective.

1.3 Definition of a hard-core system for liquids and dense gases

Before the 1970s, it was thought that nothing substantial could be added about the microscopic
origins of the properties of liquids, and it was considered that the delicate balance between entropic
and enthalpy contributions could be so intricate and specific across the phase space that it was very
difficult to develop simple models of general applicability. What partly changed this panorama was
the development of experimental techniques, such as neutron scattering and tunnel spectroscopy,
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

which allowed studying the microscopic and dynamic structure. As well as the development of molecular simulation techniques by computer. All advances allowed to test without ambiguities the molecular theories that were developed or had already been developed, discarding the unpromising ones, and continuing with the improvement of those that showed to have a future [31].

With all the above, it has been found that the most common reference system for dense gases and real liquids consists of one formed by hard-core particles, representing the molecules of the real fluid. Being the simplest case, the one constituted by hard spheres (HS) interacting among themselves by means of forces derived from spherical symmetry potentials. In fact, it is the reference system that has attracted the most attention and has been studied for decades, for example, through molecular simulation techniques. For this spherical-hard system, the particles interact by means of an intermolecular potential represented by:

\[
    u(r) = \begin{cases} 
    \infty & \text{if } r \leq \sigma \\
    0 & \text{if } r > \sigma 
    \end{cases}
\]

Where \( \sigma \) is the hard-sphere diameter.

This model of intermolecular potential is completely repulsive, and then two spheres repel each other with an infinite force when they contact each other, something like two billiard balls. The thermodynamic properties of the real fluid can then be developed as a series of powers of a certain physical magnitude that is adequate and representative. So do the so-called thermodynamic perturbation theories.

### 1.4 Thermodynamic perturbation theories (TPTs)

These theories are based upon the fact that at the extreme case of high temperatures, real fluids behave as if they were systems formed by hard molecules or hard spheres, as a special case. They are also based upon the commonly accepted fact that the structure and thermodynamic properties of real fluids are mainly determined by repulsive interactions between particles and that the attractive interactions represent a contribution of lesser quantitative importance. Therefore, this last contribution can be "seen" as a perturbation to the repulsive contribution. However, in certain regions of the phase diagram of a fluid, or its mixtures, this theoretical picture is not faithfully fulfilled (e.g., at the critical region) and, naturally, as already expressed, attractive forces are fundamental. Van der
Waals precisely applied a kind of very basic thermodynamic perturbation theory (TPT), giving the cause of the structure of the fluid to the repulsive forces provided by its repulsive term (i.e., excluded volume) and considering the attractive forces as a perturbation produced by an attractive potential of spherical symmetry (medium field theory).

The sophisticated idea of treating attractive forces in a fluid as a perturbation over a hard-core potential was first introduced by Zwanzig [32]. These theories of perturbation have been widely accepted for decades by researchers working in the field of statistical mechanics of the liquid state, the most famous being the TPTs developed by Barker and Henderson (BH) [33]-[35], Week-Chander-Andersen (WCA) [36], and Rowlinson [37]-[39]. The general success of perturbation theories for the description of dense liquids and gases is mainly due to their relative simplicity, the quality of the results they provide, and the generality of their applications. In these facts, the TPTs surpass the models obtained from the so-called integral equation theories (IET). These IETs are commonly based on the solution of the complex Ornstein-Zernike equation (OZ) [40] by using closure expressions such as Percus-Yevick (PY) [41], hypernated chain (HNC) [42], etc. Naturally, the field of research in perturbation theories: limitations, possible improvements, the extension of these to polyatomic molecules, the use of more complex intermolecular potentials, the presence of dipoles, molecular association, and electrostatic forces, is in plenty activity.

Of the three TPTs mentioned above, the most used for the development of molecular-based thermodynamic models (e.g., EoS) is that of Barker and Henderson (BH) [33]. Barker and Henderson’s TPT is based on a formulation called "discrete representation". This focus consists in dividing the intermolecular distances into discrete intervals and considering constant within each interval both the perturbative part of the additive-pair potential and the radial distribution function (RDF). This simplification allows to consider the distribution of distances between pairs instead of the spatial distribution of the particles. Barker and Henderson TPT’s makes the division of the additive-pair potential into a repulsive part (reference) and an attractive part (perturbative), as follows:

\[ u(r) = u_0(r) + u_1(r) \]  \hspace{1cm} (1.2)

Where \( u_0(r) \) is the repulsive or reference potential, and \( u_1(r) \) is the perturbing (i.e., attractive) one.
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

\[ u_0(r) = \begin{cases} u(r) & \text{if } r \leq \sigma \\ 0 & \text{if } r > \sigma \end{cases} \quad (1.3) \]

\[ u_1(r) = \begin{cases} 0 & \text{if } r \leq \sigma \\ u(r) & \text{if } r > \sigma \end{cases} \quad (1.4) \]

Here \( \sigma \) is the value of \( r \) for which the repulsive reference part is canceled. With this division, the total potential energy of the system, \( \Phi \), is then expressed as:

\[ \Phi(r \rightarrow N) = \Phi_0(r \rightarrow N) + \Phi_1(r \rightarrow N) = \Phi_0(r \rightarrow N) + \sum_i N_i u_1(r_i) \quad (1.5) \]

Wherein the summation represents the discretization of the potential. Here, \( N_i \) means the number of particles within the respective \( i \)-th range. Thus, the configurational part of the partition function in the canonical ensemble can be expressed as:

\[ Q_c = Q_c^0 \langle exp[-\beta \sum_i N_i u_1(r_i)] \rangle_0 \quad (1.6) \]

The Helmholtz free energy is given then as:

\[ (A - A_0) = -\ln(\langle exp[-\beta \sum_i N_i u_1(r_i)] \rangle_0) = \beta \sum_i \langle N_i \rangle_0 u_1(r_i) - \frac{1}{2} \beta^2 \sum_{ij}(\langle N_i N_j \rangle_0 - \langle N_i \rangle_0 \langle N_j \rangle_0) u_1(r_i) u_1(r_j) + \text{higher terms} \quad (1.7a) \]

\[ \beta \equiv \frac{1}{kT} \text{, then eqn. (1.7a) is commonly expressed as:} \]

\[ A = A_0 + \frac{A_1}{kT} + \frac{A_2}{(kT)^2} + \text{higher terms} \quad (1.7b) \]

Here, \( A_0 \) is the total Helmholtz free energy for the reference system. On the right-hand side (RHS), the first term represents the first perturbation term, \( A_1 \), and the second means the second term of perturbation, \( A_2 \). The “higher terms” obviously consider the contributions of \( A_3, A_4, \ldots, A_N \). As the term increases, so does the accuracy of the expansion, but, in turn, the complexity of the resulting model increases and the difficulties to be evaluated. In fact, it is expected that as the perturbation
term increases, it will become less important. This last fact really depends upon the fast convergence of the series. Barker Henderson’s TPT assumes that to expand the series up to $A_2$ is enough.

As seen from eqn. (1.7a), $A_2$ is directly related to the theory of fluctuations, and, naturally, it is expected that its contribution will be less important at high pressures, since at high pressures, obviously far from the critical region, the fluctuations are less important. Thus, it is expected that BH theory will be most accurate at high pressures and deteriorate at low pressures, requiring the introduction of higher terms. This is an inherent problem of the perturbation theories, and it has been studied extensively in the literature related to the molecular theory of fluids [7].

Similarly, as evident in eqn. (1.7b), better performance is expected at higher temperatures. At high temperatures, the term that contains $A_2$ in eqn. (1.7b) is less important. Similarly happens with $A_1$. Hence, $A \approx A_0$. On the contrary, the TPT is expected to be less accurate at low temperatures, in which $A_1$ and $A_2$, and maybe higher terms, are plenty relevant.

In eqn. (1.7a), the average number of molecular pairs in the reference system, at a distance within the $i$-th interval, is given as:

$$\langle N_i \rangle_0 = 2\pi Np \int_{r_i}^{r_{i+1}} g_0(r)r^2 dr$$

(1.8)

Wherein $g_0(r)$ is the RDF of the reference system. However, if the difference between $r_i$ and $r_{i+1}$ tends to zero, and assuming that $u_0(r)$ is constant in that interval, then the first perturbation term can be expressed as [33]-[35]:

$$\beta A_1 = \sum_i \langle N_i \rangle_0 u_1^*(r_i) = 2\pi Np \int_0^\infty g_0(r)u_1^*(r)r^2 dr$$

(1.9)

Where $u_1^*$ is the reduced intermolecular perturbation potential (i.e., $u_1^* = \frac{u_1}{\varepsilon}$).

The second perturbation term is given as follows:

$$\beta A_2 = -\frac{1}{2} \frac{kT}{\varepsilon^2} \sum_i \langle N_i \rangle_0 u_1^2(r_i) = -\pi Np kT \langle \frac{\partial \rho}{\partial p} \rangle_0 \int_0^\infty g_0(r)[u_1^*(r)]^2 r^2 dr$$

(1.10)
Here, $\rho$ is the density in number, and its derivative with respect to pressure, $\left(\frac{\partial \rho}{\partial p}\right)_0$, represents the compressibility of the reference system. The approximation giving as a result eqn. (1.10) was named by Barker and Henderson as “macroscopic compressibility approximation” (mc) due to $\left(\frac{\partial \rho}{\partial p}\right)_0$ is proportional to the compressibility of a macroscopic system formed by hard spheres. Nonetheless, the fluctuations in a shell of fluid are most intimately related to the local compressibility, $\left(\frac{\partial (\rho g)}{\partial p}\right)_0$ (i.e., into the same shell). For this reason, Barker and Henderson obtained an equation like eqn. (1.10) but for the local compressibility, called “local compressibility approximation” (lc). The mathematical expression is given as:

$$\beta A_2 = -\pi N p k T \int_0^\infty u_1^* (r) 2 \left(\frac{\partial (\rho g)}{\partial p}\right)_0 r^2 dr \tag{1.11}$$

If it is a soft-core potential instead of a hard-core potential; then, it would be necessary to obtain the thermodynamic properties of the "soft" reference system. For this purpose, Barker and Henderson demonstrated that the reference system can be approximated by a hard-sphere system with an effective diameter, $d$. Into the Barker and Henderson TPT, $d$ is given as [33]-[35], [7]:

$$d(T) = \int_0^\sigma [1 - \exp\{-\beta u(r)\}] dr \tag{1.12}$$

Note that this expression of effective diameter is a function of temperature, but it does not depend upon density.

BH theory has been applied to Lennard-Jones potential [34], [35], [43], and for simpler intermolecular potentials like square well, SW, and "soft" square well, SWSS [44]-[50]. By using the first-order term only, $A_1$, quite satisfactory results are obtained when this theory is applied at not too low temperatures, and the radial distribution function for the reference fluid is determined from Percus-Yevick theory. Moreover, Helmholtz free energy values are excellent if the terms $A_1$ and $A_2$ are calculated from molecular simulation data [42], [51].

When comparing BH TPT with HTA-WCA (HTA means “high-temperature approximation”), it is found that for Lennard-Jones fluids the latter TPT provides better results at high densities and not too high temperatures when compared with molecular simulation data. In addition, for low densities,
the HTA-WCA TPT is not sufficiently accurate, and it is necessary to introduce high-order terms than the first perturbative one. The HTA-WCA theory uses an effective diameter which, in addition to temperature, is also a function of density. In contrast, for reduced temperatures of the order of three or more, the Barker-Henderson theory is superior [52].

With respect to Rowlinson's TPT [37]-[39], this theory also uses an effective diameter independent of density, and it provides reasonably satisfactory results only at high temperatures and low densities. On the other hand, this TPT converges very slowly, and higher-order terms are completely necessary, but those terms cannot be mathematically obtained in a simple way [37], [38]. Nevertheless, Rowlinson’s work was essential to improve BH theory. This will be discussed later.

The three above-mentioned perturbation theories -BH, HTA-WCA, and Rowlinson- essentially differ in the way each one assumes the division of the pair-additive potential between the repulsive (reference) and attractive (perturbation) part, and whether those TPTs consider the effect of density on the effective diameter. However, the separation between repulsive and attractive forces, in which perturbation theories rely on, and the assumption that those repulsive forces are responsible for the structure of the fluid, has been questioned by several researchers. In fact, Berthier and Tarjus [53], [54] have challenged these concepts, as they showed that in some cases to ignore the effect of attractive forces on the structure of fluids leads to large errors. Similarly, Toxvaerd and Dyre [55], [56] showed that the determining factor to achieve the correct thermodynamic and dynamic description is not per se if the attractive forces are included or not in the simulations, but what is an important thing is if within the first sphere of coordination (FCS) the interactions between all particles are included or not. Attractive forces can be ignored but only at extremely high densities because under those conditions repulsive interactions are predominant. Simple liquids are then chemically characterized by the fact that their properties are completely determined by the interactions between the molecules within the FCS [4].

It should be noted that Touba and Mansoori [57] had already developed an analytical expression for the FCS of the radial distribution function (RDF), and it was applicable to several types of intermolecular potentials. Those authors concluded, when compared with computer simulations, that the information within the first coordination sphere is sufficient to calculate the thermodynamic properties. For example, with Lennard-Jones potential the cut-off radius for reproducing the computer simulation data was always within the FCS, which means that the cut-off is always within the radius that represents the first minimum of the RDF or, from an engineering viewpoint, it means
the radius in which the mean density within a sphere equals the overall particle density. Therefore, speaking strictly, attractive interactions should always be considered at least within the FCS.

1.5 Equation of state (EoS)

The progress in the development of equation of state (EoS) models has been impressive since the pioneering work carried out by van der Waals [1] to describe the liquid-vapor equilibrium of simple fluids. It is evident by the enormous amount of models and modifications now available to describe, with less or more success, the thermodynamic and equilibrium properties of fluid, solid and semi-solid systems, with diversity in types of intermolecular interaction, ranges of application (e.g., temperatures, pressures, compositions, proximity to transition points, etc.), asymmetries in molecular sizes, the inclusion of aggregation effects, adsorption, etc. [58] Theoretical advances in models based on statistical thermodynamics, molecular simulation, ab initio methods, etc., have allowed the unprecedented evolution from empirical EoS to those with robust theoretical bases [59]-[63]. The variety of equations of state with strong molecular bases is very wide, and they are generally based on one of two theoretical lines that were already mentioned above: (1) integral equation theory (IET), involving the solution of the Ornstein-Zernike equation [40] by means of a closure model such as Percus-Yevick [41] or hypernetted-chain equation [42], [64] or (2) thermodynamic perturbation theory [33]-[39]. Though EIT could be more accurate and rigorous in describing, for example, the molecular structure of fluids (i.e., the RDF), it is quite complex and has the main disadvantage that, for example, closure methods generally have no solution within the two-phase region. In addition, it suffers from the absence of thermodynamic consistency among energy, virial, and compressibility paths [65]. These drawbacks are being tried to be solved [66], [65], but now it is not easy to obtain an equation of state from EIT that has the sufficient practicality and simplicity required to be used in solving real engineering problems.

On the other hand, most EoS models in engineering are based on TPTs, as much the semi-empirical ones (e.g.: Van der Waals [1], Redlich-Kwong (RK) [67], Soave-Redlich-Kwong (SRK) [68], Peng-Robinson (PR) [69]), and those models with sound theoretical bases (e.g.: PHCT, BACK, SAFT family, etc.) [58]. Considering, as already explained above, that the structure of the fluids is given by repulsive forces, and that the attractive contribution can be considered a perturbation. Thus, it is obviously assumed that the structure of the fluid does not change when attractive forces are included. As explained above, that is not necessarily true.
The variety of EoS models combining repulsive + attractive contributions is very wide in the scientific literature, and some aspects are key in all these years of development of this type of model. For example:

1. The use of molecular simulation based on intermolecular potential models such as SW, SWSS [44]-[50], LJ [20]-[22], Kihara [27], and others, has been fundamental to elucidate the order of magnitude of these repulsive and attractive contributions in modeling molecules, such as spheres, chains, cylinders, discs, etc, allowing, for example, the development of expressions such as Carnahan-Starling [70] to describe the repulsive nature of hard spheres, the basis for the extension to chains formed by those hard spheres.

2. There is consensus that the most accurate and pioneering expression for the repulsive contribution of hard spheres for isotropic fluids is that of Carnahan-Starling, although alternative expressions have been sought to reduce computation times without losing the accuracy [71]. In fact, the number of alternative expressions is very large, and it would be interesting to investigate the sensitivity of thermodynamic calculations and computation times when using some of those alternative expressions since no direct correlation has been found between the complexity of the reference term of hard spheres and the accuracy of the resulting model [72], [73].

3. At present, there is no exact counterpart for the attractive contribution, like that of Carnahan-Starling for the repulsive part, and that expression has been very elusive for the scientific community related to fluid modeling.

4. To develop EoS models is much more than combining the best repulsive contribution (e.g., Carnahan-Starling type) with some attractive expression. In fact, these attempts have generally yielded failed models [58]; Furthermore, it can sometimes happen that combining an erroneous (or not correct) repulsive contribution expression with an erroneous attractive contribution expression results in a fairly successful model for a given application such as the Peng Robinson EoS (PR EoS). As expressed by Wu and Prausnitz [74] … "Although the literature is rich with hundreds of variations of the original van der Waals equation of the state of 1873, no variation has been as useful or as widely accepted as the PR EoS. It is no exaggeration to claim that PR EoS is one of the greatest success stories in the history of applied chemical thermodynamics. Somehow, by design, determination, experience, and a bit of luck, Peng and Robinson constructed the optimum balance of repulsive and attractive terms such that the sum of those terms gives a remarkably close
representation of the configurational thermodynamic properties of many pure fluids and their mixtures". Nevertheless, the same authors gave examples of failures for PR EoS... "the limitations of this justly famous equation of state are also well-known: inaccurate liquid densities; poor representation in the critical region; unreliable for fluids with very large molecules; and inapplicable to highly polar fluids, hydrogen-bonded fluids (especially water), and electrolytes" [74]. The following figure illustrates the failure of van der Waals' repulsive term, also used as a repulsive term in all cubic state equations.

Figure 1-1: Compressibility factor of athermic hard spheres predicted by the repulsive term of van del Waal versus molecular simulation [58].

5. There is not a generic EoS model. In fact, modeling the critical region remains to date one of the biggest problems not solved satisfactorily [75], [76].

6. Usually, new EoS models are proposed as modifications of existing ones, or successful components of one or more EoS models are reused to obtain a new equation. This reuse of components is a common practice, both in the development of empirical equations of state and those with sound theoretical bases [58]. Here, the advances in molecular simulation and structural information from analytical techniques such as SANS (small-angle neutron scattering), SAXS (small-angle X-ray scattering), etc. are important inputs for developing the EoS [66].
Of the modern EoS based upon molecular theories, SAFT-family EoS models stand out. These models are rooted in the TPTs and make use of molecular simulation results for square-well-type molecular potentials (and their modifications) and/or Lennard-Jones (and their modifications). At the same time, from the SAFT family, the perturbed chain-statistical association fluid theory equation of state (PC-SAFT EoS) stands out [50]. In fact, PC-SAFT can be considered one of the main developments in the theory of equations of state after the emergence of SAFT, and after the development of the famous semi-empirical EoS, like RK, SRK, and PR. Although PC-SAFT represents a great advance in the development of equations of state with sound molecular bases, it is also true that, due to those same molecular bases, this model has identifiable limitations. Some of them are:

(a) For pure components, PC-SAFT can predict fictitious gas-gas and/or liquid-liquid transitions. Gas-gas equilibria at low densities and high temperatures, wherein, usually, the ideal gas phase is expected. Liquid-liquid transitions at high density and low-temperature conditions, wherein a liquid-solid transition should occur [77]. Such fictitious regions predicted by PC-SAFT are mainly a consequence of the attractive term and the simplified expression for the effective diameter (see equation (1.11)).

(b) PC-SAFT presents difficulties in modeling non-spherical rigid molecules. For example, Deiters found inconveniences with PC-SAFT to model the binary system CO\textsubscript{2}-Caffeine. According to that author: "...we attributed that to the fact that the PC-SAFT EOS and mixing rules have been optimized for flexible molecules (alkanes up to polyethylene) but cannot cope well with nonspherical rigid molecules like caffeine" [78]. This is a difficult drawback to solve because that could imply having to perform, for example, a re-evaluation of the so-called "universal" constants of the model, perhaps looking for some constants that are particularly applicable to rigid molecules. Another option for this type of non-spherical rigid molecules would be to replace the Carnahan-Starlig expression [2], which is for rigid spheres, by any that is applicable to hard disks.

(c) PC-SAFT exhibits inaccuracies, or predicts strange phase behavior, in modeling macromolecular substances (e.g., polymers), especially at low temperatures. For example, Van Schilt et al. found problems in modeling the density of polybutadiene at ambient temperature. This author expressed that "...discrepancies in modeling the polymer density at ambient temperature and high pressure can be traced back to the (artificial) liquid-liquid phase separation predicted by the equation of state at low temperatures" [79]. This drawback may be linked not only to that expressed by Van Schilt et al.
but also to the simplified expression for the effective diameter, inherited from the Barker-Henderson perturbation theory (BH), and to the universal constants used in the attractive part of this EoS model.

(d) PC-SAFT is between 1.5 and 2.2, slower than a cubic EoS like PR. Therefore, this computational cost limits its implementation into engineering simulators, such as petroleum reservoir simulators [80]. Here, both the complexity of the term repulsive and the attractiveness contribute to this problem.

Recently, there has been interest in developing SAFT EoS models, but with more flexible intermolecular potential like Mie’s one, and with a variable range [18], [81], [82]. However, such a combination produces a more complex model and, therefore, a most-restricted EoS for its application in modeling thermodynamics of fluids into an engineering simulator.

1.6 Asphaltene precipitation and modeling

As reported in the literature [83], calorimetric measurements related to flocculation enthalpies, and the composition of asphaltene deposits support the idea that this flocculation process is a "liquid-liquid" transition from a liquid phase, crude oil, to a second liquid phase, rich in asphaltenes. The most widespread assumption to date is that in crude oils the asphaltenes are present in a colloidal state. Resins and other aromatic components play a role in stabilizing the asphaltenes due to solubility effects and/or favorable molecular interactions between resin-asphaltene molecules instead of asphaltene-asphaltene interactions. An illustration showing this scenario is presented below:

Figure 1-2: Colloidal model of asphaltenes [84]
Over the past 40 years, several thermodynamic models have been developed to predict the precipitation of asphaltenes in asymmetric mixtures typical of petroleum reservoir fluids. At present, models based upon EoS are the most used. In fact, irreversible colloidal models [85], and micellar ones [86], [87] have lost their validity. Furthermore, it is important to differentiate the models that use cubic EoS [88]-[98], with or without association, from those EoS models with the soundest theoretical bases. The last EoS models are rooted in the TPTs of Barker-Henderson [33]- [35], and Werthein [99]-[104]. Such as the SAFT-family EoS models [50], [105]-[113]. Nonetheless, from the cubic equations, the CPA (Cubic Plus Association) [95], [96], [98] stands out, in which the association term is based on Werthein's TPT; while from the SAFT family, the most used EoS to model the asphaltene phase behavior is undoubtedly the PC-SAFT EoS [50], either with or without the association contribution. Recently, articles have been published in the scientific literature focused on comparing the performance of PC-SAFT versus CPA for the modeling of hydrocarbon mixtures prone to asphaltene precipitation [93], [114], [115]. CPA has a theoretical consistency problem since the physical part- i.e., attractive, and repulsive- is taken from cubic EoS models, such as SRK [67] or Peng-Robinson [68]. As mentioned above, cubic EoS models are theoretically incorrect. However, the CPA Eos is a model widely used in chemical and petroleum engineering. According to Arya et al. [115], to consider only van Waals forces is not enough to model asphaltene precipitation with PC-SAFT, and an association term should be included. Following Arya et al., both PC-SAFT and CPA are promising models for describing the asphaltene precipitation in petroleum fluids, if the association term is included. Those authors report results showing that PC-SAFT without the association term is unable to correctly correlate the experimental asphaltene onset pressures (AOPs) for several reservoir fluids. Figure 1-3 presents an example reported by Arya et al. [115]. According to this figure, PC-SAFT with or without the association term has the tendency of predicting very high AOPs as the temperature decreases.

Naturally, the inclusion of an association term makes PC-SAFT a "heavier" model, computationally speaking. Hence, CPA EoS would be much more practical to be incorporated in engineering simulators, even though its theoretical basis is quite deficient because its physical reference is a semi-empirical cubic EoS. However, it is very difficult to know for PC-SAFT what the real contribution of the association term would be if the non-associative part (i.e., physical) was not first studied deeper to understand and propose possible theoretical improvements. It is important to consider that both models, PC-SAFT and CPA, are generally used in the scientific literature to correlate experimental AOPs and Bubblepoits (BPs), and not in a predictive manner [96], [98], [115]-[120]. The correlative ability of CPA to model AOPs depends strongly on the association term. This
associative term must be forced to be able to reproduce the experimental information and cover the deficiencies of the cubic EoS used to account for the repulsive and non-directional attractive contributions [96], [115]. Among other things, it is necessary to use temperature-dependent association parameters to correlate the experimental AOPs. This fact is clearly undesirable and reduces the predictive capability for these EoS models [96], [115].

**Figure 1-3:** Modeling of AOPs with PC-SAFT and CPA by Arya et al. [115].

1.7 **Effective diameter of Barker and Henderson**

The effective sphere diameter is a variable of primary interest due to several reasons. For example, it can be interpreted in terms of other molecular properties, such as the collision diameter of the repulsive part of the pair interactions. Furthermore, it is a well-known fact that any EoS of the hard-sphere type is highly sensitive to that diameter because, for example, at liquid state densities the molecules are very close together, such that a small increase in the size of these diameters produces a huge increase in pressure [121].

As mentioned above, there are several theories of statistical mechanics that provide the dependence of the effective diameter on thermodynamic variables. In general, the effective diameter should decrease with increasing the temperature because the kinetic energy increases, while its dependence upon density is not so obvious [121]. Usually, an effective diameter decreasing with density is expected.
As already mentioned also, the effective diameter of Barker and Henderson is an exponential Boltzmann-type function that depends only on temperature (see eqn. (1.12)). Therefore, this diameter is really an approximation, which for simple fluids may be enough. It has been shown that even in Barker and Henderson's theory the effective diameter should also be a function of the density [43]. In part, this simplification represented by eqn. (1.12) was because in the 1960s, in which the work of Barker and Henderson was developed [33]-[35], the computational cost was very high, and then using a simplified expression like the previous one was a good compromise between accuracy and computational efficiency [43]. But such a diameter is not physically correct and has a too simple and unique dependence on temperature [78].

Thermodynamic calculations are very sensitive to effective diameter. Moreover, BH theory strongly underestimates enthalpy at low and moderate temperatures, and this problem is more severe for mixtures. Enthalpy contributions directly affect the performance of an equation of state like PC-SAFT at low temperatures [121].

The EoS PC-SAFT uses the potential of Chen-Kreglewski [122], given by:

\[
\begin{align*}
  u(r) &= \begin{cases} 
    \infty & \text{if } r < (\sigma - s_1) \\
    3\epsilon & \text{if } (\sigma - s_1) \leq r \leq \sigma \\
    -\epsilon & \text{if } \sigma < r \leq \lambda \sigma \\
    0 & \text{if } r > \lambda \sigma 
  \end{cases} 
\end{align*}
\]

(1.13)

In which $3\epsilon$ and $s_1$ are the height and width of the repulsive "shoulder". On the other hand, $-\epsilon$ and $\lambda$ represent the depth and width of the attractive well.

Therefore, by using eqn. (1.13) in eqn. (1.12) the resulting effective diameter is:

\[
d_i = \sigma_i \left[1 - 0.12 \exp \left(-3 \frac{\epsilon_i}{kT} \right) \right]
\]

(1.14)

This could explain, in part, the tendency of PC-SAFT to over-predict the onsets of asphaltene precipitation and polymer cloud points at low temperatures [78], [123].
Boltzmann-type temperature dependency may be the reason why PC-SAFT predicts Amagat curves (i.e., Joule effect inversion curves) without physical sense. It also causes the zero effective diameter limit (i.e., ideal gas limit) not to be met when the temperature tends to be infinite [124]. Although the fact that PC-SAFT does not predict consistent Amagat curves may not have an impact on asphalt modeling, it is important, from a theoretical viewpoint, that this EoS reproduce them.

More robust features are needed for the effective diameter. However, at present, no attempts have been published in the literature to theoretically deduce alternative expressions for the effective diameter and replace the original BH expression. As PC-SAFT uses Chen-Kreglewski potential [122] for the repulsive part, then any theoretical deduction of a more rigorous effective diameter expression to be used in PC-SAFT should consider this potential and to be a function of both temperature and density.

As explained above, in Barker and Henderson's theory the molecular potential is separated into a repulsive and an attractive part:

\[ u(r) = u_{\text{rep}}(r) + u_{\text{att}}(r) \]  \hspace{1cm} (1.15)

Where \( u_{\text{rep}}(r) \) is the repulsive or reference potential, and \( u_{\text{att}}(r) \) is the attractive part (perturbation), given by:

\[ u_{\text{rep}}(r) = \begin{cases} u(r) & \text{if } r \leq \sigma \\ 0 & \text{if } r > \sigma \end{cases} \]  \hspace{1cm} (1.16)

\[ u_{\text{att}}(r) = \begin{cases} 0 & \text{if } r \leq \sigma \\ u(r) & \text{if } r > \sigma \end{cases} \]  \hspace{1cm} (1.17)

In this case, the separation occurs at \( r = \sigma \). Wherein \( \sigma \) is the hard-core diameter and it is independent of both temperature and density.

Barker and Henderson took as a reference a pseudofluid made-up of molecules interacting according to the repulsive potential (i.e., eqn. (1.16)), while the attractive contribution was considered as a perturbation on such a reference fluid. Since in general both free energy and RDF are not analytically obtainable for an arbitrary reference system, then the reference system is in turn mapped to one of
hard spheres by using the effective diameter concept. As explained later, the properties of the hard-
sphere system have been amply studied by theory and machine calculations. Hence, Barker and
Henderson [33] made an expansion of the free energy of Helmholtz with respect to $\alpha$ and $\gamma$ to obtain
a diameter for the reference system based on the diameter of hard spheres. Here, $\alpha$ and $\gamma$ are the
slope and depth of the potential function [43], respectively.

The first term of the expansion is given by:

$$a = a_{HS} - 2\pi \rho g_{HS}(d)d^2\left( d - \int_{0}^{d} (1 - e^{-\beta u(r)}) dr \right) + \ldots$$ (1.18)

Wherein the sub-index $HS$ refers to the system of hard spheres, $d$ is the effective diameter, $g_{HS}$ is
the RDF, and $\beta \equiv 1 / kT$. Being $k$, Boltzmann's constant. The suspension points in eqn. (1.18)
indicate that other higher terms were omitted in the expansion. This fact would be analyzed after.

Note that a simple choice for the effective diameter, $d$, emerges by taking $a = a_{HS}$ in eqn. (1.18).
That is to say, that the free energy of Helmholtz equals the free energy of hard spheres, which is
obtained by making the first term of the expansion null, leading to eqn. (1.12) already discussed (i.e.,
$d = \int_{0}^{d} (1 - e^{-\beta u(r)}) dr$). Equation (1.12) is a function of temperature and the form of the potential
$u_{r}$ used. As previously expressed, in the 60s of the past century, when the work of Barker and
Henderson was developed [33]-[35], the computational cost was very high and by using a simplified
expression such as eqn. (1.12) meant a compromise between accuracy and computational efficiency
[43]. Nevertheless, in principle, alternative expressions of the effective diameter can be derived by
using the Mayer function [125], $f$, and then performing a perturbative expansion of the Helmholtz
free energy of the pseudofluid around a system of hard spheres with diameter $d$ [43], [125], [126]:

$$a_{rep} = a_{HS} + \int \left( \frac{\partial a}{\partial f(r)} \right)_{HS} \left( f_{rep}(r) - f_{HS}(r) \right) dr$$

$$= a_{HS} - \frac{1}{2} \rho \int y_{HS}(r) \left( e^{-\beta u_{rep}(r)} - e^{-\beta u_{HS}(r)} \right) dr,$$ (1.19)

Here:

$$\frac{\partial a}{\partial f(r)} = -\frac{1}{2} \rho y(r),$$ (1.20)
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

\[ y(r) = e^{\beta u(r)} g(r), \quad (1.21) \]

\[ f(r) = e^{-\beta u(r)} - 1 \quad (1.22) \]

As will be seen later, eqns. (1.21) and (1.22) are related to the Percus-Yevick closure approximation [41] used to solve the Ornstein-Zernike integral equation [40]. Equation (1.19) can be reduced to:

\[ a_{rep} = a_{HS} - 2\pi \rho \int_0^\sigma y_{HS}(r) \left( e^{-\beta u_{rep}(r)} - e^{-\beta u_{HS}(r)} \right) r^2 dr \quad (1.23) \]

Again, a choice for the effective diameter, \( d \), emerges by taking \( a_{rep} = a_{HS} \). Namely, that the repulsive Helmholtz free energy equals the Helmholtz free energy of hard spheres, being this true if the first term of the expansion is null, i.e.,

\[ 2\pi \rho \int_0^\sigma y_{HS}(r) \left( e^{-\beta u_{rep}(r)} - e^{-\beta u_{HS}(r)} \right) r^2 dr = 0 \quad (1.24) \]

Which ultimately becomes:

\[ \int_0^\sigma y_{HS}(r) e^{-\beta u_{rep}(r)} r^2 dr = \int_d^\sigma y_{HS}(r) r^2 dr, \quad (1.25) \]

Wherein:

\[ y_{HS}(r) = \begin{cases} 
- c_{HS}(r) & \text{if } r < d \\
g_{HS}(r) & \text{if } r > d 
\end{cases} \quad (1.26) \]

Note that, according to eqns. (1.21) and (1.26), \( y_{HS}(r) \) is related to the RDF, \( g_{HS}(r) \), and it is known as a cavity function. \( c_{HS}(r) \) represents the direct correlation function obtained from the Ornstein-Zernike EIT, as will be explained later.

This implies that the effective diameter, \( d \), in eqn. (1.25) not only will depend on temperature but also upon density, due to RDF depends on density. Therefore, to be able to use eqn. (1.25) to find \( d \), it is necessary to know \( y_{HS}(r) \). For this purpose, one option is to use Percus-Yevick cavity function obtained from the EIT. In other words, the complexity to determine the effective diameter using
equation (1.25) depends on having the expressions $c_{HS}(r)$ and $g_{HS}(r)$ for the repulsive potential of interest. As stressed before, PC-SAFT uses Chen-Kreglewski potential [122], which is an SWSS-type potential. Until now, none work had been performed in the scientific literature focused on using the equation (1.25) to determine an analytical expression for the Barker-Henderson effective diameter of SWSS potentials, thus dependent not only on temperature but also on density. Speaking strictly, theoretically deduced temperature-and density-dependent effective diameter expressions had not been used in PC-SAFT.

For completeness, Ornstein-Zernike (OZ) integral equation is given in general form by [40]:

$$h(r) = c(r) + \rho \int c(r')h(|r - r'|)dr'.$$  \hspace{1cm} (1.27)

Where $\rho$ is the density of particles, $h(r)$ is known as the total correlation function. The OZ equation defines the direct correlation function, $c(r)$, depending on $h(r)$. In addition, $h(r) = g(r) - 1$.

It is necessary to have additional relationships that link the structure functions [i.e., $h(r)$ and $c(r)$] to the intermolecular potential to solve equation (1.27). These relationships are commonly called closure relationships [127]. For example, the well-known Percus-Yevick closure approximation [41] is very useful for systems with repulsive short-range interactions, and it is given by:

$$c(r) = [e^{-\beta u(r)} - 1]y(r) = f(r)y(r)$$  \hspace{1cm} (1.28)

Where $y(r) = e^{\beta u(r)}[h(r) + 1] = e^{\beta u(r)}g(r)$, which is simply eqn. (1.21); $f(r)$ is Mayer's function, given already in eqn. (1.22).

For SW and SWSS potentials [128]-[134], different methods have been recently proposed in the literature to solve the OZ integral equation and obtain numerical and analytical solutions for $c(r)$. These developments are promising to be used in the theoretical development of an alternative expression of the effective diameter as a function of temperature and density for PC-SAFT.
2. Main theoretical developments from this thesis

Almost all the material presented in this chapter has already been published by the author in the following list of papers (this is also stressed at the beginning of each section):


- Wilson A. Cañas-Marín, Bibian A. Hoyos. Role of the soft-core repulsion upon the prediction of characteristic curves with PC-SAFT. Fluid Phase Eq. 499 (2019) 112247.


2.1 Mathematical generalities of PC-SAFT

As mentioned before, PC-SAFT is based upon Barker and Hederson’s TPT. At present, this EoS represents one of the most modern and versatile models published in the literature. Gross and Sadowski [50] presented all mathematical details for PC-SAFT, and the assumptions underlying this molecular model in their Appendix A, entitled “Summary of Equations for Calculating Pressure, Density, Fugacity Coefficients, and Caloric Properties Using the Perturbed-Chain SAFT Model”. In short, PC-SAFT EoS is represented by a summation of several contributions to the residual Helmholtz free energy:

\[
\frac{A_{res}}{NkT} = \frac{A_0}{NkT} + \frac{A_{disp}}{NkT} + \frac{A_{assoc}}{NkT}
\]  

(2.1)

Where \(A\) is, again, the Helmholtz free energy. Super indexes \(disp\), and \(assoc\) stand for the respective contributions of the terms of dispersion and association to the residual Helmholtz free energy \(res\).

The repulsive (reference) contribution to PC-SAFT is given by a hard-chain term formed by hard-spheres, as follows:

\[
\frac{A_0}{NkT} = \frac{A_{hc}}{NkT} = \bar{m} \frac{A_{hs}}{NkT} - \sum_i x_i (m_i - 1) \ln(g_i^{hs})
\]  

(2.2)

\[
\bar{m} \equiv \sum_i x_i m_i
\]  

(2.3)

\(m_i\) is the number of segments per chain, \(\bar{m}\) stands for the mean segment number in the system, and \(x\) represents the molar fraction. The summation at RHS of equation (2.2) considers the contribution given by the connectivity of the hard spheres to form the hard-sphere chains. The main difference between SAFT EoS [105]-[107] and PC-SAFT is precisely the selection of \(\frac{A_0}{NkT}\). While in SAFT a hard-sphere system was chosen, PC-SAFT works with a chain formed by hard spheres.
In eqn. (2.2) of PC-SAFT, the hard-sphere contribution is given by:

\[
\frac{A_{hs}^{NkT}}{NkT} = \frac{1}{\xi_0} \left[ \frac{3\xi_1\xi_2}{(1-\xi_3)} + \frac{\xi_2^2}{2(1-\xi_3)} + \left( \frac{\xi_2^2}{\xi_0} - \xi_0 \right) \ln(1 - \xi_3) \right]
\]

(2.4)

Here, \( g_{hs} \) is the RDF for hard spheres, \( g_{hs}^{ij} \),

\[
g_{hs}^{ij} = \frac{1}{(1-\xi_3)} + \left( \frac{d_id_j}{d_i+d_j} \right) \frac{3\xi_2}{(1-\xi_3)^2} + \left( \frac{d_id_j}{d_i+d_j} \right)^2 \frac{2\xi_2^2}{(1-\xi_3)^3},
\]

(2.5)

And \( \xi_n \ (n = 0, 1, 2, 3) \) are defined as follows:

\[
\xi_n \equiv \frac{\pi}{6} \rho \sum x_i m_i d_i^n
\]

(2.6)

\( d_i \) is the effective diameter defined for PC-SAFT given in eqn. (1.14).

On the other hand, the perturbative (attractive) part in PC-SAFT is represented as:

\[
\frac{A_{disp}^{NkT}}{NkT} = \frac{A_1}{NkT} + \frac{A_2}{NkT}
\]

(2.7)

Wherein \( \frac{A_1}{NkT} \) and \( \frac{A_2}{NkT} \) represent the first- and second-order contributions already discussed before.

Then, \( \frac{A_{disp}^{NkT}}{NkT} \) was represented by Gross and Sadowski as:

\[
\frac{A_{disp}^{NkT}}{NkT} = \frac{A_1}{NkT} + \frac{A_2}{NkT} = -2\pi \rho l_1(\eta, \bar{m})\bar{m}^2 \epsilon \sigma^3 - \pi \rho \bar{m} C_1 l_2(\eta, \bar{m})\bar{m}^2 \epsilon^2 \sigma^3
\]

(2.8)

Being,

\[
l_1(\eta, \bar{m}) \equiv \sum_{i=0}^{6} a_i(m)\eta^i
\]

(2.9)

\[
l_2(\eta, \bar{m}) \equiv \sum_{i=0}^{6} b_i(m)\eta^i
\]

(2.10)

\[
\bar{m}^2 \epsilon \sigma^3 \equiv \sum_i \sum_j x_i x_j m_i m_j \left( \frac{\epsilon_{ij}}{\kappa T} \right) \sigma_{ij}^3
\]

(2.11)
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

\[ \overline{m^2 \varepsilon^2 \sigma^3} \equiv \sum_i \sum_j x_i x_j m_i m_j \left( \frac{\varepsilon_{ij}}{kT} \right)^2 \sigma_{ij}^3 \]  
(2.12)

\[ C_1 \equiv \left[ 1 + \overline{m} \frac{8 \eta - 2 \eta^2}{(1 - \eta)^2} + (1 - \overline{m}) \frac{20 \eta - 27 \eta^2 + 12 \eta^3 - 2 \eta^4}{[(1 - \eta)(2 - \eta)]^2} \right]^{-1} \]  
(2.13)

Other relationships required to calculate the terms of PC-SAFT are:

\[ \eta = \frac{\pi \rho}{6} \sum_i x_i m_i d_i^3 \]  
(2.14)

\[ \rho = \frac{\overline{\rho}}{N_{AV}} \]  
(2.15)

\[ a_i(m) = a_{0i} + \overline{m} a_{1i} + \left( \frac{m-1}{m} \right) a_{2i} \text{ (universal constants, } a_{ji} \text{) } \]  
(2.16)

\[ b_i(m) = b_{0i} + \overline{m} b_{1i} + \left( \frac{m-1}{m} \right) b_{2i} \text{ (universal constants, } b_{ji} \text{) } \]  
(2.17)

Here, \( \eta \) is the packing fraction (i.e., reduced density), \( \sigma \) is the hard-sphere diameter, \( \varepsilon \) is the depth of the pair potential, \( \overline{\rho} \) is the molar density, \( \rho \) is the number density of molecules, \( N_{AV} \) is Avogadro’s number. \( a_{ji} \) and \( b_{ji} \) are called “universal constants”, and Gross and Sadowski [50] fitted these constants to n-alkane properties. Hence, several sets of “universal constants” could be used in PC-SAFT, depending on the components used to fit them. As will be discussed in this work, calculations with PC-SAFT are very sensitive to the set of universal constants appearing in eqns. (2.15) and (2.16). It will be analyzed in enough detail later.

In addition, the cross diameter of segment, \( \sigma_{ij} \), and cross energies, \( \varepsilon_{ij} \), are calculated by using the simple Berthelot combination rules,

\[ \sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \]  
(2.18)

\[ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j (1 - k_{ij})} \]  
(2.19)

Finally,
\[
\frac{A_{\text{assoc}}}{RT} = \Sigma_{i} x_{i} \left[ \Sigma_{A_{i}} \left( \ln X_{A_{i}} - \frac{X_{A_{i}}}{2} \right) + \frac{M_{i}}{2} \right]
\] (2.20)

PC-SAFT really results from combining several theoretical developments: (a) IET, represented by the RDF (i.e., eqn. (2.5)), (b) conformal mixtures/solutions theory, given by the van de Waals one-fluid mixing rule (double summations in eqns. (2.11) and (2.12)), (c) Barker and Henderson TPT (eqns. (2.7) and (2.8)), and (d) Wertheim’s TPT (eqn. (2.20)). As mentioned above, eqn. (2.20) has not been considered in the present work. Less evident, PC-SAFT is also related to the theory of fluctuations through Barker and Henderson’s TPT.

### 2.2 Some mistakes and misprints in the original paper of PC-SAFT by Gross and Sadowski

From thermodynamics, the fugacity coefficient, \( \varphi \), for a component \( i \), is related to the residual chemical potential, \( \mu \), according to,

\[
\ln \varphi_{i}(T, P) = \frac{\mu_{i}^{\text{res}}(T, P)}{kT} - \ln Z
\] (2.21)

For PC-SAFT [50], the reduced residual chemical potential, \( \frac{\mu_{i}^{\text{res}}}{kT} \), is given as,

\[
\frac{\mu_{i}^{\text{res}}(T, \rho)}{kT} = \tilde{\alpha}^{\text{res}} + (Z - 1) + \left( \frac{\partial \tilde{\alpha}^{\text{res}}}{x_{i}} \right)_{T, \rho, x_{j} \neq i} - \Sigma_{j} x_{j} \left( \frac{\partial \tilde{\alpha}^{\text{res}}}{x_{j}} \right)_{T, \rho, x_{l} \neq j}
\] (2.22)

Wherein \( \tilde{\alpha} \equiv \frac{A}{NkT} \), and, in eqn. (2.22):

\[
\left( \frac{\partial \tilde{\alpha}^{\text{res}}}{x_{i}} \right)_{T, \rho, x_{j} \neq i} = \left( \frac{\partial \tilde{\alpha}^{hc}}{x_{i}} \right)_{T, \rho, x_{j} \neq i} + \left( \frac{\partial \tilde{\alpha}^{\text{disp}}}{x_{i}} \right)_{T, \rho, x_{j} \neq i}
\] (2.23)

Gross and Sadowski gave the mathematical expression for the compositional derivative of \( \tilde{\alpha}^{hc} \) as (see eqn. A.35 in [50]):

\[
\left( \frac{\partial \tilde{\alpha}^{hc}}{x_{i}} \right)_{T, \rho, x_{j} \neq i} = m_{l} \tilde{\alpha}^{hs} + \bar{m} \left( \frac{\partial \tilde{\alpha}^{hs}}{x_{l}} \right)_{T, \rho, x_{j} \neq i} - \Sigma_{l} x_{l} (m_{l} - 1) \left( g_{ll}^{hs} \right)^{-1} \left( \frac{\partial g_{ll}^{hs}}{x_{l}} \right)_{T, \rho, x_{j} \neq i}
\] (2.24)
But eqn. (2.24) is incorrect, being the following expression the correct one:

\[
\left( \frac{\partial \tilde{a}^{hc}}{x_i} \right)_{T,\rho,x_{j\neq i}} = m_i \tilde{a}^{hs} + \bar{m} \left( \frac{\partial \bar{a}^{hs}}{x_i} \right)_{T,\rho,x_{j\neq i}} - (m_i - 1) \ln g_{ii}^{hs} - \sum_i x_i (m_i - 1) \left( g_{ii}^{hs} \right)^{-1} \left( \frac{\partial g_{ii}^{hs}}{x_i} \right)_{T,\rho,x_{j\neq i}} - 1 \]

(2.25)

In short, the third term on the RHS [i.e., \(-(m_i - 1)\ln g_{ii}^{hs}\)] is missing in the original paper, and this absent term could contribute to produce erroneous or extraneous predictions by using PC-SAFT without checking the consistency of the respective mathematical expressions. This mistake was recently exposed by Cañas-Marín et al. [135]. In the reply by Gross and Sadowski [136], they considered this missing as a “misprint”, and expressed that “We are aware of three misprints in that article. Our discussions with scientists who implemented the equations of the PC-SAFT model showed that, fortunately, these misprints are rather easy to detect. The most subtle misprint is indeed the one commented by Cañas-Marín et al.”

The missing term in eqn. A35 in the original paper by Gross and Sadowski is difficult of being detected. The only way of finding this mistake is by carrying out a careful mathematical derivation of \( \tilde{a}^{hc} \) from eqn. (2.2). In terms of \( \tilde{a} \), eqn. (2.2) is given as:

\[
\tilde{a}^{hc} = \bar{m} \tilde{a}^{hs} - \sum_i x_i (m_i - 1) \ln g_{ii}^{hs}
\]

(2.26)

In fact, some authors in the literature have published the wrong equation (i.e., eqn. (2.24)) in their papers. See, for example, [137].

Gross and Sadowski [136] used their reply to highlight two most “misprints” in their original paper:

- “the right-hand side of eq. (A.11) should be raised to the power of -1. It is then consistent with eq. (13) and eq. (25).”

- “the superscript of eq. (A.38) should be ‘disp’ instead of ‘hs’, in agreement to the headline of the sub-section.”
Nevertheless, another misprint not reported by Gross and Sadowski in their reply is that eqn. (1.18) of their original paper is wrong. The correct term is \( \frac{3\xi_2}{(1-\xi_2)^2} \), i.e., the power 2 was missing.

By concreteness, the tilde (\(~\)) is dropped in the rest of this work to define the reduced Helmholtz free energies. Thus, \( \tilde{a} \) is simplified as \( a \).

### 2.3 A modified Barker and Henderson’s second-order dispersive term

The following derivation and discussion were already published by Cañas-Marín et al. (see reference [138]).

This section presents a modified perturbed chain-statistical association fluid theory (mod-PC-SAFT EoS) obtained by including into PC-SAFT the second-order dispersion term developed originally by Zhang [139] for pure components but extended in this thesis to mixtures. This version of PC-SAFT is then used to predict asphaltene onset pressures (AOPs) for nine petroleum reservoir fluids with asphaltene contents, based on saturates-aromatics-resins-asphaltenes (SARA) analyses varying from 0.80 to 16 wt.%. In all modeled cases, this new version predicts less accelerated AOPs at low temperatures than the original PC-SAFT, and then the well-known and widely discussed tendency of PC-SAFT of predicting very high AOPs at these conditions is corrected. The new model also reduces or eliminates the crossover temperatures predicted by PC-SAFT when a reservoir fluid, prone to precipitate asphaltenes, is enriched with CO2.

Asphaltene precipitation is a serious problem in the production, transport, and processing of reservoir fluids. This phenomenon is directly influenced by changes in temperature, pressure, and composition. However, it is an arduous task to predict the conditions (e.g., pressures) under which asphaltene becomes unstable, because, among other aspects, this substance is a solubility class [140], [141]. Following Szewczyk and Béhar [83], calorimetric measurements of asphaltene flocculation enthalpies and compositional analysis support the idea that the asphaltene flocculation process, at reservoir conditions, is a thermodynamic transition from one liquid phase (crude oil) to another liquid phase (asphaltene rich phase). Knowledge of the physicochemical characteristics of phases present during the asphaltene precipitation process has promoted the development, use, and modification of many thermodynamic models (e.g., equations of state) for predicting asphaltene onset pressures (AOPs) [95], [96], [98], [111], [114], [116], [119], [120], [142], [143], [144]. For example, Chapman...
et al. [116]-[118] and Vargas et al. [114], [119], [120] have used PC-SAFT to calculate the AOPs of petroleum reservoir fluids under pressure depletion and gas injection processes, showing that PC-SAFT is a very promising equation of state (EoS) to describe AOPs in multicomponent mixtures. This EoS has shown good performance in modeling diverse fluid systems ranging from light gases up to polymeric systems. PC-SAFT performs well for AOPs, but its predictive capability deteriorates at low temperatures [79], [115].

Recently, Abutaqiya et al. [145] discussed the presence of a minimum upper critical solution temperature (MUCST) predicted by PC-SAFT. At this MUCST, the AOP curve given by this EoS tends to infinity. Similar predictions with PC-SAFT were reported by Arya et al. [115]. In addition, Abutaqiya et al. [145] systematically modified the PC-SAFT molecular parameters without finding different behavior with respect to predictions of MUCSTs. PC-SAFT also predicts a hypothetical hyper asphaltene onset curve (HAOP), which occurs because the upper AOP curve returns from the MUCST up to higher temperatures, forming a new phase boundary [145]. The HAOP occurs at extremely high pressures [145], outside the range of interest for the petroleum industry, and it appears to be a mere artifact of PC-SAFT. As discussed later, this PC-SAFT behavior at low temperatures is independent of the characterization method used to describe the reservoir fluid.

Van Schilt et al. [79] used PC-SAFT to predict cloud points (CPs) of polymeric ternary systems composed of poly cyclohexane carbonate-cyclohexane oxide-carbon dioxide (PCHC-CHO-CO$_2$). These CPs are modeled as liquid-liquid equilibria. At high temperatures, PC-SAFT described the CPs well, whereas at lower temperatures it overestimated the experimental cloud-point pressures. At low temperatures, the CP pressures in polymer systems often increase due to unfavorable enthalpic interactions between polymer and solvent (i.e., upper critical solute temperature (UCST) demixing), which is very similar to the behavior in asphaltenic systems. As explained by Van Schilt et al. [79], “since the density is increasing toward lower temperatures, the mixtures become more incompressible in this region, then the UCST phase transition is less sensitive to pressure, resulting in a steep slope of the cloud-point curve”. Yelash et al. [77] conducted a global investigation of phase equilibria using PC-SAFT and found drawbacks when modeling polybutadiene densities at ambient temperature and high pressures. According to these authors, discrepancies in these densities could be traced back to the liquid-liquid phase separation predicted by PC-SAFT at low temperatures. Yelash et al. concluded that: “liquid-liquid demixing predicted by PC-SAFT is due to inappropriate approximations in the dispersion term” [77]. Additionally, Liang and Kontogeorgis [146] found that the PC-SAFT EoS exhibited more than three volume (density) roots, or two stable
liquid volume roots. In addition, discontinuous volume roots were observed as the pressure increased, which led to an unrealistic prediction of phase behavior.

The comparisons in the literature between PC-SAFT and the cubic plus association EoS (CPA) to predict AOPs have been contradictory, and there is a debate over which of these models is correct [114], [115]. For instance, Arya [14] reported that an association term should be included in PC-SAFT to correlate better the experimental AOPs with this EoS, and that the original PC-SAFT without association (WOA) is inferior to both CPA and PC-SAFT with an association term. In fact, Arya et al. [115] concluded that “PC-SAFT (WOA) approach has convergence problem at low temperatures”, and that “…It also raises questions whether only van der Waals interactions are responsible for asphaltene precipitation or association forces also contribute to asphaltene precipitation. If only van der Waals interactions are responsible, then we need to modify the modeling approach for the PC-SAFT (without association) to characterize the stock tank oil components”. On the contrary, AlHammadi et al. [114] using PC-SAFT without association concluded that “…with an optimized characterization, both EOS give reasonable predictions of the phase behavior and asphaltene precipitation tendency, with the PC-SAFT predictions of asphaltene precipitation closer to experimental results compared to CPA”.

The hypothesis in the present work is that both the repulsive and attractive parts of the original PC-SAFT (i.e., without association) can be theoretically improved to avoid the over predictions of AOPs at low temperatures. Hence, in this first section, a theoretically modified PC-SAFT EoS (mod-PC-SAFT) is presented as a result of changing the second-order dispersion term (i.e., the attractive part) in the original PC-SAFT (O-PC-SAFT). The mod-PC-SAFT and O-PC-SAFT are compared in terms of predicting AOPs for nine petroleum reservoir fluids with asphaltene contents, based on SARA analyses, varying from 0.80 to 16 wt.%. Both models are used to perform sensibility analysis of AOPs to changes in molecular weights of resin and asphaltenes. Finally, these two models are utilized to perform sensibility calculations of crossover temperatures for a reservoir fluid under CO₂ injection. It is important to highlight that soft-core repulsion also plays a fundamental role in smoothing AOPs predicted by PC-SAFT at low temperatures (high densities), and this topic will be theoretically analyzed after. Both theoretical modifications should be introduced into PC-SAFT before comparing this model against other EoS models published in the literature.

Several practical approaches could be considered to improve the capability of PC-SAFT in describing liquid-liquid equilibrium at low temperatures. For instance, one option would be
introducing, as suggested by Van Schilt et al. [79], temperature-dependent binary interaction coefficients, $k_{ij}(T)$, into the combination rule used by the PC-SAFT EoS to calculate the cross-energetic interaction, $\varepsilon_{ij}$ [50]:

$$
\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j (1 - k_{ij}(T))}
$$

(2.27)

However, this approach could be inadequate because at least two experimental points, at two different temperatures, would be necessary to describe $k_{ij}$’s dependency on temperature, affecting the predictive capability of PC-SAFT. Moreover, this option does not have a theoretical basis because it is empirical. Thus, it is most convenient to use temperature-independent $k_{ij}$ terms.

As PC-SAFT is a theoretically based EoS and its second-order term is founded on Barker and Henderson’s TPT, its improvement should also be theoretical in nature. For example, the perturbative term could be modified to describe the effects of attractive contributions on thermodynamics. This last approach can be justified for the following reasons: (a) thermodynamic calculations are very sensitive to the perturbative contribution [147], (b) the attractive interactions are crucial to calorific properties [148], and (c) enthalpic interaction directly affects the performance of the PC-SAFT at low temperatures [79]. Furthermore, Barker and Henderson theory strongly underestimates the excess heat capacity (enthalpy) at low and moderate temperatures [147]. The reader is remitted to [33]-[35] for a full description of this seminal molecular theory. This theoretical approach assumed that the repulsive and attractive (e.g., dispersion) contributions were separable. The influence of attractive forces could be considered a perturbation upon repulsive forces. Repulsive forces are mainly responsible of the structure of the fluids at conditions far from the critical point. For a pure molecular component, Barker and Henderson mathematically described the theory as:

$$
\frac{A}{NkT} = \frac{A_0}{NkT} + \frac{A_1}{NkT} + \frac{A_2}{NkT} + \cdots
$$

(2.28)

where,

$$
\frac{A_1}{NkT} = 2\pi \rho \beta \int_{\sigma}^{\infty} g_0(d,R)u^*(R)R^2 dR
$$

(2.29)
and,

\[
\frac{A_2}{NkT} = -\pi \rho \beta \left( \frac{\partial \rho}{\partial p} \right)_0 \frac{\partial}{\partial \rho} \left[ \rho \int_\sigma^\infty \int g_0(d,R)u^*(R)R^2dR \right]
\]  (2.30)

Here, as was discussed before in this work, \( \frac{A_0}{NkT} \), \( \frac{A_1}{NkT} \), and \( \frac{A_2}{NkT} \) are the reduced Helmholtz free energies representing the repulsive (i.e., hard spheres) term, and the first- and second-order perturbation contributions, respectively. \( N, k, T, \rho, g_0, \) and \( u \) represent the number of molecules, the Boltzmann constant, temperature, molecular density, the hard sphere radial distribution function, and the attractive portion of the intermolecular potential, respectively. Finally, \( \sigma \) and \( d \) are the hard- and soft- sphere diameters. Other variables were not relevant to the present discussion and can be found in [33].

Barker and Henderson derived \( \frac{A_2}{NkT} \) by assuming during the process of mathematical integration that the molecules form non-correlated shells [33]. This assumption simplifies the mathematics involved and has had consequences on all models based on this theory, such as PC-SAFT. Thus, it should be possible to improve the Baker and Henderson TPT by removing this restriction.

For instance, Zhang [139], [149], [150] presented an improved Barker and Henderson TPT by allowing for a statistical correlation between two neighboring shells of fluid. Subsequently, a mathematical expression for \( \frac{A_2}{NkT} \) was determined based on the microscopic version of Barker and Henderson’s TPT (i.e., the local compressibility approximation, lc, discussed above), which is the same version used by PC-SAFT. Finally, Zhang demonstrated, based on Monte Carlo simulations for a square-well potential, that the results obtained were superior to that from the original Barker and Henderson TPT, especially at higher densities [139]. From eqn. (2.28), an improvement in \( \frac{A_2}{NkT} \) would results in a lower contribution from the terms \( \frac{A_3}{NkT}, \frac{A_4}{NkT} \), and the higher terms. Hence, the TPT in eqn. (2.28) should converge faster.

Instead of eqn. (2.30), Zhang presented the second-order perturbation term for a pure molecular component as [139]:

\[
\frac{A_2}{NkT} = -\pi \rho \beta (1 + 2\Psi \eta^2) \left( \frac{\partial \rho}{\partial p} \right)_0 \frac{\partial}{\partial \rho} \left[ \rho \int_\sigma^\infty \int g_0(d,R)u^*(R)R^2dR \right]
\]  (2.31)
Where Ψ results from assuming a linear statistical correlation between two neighbor shells of fluid, with probability one if the fluid is condensed. Ψ is equal to 2.028397566. Here, η is the packing fraction. If η \rightarrow 0, then eqn. (1.5) becomes Eqn. (1.4) (i.e., the original one). From eqn. (2.31), this theoretical modification should have a direct effect on condensed phases, such as liquids, and its contribution should increment at low temperatures and/or high pressures (i.e., high densities).

Eqn. (2.8) before discussed represents the original dispersion term for PC-SAFT [50]:

\[
\tilde{a}_{disp} = \frac{A_1}{NkT} + \frac{A_2}{NkT} = -2\pi\rho l_1(\eta, \bar{m})\frac{m^2\varepsilon\sigma^3}{} - \pi\rho \bar{m} C_1 l_2(\eta, \bar{m})m^2\varepsilon^2\sigma^3
\] (2.32)

Where \(-\pi\rho \bar{m} C_1 l_2(\eta, \bar{m})m^2\varepsilon^2\sigma^3\) corresponds to the second-order perturbation contribution.

By introducing the expression given by Zhang [139] into eqn. (2.32), the resultant modified dispersion term is here presented as:

\[
\tilde{a}_{disp,mod} = -2\pi\rho l_1(\eta, \bar{m})\frac{m^2\varepsilon\sigma^3}{} - \pi\rho \bar{m} C_1 l_2(\eta, \bar{m})(1 + 2\Psi \eta^2)m^2\varepsilon^2\sigma^3
\] (2.33)

Eqn. (2.33) had not been published in the literature. Notice that if η \rightarrow 0, then eqn. (2.33) becomes eqn. (2.32) of Gross and Sadowski [50]. Clearly, a higher difference between these two PC-SAFT versions is expected at low temperatures and/or high pressures (i.e., higher densities), which will be presented later in this chapter.

The mathematical expressions and the derivatives required to use PC-SAFT with this theoretical modification given by eqn. (2.33) are presented as:

\[
\left(\frac{\partial \tilde{a}_{disp}}{\partial x_k}\right)_{T,\rho,\eta ≠ k} = -2\pi\rho \left[l_{1x_k}\frac{m^2\varepsilon\sigma^3}{} + l_{1}m^2\varepsilon\sigma^3\right] - \pi\rho \left[mk C_1 l_2 + \bar{m} C_{1x_k} l_2 + \bar{m} C_{2x_k} l_2 + \bar{m} C_{3x_k} l_2 + \bar{m} \eta^2 C_{1x_k} l_2 + \bar{m} \eta^2 C_{2x_k} l_2 + \bar{m} \eta^2 C_{3x_k} l_2 + \bar{m} \eta^2 C_{4x_k} l_2 \right] - \pi\rho 2\Psi^2 \left[m_{x_k} \cdot \eta^2 C_1 l_2 + \bar{m}\eta \eta_{x_k} C_1 l_2 + \bar{m}\eta^2 C_{1x_k} l_2 + \bar{m}\eta^2 C_{2x_k} l_2 + \bar{m}\eta^2 C_{3x_k} l_2 + \bar{m}\eta^2 C_{4x_k} l_2 \right]
\] (2.34)

\[
\xi_{n,xk} = \left(\frac{\partial \xi_n}{\partial x_k}\right)_{T,\rho,\eta ≠ k} = \frac{\pi}{6} \rho m_k (d_k)^n \Rightarrow \eta_{xk} = \xi_{3,xk} = \frac{\pi}{6} \rho m_k d_k^3
\] (2.35)
\[ Z^{\text{disp}} = -2\pi p \frac{\partial (\eta l_2)}{\partial \eta} m^2 \varepsilon \sigma^3 - 2\pi \rho m \left( C_1 \frac{\partial (\eta l_2)}{\partial \eta} + (\eta l_2) \frac{\partial C_1}{\partial \eta} \right) m^2 \varepsilon^2 \sigma^3 - 2\pi \rho m \Psi^2 \left( \eta^2 C_1 \frac{\partial (\eta l_2)}{\partial \eta} + \eta^2 \frac{\partial C_1}{\partial \eta} (\eta l_2) \right) m^2 \varepsilon^2 \sigma^3 - \]
\[ \left( \frac{2\pi \rho \mu_{\text{SAFT}}}{\eta} \right) \left\{ n^2 C_1 \frac{\partial (\eta l_2)}{\partial \eta} + \eta^2 \frac{\partial C_1}{\partial \eta} (\eta l_2) \right\} m^2 \varepsilon^2 \sigma^3 - 2\pi \rho \frac{\partial^2 (\eta l_2)}{\partial \eta^2} m^2 \varepsilon^2 \sigma^3 - \]
\[ \pi \rho m \left\{ C_1 \frac{\partial^2 (\eta l_2)}{\partial \eta^2} + \frac{\partial C_1}{\partial \eta} \frac{\partial (\eta l_2)}{\partial \eta} + (\eta l_2) \right\} m^2 \varepsilon^2 \sigma^3 - 2\pi \rho m \Psi^2 \left( \eta^2 C_1 \frac{\partial (\eta l_2)}{\partial \eta^2} + \eta^2 \frac{\partial C_1}{\partial \eta} \frac{\partial (\eta l_2)}{\partial \eta} + \eta^2 \frac{\partial^2 C_1}{\partial \eta^2} (\eta l_2) + 2\eta \frac{\partial C_1}{\partial \eta} (\eta l_2) + 2\eta C_1 \frac{\partial (\eta l_2)}{\partial \eta} + \right\} \]
\[ + 2\eta \frac{\partial C_1}{\partial \eta} (\eta l_2) + 2C_1 (\eta l_2) \left( \frac{\partial (\eta l_2)}{\partial \eta} \right) m^2 \varepsilon^2 \sigma^3 \]  

(2.37)

The meaning of symbols, mathematical expressions, and derivatives can be found in the original paper by Gross and Sadowski [50]. Obviously, the original terms of Gross and Sadowski are recovered by taking \( \Psi = 0 \) in eqns. (2.34), (2.36), and (2.37).

### 2.3.1 Fluids, assumptions, results, and discussion

In the following sub-sections, details on the properties of the reservoir fluids modeled, and the approaches and assumptions used to predict AOPs with PC-SAFT are presented.

- **Reservoir Fluids used**

Nine reservoir fluids from the literature and one unpublished fluid are used to conduct the comparative calculations of AOPs using both the original PC-SAFT (O-PC-SAFT, or also called “GS-PC-SAFT” in this thesis), and its modified version presented here (i.e., mod-PC-SAFT). The fluids are denoted as follows: Fluid 1 [151], Fluid 2 [152], Fluid 3, Fluid 4 [151], Fluid 5 [153], Fluid 6 [151], Fluid 7 [154], Fluid 8 [155], and Fluid 9 [155]. Based on SARA analyses, these fluids covered an asphaltene content range from 0.80 to 16 wt.%. Table 2-1 presents these fluids in ascending order of asphaltene content. Additionally, depending on the PC-SAFT version, this table depicts the pre-aggregate (or monomeric) asphaltene molecular weights used.
Table 2-1: Asphaltene contents and asphaltene molecular weights for the nine petroleum reservoir fluids modeled in this section.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Asphaltene content wt. %</th>
<th>Asphaltene molecular weight Da</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid 1 [151]</td>
<td>0.82</td>
<td>2500</td>
</tr>
<tr>
<td>Fluid 2 [152]</td>
<td>1.04</td>
<td>700</td>
</tr>
<tr>
<td>Fluid 3</td>
<td>1.14</td>
<td>1400</td>
</tr>
<tr>
<td>Fluid 4 [151]</td>
<td>1.23</td>
<td>2500</td>
</tr>
<tr>
<td>Fluid 5 [153]</td>
<td>1.40</td>
<td>800</td>
</tr>
<tr>
<td>Fluid 6 [151]</td>
<td>2.11</td>
<td>1000</td>
</tr>
<tr>
<td>Fluid 7 [154]</td>
<td>3.25</td>
<td>1000</td>
</tr>
<tr>
<td>Fluid 8 [155]</td>
<td>7.00</td>
<td>3200</td>
</tr>
<tr>
<td>Fluid 9 [155]</td>
<td>15.58</td>
<td>4000</td>
</tr>
</tbody>
</table>

Finally, Tables 2-2 to 2-4 show relevant information for Fluid 3.

Table 2-2: Fluid 3: SARA analysis

<table>
<thead>
<tr>
<th>Saturates</th>
<th>Aromatics</th>
<th>Resins</th>
<th>Asphaltenes</th>
<th>wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.36</td>
<td>22.74</td>
<td>6.76</td>
<td>1.14</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-3: Fluid 3: Experimental bubblepoint and asphaltene onset pressures (AOPs)

<table>
<thead>
<tr>
<th>Temperature/ K</th>
<th>Exp. AOP/ bar</th>
<th>Exp. Bubblepoint/ bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>418.71</td>
<td>351.82</td>
<td>247.26</td>
</tr>
<tr>
<td>366.48</td>
<td>387.01</td>
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</tr>
<tr>
<td>322.04</td>
<td>492.55</td>
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### Table 2-4: Fluid 3: Composition, gas-oil ratio, molecular weight, and API Gravity.

<table>
<thead>
<tr>
<th>Components</th>
<th>Flashed Liquid</th>
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<th></th>
<th>Flashed Gas</th>
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<th></th>
<th>Monophasic Fluid</th>
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<tbody>
<tr>
<td></td>
<td>mol. %</td>
<td>wt. %</td>
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</tr>
<tr>
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<td>0.53</td>
<td>0.33</td>
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<td>0.00</td>
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</tr>
<tr>
<td>C₁</td>
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<td>0.00</td>
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<tr>
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<tr>
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<td>0.14</td>
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<td>16.07</td>
<td>6.61</td>
<td>3.24</td>
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<tr>
<td>i - C₄</td>
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<td>0.11</td>
<td>2.10</td>
<td>4.62</td>
<td>1.53</td>
<td>0.99</td>
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<td>3.13</td>
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<td>C₇</td>
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<tr>
<td>C₂₈</td>
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<td>1.46</td>
<td>0.28</td>
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<tr>
<td>C₃₀⁺</td>
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<td>25.41</td>
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<tr>
<td>GOR</td>
<td>186 m³/m³</td>
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</tr>
<tr>
<td>API Gravity</td>
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</tr>
</tbody>
</table>

- **Assumptions for modeling the reservoir fluids**

Experimental evidence presented by several researchers supports the assumption that the dispersion forces (i.e., polarizability) govern asphaltene phase behavior. For a complete discussion on this topic, see [156] (chap. 12 in that reference). Because of this, and the exclusive goal of the present section of comparing O-PCSAFT versus mod-PCSAFT, an association term in SAFT is not used. PC-SAFT, for a pure component, requires just three molecular parameters, \( m, \sigma, \text{ and } \epsilon/k \), related to repulsion...
and dispersion contributions [114]. In mixtures, binary interaction coefficients, \( k_{ij} \) terms, are also required. Thus, Rice University's approach [114], [116], [120], [142], [143] was followed to model AOPs with PC-SAFT. This approach assumes that the asphaltenes are pre-associated in crude oils, forming aggregates. Hence, asphaltene molecular weights in Table 1 represent the values for a monomer or pre-aggregate “compound” [118]. In principle, these molecular weights should be dependent upon the chemical composition and the amount of asphaltenes present in each reservoir fluid. Zhang's TPT influences Eqn. (2.33) [139], which implies that two neighbor shells of pre-aggregates would be statistically correlated.

All experimental AOP data were assumed to correspond to true liquid-liquid equilibria. Thus, possible kinetic effects discussed in the literature were not considered [157]. As mentioned before, the goal here is to exclusively compare, under the same conditions, the AOPs predicted by O-PC-SAFT and mod-PC-SAFT at low temperatures. Hence, only experimental bubblepoint and AOP data were included in the regression of PC-SAFT parameters. Experimental density or derivative property data were intentionally excluded. The following specific procedure for characterizing and tuning PC-SAFT parameters is used:

1. Each reservoir fluid was characterized by using nine components: \( \text{N}_2 \), \( \text{CO}_2 \), \( \text{H}_2\text{S} \), \( \text{CH}_4 \), “heavy-gas”, “saturate”, “aromatic”, “resin”, and “asphaltene”. This specific characterization allowed for AOPs’ sensibility analyses to changes in both resin and asphaltene molecular weights.

2. For pure components (\( \text{N}_2 \), \( \text{CO}_2 \), \( \text{H}_2\text{S} \), \( \text{CH}_4 \)), O-PC-SAFT parameters published in the literature [119] can be used in mod-PC-SAFT. Liang and Kontogeorgis [146] made a similar assumption after modifying the PC-SAFT universal constants. However, a better description of phase behavior and physical properties could be obtained if the pure component parameters were refitted to the new dispersion term [146]. To compare, under the same conditions, the AOPs predicted by both PC-SAFT models, the use of the original PC-SAFT parameters in mod-PC-SAFT is justified.

3. All PC-SAFT parameters (i.e., \( m \), \( \sigma \), and \( \varepsilon/\kappa \)) for the pseudo-component “heavy-gas” were obtained from Panuganti et al. [119].
4. Two PC-SAFT parameters ($m$ and $\sigma$) for the pseudo-component “saturate” were also obtained from Panuganti et al. [119]. As explained below, $\epsilon/\kappa$ was initially calculated from [119] and then regressed.

5. All PC-SAFT parameters for the pseudo-component “resin” were regressed.

6. For the pseudo-component “asphaltene”, two PC-SAFT parameters ($m$ and $\sigma$) and an initial value for $\epsilon/\kappa$ were calculated from [119] by assuming the component as a full polynuclear aromatic (i.e., $\gamma = 1$ in correlations from [119]). Thus, $\epsilon/\kappa$ was also regressed.

7. Finally, the same internal numerical strategy in commercial PVT software to tune parameters of cubic EoS models to experimental data was used [67]-[69]. In this work, the couple given by the experimental AOP and bubblepoint reported at the highest temperature was fitted without including densities or other experimental data in the parametric regression process. The approach in commercial software is commonly based on pre-multipliers, which permit “smooth” numerical changes in parameters during the regression. For both PC-SAFT EoS models, a Levenberg-Marquardt (LM) algorithm was used with two pre-multipliers, $\psi$ and $\chi$, both varying, following the common practice, between zero and one. $\psi$ was used to simultaneously change the $\epsilon/k$ values for the pseudo-components “saturate”, “aromatic”, “resin”, and “asphaltene”. $\chi$ was used to simultaneously modify $k_{ij}$ values for the following couples: CH$_4$-saturate, CH$_4$-aromatic, CH$_4$-resin, and CH$_4$-asphaltene. The regression procedure is presented schematically in Appendix A. Hence, only three variables were adjusted to tune the PC-SAFT parameters: $\gamma$ (i.e., aromaticity), $\psi$, and $\chi$.

The above approach was compared to that from Gonzalez et al. [143], [158], which uses the reservoir fluid stock-tank oil densities (STO) as additional experimental data to be fitted. Aromatics and resins were joined in a pseudo-component termed “aromatics + resins”. As seen in Figure 2-1, both procedures predicted similar AOPs for the two PC-SAFT models. Regardless of the characterization strategy and parametric tuning, O-PC-SAFT consistently predicts higher AOPs at low temperatures than mod-PC-SAFT.
It is important to stress that for practical applications in the petroleum industry, models such as O-PC-SAFT and mod-PC-SAFT require most sophisticated methodologies to calibrate the molecular parameters. Pure component parameters must be recalibrated, and densities included, along with other experimental data, to correctly predict a wider range of thermodynamic properties. Here, methodologies such as those developed by Gonzalez et al. [143], [158] and Vargas et al. [114], [119], [120] would be recommended. Burgess et al. [159] recently presented an alternative characterization procedure based on elemental analysis to improve the performance of O-PC-SAFT in predicting densities and isothermal compressibilities for two reservoir oils under high pressure-high temperature (HPHT) conditions. Molecular parameters fitted at conventional pressures did not perform well under severe conditions. The low-pressure parameters under-predicted the density data at low pressures but over-predicted the data at high pressures. Thus, the slope of the predicted density versus pressure curves were incorrect. Therefore, “predictions made using PC-SAFT with the low-pressure parameters for the isothermal compressibility and other derivative properties, which depend on the derivative \((dV/dP)T\), are expected to be erroneous” [159].

The resin molecular weight (MWres) was initially set to 600 Da, while the asphaltene molecular weight (MWAsph) was modified to study the AOPs’ sensibility, as predicted for both PC-SAFT models. Thereafter, for the same purpose, MWres was varied between 500 and 800 Da [156], [160].
2.3.2 Modeling

Figure 2-2 presents AOPs predicted by both models for Fluid 1 (panel A), Fluid 2 (panel B), and Fluid 3 (panel C).

![Figure 2-2:](image)

As depicted in Table 2-1 above, Fluid 1 was modeled using a MW asph of 2500 and 1000 Da for O-PC-SAFT and mod-PC-SAFT, respectively. Both EoS models provided a correct representation of the experimental AOPs. However, as seen in panel A for Fluid 1, O-PC-SAFT deviated at temperatures lower than 363 K. For Fluids 2 and 3, O-PC-SAFT behaved qualitatively much better. In fact, for Fluid 3 both models coincided down to 350 K, but O-PC-SAFT was very sensible at lower temperatures, predicting higher AOPs than mod-PC-SAFT. As expected from eqn. (2.33), mod-PC-SAFT predicted lower AOPs than O-PC-SAFT, mainly at low temperatures, and substantially reduced the liquid-liquid region.
Figure 2-3 and Figure 2-4 depict a scenario like Figure 2-2, but for Fluids 4 to 6 (Figure 2-3) and Fluids 7 to 9 (Figure 2-4).

**Figure 2-3:** Fluid 4 (A), Fluid 5 (B), Fluid 6 (C). O-PC-SAFT: (—) AOP, (---) Bubblepoint. mod-PC-SAFT: (——) AOP, (-----) Bubblepoint. Exp: (○) AOP, (△) Bubblepoint.

![Graph A](image1)

Again, mod-PC-SAFT predicted lower AOPs and MUCSTs than O-PC-SAFT. In general, Figures 2-2 to 2-4 show that, as expected, O-PC-SAFT and mod-PC-SAFT predicted similar bubblepoints, and the difference was in representing liquid-liquid equilibria (i.e., AOPs).
Fluids 5 and 9 (1.04 and 15.58 wt.\% asphaltene content, respectively) were chosen to predict AOP sensibilities with respect to MW_{asph} values. In this work, 700, 800, 900, and 1000 Da for Fluid 5 and 2500, 3000, 3500, and 4000 Da for Fluid 9 were used. Figure 8 shows both O-PC-SAFT and mod-PC-SAFT predictions for Fluid 5 (panel A) and Fluid 9 (panel B).
Figure 2-5: Sensibility of AOPs to asphaltene molecular weight (MW_{asph}, Da). Fluid 5 (A), MW_{asph} outside brackets, Fluid 9 (B), MW_{asph} inside brackets. O-PC-SAFT: (---) 700 [2500], (---) 800 [3000], (---) 900 [3500], (---) 1000 [4000]. mod-PC-SAFT: (—) 700 [2500], (—) 800 [3000], (—) 900 [3500], (—) 1000 [4000].

Clearly, both EoS models present high sensibility to MW_{asph} values, and both predicted lower AOPs and MUCSTs at higher MW_{asph} values. Nevertheless, mod-PC-SAFT gave lower AOPs and MUCSTs than O-PC-SAFT. For Fluid 5 (panel A), mod-PC-SAFT predicted AOPs down to 272 K and the MUCST value for O-PC-SAFT was 316 K. The same behavior was observed for Fluid 9 (panel B), where mod-PC-SAFT predicted a MUCST 35 K lower than O-PC-SAFT. mod-PC-SAFT did not eliminate MUCSTs but moved MUCSTs to lower temperatures. As said before, the dispersion term is not the only term responsible for mitigating or eliminating MUCSTs. Soft repulsion plays a fundamental role in smoothing AOPs predicted by PC-SAFT at low temperatures (high densities). In fact, soft-core repulsion in PC-SAFT is not correct [78]. As expressed by Nezbeda et al. [161], [162], at high densities, for example, the particles or molecules are closer, such that a small increment in the effective diameter could induce a large increase in pressure. This topic will be analyzed in an ongoing section [163].

Fluids 5 and 9 were also chosen to predict the sensibilities of AOPs to MW_{res}. In this case, MW_{res} values of 500, 600, 700, and 800 Da were used, which are consistent with measurements reported in the literature [156], [160]. Figure 2-6 presents the results for both O-PC-SAFT and mod-PC-SAFT, with Fluid 5 in panel A and Fluid 9 in panel B.
Figure 2-6: Sensibility of AOPs to resin molecular weight (MWres, Da). Fluid 5 (A); Fluid 9 (B). O-PC-SAFT: (---) 500, (•••) 600, (---) 700; (---) 800. mod-PC-SAFT: (——) 500, (——) 600, (——) 700, (——) 800. Exp: (◯) AOP.

At higher MWres values, both models predicted higher AOPs, but the effect was practically indistinguishable. Hence, setting a value for MWres (e.g., 600 Da) is justified.

Finally, results published in the literature about the effects of injecting CO\textsubscript{2} into reservoir fluid prone to asphaltene precipitation are contradictories. For instance, Gonzalez et al. [143], [158] were the first to report that O-PC-SAFT predicts a crossover temperature, where an increment in CO\textsubscript{2} injection does not promote asphaltene precipitation, but its solubility. Recently, Baharani et al. [164], using a cubic EoS with an association term, conducted predictive calculations of AOPs for 10, 25, and 50\% mol of CO\textsubscript{2} injected into a reservoir fluid, and concluded that “the CO\textsubscript{2} injection causes asphaltene precipitation to increase at high temperatures but below at certain crossover, the asphaltene stability increases. Then the CO\textsubscript{2} can behave like an inhibitor or a precursor of asphaltene precipitation” [164]. Thus, both O-PC-SAFT and cubic EoS predict crossover temperatures. For other investigations, the crossover temperatures predicted by O-PC-SAFT were not real and depended heavily on the CO\textsubscript{2}-asphaltene binary interaction coefficient (\(k_{ij}\)) used [115]. Thus, an AOP sensibility analysis to CO\textsubscript{2}-asphaltene \(k_{ij}\) values was performed on Fluid 5 for both O-PC-SAFT and mod-PC-SAFT. Fluid 5 originally has 0.5 \% mol of CO\textsubscript{2}. Figure 2-7 shows AOP predictions by O-PC-SAFT and mod-PC-SAFT for three CO\textsubscript{2} molar percentages injected: 10, 20, and 30 \% mol. Three different \(k_{ij}\) values were used: 0.10 (panels A and B), 0.15 (panels C and D), and 0.19 (panels E and F).
The crossover temperature predicted by O-PC-SAFT was reduced from 385 to 350 K as the interaction coefficient varied from 0.10 (panel A) to 0.15 (panel C), and the crossover disappeared for a $k_{ij}$ of 0.19 (Panel E). In contrast, the mod-PC-SAFT model softened the crossover phenomenon, and the crossover temperature disappeared (panel D) for a $k_{ij}$ value of 0.15. In fact, for this model, AOP curves diverged for 0.19 (panel F) and a crossover temperature was no longer possible. Thus, the mod-PC-SAFT EoS required smaller $k_{ij}$ values between asphaltene and CO$_2$ than that of O-PC-SAFT to eliminate crossover temperatures. Unfortunately, exhaustive experimental evidence to corroborate or rule out these predictions, involving direct experimental measurements of AOPs for reservoir fluids under injection of variant CO$_2$ concentrations, is lacking.

For all simulations performed in this section, mod-PC-SAFT-EoS showed excellent numerical stability, superior to O-PC-SAFT. This could be due to its ability to predict smoother AOP curves. As discussed later, it would be related to a wider range of isotropic conditions, T and P, given by mod-PC-SAFT than O-PC-SAFT.
**Figure 2-7:** Fluid 5. Sensibility of AOPs to the CO$_2$-asphaltene binary interaction coefficient. $k_{ij} = 0.10$ (Panels A and B); $k_{ij} = 0.15$ (Panels C and D); $k_{ij} = 0.19$ (Panels E and F). O-PC-SAFT: (- - -) 0.5% CO$_2$, (- - -) 10% CO$_2$, (- - -) 20% CO$_2$, (- - -) 30% CO$_2$. mod-PC-SAFT: (---) 0.5% CO$_2$, (---) 10% CO$_2$, (---) 20% CO$_2$, (---) 30% CO$_2$. (A) (B) (C) (D) (E) (F)
2.3.3 Conclusions for section 2.3

A modified Barker and Henderson’s second-order perturbation term was introduced into PC-SAFT EoS to predict AOPs. mod-PC-SAFT predicted lower AOPs and MUCSTs than O-PC-SAFT, reducing the liquid-liquid region at the same temperature. These findings did not depend on the asphaltene molecular weight nor the characterization and parametric regression methods used. While AOPs predicted by both models were very sensible to asphaltene molecular weight, the effect of varying the molecular weight of the resin was marginal. Finally, the crossover temperature predicted by PC-SAFT as CO$_2$ was injected into a reservoir fluid heavily depended upon both the CO$_2$-asphaltene binary interaction coefficient values and the PC-SAFT EoS version used. The mod-PC-SAFT EoS required lower CO$_2$-asphaltene $k_{ij}$ values than O-PC-SAFT to eliminate the crossover phenomenon. However, more experimental data are required to corroborate these predictions.

2.4 A temperature-and density-dependent effective diameter for PC-SAFT

The following derivation and discussion were already published by Cañas-Marín et al. [165].

In this section, a simple effective diameter expression as a function of both temperature and density is presented. This new effective diameter is theoretically deduced by combining a modified Percus-Yevick (PY) cavity function with the square-shoulder soft-core repulsion of Chen and Kregleswski. Then, for illustrative purposes, this new expression is introduced into the PC-SAFT EoS to perform predictive thermodynamic calculations for simple hydrocarbon systems, and more complex mixtures such as polymers, and petroleum reservoir fluids. The predictive calculations demonstrate that a temperature-and density-dependent effective diameter only significantly affects the phase behavior of dense and complex systems and does not have an important impact on systems formed by simple molecules under ordinary conditions. With this new effective diameter, PC-SAFT generally tends to predict both asphaltene onset pressures (AOPs) and cloud-point pressures (CPs) lower than the original EoS.

As discussed before, the effective diameter has a central role in the most famous thermodynamic perturbation theories (TPT) of fluids, such as those by Barker and Henderson (BH) [33]-[35] and Weeks-Chandler-Andersen (WCA) [36]. Because, for example, such as diameter is responsible for introducing the soft-core repulsion between two molecules or segments interacting closely with each
other. In fact, in Barker and Henderson TPT framework, the effective diameter can be interpreted as the mean distance of the closest approach for an interparticle potential $u(r)$ [166].

As already pointed out, Barker and Henderson derived a mathematical expression to describe the reduced Helmholtz free energy for a fluid [34]. From eqn. (1.18),

$$a = a_{HS} - 2\pi \rho d^2 g_{HS}(d) \left( d - \int_0^d (1 - \exp(-\beta u(r))) dr \right) + \gamma 2\pi \rho \beta \int_0^\infty g_{HS}(r) u(r)r^2 dr + \text{higher order terms.} \quad (2.38)$$

Again, as discussed before, the easier manner to make that $a$ becomes $a_{HS}$ in eqn. (2.38) is by taking $(d - \int_0^d (1 - \exp(-\beta u(r))) dr) = 0$, and additionally discarding all the higher-order terms appearing at the RHS. That produces as a result the simple BH effective diameter expression:

$$d(T) = \int_0^\sigma [1 - \exp(-\beta u(r))] dr \quad (2.39)$$

Nevertheless, speaking strictly, $d$ should also be a function of density (i.e., of the packing fraction, $\eta$). This fact is most evident from eqn. (2.38), wherein, for example, the explicit third term at the right-hand, given by $\gamma 2\pi \rho \beta \int_0^\infty g_{HS}(r) u(r)r^2 dr$, depends on the RDF, $g_{HS}$, which is, in turn, a function of the packing-fraction (see eqns. (2.5) and (2.6), and (2.46) below). As already mentioned, the thermodynamic calculations are very sensitive to the effective diameter, and then the possible impact of the density contribution to this parameter should be considered and evaluated, mainly in the thermodynamic modeling of dense phases. For simple systems, the effect of density on the effective diameter is expected to be marginal [43], [167]. Particularly, the effective diameter directly impacts the performance of an equation of state (EoS), such as PC-SAFT [50], to predict the enthalpic contributions at low and moderate temperatures. This effect is especially important for mixtures [43], [161]. As discussed in the last section, the original PC-SAFT has the tendency of predicting high asphaltene onset pressures (AOPs) at low temperatures [115], [163]. Although PC-SAFT has shown relatively good performance in describing AOPs, normally its predictive capability becomes deteriorated as the temperature is reduced [115], [163]. For example, Gonzalez [158] modeled the AOPs for one synthetic model oil formed by the ternary system methane-toluene-asphaltene and found that “the PC-SAFT predictions deviate from experimental data at low temperatures”. Ting [116] attributed these deviations of PC-SAFT to the non-inclusion of the polydispersity of the asphaltenes. Nevertheless, as illustrated later, a temperature-and density-
dependent effective diameter helps to correct those high deviations in AOPs without the need of including such an asphaltenic polydispersity. The same behavior of PC-SAFT at low temperatures has been reported in the literature to describe other kinds of systems, such as the cloud points (CPs) of polymeric mixtures. For example, Van Schilt et al. [79] used PC-SAFT to study the phase behavior of the ternary polymeric system given by poly cyclohexane carbonate (PCHC)-cyclohexane oxide (CHO)-carbon dioxide (CO$_2$) at high pressures. Those researchers found that at high temperatures the PC-SAFT EoS allowed for a quantitative description of the phase behavior, whereas PC-SAFT tended to strongly overestimate the CPs at low temperatures. Those authors explained that at low temperatures the CPs in polymer systems often increase due to unfavorable enthalpic interactions of polymer and solvent (i.e., UCST demixing); which is like the behavior currently expected in asphaltenic systems [138]. For illustrative purposes, this ternary polymeric system is also modeled in the present section. In fact, this is the first time that a temperature-and density-dependent effective diameter is theoretically deduced and published in the literature as an extension of the original effective diameter used by Gross and Sadowski for PC-SAFT [50].

As presented before, Gross and Sadowski [50] derived the effective diameter for PC-SAFT by using the “soft-core” repulsion of the square-shoulder potential, given by Chen and Kregleswki [122], into eqn. (2.39). Thus, the resulting expression for the original PC-SAFT effective diameter of a component $i$ is given by [50]:

$$d_i(T) = \sigma_i \left[1 - 0.12 \exp \left(-\frac{3\varepsilon_i}{kT}\right)\right]$$

Eqn. (2.40) is a simple expression and very convenient for most engineering applications. However, speaking strictly, that effective diameter model is theoretically incorrect [43], [163]. But, as discussed by Tang [43], at normal conditions a temperature-and density-dependent effective diameter is expected to produce almost the same results as the original Barker and Henderson one. Nevertheless, different behavior is expected to occur at extreme temperatures and pressures or in dense and complex phases. Hence, in this section, an extension to Gross and Sadowski’s work is proposed by theoretically including the effect of the density upon the effective diameter. In fact, as demonstrated in this work, the model here formulated tends to that of Gross and Sadowski when the density approaches zero.
The effective diameter expression proposed in this work is derived by resorting to the Mayer function, \( f \), and making a perturbative expansion of the repulsive Helmholtz free energy, \( a_{\text{rep}} \), of the real fluid around a reference pseudo-fluid made-up by hard spheres of diameter \( d \), as follows [43], [168], [169]:

\[
a_{\text{rep}} = a_{\text{HS}} + \int \left( \frac{\partial a}{\partial f(r)} \right)_{\text{HS}} \left( f_{\text{rep}}(r) - f_{\text{HS}}(r) \right) dr \\
= a_{\text{HS}} - \frac{1}{2} \rho \int y_{\text{HS}}(r) \left( e^{-\beta u_{\text{rep}}(r)} - e^{-\beta u_{\text{HS}}(r)} \right) r^2 dr,
\]

(2.41)

Wherein \( u_{\text{rep}}(r) \) is the repulsive part of the intermolecular potential, and \( u_{\text{HS}}(r) \) is the hard-sphere potential. Also \( \frac{\partial a}{\partial f(r)} = -\frac{1}{2} \rho y(r) \), \( y(r) = e^{\beta u(r)} g(r) \), and \( f(r) = e^{-\beta u(r)} - 1 \). Here, \( y(r) \) (i.e., the cavity function, which depends on both temperature and density) and \( f(r) \) are related to the Percus-Yevick (PY) closure function [41], commonly used to solve the Ornstein-Zernike integral equation (OZ) [40]. It is easily demonstrated that eqn. (2.41) can be reduced to:

\[
a_{\text{rep}} = a_{\text{HS}} - 2\pi \rho \int_0^d y_{\text{HS}}(r) \left( e^{-\beta u_{\text{rep}}(r)} - e^{-\beta u_{\text{HS}}(r)} \right) r^2 dr
\]

(2.42)

Then, \( a_{\text{rep}} \) becomes \( a_{\text{HS}} \) if \( 2\pi \rho \int_0^d y_{\text{HS}}(r) \left( e^{-\beta u_{\text{rep}}(r)} - e^{-\beta u_{\text{HS}}(r)} \right) r^2 dr = 0 \). Which is equivalent to [5]:

\[
\int_0^d y_{\text{HS}}(r) e^{-\beta u_{\text{rep}}(r)} r^2 dr = \int_d^\sigma y_{\text{HS}}(r) r^2 dr
\]

(2.43)

Here, \( y_{\text{HS}}(r) \) is the cavity function for the reference pseudo-fluid made-up of hard spheres, and it is given by [43]:

\[
y_{\text{HS}}(r) = \begin{cases} 
-c_{\text{HS}}(r) & \text{if } r < d \\
g_{\text{HS}}(r) & \text{if } r > d
\end{cases}
\]

(2.44)

The PY direct correlation function for hard spheres, \( c_{\text{HS}}(r) \), and the respective PY RDF, \( g_{\text{HS}}(r) \), are usually found by solving the OZ integral equation around \( d \). In this work, the modified expression given by Henderson and Grundke [170] was used for \( c_{\text{HS}}(r) \):
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\[ c_{HS}(r) = \xi \left[ \frac{\eta (1+2\eta)^2}{2(1-\eta)^4} \left( \frac{r}{d} \right)^3 + \frac{6\eta (1+\eta/2)^2}{(1-\eta)^4} \frac{r}{d} + \frac{(1+2\eta)^2}{(1-\eta)^4} \right] \]  

(2.45)

Where \( \xi = 1 - 0.127 \rho^2 \sigma^6 \) was the parameterization introduced by Henderson and Grundke for \( r < \sigma \), and the term in brackets is the original expression of PY for \( c_{HS}(r) \) [52]. This ansatz introduced by Henderson and Grundke [170] has been used by several researchers to improve the description of the thermodynamics and structure factors of, for example, dense simple fluids [171], [172], liquid metals [173], plasma liquid [174], and colloids [175].

For \( g_{HS}(r) \), the expression derived by Tang and Lu [176] was chosen:

\[ g_{HS}(r) = \frac{1+\eta/2}{(1-\eta)^2} \frac{d}{r} + \frac{1-5\eta-5\eta^2 - d}{(1-\eta)^3} \frac{r-d}{r} + \frac{-3\eta + 6\eta^2 + 21/2\eta^3}{(1-\eta)^4} (r-d)^2 \frac{d}{rd} \]  

(2.46)

Finally, an expression for the \( u_{rep}(r) \) is required. In the present section, like Gross and Sadowski [50], the soft-core square-shoulder potential of Chen and Kregleswki [122] was used.

\[ u(r) = \begin{cases} 
\infty & \text{if } r < (\sigma - s_1) \\
3\epsilon & \text{if } (\sigma - s_1) \leq r \leq \sigma \\
-\epsilon & \text{if } \sigma < r \leq \lambda \sigma \\
0 & \text{if } r > \lambda \sigma 
\end{cases} \]  

(2.47)

Wherein \( 3\epsilon \) and \( s_1 \) are the height and the wide of the soft repulsive square shoulder, respectively, and \( s_1 = 0.12\sigma \) for PC-SAFT. In other words, the simplicity given by this “soft-core” repulsion is conserved in the present work with the purpose of having a temperature-and density-dependent effective diameter as simple as possible, and to be able to determine clearer the contribution of the density on this molecular parameter, as well as the performance of this new diameter in comparison to the original one used in PC-SAFT (i.e., eqn. (2.40)). Hence, by using eqns. (2.44) - (2.47) into (2.43), the new temperature-and density-dependent effective diameter expression proposed in this work is obtained as:

\[ \varphi d^6 + \delta d^4 + \theta d^3 + \theta d^2 + \tau = 0 \]  

(2.48)

Wherein the coefficients \( \varphi, \delta, \theta, \theta \) and \( \tau \) depend upon density and temperature. These terms are given as:
\( \varphi = \bar{A} - \overline{EXPP} \cdot \bar{H} \) \tag{2.49}

\( \delta = \overline{EXPP} \cdot \bar{E} \) \tag{2.50}

\( \bar{\theta} = \overline{EXPP} \cdot \bar{G} - \bar{D} \) \tag{2.51}

\( \theta = \overline{EXPP} \cdot \bar{F} - \bar{C} \) \tag{2.52}

\( \tau = -\bar{B} \) \tag{2.53}

\[
\overline{EXPP} = \frac{1 - e^{-\beta \mu_{\text{rep}}(r)}}{e^{-\beta \mu_{\text{rep}}(r)}}
\] \tag{2.54}

\( \bar{A} = \left[ \frac{1}{6} \bar{\alpha}_1 + \frac{1}{4} \bar{\alpha}_2 + \frac{1}{3} \bar{\alpha}_3 \right] \) \tag{2.55}

\( \bar{B} = \frac{1}{6} \bar{\alpha}_1 \psi^6 \) \tag{2.56}

\( \bar{C} = \frac{1}{4} \bar{\alpha}_2 \psi^4 \) \tag{2.57}

\( \bar{D} = \frac{1}{3} \bar{\alpha}_3 \psi^2 \) \tag{2.58}

\( E = \left[ \frac{\bar{\delta}_1 \sigma^2}{2} - \frac{\bar{\delta}_2 \sigma^2}{2} + \frac{\bar{\delta}_3 \sigma^2}{2} \right] \) \tag{2.59}

\( F = \left[ \frac{\bar{\delta}_3 \sigma^4}{4} \right] \) \tag{2.60}

\( \bar{G} = \left[ \frac{\bar{\delta}_2}{3} \cdot \sigma^3 - \frac{2}{3} \bar{\delta}_3 \sigma^3 \right] \) \tag{2.61}

\( \bar{H} = \left[ \frac{\bar{\delta}_1}{2} + \frac{\bar{\delta}_2}{3} - \frac{\bar{\delta}_2}{2} + \frac{\bar{\delta}_3}{4} - \frac{2}{3} \bar{\delta}_3 + \frac{\bar{\delta}_3}{2} \right] \) \tag{2.62}

\( \bar{\alpha}_1 = \xi \frac{\eta(1+2\eta)^2}{2(1-\eta)^2} ; \bar{\alpha}_2 = \xi \frac{6\eta (1+\eta/2)^2}{(1-\eta)^4} ; \bar{\alpha}_3 = -\xi \frac{(1+2\eta)^2}{(1-\eta)^4} ; \xi = 1 - 0.127 \rho^2 \sigma^6 \) \tag{2.63}
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\[
\bar{\delta}_1 = \frac{1+\eta}{(1-\eta)^2} ; \quad \bar{\delta}_2 = \frac{1-5\eta-5\eta^2}{(1-\eta)^3} ; \quad \bar{\delta}_3 = \frac{-3\eta+6\eta^2+21/2\eta^3}{(1-\eta)^4}
\]  

\[
\psi^6 = (\sigma - s_1)^6 ; \quad \psi^4 = (\sigma - s_1)^4 ; \quad \psi^3 = (\sigma - s_1)^3
\]

\(s_1 = 0.12\sigma\) for the square-shoulder repulsive potential of Chen and Kreglewski used in PC-SAFT [50], [122]. If \(\xi = 1\), the original PY expression is recovered.

Brent’s algorithm [177] was chosen to easily solve this polynomial and obtain \(d\). This algorithm guarantees convergence for finding a zero of a function without needing derivatives. Obviously, other mathematical routines could be used for this purpose. In the mathematical strategy, the original effective diameter of Gross and Sadowski (i.e., eqn. (2.40)) was chosen as an initial guess for the iterative process involved in solving eqn. (2.48). With Brent’s algorithm, the \(d\)-values, dependent upon both temperature and density, were always found. Then, the new temperature- and density-dependent effective diameter is introduced into PC-SAFT, and the resultant EoS model is again denoted as “mod-PC-SAFT”, and the original PC-SAFT as “O-PC-SAFT”.

Figure 2-8 (panel A) depicts the reduced temperature- and density-dependent effective diameters, \(d^* = d/\sigma\), calculated from eqn. (2.48) as a function of reduced temperature, \(\tau \equiv kT/\epsilon\), and for different packing fractions, \(\eta\) (i.e., reduced density). If \(\xi = 1\) in eqn. (2.48), then the effective diameter is denoted as “PY”; but if the complete \(c_{HS}(r)\) expression of Henderson and Grundke [170] is used instead, then it is named as “PYHG”.
Figure 2-8: Reduced effective diameter versus reduced temperature as a function of packing fraction and Percus-Yevick cavity function. (A) mod-PC-SAFT: PY and PYHG for different packing fractions. (B) Comparison between the Gross-Sadowski effective diameter (i.e., O-PC-SAFT, eqn. 68) and the mod-PC-SAFT (i.e., eqn. 76) for packing fraction equal to zero.

Notice that, as theoretically expected, the effective diameter diminishes as the temperature or the density increase [167]. The density effect upon the effective diameter is evident in Figure 2-8, and it should not be a priori discarded. In fact, the most important contribution of the density to the effective diameter occurs inside the range of practical engineering applications, and the density contribution is stronger at lower temperatures. Also notice that, even though the PY diameters appear smaller than the PYHG ones, especially at higher densities, really the differences between them, at the same packing fraction ($\eta$), are insignificant. For instance, at $\tau = 5$ and $\eta = 0.8$ the difference between PY and PYHG is only 0.22%. In Figure 11, the $\tau$-values are presented between 0 and 40, which corresponds to temperatures between 0 and 10000 K, respectively. For example, if a very extreme high-temperature petroleum reservoir hypothetically has a reservoir temperature of 600 K, these values in the present context would correspond to $\tau = 2.4$, and it is evident from Figure 11 that PY and PYHG predict the same effective diameter for the same packing fraction value. It is most apparent for conventional reservoir wherein the reservoir temperatures are lower than 463 K [178]. Notice that both eqn. (2.40) and eqn. (2.48) fulfill the theoretical limit that $d \to \sigma$ as $T \to 0$. However, a smaller collision diameter occurs as the temperature increases. In the cases of both eqn. (2.40) and eqn. (2.48), $d$ takes the limit $0.88\sigma$ if the temperature tends to infinity, while the correct theoretical limit under this condition would be that $d \to 0$ (i.e., the ideal gas limit). This last fact is due to the soft-core repulsion given by the square-shoulder potential of Chen and Kreglewski [122] and used for PC-SAFT (i.e., eqn. (2.47)). Nevertheless, as indicated by Jiu-Xun [179], the
accomplishment of both limits is not relevant for practical applications. The first reason is that most materials are in the solid state at temperatures lower than \( \tau = 0.4 \), and a liquid theory is naturally inapplicable. The second one is that the limit \( \tau \to \infty \) is not the interest for the typical material used for engineering purposes. Then, even though to fulfill these limits is highly desirable from a theoretical viewpoint, it is not a limitation for engineering applications [179].

In Figure 2-8 (panel B) the original temperature-dependent PC-SAFT effective diameter (i.e., eqn. (2.40)) is also graphed as O-PC-SAFT, but it coincides with the curves of mod-PC-SAFT at \( \eta = 0 \). More exactly, when the density tends to zero (i.e., \( \eta \to 0 \)) the effective diameter given by eqn. (2.48) depends only upon temperature. This fact is evident from eqn. (2.45) for \( c_{HS}(r) \), and eqn. (2.46) for \( g_{HS}(r) \). More clearly, when \( \eta \to 0 \) then \( c_{HS}(r) \to -1 \), and \( g_{HS}(r) \to 1 \). Thus, when \( \rho \to 0 \), then \( d(T, \rho) \to d(T) \). Hence, eqn. (2.48) fulfills exactly the theoretical restriction that the second virial coefficient, \( B \), depends upon temperature and not on density. \( B \) is defined here as:

\[
B(T) = \lim_{\rho \to 0} \left( \frac{Z-1}{\rho} \right) = \lim_{\rho \to 0} \left( \frac{\partial (a^R/RT)}{\partial \rho} \right) \tag{2.66}
\]

In Eqn. (2.66), \( Z \) and \( a^R \) mean the compressibility factor and the residual Helmholtz free energy [180].

For illustrative purposes only, the effect of the new effective diameter expression upon the thermodynamic calculations of critical loci, densities, and speeds of sound for simple systems are first presented and discussed. After that, the predictions of the CPs in a ternary polymeric system reported by van Schilt et al. [79] are presented. Finally, the predictions of asphaltene onset pressures (AOPs) for seven hydrocarbon systems prone to asphaltene precipitation are reported. One of them being a ternary mixture made up of methane-toluene-asphaltene [116], [142], and the rest of those hydrocarbon mixtures modeled correspond to real petroleum reservoir fluids. One of those real reservoir fluids has not been published before. For completeness, and comparative purposes, the same calculations are performed by using the original PC-SAFT (O-PC-SAFT), which, as said before, uses eqn. (2.40) to determine the effective diameters.
2.4.1 Well-defined components and mixtures

As expressed above, PC-SAFT requires just three molecular parameters for a non-associating pure component: $m$, $\sigma$, and $\varepsilon/k$, related to repulsion and dispersion contributions [50]. For simple pure components, typical in natural gases, the same molecular parameters of Gross and Sadowski can be used for O-PC-SAFT and mod-PC-SAFT. For example, Figure 2-9 depicts the prediction of densities at 300 K for methane, propane, pentane, and decane.

**Figure 2-9:** Densities at 300 K predicted with O-PC-SAFT (Dens0); mod-PC-SAFT (Dens1) using the parameters of Gross-Sadowski [50]; mod-PC-SAFT (Dens2) using parameters refitted in this work to saturated liquid densities and vapor pressure for each component. CH$_4$, C$_3$H$_8$, C$_5$H$_{12}$, and C$_{10}$H$_{22}$.

In the first case, the parameters of Gross and Sadowski [50] were first used for both O-PC-SAFT (Dens0) and mod-PC-SAFT (Dens1), and after mod-PC-SAFT (Dens2) was used with parameters
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refitted to saturated liquid densities and vapor pressures data from the triple point up to the critical point for each component. As a result, the densities predicted in all cases are practically the same.

Table 2-5 depicts the comparison between the Gross-Sadowski parameters [50] and the ones refitted for mod-PC-SAFT for several pure components, typical of petroleum reservoir fluids. As can be seen, the numerical differences are negligible. Then, the same parameters of O-PC-SAFT for the light components present in the petroleum reservoir fluids can be used for mod-PC-SAFT.

**Table 2-5:** Original parameters for some pure components present in petroleum reservoir fluids. O-PC-SAFT [50] versus parameters refitted for mod-PC-SAFT.

<table>
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<th>Component</th>
<th>O-PC-SAFT</th>
<th>mod-PC-SAFT</th>
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<td></td>
<td>( m )</td>
<td>( \sigma )</td>
</tr>
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</tr>
<tr>
<td>H(_2)S</td>
<td>1.7163</td>
<td>3.0090</td>
</tr>
<tr>
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</tbody>
</table>

Figure 2-10 presents the speeds of sound for methane, propane, pentane, and decane, at 300 K, by using first the parameters of Gross and Sadowski [7] for both O-PC-SAFT (SS0) and mod-PC-SAFT (SS1). After that, by using mod-PC-SAFT (SS2) with parameters refitted for each component.

Both O-PC-SAFT and mod-PC-SAFT present the same well-known problems to reproduce speeds of sound [146], [181], 182]. This inconvenient can be solved for both models, O-PC-SAFT and mod-PC-SAFT, by incorporating the approach published by Liang et al. [146], [181]. That idea is based on refitting the universal constants of PC-SAFT but including explicitly the derivatives \( \frac{dV}{dP} \) into the refitting procedure. One of the reasons expressed by these researchers [146] is that the “current PC-SAFT framework is not enough for a simultaneous accurate description of the first-and second-
order derivative properties over a wide range of temperature”. As emphasized by Polishuk et al. [182], the approach of Liang et al. [146], [181] “practically eliminates predicting unrealistic critical points”. Furthermore, improves the predictions of the second-derivative properties, including obviously the speeds of sound.

**Figure 2-10:** Speeds of sound (SS) at 300 K predicted with O-PC-SAFT (SS0); mod-PC-SAFT (SS1) using the parameters of Gross-Sadowski [50]; mod-PC-SAFT (SS2) using parameters refitted in this work to saturated liquid densities and vapor pressure for each component. CH₄, C₃H₈, C₅H₁₂, and C₁₀H₂₂.

However, as expressed by Polishuk also [182], “…the original PC-SAFT parameters are not usable in the PC-SAFT working with the Liang’s et al.’s universal parameter matrix”. Then, the PC-SAFT parameters should be refitted to account for those new universal constants. Moreover, Piracaud [183] proposed another approach focused on eliminating artifacts in PC-SAFT without modifying the
universal constants, which was recommended recently by Gross and Sadowski [184]. Nevertheless, it is important to emphasize that the goal of the present work is to use the original version of PC-SAFT as the basis to introduce the effect of a temperature-and density-dependent effective diameter. However, the effects of using Liang et al.´s universal parameter matrix and the Paricaud approach [183] will also be discussed in this thesis.

Figure 2-11 presents critical loci measured for the binary systems methane-propane, methane-pentane, and methane-decane [185], and the predictions by using the same molecular parameters for both O-PC-SAFT and mod-PC-SAFT.

**Figure 2-11:** Critical loci for three simple hydrocarbon binary systems: CH$_4$-C$_3$H$_8$; CH$_4$-C$_5$H$_{12}$; CH$_4$-C$_{10}$H$_{22}$. Exp. data from [185].
As can be seen in figure 2-11, the inclusion of a temperature-and density-dependent effective diameter is practically irrelevant for these simple systems. The main reason is that the packing fractions for these calculations and simple binary systems are usually small ($\eta \leq 0.14$). The differences between O-PC-SAFT and mod-PC-SAFT for the critical loci are more evident at the respective highest critical pressures.

Figure 2-12 shows the predictions of CPs for the well-defined ternary polymeric system given by poly cyclohexane carbonate-cyclohexane oxide-carbon dioxide (i.e., PCHC-CHO-CO$_2$) [14] with weight concentrations of 1% (PCHC), 15.46% (CHO), and 83.54%, respectively. The molecular weight for PCHC is 25000. The details of this system can be found in Van Schilt et al. [79]. These authors reported that at high temperatures the PC-SAFT EoS was able to reproduce the experimental cloud-points for this system, whereas at lower temperatures this EoS tended to strongly overestimate these data. In the present work, the intention was not to correlate the cloud-points for this polymeric system. On the contrary, the approach used was of fitting only the cloud-point measured at the highest temperature by varying the energetic parameter, $\varepsilon/k$, for PCHC. Then, after this cloud-point was fitted, the remaining cloud-points, at lower temperatures, were predicted. This approach allows studying better the predictive capability of PC-SAFT and not simply its ability to correlate cloud-points, which is the common focus used in the literature. The other parameters for PCHC (i.e., $m$ and $\sigma$) and all the parameters for CHO and CO$_2$ were taken from [79].

**Figure 2-12:** Cloud-points predicted by O-PC-SAFT and mod-PC-SAFT for the polymeric ternary systems PCHC-CHO-CO$_2$. Exp. data from [79].
It is evident from Figure 2-12 that mod-PC-SAFT predicts lower cloud-points for this system than O-PC-SAFT. In contrast to the simple systems discussed above, $\eta$ has values commonly superior to 0.45, then the density effect upon the effective diameter is not negligible. The optimum $\varepsilon/k$ found for O-PC-SAFT and mod-PC-SAFT were 424.3 and 424.1 K, respectively. Hence, at low temperatures the difference in the predictions of these two models is clearly linked to the effect of the density upon the effective diameter.

Finally, figure 2-13 depicts the prediction of AOPs for the well-defined ternary systems given by methane-toluene-asphaltene reported by Ting [116] and modeled with O-PC-SAFT by Ting [116] and Gonzalez [158].

**Figure 2-13:** AOPs predicted by O-PC-SAFT and mod-PC-SAFT for the asphaltenic ternary systems methane-toluene-asphaltene. Exp. data from [116], [158].

As can be seen, at 20°C (263.15 K) the O-PC-SAFT really overpredicts the AOPs; which is in accordance with the results and comments presented by both researchers. In contrast, the mod-PC-SAFT model predicts very well the AOPs for this ternary system and without including the asphaltene polydispersity suggested by Ting [116]. The same PC-SAFT parameters reported by those authors [116], [158] were used in the present work for both O-PC-SAFT and mod-PC-SAFT. Then, like the polymeric system discussed before, the difference between the predictions of these two models at low temperatures is again linked to the effect of the density on the effective diameter.
2.4.2 Ill-defined mixtures: Petroleum reservoir fluids

Six petroleum reservoir fluids prone to precipitate asphaltenes, five from the literature and one not published before, were used to conduct predictive calculations of AOPs using both O-PC-SAFT and mod-PC-SAFT EoS. The fluids here modeled are denoted as follows: Fluid 1, Fluid 2 [153], Fluid 3 [138], Fluid 4 [186], Fluid 5 [154], and Fluid 6 [151]. Tables 2-6 to 2-8 show relevant information for Fluid 1.

Table 2-6: Fluid 1: Composition and molecular weight data.

<table>
<thead>
<tr>
<th>Components</th>
<th>Monophasic Fluid mol. %</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>0.963</td>
<td>28.013</td>
</tr>
<tr>
<td>CO2</td>
<td>2.549</td>
<td>44.010</td>
</tr>
<tr>
<td>C1</td>
<td>37.465</td>
<td>16.043</td>
</tr>
<tr>
<td>C2</td>
<td>11.169</td>
<td>30.070</td>
</tr>
<tr>
<td>C3</td>
<td>9.475</td>
<td>44.094</td>
</tr>
<tr>
<td>i-C4</td>
<td>1.667</td>
<td>58.124</td>
</tr>
<tr>
<td>n-C4</td>
<td>4.270</td>
<td>58.124</td>
</tr>
<tr>
<td>i-C5</td>
<td>1.696</td>
<td>72.151</td>
</tr>
<tr>
<td>n-C5</td>
<td>1.801</td>
<td>72.151</td>
</tr>
<tr>
<td>C6</td>
<td>2.127</td>
<td>84</td>
</tr>
<tr>
<td>C7</td>
<td>3.091</td>
<td>96</td>
</tr>
<tr>
<td>C8</td>
<td>3.496</td>
<td>107</td>
</tr>
<tr>
<td>C9</td>
<td>2.501</td>
<td>121</td>
</tr>
<tr>
<td>C10</td>
<td>2.061</td>
<td>134</td>
</tr>
<tr>
<td>C11</td>
<td>1.527</td>
<td>147</td>
</tr>
<tr>
<td>C12</td>
<td>1.271</td>
<td>161</td>
</tr>
<tr>
<td>C13</td>
<td>1.322</td>
<td>175</td>
</tr>
<tr>
<td>C14</td>
<td>1.058</td>
<td>190</td>
</tr>
</tbody>
</table>
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

Table 2-6:  (Continuation)

<table>
<thead>
<tr>
<th>Components</th>
<th>Monophasic Fluid mol. %</th>
<th>MW</th>
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<tr>
<td>C15</td>
<td>1.111</td>
<td>206</td>
</tr>
<tr>
<td>C16</td>
<td>0.887</td>
<td>222</td>
</tr>
<tr>
<td>C17</td>
<td>0.735</td>
<td>237</td>
</tr>
<tr>
<td>C18</td>
<td>0.724</td>
<td>251</td>
</tr>
<tr>
<td>C19</td>
<td>0.644</td>
<td>263</td>
</tr>
<tr>
<td>C20</td>
<td>0.509</td>
<td>275</td>
</tr>
<tr>
<td>C21</td>
<td>0.485</td>
<td>291</td>
</tr>
<tr>
<td>C22</td>
<td>0.422</td>
<td>300</td>
</tr>
<tr>
<td>C23</td>
<td>0.383</td>
<td>312</td>
</tr>
<tr>
<td>C24</td>
<td>0.340</td>
<td>324</td>
</tr>
<tr>
<td>C25</td>
<td>0.334</td>
<td>337</td>
</tr>
<tr>
<td>C26</td>
<td>0.271</td>
<td>349</td>
</tr>
<tr>
<td>C27</td>
<td>0.299</td>
<td>360</td>
</tr>
<tr>
<td>C28</td>
<td>0.237</td>
<td>372</td>
</tr>
<tr>
<td>C29</td>
<td>0.246</td>
<td>382</td>
</tr>
<tr>
<td>C30+</td>
<td>2.865</td>
<td>580</td>
</tr>
</tbody>
</table>

100.00

Table 2-7: Fluid 1: SARA analysis.

<table>
<thead>
<tr>
<th>Saturates</th>
<th>Aromatics</th>
<th>Resins</th>
<th>Asphaltenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54.03</td>
<td>26.70</td>
<td>19.07</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Table 2-8: Fluid 1: Experimental bubblepoints and asphaltene onset pressures (AOPs).

<table>
<thead>
<tr>
<th>Temperature/ K</th>
<th>Exp. AOP/ bar</th>
<th>Exp. Bubblepoint/ bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>378.15</td>
<td>245.39</td>
<td>220.09</td>
</tr>
<tr>
<td>348.15</td>
<td>254.76</td>
<td>201.82</td>
</tr>
<tr>
<td>329.15</td>
<td>257.31</td>
<td>189.55</td>
</tr>
</tbody>
</table>

All these reservoir fluids have conventional reservoir temperatures. This fact is typical of the literature related to the modeling of AOPs in petroleum fluids prone to precipitate asphaltenes. All assumptions used in the present section to model asphaltene onset pressures (AOPs) for these ill-defined mixtures were already amply discussed and supported in section 2.2.1.

Petroleum reservoir fluids are ill-defined multicomponent mixtures, then it is better to perform, under the same conditions, sensibility analyses of AOPs calculations predicted by O-PC-SAFT and mod-PC-SAFT to changes of a key property. In this way, Figure 2-14 presents the AOPs and bubblepoints (BPs) for Fluid 1 (panels A and B), Fluid 2 (panels C and D), and Fluid 3 (panels E and F) for different asphaltene molecular weight values (MWasph). For Fluid 1 the MWasph values chosen were: 1800, 1900, and 2000. For Fluid 2: 600, 700, and 800. For Fluid 3: 1400, 1500, and 1600.

As clearly depicted, mod-PC-SAFT EoS generally predicts lower AOPs than O-PC-SAFT at the same MWasph value or the three fluid. Additionally, it is important to report that mod-PC-SAFT usually requires a lower $\epsilon/k$ value to fit the highest temperature AOP. This last fact is subtly shown in Table 2-5 but the differences are trivia for those simple components. The insensibility of the BPs (i.e., liquid-vapor equilibria) with respect to variations in MWasph, and the PC-SAFT model, is also evident from Figure 2-11. This insensibility is contrary to AOPs behavior (i.e., liquid-liquid equilibria). Figure 2-15 corroborates these same facts for Fluids 4-6, respectively.
Figure 2-14: AOPs and Bubble-points predicted by O-PC-SAFT and mod-PC-SAFT for different asphaltene molecular weight values (MW_{Asph}). Panels (A) and (B) for Fluid 1 [this work]; panels (C) and (D) for Fluid 2 [153]; panels (E) and (F) for Fluid 3 [138]. Panels (A), (C), and (D) are for AOPs. Panels (B), (D), and (F) are for bubblepoints (BPs).
**Figure 2-15:** AOPs and Bubble-points predicted by O-PC-SAFT and mod-PC-SAFT for different asphaltene molecular weight values (MW_{Asph}). Panels (A) and (B) for Fluid 4 [186]; Panels (C) and (D) for Fluid 5 [154]; Panels (E) and (F) for Fluid 6 [151]. Panels (A), (C), and (D) are for AOPs. Panels (B), (D), and (F) are for bubblepoints (BPs).
Notice that this insensibility of the liquid-vapor (i.e., bubble-points) for these ill-defined petroleum reservoir fluids is like the insensibility of the critical loci discussed above for the well-defined binary systems presented in Figure 2-11.

As explained before, the approach used was to fit only the AOP and bubblepoint measured at the highest temperature [138]. Then, after that, the remaining AOPs, at lower temperatures, were predicted. This approach allows studying better the predictive capability of PC-SAFT and not simply its ability to correlate AOPs for these ill-defined mixtures, which is contrary to the approach commonly used in the literature focused on correlating AOPs for this kind of mixtures prone to precipitate asphaltenes. Hence, the results show that, in comparison with using an effective diameter dependent only upon temperature, PC-SAFT with this new effective diameter (i.e., mod-PC-SAFT) predicts substantially lower AOP curves than the original PC-SAFT [50]. This new effective diameter significantly reduces the liquid-liquid region. It is important to stress again that the goal of this work was to extend the original idea of Gross and Sadowski [50] of using a simple intermolecular potential (i.e., square-shoulder one) to consider the soft-core repulsion into the effective diameter and to obtain an effective diameter as simple as possible. Thus, the same approach was followed in the present work, but including the density effect on the effective diameter for performing practical engineering calculations. The use of other more complex intermolecular potentials would produce more complicated effective diameter expressions, which usually would require numerical integrations to obtain the effective diameter values for each thermodynamic condition evaluated. This fact will be demonstrated later.

As emphasized above, the experimental AOPs are assumed as true liquid-liquid equilibria, and kinetic effects on the AOPs are not considered. In fact, the magnitude of these kinetic effects is not plenty determined or understood. For example, these kinetic effects should depend on the asphaltenes present in each reservoir fluid (molecular composition, polarizability, etc.), rates of depressurization used in the experiments, mixing and relaxing times used in the PVT cell, PVT technology chosen, etc. Nevertheless, very interesting efforts to improve the comprehension of these kinetic effects are being realized [157]. It is also important to highlight that the amply literature related to thermodynamic models to predict AOPs of petroleum reservoir fluids, included very recent works [187], intrinsically assume the AOPs are true liquid-liquid equilibria. Thus, the approach used in this work is the conventional one followed by hundreds of papers published in the literature (e.g., [114]-[120], [123], [138], [142], [143], [187]).
2.4.3 Conclusions for section 2.4

Based on a modified Percus-Yevick cavity function (PYHG), a temperature-and density-dependent effective diameter was theoretically deduced and used to predict AOPs with PC-SAFT EoS. This new expression of effective diameter is a polynomial and can be easily solved by a simple numerical routine. Even though the ansatz introduced by Henderson and Grundke has been used in the literature to improve the description of the thermodynamics and the structure factors of different kinds of fluids, no advantage of using PYHG over PY was found in this work. Globally, the results show that PC-SAFT with this new effective diameter (i.e., mod-PC-SAFT) predicts substantially lower AOP and CP curves than the original PC-SAFT EoS, reducing then the liquid-liquid region. For simple systems, under ordinary conditions, the effect of density upon the effective diameter is generally irrelevant.

2.5 Four PC-SAFT versions: Effect of “universal constants” and “effective diameter” on liquid-liquid equilibria of polymer and asphaltene systems at low temperatures

The following material was already published by Cañas-Marín et al. (see reference [188]).

In this section, the simple temperature-and density-dependent effective diameter expression present in the precedent section is combined with a new set of universal constants for the perturbed chain-statistical association fluid theory equation of state (PC-SAFT EoS). Then, the resulting modified PC-SAFT version is used to perform thermodynamic calculations of Brown’s first-order ideal curves, phase behavior for simple hydrocarbon binary mixtures (critical loci), cloud points (CP) for ternary polymeric mixtures, and asphaltene onset pressures (AOPs) for ill-and well-defined hydrocarbon mixtures prone to precipitate asphaltenes. In addition, the new PC-SAFT version is utilized to predict the crossover temperatures of one of the ill-defined petroleum mixtures under the injection of different amounts of CO$_2$.

The simple polynomial effective diameter equation presented above is a function of both temperature and density for PC-SAFT, and it does not require the numerical evaluation of integrals. This new model was theoretically obtained by combining a modified Percus-Yevick (PY) [41] cavity function with the square-shoulder soft-core repulsion of Chen and Kreglewski [122]. Furthermore, Liang and Kontogeorgis (LK) [146] published a new set of universal constants (see Table 1 in [146]) for evaluating the second-order dispersion term of the perturbed chain-statistical association fluid
theory equation of state (PC-SAFT EoS). This set reduces numerical pitfalls commonly found with the use of the original universal constants of Gross and Sadowski (GS) [50]. For instance, the presence of more than three roots of volume at real application conditions. This fact is especially found with the GS universal constants at low temperatures. Hence, it is very interesting to study the performance of PC-SAFT at low temperatures by using the new temperature-and density-dependent effective diameter expression [165] in combination with the set of universal constants of Liang and Kontogeorgis [146]. Original PC-SAFT performance usually worsens at low temperatures [79], [115], or extreme temperature and pressure conditions [163]. In addition, Abutaqiya et al. [145] reported that PC-SAFT predicts a minimum upper critical solution temperature (MUCST) in petroleum mixtures prone to precipitate asphaltenes. At this MUCST, the asphaltene onset pressure (AOP) curve given by this EoS tends to infinity. PC-SAFT also predicts a hypothetical hyper-asphaltene onset pressure curve (HAOP), which occurs because the upper AOP curve returns from the MUCST up to higher temperatures forming a new phase boundary [145]. However, the HAOP occurs at extremely high pressures [145], outside the range of interest for the petroleum industry, and it appears to be an artifact of PC-SAFT. This finding is independent of the characterization method chosen to characterize the petroleum reservoir mixtures [138].

LK [146] showed that PC-SAFT exhibits more than three roots of volume (density), or two stable liquid volume roots, at real application conditions. Moreover, discontinuous volume roots were observed as the pressure increases, which produces unrealistic predictions of phase behavior. As well recognized, PC-SAFT also presents difficulties to model speeds of sound [146], [181], [182], because of the limitation of this model for describing simultaneously the first-and second-order derivative properties over a wide range of temperatures. In principle, this difficulty is intimately linked to the dispersion term in PC-SAFT (i.e., attractive contribution). In fact, this drawback could be solved by incorporating the set of universal constants originally published by Liang et al. [181]. This new set of constants was obtained by refitting them to saturation pressures, saturation densities, and $dV/dP$ experimental data. As mentioned by Polishuk et al. [182], besides improving the predictions of the second-order derivative properties, this set of universal constants [181] practically eliminates the prediction of unrealistic critical points with PC-SAFT. However, as expressed by those authors [182], the original PC-SAFT parameters (i.e., $m$, $\sigma$, and $\epsilon/\kappa$) are not usable in the PC-SAFT EoS working with the Liang et al.’s universal constants [181]. Then, the PC-SAFT parameters should be refitted to account for those new universal constants. Nonetheless, to fit the universal constants of PC-SAFT to reproduce explicitly the second order-derivative properties could be not
recommendable for modeling ill-defined mixtures, such as the petroleum’s ones, because that procedure biases the EoS. Moreover, that first set of universal constants of Liang et al. [181] showed a bad performance to predict densities of long-chain fluids [146]. Due to drawbacks like those, LK [146] revisited that first set of universal constants for PC-SAFT and proposed a new set. These last constants can be applied to ill-defined mixtures and, in principle, as demonstrated by those researchers, and later in this work, the original PC-SAFT EoS parameters can also be used without refit [146]. LK reported a slight improvement of these new constants for reproducing vapor pressures and saturated densities for \( n \)-alkanes from \( C_1-C_{20} \) [146]. However, this new set of universal constants does not eliminate the difficulties of PC-SAFT to reproduce second-order derivative properties, such as the speeds of sound. Paricaud [183] proposed another approach focused on eliminating artifacts in PC-SAFT without modifying the universal constants, and it was recommended recently by Gross and Sadowski [184]. Nonetheless, though this last option is a very attractive theoretical approach, this one requires a non-trivial modification of the repulsive part of the PC-SAFT EoS, producing a more complex PC-SAFT version for engineering purposes.

Finally, as will be discussed in other sections, it is important to emphasize that PC-SAFT does not trace physically coherent Amagat curves. These curves represent one of the types of Brown’s first-order ideal curves [189]. In fact, to predict coherent Amagat loci represents a very demanding test for any EoS [190].

This section is organized as follows: first, the temperature-and density-dependent effective diameter is combined with the new set of universal constants of LK [146] to perform predictive calculations of Brown’s first-order ideal curves and critical loci for simple components. second, with that combination, CPs for polymeric systems and AOPs for asphaltene mixtures are also modeled. Third, this new PC-SAFT version was used to predict the effect of injecting varying amounts of \( CO_2 \) into one ill-defined petroleum mixture prone to precipitate asphaltenes. It is important to highlight that for each asphaltene (or polymeric) mixture, the experimental AOP (or CP) at the highest temperature is first fitted, and then the AOPs (or CPs) at lower temperatures are predicted. This focus is different from the one usually chosen in the literature, wherein PC-SAFT is used to correlate the experimental data.

As was already discussed, the original effective diameter used in PC-SAFT is given by eqn. 68, and it represents a temperature-dependent effective diameter. But in the last section, a density-and temperature-dependent effective diameter was presented and discussed. This model is given as a
sixth-degree polynomial: \( \phi d^6 + \delta d^4 + \theta d^3 + \vartheta d^2 + \tau = 0 \). Wherein the coefficients \( \phi, \delta, \theta, \vartheta \) and \( \tau \) depend upon density and temperature [165]. Like Eqn. (2.40), eqn. (2.48) is also based on Chen and Kregleswski’s square-shoulder potential [122] to account for the soft-core repulsion. In principle, eqn. (2.48) could be used in other molecular-based EoS different to PC-SAFT but obviously wherein the soft-core repulsion be also considered by using Chen and Kregleswski potential.

In this section, four PC-SAFT versions are tested. These models are the result of combining two different PC-SAFT universal constants sets with two different PC-SAFT effective diameter expressions. The first PC-SAFT version is the original PC-SAFT of Gross and Sadowski (hereafter called GS-PC-SAFT instead of “O-PC-SAFT“). The second one is given by combining the PC-SAFT universal constants reported by LK [146] with the original PC-SAFT effective diameter expression presented in eqn. (2.40) (i.e., LK-PC-SAFT). The third model results of using the original PC-SAFT universal constants of GS [50] united to the temperature-and density-dependent effective diameter given by eqn. (2.48) (i.e., GS-PC-SAFT- \( d(T, \rho) \)). Finally, the fourth version is given by combining the LK’s PC-SAFT universal constants with eqn. (2.48) (i.e., LK-PC-SAFT- \( d(T, \rho) \)). As emphasized by LK [146], the set of universal constants is not exclusive, and “different universal constant sets could give equally good correlations for vapor pressure and density, but it does not seem possible to obtain a unique set having the best description for all properties”. Hence, to test the relative performance of these four PC-SAFT versions for engineering applications makes full sense. The approach used to calculate the fugacity coefficients for GS-PC-SAFT- \( d(T, \rho) \) and LK-PC-SAFT- \( d(T, \rho) \) was that reported by Boshkova and Deiters [190].

### 2.5.1 Well-defined components and mixtures

Figure 2-16 presents Brown’s first-order ideal curves for \( \text{Ar}, \text{CO}_2, \text{CH}_4, \) and \( \text{C}_{10}\text{H}_{22} \). Coherent Amagat curves are dome-shaped envelopes like those of Boyle and Charles ones. In fact, for each substance the Boyle and Charles envelopes are inside the Amagat one [124].
Figure 2-16: Brown’s first-order curves predicted by PC-SAFT. — GS-universal constants, — LK-universal constants.

Amagat | Boyle | Charles

CH4

Ar

C_{10}H_{22}

CO_2
As seen from this figure, the GS-and LK-universal constants predict coherent Boyle and Charles curves but incoherent Amagat envelopes, being unable of producing dome-shaped Amagat curves. The use of the LK universal constants (i.e., LK-PC-SAFT) worsen the numerical stability to calculate the Amagat curves, and the incoherent results persist. This failure of PC-SAFT to predict coherent Amagat curves has been amply discussed in the literature [124], [165], emphasizing that “to predict physically reasonable Amagat curves is really a demanding test for PC-SAFT, and the success depends heavily on the soft-repulsion model used to obtain the effective diameter expression”. Then, the Chen-Kreglewski intermolecular potential [122] is not a good model to capture the “soft-repulsion” in PC-SAFT, and other intermolecular potential are then required to predict coherent Amagat curves [163]. However, at present, and excepting some components like hydrogen [163], these Amagat curves are usually outside the range of engineering applications. Thus, because of its simplicity and versatility at engineering conditions, the Chen-Kreglewski intermolecular potential [122] continues to be relevant into PC-SAFT [5]. Finally, as noted in Figure 1, for the Boyle and Charles curves the respective predictions by using GS or LK universal constants in PC-SAFT are indistinguishable. This topic will be discussed most amply in section 2.8.

As reported by LK [146], the original PC-SAFT parameters ($m$, $\sigma$, and $\varepsilon/k$) given by Gross and Sadowski [50] are reusable with the new universal constants. In fact, a similar result for the temperature-and density-dependent effective diameter, given by eqn. 76, was already presented in table 2-5. Even so, in this section, for each PC-SAFT version used, the PC-SAFT parameters were again refitted for the main pure components present in the gases coming from petroleum reservoir fluids. During the regression procedure for each component, $m$ was set to the Gross and Sadowski value, and $\sigma$ and $\varepsilon/k$ were modified to fit both the saturated densities and vapor pressures. The results are reported in Table 2-9.
Table 2-9: Parameters for the different PC-SAFT versions.

<table>
<thead>
<tr>
<th>Component</th>
<th>GS-PC-SAFT [50]</th>
<th>LK-PC-SAFT</th>
<th>GS-PC-SAFT $d(T,\rho)$</th>
<th>LK-PC-SAFT $d(T,\rho)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m^*$ [-]</td>
<td>$\sigma$ [Å]</td>
<td>$\varepsilon/k$ [K]</td>
<td>$\sigma$ [Å]</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.2053</td>
<td>3.3130</td>
<td>90.96</td>
<td>3.3150</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>1.7163</td>
<td>3.0090</td>
<td>224.96</td>
<td>3.0060</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.0729</td>
<td>2.7852</td>
<td>169.21</td>
<td>2.7682</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1.0000</td>
<td>3.7050</td>
<td>150.03</td>
<td>3.7005</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>1.6069</td>
<td>3.5206</td>
<td>191.42</td>
<td>1.6069</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>2.0020</td>
<td>3.6184</td>
<td>208.11</td>
<td>3.6024</td>
</tr>
<tr>
<td>iC$<em>4$H$</em>{10}$</td>
<td>2.2618</td>
<td>3.7574</td>
<td>216.53</td>
<td>3.7520</td>
</tr>
<tr>
<td>nC$<em>4$H$</em>{10}$</td>
<td>2.3316</td>
<td>3.7086</td>
<td>222.88</td>
<td>3.7076</td>
</tr>
<tr>
<td>iC$<em>5$H$</em>{12}$</td>
<td>2.5620</td>
<td>3.8296</td>
<td>230.75</td>
<td>3.8156</td>
</tr>
<tr>
<td>nC$<em>5$H$</em>{12}$</td>
<td>2.6896</td>
<td>3.7729</td>
<td>231.20</td>
<td>3.7700</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{14}$</td>
<td>3.0576</td>
<td>3.7983</td>
<td>236.77</td>
<td>3.7923</td>
</tr>
</tbody>
</table>

* $m$ values from [50] are the same for all PC-SAFT versions.

As can be seen, the variations in the PC-SAFT parameters among these different PC-SAFT versions are small, usually less than 1%. The details upon the strategy and assumptions used for regressing the PC-SAFT parameters for the four PC-SAFT versions were amply discussed in 2.2.1 (see section 3 in [138] also), wherein the numerical regression for the PC-SAFT parameters was based on the Levenberg-Marquardt (LM) algorithm. A detailed and illustrative schematic diagram for LM was also presented in Appendix A (see also [138]). The characterization for the fluids modeled in the present section are depicted in Appendix B. For the pure components in Table 2-9, the uncertainties in the values of $\sigma$ and $\varepsilon/k$ are in the second and fourth decimal, respectively. The respective $m$ value was taken from [50].
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

**Figure 2-17:** Critical Loci. — GS-PC-SAFT, — LK-PC-SAFT, — GS-PC-SAFT-d (T, ρ), — LK-PC-SAFT-d (T, ρ), ○ Exp. critical locus [185].

![Critical Loci](image)

Figure 2-17 depicts the critical loci for \( \text{CH}_4-\text{C}_3\text{H}_8 \), \( \text{CH}_4-\text{C}_5\text{H}_{12} \), and \( \text{CH}_4-\text{C}_{10}\text{H}_{22} \) [185]. As can be seen, these four PC-SAFT versions practically predict the same results.

As can be seen, these four PC-SAFT versions practically predict the same results. For these simple systems, the packing fractions are usually small \( (η ≤ 0.14) \), and the small differences in predictions occur at the respective highest critical pressures.

Figure 2-18 shows the CPs predicted by the four PC-SAFT versions for a well-defined ternary polymeric system made-up by poly cyclohexane carbonate (PCHC)-cyclohexane oxide (CHO)-carbon dioxide (CO2) [79] with weight concentrations of 0.94 % (PCHC), 12.46% (CHO), and 86.60% (CO2), respectively. The molecular weight for the polymer PCHC is 12000. This figure also presents the packing fraction variation versus temperature for the overall liquid phase and the incipient polymeric rich phase at the respective CP.
As easily seen in that figure, the LK universal constants (continuous curves) predict a smoother and less accelerated behavior for the CPs at both high and low temperatures as compared to the GS ones (dashed curves). For this ternary system, the GS universal constants cause problems at low temperatures, producing accelerated curvatures of the packing fraction versus temperature plots. In fact, the high densities predicted by GS universal constants are evident for both liquid phases at lower temperatures. As said before, one of the characteristics of the LK universal constants is to reduce the numerical pitfalls in PC-SAFT.

**Figure 2-18:** CPs and densities for the ternary polymer mixture 0.94% (PCHC)- 12.46% (CHO)- 86.60% (CO₂). --- GS-PC-SAFT, --- GS-PC-SAFT- d (T, ρ), — LK-PC-SAFT, — LK-PC-SAFT- d (T, ρ), ○ Exp. CP [79].
Like Figure 2-18, figure 2-19 shows the same curves but for the weight concentrations of 1% (PCHC), 15.46% (CHO), and 83.54% (CO2). In short, for both ternary systems the LK-PC-SAFT-\(d(T, \rho)\) version predicts the lower CPs.

**Figure 2-19:** CPs and densities for a ternary polymer mixture 1% (PCHC) - 15.46% (CHO) - 83.54% (CO2). --- GS-PC-SAFT, --- GS-PC-SAFT- \(d(T, \rho)\), — LK-PC- SAFT, — LK-PC-SAFT- \(d(T, \rho)\), O Exp. CP [79].

In the present work, the purpose was not to correlate the CPs for these ternary polymeric systems, and, on the contrary, the approach used consisted in fitting only the experimental CP at the highest temperature by varying the PC-SAFT energetic parameter, \(\varepsilon/k\), for PCHC. After this CP was fitted, the rest of CPs at lower temperatures were predicted. This approach allows studying the predictive capability of the different PC-SAFT versions and not simply the ability to correlate CPs. The parameters \(m\) and \(\sigma\) for PCHC were taken from [79].
Figure 2-20 presents the predictions of AOPs for the well-defined ternary systems at 20 °C (263.15 K) given by methane-toluene-asphaltene reported by Ting [116], and Gonzalez [142].

**Figure 2-20:** AOPs and BPs for the ternary mixture made-up by methane-toluene-asphaltene.

AOPs: --- GS-PC-SAFT, --- GS-PC-SAFT- d (T, \(\rho\)), — LK-PC-SAFT, — LK-PC-SAFT- d (T, \(\rho\)).

BPs: ··· GS-PC-SAFT, ··· GS-PC-SAFT- d (T, \(\rho\)), ··· LK-PC-SAFT, ··· LK-PC-SAFT- d (T, \(\rho\)), O Exp. AOP [116], [142], △ Exp. BP [116], [142].

As can be seen, the GS-PC-SAFT overpredicts the AOPs; which is in concordance with the results and comments presented by both researchers [116], [142]. For this system, the LK universal constants (continuous curves) produce a slightly smoother and less accelerated behavior for the AOPs than the GS ones (dashed curves). The GS-PC-SAFT- \(d(T, \rho)\) model predicts very well the AOPs for this ternary system, and better than LK-PC-SAFT or LK-PC-SAFT- \(d(T, \rho)\). The same PC-SAFT parameters reported by those authors [116], [142] were used in the present work for all four PC-SAFT versions. Nevertheless, analyzing carefully the AOP slopes predicted by the four PC-SAFT versions, it could be realized that by moving slightly the PC-SAFT parameters is possible that LK-PC-SAFT- \(d(T, \rho)\)- i.e., the continuous red line- were closer to the experimental AOPs than GS-PC-SAFT- \(d(T, \rho)\). In addition, figure 2-21 shows the global- and asphaltenic- liquid phase densities for this mixture, respectively.
Figure 2-21: Densities for the ternary mixture made-up by methane- toluene asphaltene. — GS-PC-SAFT, --- GS-PC-SAFT- d (T, ρ), — LK-PC-SAFT, — LK-PC-SAFT- d (T, ρ).

As depicted, the effect of the LK universal constants is to predict a smoother and less accelerated density slope for the asphaltene-rich phase, and this effect is more evident for the LK-PC-SAFT- \(d(T, \rho)\) model. As an evident fact, the inclusion of \(d(T, \rho)\) always produces the lowest densities. In other words, this kind of effective diameter moves the reduced density values towards isotropic conditions, wherein the TPTs are more reliable. This last point will be discussed in section 2.6, and 2.7.

### 2.5.2 Ill- defined mixtures: Petroleum reservoir fluids

In this work, six real petroleum reservoir fluids prone to precipitate asphaltenes were used to perform predictive calculations of AOPs and bubble-points (BPs) using the four PC-SAFT versions. These fluids are denoted as follows: Fluid 1 [165], Fluid 2 [153], Fluid 3 [138], Fluid 4 [186], Fluid 5 [113], and Fluid 6 [191].

Figure 2-22 presents the AOPs and the respective BPs for Fluids 1-3 predicted by the four PC-SAFT
As depicted, for these petroleum fluids the LK-PC-SAFT- \( d(T, \rho) \) model generally predicts lower AOPs than the other ones, followed by LK-PC-SAFT. Then, the combination of a temperature- and density-dependent effective diameter with the LK universal constants results in the biggest reduction of AOPs at low temperatures. In fact, as seen in this figure, the LK universal constants (continuous curves) provoke also lesser curvatures of the AOPs at low temperatures than the GS ones (dashed curves).
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation curves). This is due to the trend of the LK universal constants to accelerate the AOPs at significantly lower temperatures than the GS ones. In addition, the effect of introducing a temperature- and density-dependent effective diameter is evident by comparing for example the AOPs predicted by LK-PC-SAFT (continuous green color curve) versus LK-PC-SAFT-\(d(T, \rho)\)-i.e., continuous red color curve.

This new density-and-temperature dependent effective diameter [1] does not change the curvatures of the AOPs but its effect on the reduction in AOPs is clear by comparing GS-PC-SAFT (yellow dashed curves) versus GS-PC-SAFT-\(d(T, \rho)\) (blue dashed curves), or LK-PC-SAFT (green continuous curves) versus LK-PC-SAFT-\(d(T, \rho)\) (red continuous curves). The use of the GS universal constants in GS-PC-SAFT- \(d(T, \rho)\) provokes a most accelerated AOP curve at low temperatures than LK-PC-SAFT- \(d(T, \rho)\). It is important to report that LK-PC-SAFT- \(d(T, \rho)\) usually requires the lowest \(\epsilon/k\) values to fit the respective experimental AOPs at the highest temperatures.

Figure 2-23 depicts the overall liquid phase reduced densities (packing fraction) and the asphaltenic-rich liquid phase reduced densities at the AOPs for these tree fluids.

As seen, the inclusion of \(d(T, \rho)\) predicts the lowest densities for both liquid phases and both universal constant sets. The same findings are shown in figures 2-18, 2-19, and 2-21 for the three well-defined ternary mixtures above discussed, respectively. The changes of curvature appear by changing the PC-SAFT universal constants. As shown, LK-PC-SAFT- \(d(T, \rho)\) produces the lowest densities and curvatures for both phases, which explains the results for AOPs reported in figure 2-22.
**Figure 2-23:** Densities (packing fractions, $\eta$) for the reservoir fluids 1-3. — GS-PC-SAFT, -- GS-PC-SAFT- $d(T, \rho)$, — LK-PC-SAFT, — LK-PC-SAFT- $d(T, \rho)$.

Figure 2-24 shows the AOPs and the respective BPs for fluids 4- 6 predicted by the four different PC-SAFT versions. The results depicted by this figure are as those presented above for Fluids 1- 3 in figure 2-22. Like figure 2-22, LK- PC-SAFT- $d(T, \rho)$ generally predicts the lowest AOPs for these other three petroleum reservoir fluids, followed by LK-PC-SAFT. Then an additional discussion respect to this figure and these fluids would be redundant.
Figure 2-24: AOPs and BPs for the reservoir fluids 4-6. --- GS-PC-SAFT, --- GS-PC-SAFT- d (T, p), — LK-PC-SAFT, — LK-PC-SAFT- d (T, p), O Exp. [186, 113, 191].

Figure 2-25 shows the AOPs predicted by GS-PC-SAFT and LK-PC-SAFT (i.e., both without considering the density effect upon the effective diameter) for three CO₂ molar percentages injected to Fluid 2: 10, 20, and 30 % mol. Four different CO₂- asphaltene BICs were used: 0.10, 0.15, 0.17, and 0.19. The first goal was studying the effect of changing the PC-SAFT universal constants upon the crossover temperatures [138], and curvatures, of the AOPs at different CO₂ concentrations injected to this reservoir fluid.
Figure 2-25: AOPs for CO₂ injection to fluid 2 predicted by GS-PC-SAFT and LK-PC-SAFT. GS-PC-SAFT: ---0.5%, ---10%, ---20%, ---30%. LK-PC-SAFT: ---0.5%, ---10%, ---20%, ---30% mol.
As seen, to change the universal constants does not affect the crossover temperature values, but the effect upon the AOP values and curvatures is evident. Clearly, the LK universal constants (continuous curves) reduce both the AOPs values and the curvatures and contribute to eliminate the crossover temperatures at a lower \( \text{CO}_2 \)-asphaltene BIC than the GS ones (dashed curves). For instance, for a \( \text{CO}_2 \)-asphaltene binary interaction coefficient of 0.17 the GS universal constants cause the divergence of the AOP curves at 320 K, while the LK ones even give finite AOPs at the same temperature.

Figure 2-26 presents the AOP predictions given by both the original PC-SAFT (i.e., GS-PC-SAFT) and GS-PC-SAFT- \( d(T, \rho) \) - (i.e., considering the density effect upon the effective diameter) - for the same three \( \text{CO}_2 \) molar percentages injected to Fluid 2: 10, 20, and 30 % mol. The same four different \( \text{CO}_2 \)-asphaltene BICs were used: 0.10, 0.15, 0.17, and 0.19. The aim here was studying the effect of changing the effective diameter expression upon the crossover temperatures and curvatures.

As a result, the temperature-and density-dependent effective diameter moves the crossover temperatures towards lower temperatures. For instance, for a \( \text{CO}_2 \)-asphaltene BIC of 0.10 the crossover temperature given by GS-PC-SAFT is 383 K while for GS-PC-SAFT- \( d(T, \rho) \) is 372 K. In addition, the reduction in AOPs given by GS-PC-SAFT- \( d(T, \rho) \) versus GS-PC-SAFT is evident. For instance, at the same \( \text{CO}_2 \)-asphaltene BIC of 0.10 and \( T = 316 \) K, the AOPs predicted by GS-PC-SAFT and GS-PC-SAFT- \( d(T, \rho) \) are, respectively, 648 and 484 bar at 10% mol of \( \text{CO}_2 \), 358 and 326 bar at 20% mol, and 326 and 288 bar at 30% mol. A similar behavior is seen for the BICs values of 0.15, 0.17, and 0.19. In fact, by increasing the BIC value to 0.17 the crossover temperature has practically disappeared.
**Figure 2-26:** AOPs for CO$_2$ injection to fluid 2 predicted by GS-PC-SAFT and GS-PC-SAFT-d (T, $\rho$). --- 0.5%, --- 10%, --- 20%, --- 30% mol.
Finally, Figure 2-27 depicts the same kind of pictures like figure 2-26, but the comparison is for LK-PC-SAFT and LK-PC-SAFT- $d(T, \rho)$. In short, LK-PC-SAFT- $d(T, \rho)$ predicts lower AOPs than LK-PC-SAFT.

Again, the use of a temperature-and density-dependent effective diameter produces a reduction of approximately 10 K in the crossover temperatures. Globally, from Figures 2-25 to 2-27 the combination of the LK universal constants and the temperature-and density-dependent effective diameter (i.e., LK-PC-SAFT- $d(T, \rho)$) predicts the lowest AOPs, crossover temperatures, and curvatures of the four PC-SAFT versions studied in this work. LK-PC-SAFT- $d(T & \rho)$ significantly reduces the liquid-liquid region.

As presented before, Baharani et al. [164] used a cubic EoS with an association term (i.e., a cubic EoS plus association- CPA) to performance predictive calculations of AOPs for 10, 25, and 50% mol of CO$_2$ injected into a reservoir fluid. These researchers found that “the CO$_2$ injection causes asphaltene precipitation to increase at high temperatures but below at certain crossover, the asphaltene stability increases. Then the CO$_2$ can behave like an inhibitor or precursor of asphaltene precipitation” [164]. Thus, both PC-SAFT without association and the CPA used by Baharani et al. [164] predict crossover temperatures. In fact, Arya et al. [115] found that PC-SAFT with or without an association term predicts crossover temperatures. However, the same researchers reported that the crossover temperatures predicted by PC-SAFT were not real and depended heavily on the CO$_2$-asphaltene binary interaction coefficient ($k_{ij}$) used [115]. As said before, more experimental AOPs measurements for real reservoir oils under CO$_2$ injection are required to validate whether the crossover temperatures really exist. As a matter of fact, to include an association term in PC-SAFT for modeling AOPs results in a more complex EoS, with two additional parameters to be fitted, and commonly requiring considering the temperature-dependence for the association energy, $\varepsilon$. Thus, before including an association term, it is more practical to explore first how theoretically to improve the physical repulsive- and attractive- parts of PC-SAFT, because both contributions are based on fluid molecular theories, which obviously are not exact [33-35], [40], [41], [50], [105-107].
Figure 2-27: AOPs for CO₂ injection to fluid 2 predicted by LK-PC-SAFT and LK-PC-SAFT- d (T, ρ). — 0.5%, — 10%, — 20%, — 30%.

LK-PC-SAFT

LK-PC-SAFT- d (T, ρ)

BIC=0.10

BIC=0.15

BIC=0.17

BIC=0.19
It is important to highlight that the goal of this work is like the original idea of Gross and Sadowski [50] of using a simple intermolecular potential (i.e., the Chen and Kregleswski’s square-shoulder potential [122]) to consider the soft-core repulsion into the effective diameter expression. However, the difference was the theoretical inclusion of the density effect (i.e., eqn. (2.48)) upon such as diameter for performing engineering calculations. A soft-core repulsion “softer” than that of Chen and Kregleswski (e.g., a Lennard-Jones potential) would result in a mathematical expression requiring numerical integrations for obtaining, iteratively, the temperature-and density-dependent effective diameter [43], [124]. This fact could not be practical for some time-consuming engineering calculations. On the contrary, eqn. (2.48) is polynomial and can be easily solved by a simple numerical routine [165].

Finally, as already emphasize above, the experimental AOPs are assumed as true liquid-liquid equilibria, and then kinetic effects upon AOPs are ruled out. Moreover, the magnitude of these kinetic effects is not totally understood at present. Nevertheless, very interesting efforts to improve the comprehension of these kinetic effects are being carried out [157]. It also is important to stand out that the amply literature related to thermodynamic models to predict AOPs of petroleum reservoir fluids, including very recent works [187], intrinsically assume that the experimental AOPs are true liquid-liquid equilibria. Thus, the assumption used in this work is the conventional one followed by hundreds of papers published in the literature (e.g., [113]-[120], [187]).

### 2.5.3 Conclusions for section 2.5

Two sets of PC-SAFT universal constants and two effective diameter expressions were combined to predict different thermodynamic phase equilibria for simple and complex fluid mixtures. For simple mixtures, the variations in PC-SAFT universal constants or effective diameter expressions did not have a significant influence on the results predicted here. Nevertheless, for complex mixtures characterized by denser fluids, the predicted effect on the liquid-liquid phase behavior was evident. The PC-SAFT version given by LK-PC-SAFT- \(d(T, \rho)\) generally predicted lower cloud-points and AOPs than the other versions used, causing a significant reduction of the liquid-liquid region. Furthermore, the temperature-and density-dependent effective diameter moved the predicted crossover temperatures towards lower values. On the contrary, these crossover temperatures are insensitive to changes in the PC-SAFT universal constants. Also, the liquid-vapor equilibria showed to be significantly most insensitive to the PC-SAFT versions here used than the liquid-liquid equilibria. In addition, the Amagat curves are a challenge for PC-SAFT, and to change the set of
universal constants did not improve its performance for this kind of calculations. As explained after, those curves are mainly influenced by the “soft-core” expression used into the intermolecular potential, and the inclusion of more sophisticated “soft-core” repulsion potential, to improve the Amagat predictions with PC-SAFT, could produce density-and temperature-dependent effective diameter expressions most complex; requiring solving numerical integrals to obtain the effective diameter for each segment or molecule. The last fact could be impractical for some time-demanding engineering calculations; for instance, those related to petroleum reservoir simulators. This last topic will be discussed in most detail later.

2.6 Prediction of extreme asphaltene onset pressures with PC-SAFT for petroleum reservoir fluids

The following material was already published by Cañas-Marín et al. (see reference [192]).

In this section, the four versions of the PC-SAFT EoS presented in the last section were used to predictive upper asphaltene onset pressures (UAOPs), minimum upper critical solution temperatures (MUCSTs), and hyper asphaltene onset pressures (HAOPs) for real petroleum reservoir fluids. As a result, the PC-SAFT models using the Liang and Kontogeorgis universal constants (LKUCs) predicted lower UAOPs and MUCSTs than the PC-SAFT versions utilizing the original Gross and Sadowski set (GSUCs). That is especially valid for the PC-SAFT EoS that combines the LKUCs with the temperature-and density-dependent effective diameter given in eqn. (2.48). Moreover, all the PC-SAFT versions predict ascending branches of UAOPs. Nevertheless, none of these branches tends to infinity. In addition, LKUCs try to suppress or eliminate the predictions of HAOP curves.

Not long ago, Abutaqiya et al. [145] reported that the original PC-SAFT [50] predicts a minimum upper critical solution temperature (MUCST) and a hyper-asphaltene onset pressure (HAOP) curve for petroleum mixtures prone to precipitate asphaltenes. The HAOPs result because the UAOP curves return from the respective MUCST up to more elevated temperatures (see figure 2 in [145]). This last finding appears to be independent of the characterization method chosen to describe the petroleum fluid [145]. In this section, UAOP and HAOP curves are predicted for six real petroleum reservoir fluids by employing the four distinct PC-SAFT versions [188] presented in the last section. In short, these four PC-SAFT models result by combining two distinct sets of universal constants for the second-order dispersion with two different expressions of effective diameter [188]. The first model considered is the original PC-SAFT EoS [50], hereafter called as GS-PC-SAFT. This one
Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

employs the Gross and Sadowski universal constants (GSUCs) and the original PC-SAFT temperature-dependent effective diameter, \( d(T) \), displayed by eqn. (2.40). The second one is the result of combining Liang-Kontogeorgis universal constants (LKUCs) [146] with the original PC-SAFT effective diameter, named hereafter as LK-PC-SAFT [188]. The third PC-SAFT version combines the GSUCs with the recently discussed temperature-and density dependent effective diameter given by eqn. (2.48) [165], [188], resulting in the GS-PC-SAFT- \( d(T, \rho) \) model. Wherein \( d(T, \rho) \) means an effective diameter dependent upon temperature and density. This diameter is theoretically supported, and its contribution occurs principally at low temperatures, high pressures, and for dense (condensed) phases like asphaltenes [165], [188]. Ultimately, the latter PC-SAFT model is given by combining the LKUCs with \( d(T, \rho) \), resulting in the LK-PC-SAFT- \( d(T, \rho) \) version.

As mentioned before, Liang and Kontogeorgis (LK) [146] showed that under actual application conditions the original PC-SAFT [50] predicts more than three volume (density) roots or two stable liquid volume roots. In addition, discontinuous volume roots were obtained as the pressure increases, which produces unrealistic predictions of phase behavior [146], [188]. LK reformulated the universal constants used in the dispersion part of PC-SAFT to eliminate that drawback. The resulting universal constants are here called LKUCs. In addition, those constants usually produce lower densities at reduced temperatures or higher pressures than GSUCs [50]. This last fact increases the pressure and temperature range wherein the fluid is isotropic, relegating the metastable conditions to very low temperatures or very high pressures. In fact, at conditions practically out of the most relevant engineering applications. It is important to stress that the TPT of Barker and Henderson, the basis for PC-SAFT, was really formulated for fluid phases under isotropic conditions [33]-[35].

Six real petroleum reservoir fluids were chosen to perform predictive calculations of UAOPs, MUCSTs, and HAOPs. Here called again as: Fluid 1 [153], Fluid 2 [186], Fluid 3 [151], Fluid 4 [191], Fluid 5 [165], and Fluid 6 [138]. All assumptions used in the present section to model the liquid-liquid (UAOPs, MUCSTs, and HAOPs) and liquid-vapor (bubblepoints- BPs) equilibria for these hydrocarbon mixtures were amply discussed in the last sections. The mathematical approach used to calculate the fugacity coefficients for GS-PC-SAFT- \( d(T, \rho) \) and LK-PC-SAFT- \( d(T, \rho) \) was the same reported by Boshkova and Deiters [124]. For all the four PC-SAFT versions and each petroleum reservoir fluid modeled, the complete characterization data are presented in Appendix C.

It is significant to highlight that the \( \text{CH}_4 \) usually represents the most abundant pure component in
real petroleum reservoir fluids. For the six petroleum mixtures modeled here, the CH$_4$ concentration is between 27 (Fluid 1) to 42 mol % (Fluid 6). Because of this fact, traditional approaches in the petroleum industry commonly utilize the regression of BICs between CH$_4$ and the heavier components to fit the experimental saturation pressures (e.g., bubblepoints) with a cubic equation of state (CEoS) [193], [194]. On the contrary, excepting the CO$_2$ amount in Fluid 1, the concentration of the rest of the pure components (i.e., N$_2$, CO$_2$, H$_2$S) in the six reservoir fluids here modeled is less than 1.3 mol %. Thus, the phase behavior of these fluids is significantly insensitive to the BICs between those pure components and the heavier components. Fluid 1 has a CO$_2$ concentration of 11.37 mol %, and, in principle, the phase behavior of this fluid could be sensible due to variations in the BICs between CO$_2$ and the heavier components.

### 2.6.1 Results and discussion

For Fluids 1-6, figure 2-28 compares the UAOPs, MUCSTs, and HAOPs predicted by the four PC-SAFT versions. For completeness, the meaning of these curves is explicitly depicted for fluid 1 also, including the presence of very steep ascending AOP branches. Figure 2 in [6] also presents the meaning of UAOPs, MUCSTs, and HAOPs. Those authors were the first in publishing MUCSTs and HAOPs predicted by the original PC-SAFT [50]. However, ascending AOP branches were unreported.

As shown in figure 2-28, the LK-PC-SAFT- $d(T, \rho)$ model- i.e., red continuous curves- generally predicts the lowest UAOPs and MUCSTs, followed by LK-PC-SAFT. Both EoS models employ the LKUCs. In addition, LK-PC-SAFT- $d(T, \rho)$ tends most to suppress or eliminate the HAOPs than the other models. Except for fluids 5 and 6, the MUCST curves predicted by this last model finish at a finite point of pressure and temperature. This point connects a straight line of AOPs. For fluids 5 and 6, both LK-PC-SAFT- $d(T, \rho)$ and LK-PC-SAFT qualitatively predict the same phase behavior at low temperatures, and these models explicitly exhibit the presence of a HAOP curve and an ascendant branch. That branch finishes again at a finite point of temperature and pressure. From this last finite point, the AOPs predicted by both models begin to diminish linearly as the temperature is reduced. For these last two fluids and the four PC-SAFT versions, the numerical routine used in the present work did not find the existence of a continuation of the straight line at more elevated temperatures than the finite point one. Because of the steepness, it is important to highlight the numerical difficulties to trace the ascending AOP branches and the straight lines connecting them. In fact, it was impossible to find these branches with the GS-PC-SAFT- $d(T, \rho)$ model, although
temperature steps as small as 0.001 K were used to try to locate them. It does not mean that GS-PC-SAFT- \( d(T, \rho) \) is unable to predict ascending AOP branches, but the numerical routine used here could need improvements to this purpose.

**Figure 2-28:** AOP diagrams and BPs predicted for fluids 1-6 by the four PC-SAFT versions.
Agger and Sorensen [195] presented an algorithm to construct asphaltene PT and Px phase diagrams, which was used by Boesen et al. [196] to trace the asphaltene phase envelopes for 36 petroleum reservoir fluids. Nevertheless, neither Agger and Sorensen [195] nor Boesen et al. [196] reported HAOPs or ascending AOP branches with that numerical routine. In fact, this type of curves does not appear in the “generic asphaltene PT phase diagram” presented in Figure 1 of [195]. Hence, to author’s knowledge, this type of phase diagrams predicted by PC-SAFT with an ascending AOP branch at MUCST had been unreported in the literature. Boesen et al. [196] found that PC-SAFT and the Soave-Redlich-Kwong (SRK) cubic EoS [197] predict similar asphaltene PT phase diagrams for the 36 reservoir fluids tested. Nevertheless, to author’s knowledge, an analogous comparison at low temperatures between PC-SAFT and CEoS has not been reported in the literature, and it is out of the purpose of the present work.

LKUCs into PC-SAFT - i.e., continuous curves in figure 2-28- reduces between 30 to 42 K the MUCSTs in comparison to GSUCs. Moreover, the inclusion of a density-and temperature-dependent effective diameter, \( d(T, \rho) \), provokes an additional reduction of 3 to 10 K in these MUCSTs. In addition, LKUCs into PC-SAFT predicts less curved UAOPs than GSUCs but does not eliminate the prediction of HAOPs. Nevertheless, on the contrary to the GSUCs (broken curves), the LKUCs displace the HAOP curves towards remarkably low temperatures. Conversely, the BP curves presented in figure 2-28 were obtained using LK-PC-SAFT- \( d(T, \rho) \). Because, as discussed before [188], the predictions of BPs (i.e., liquid-vapor equilibria) are practically insensible to the PC-SAFT version used.

To the author’s knowledge, the HAOP curves predicted by PC-SAFT have been unmeasured experimentally to corroborate whether they undoubtedly exist or merely are an artifact of PC-SAFT. For this purpose, experiments would have to be performed at most reduced temperatures than the reservoir ones. At reservoir temperatures, these HAOPs are predicted at extremely elevated pressures, practically unreachable with the experimental PVT technologies available at present. More concretely, the PVT cells normally used to measure AOPs do not operate at pressures higher than 20000 psia (~1379 bar). This limit represents a pressure well below the HAOPs predicted by PC-SAFT at the reservoir temperature conditions. Figures 2-29 and 2-30 depict packing fraction values, \( \eta \), for both the global and incipient asphaltene-rich liquid phases. \( \eta \) values for UAOPs, MUCSTs, HAOPs, and ascending AOP branches are presented.
**Figure 2-29:** Global phase reduced densities predicted for fluids 1-6 by the four PC-SAFT versions.
Figure 2-30: Incipient (asphaltenes-rich) phase reduced densities predicted for fluids 1-6 by the four PC-SAFT versions.
As noted, the inclusion of a temperature- and density-dependent effective diameter into PC-SAFT systematically produces the lowest reduced densities and increases the isotropic fluid range. As expected, the differences in density for these four models are most evident for the incipient (i.e., denser) asphaltene-rich liquid phase (see figure 2-30). It is important to consider that the phase diagram for the hard-sphere reference system used by TPTs like Barker and Henderson [33]-[35] presents only a stable fluid branch (i.e., isotropic) from $\eta = 0$ up to the freezing point ($\eta \approx 0.492$), wherein the fluid-solid transition occurs. From the freezing point up to $\eta \approx 0.543$ a solid phase and a liquid phase coexist. Nevertheless, for higher $\eta$ values up to the close-packing fraction ($\eta \approx 0.74$) a (crystalline) solid exists only. Moreover, beyond the freezing point, there is also a region of metastable fluid states that is supposed to end at the packing fraction $\eta \approx 0.58$, where a widely accepted glass transition occurs. The glass branch finishes at $\eta \approx 0.64$, corresponding to the random close packing of an amorphous solid [198]. In addition, near the freezing line, the TPTs are usually less accurate [199]. As expressed above, the trend of obtaining metastable conditions is reduced by using an effective diameter dependent on density. As said before, the more common TPTs were formulated for fluid phases under isotropic (stable) conditions [33]-[35]. Thus, phase behavior predictions with SAFT-type versions at packing fractions superior to $\eta \approx 0.492$ should be considered with caution. Because other contributions (e.g., kinetic effects) not considered into the TPTs take place under those conditions. Non-isotropic conditions are most feasible to occur in the asphaltene-rich phases (figure 2-27) than for the global phases (figure 2-26) due to the high densities predicted, mainly by GS-PC-SAFT. The inclusion of LKUCs and an effective diameter dependent on density (i.e., LK-PC-SAFT- $d(T, \rho)$) displaces these non-isotropic states at conditions practically not important for engineering applications. In addition to presenting multiple volumetric roots at low temperatures, another drawback of using GSUCs into PC-SAFT (e.g., GS-PC-SAFT) is the trend of the resulting model of predicting high densities at relatively high temperatures, favoring the occurrence of non-isotropic conditions. As seen in figure 2-27, the asphaltene-rich phase densities at the HAOP curves represent metastable states for GS-PC-SAFT and GS-PC-SAFT- $d(T, \rho)$ at relatively high temperatures.

Figure 2-31 depicts precipitated asphaltene amounts versus pressure for fluid 1 at different temperatures. These temperatures are high enough to represent isotropic conditions at the respective UAOP curves.
**Figure 2-31:** Precipitated asphaltene amounts (wt. %) versus pressure predicted for fluids 1 [153] by the four PC-SAFT versions. LAOPs predicted by the four PC-SAFT versions are also shown in the last panel.

The sequence of phase transitions taking place for the path UAOP- BP- LAOP (i.e., lower asphaltene onset pressure) is well known and amply discussed in [145]. As depicted in figure 1 from [145], by
taking a trajectory of descending pressure from A to F, at constant temperature, the UAOPs are modeled as transitions from a liquid phase to a liquid-liquid equilibrium, BPs are liquid-liquid to liquid-liquid-vapor changes, and LAOPs are liquid-liquid-vapor to liquid-vapor transitions. In this work, each trajectory presented in figure 2-28 was modeled by solving a sequence of multiphase flashes [200], [201] with prior tests of phase stability by applying the Michelsen’s tangent plane [202], [203]. Initial liquid-vapor or liquid-liquid K-values to solve the tangent plane algorithm were taken from Trebble [204]. A step-by-step discussion on how to solve the multiphase flash can be found elsewhere [205] (see chapters 8 and 10 in that reference).

As expected, the differences among the PC-SAFT versions are most evident at low temperatures. It is important to highlight that LK-PC-SAFT- \( d(T, \rho) \) predicts the highest LAOPs and the lowest UAOPs also. Hence, this model produces the most shrunken asphaltene precipitation diagrams, reducing the pressure ranges in which the asphaltene precipitation occurs. LAOPs are graphically presented in the last panel in figure 31 to depict the sensibility of these AOPs to the PC-SAFT models.

Finally, Figure 2-32 presents the effect of varying the BICs between \( \text{CO}_2 \) and the heavier components upon the PT phase diagram for fluid 1 modeled with GS-PC-SAFT.

**Figure 2-32:** Effect of varying the BICs between \( \text{CO}_2 \) and the heavier components for fluid 1 [153] using GS-PC-SAFT.
As discussed above, this reservoir fluid has a CO$_2$ amount of 11.37 mol%. Then, the phase behavior of this fluid could be sensible to those BICs. As shown in that figure, the variation in BICs produces a relatively small displacement of the curves, but these conserve the same qualitative phase behavior. Hence, the variation in the phase behavior of the reservoir fluids predicted by the PC-SAFT models is mainly given by changing the universal constants.

2.6.2 Conclusions for section 2.6

Again, LK-PC-SAFT- $d(T, \rho)$ generally predicts inferior UAOPs and MUCST than the other three PC-SAFT versions investigated. This model produces the lowest densities for the global and incipient liquid phases. Hence, this EoS increases the range of the isotropic fluid conditions in which the TPTs are expected to perform better. Hence, phase behavior predictions with SAFT-type versions at packing fractions superior to $\eta \equiv 0.492$ should be considered with caution. LKUCs try to suppress or eliminate the predictions of HAOP curves. LK-PC-SAFT- $d(T, \rho)$ predicts also the lowest LAOPs. Thus, this model produces the most shrunken asphaltene precipitation diagrams and reduces the pressure ranges in which the asphaltene precipitation occurs. Finally, none of the PC-SAFT models determines ascending AOP branches tending towards infinity. The branches finish at a finite point of pressure and temperature.

2.7 Role of the soft-core repulsion upon density-and temperature-dependent effective diameters from two thermodynamic perturbation theories.

The following material was already published by Cañas-Marín et al. (see reference [206]).

In this section, density-and temperature-dependent effective diameters from two different thermodynamic perturbation theories (TPTs) are presented. The first theory is the already discussed Barker and Henderson´s TPT, and the second one is based on the pioneering work by Rowlinson but applied to steeply repulsive potentials by Heyes. Three intermolecular potentials- generalized Lennard-Jones (GLJ), inverse power (IP), and square-well square shoulder (SWSS)- are considered to study the steepness effect, $n$, upon the theoretically deduced effective diameters. As a result, for $n \geq 12$, and both TPTs, GLJ, and IP produce numerically equivalent effective diameters for packing fractions ($\eta$) less than 0.7. Moreover, for the SWSS potential, Rowlinson´s TPT gives a simple cubic polynomial for the effective diameters, in comparison to the sixth-degree polynomial obtained from Barker and Henderson´s approach. Both polynomials from these two different TPTs essentially
predict the same values of effective diameter for \( \eta \leq 0.7 \). Thus, the theoretically based cubic polynomial presented in this work could be used into the molecular-based equations of state (EoS) to perform phase equilibrium calculations at conditions wherein an effective diameter dependent upon both temperature and density is expected to be more relevant (i.e., low temperatures, high pressures, and dense phases).

As expressed by Henderson [207], Rowlinson’s concept [37]-[39] of considering an effective hard-sphere diameter allowed to complete the three key theoretical developments required to formulate a more successful thermodynamic perturbation theory (TPT) for fluids. Being the other two requirements, to have a reference fluid (unperturbed) whose RDF and thermodynamics were well known (i.e., the hard-sphere system) [208], and convenient expressions for the second-and higher-order dispersion contributions to the perturbative part of the TPT [33]. As amply discussed before, and in the literature [33]-[39], the effective diameter is essential into the TPTs of fluids such as those by Barker and Henderson (BH) [33], [34], Rowlinson [37]-[39], and Weeks-Chandler-Andersen (WCA) [36], because this diameter permits to link the reference system properties to those of a hard-sphere system [34], [36], [207]. Without the concept of an effective diameter, the TPTs would be limited to hypothetical molecules having infinity hard repulsive cores, being impossible to extend the TPTs to real fluids. The role of the effective diameter is to introduce a soft-core repulsion between two molecules or segments close interacting with each other [147], [166], [167]. Speaking strictly, the effective diameter is a function of the thermodynamic state [147]. Then the impact of the density contribution to this parameter should be considered in the thermodynamic modeling of, for example, dense phases at low temperatures and high pressures. For simple systems, the effect of density on the effective diameter has been already tested to be marginal [33], [34]. Particularly, the effective diameter directly impacts the performance of the molecular-based equation of state (EoS) models based upon TPTs, such as PC-SAFT [50].

In the following discussion, some nomenclature will be intentionally changed to be in line to Rowlinson’s TPT, such as this TPT was applied by Heyes [209]. Particularly, \( d \) is changed to \( \sigma_{HS} \) for the effective diameter. Hence, eqn. (2.40) of Barker and Henderson’s TPT is here rewritten as [34]:

\[
a = a_{HS} - a \pi \rho \sigma_{HS}^2 g_{HS}(\sigma_{HS})(\sigma_{HS} - \int_0^\sigma (1 - e^{-\beta \phi(r)}) dr) + \gamma 2 \pi \rho \beta \int_\sigma^\infty g_{HS}(r) \phi(r) r^2 dr + \text{ higher terms.}
\]  

(2.67)
Wherein, again, \(a\) and \(a_{HS}\) are the reduced Helmholtz free energy for the real and the reference fluid (i.e., hard-sphere fluid), respectively. \(\phi\) is the intermolecular potential used to consider the soft-core repulsion. \(r\) is the distance between two molecules or segments. \(\rho\) is density. \(g_{HS}\) is the RDF, dependent upon density (i.e., packing fraction, \(\eta\)). Also, \(\beta \equiv 1/kT\), where \(k\) and \(T\) are the Boltzmann constant and the temperature, respectively. In addition, \(\sigma\) and \(\sigma_{HS}\) are the hard-sphere and effective hard-sphere diameters [34].

In eqn. (2.67), as already mentioned before, \(a\) equals \(a_{HS}\) simply by taking \((\sigma_{HS} - \int_0^\sigma \{1 - e^{-\beta \phi(r)}\}dr) = 0\), and ruling out all the “higher terms” at the right-hand side (RHS). Thus, simple Barker and Henderson’s effective diameter, dependent on temperature only, is obtained as \(\sigma_{HS} (T) = \int_0^\sigma \{1 - e^{-\beta \phi(r)}\}dr\). In which the soft-core repulsion depends on the softness (or steepness) of the intermolecular potential used, \(\phi(r)\).

From eqn. (2.67), as already discussed in other sections, the effective diameter should also be a function of density because the third term at the right-hand side depends on \(g_{HS}\), that depends upon density. Hence, in the present section, two polynomial expressions for the temperature-and density-dependent effective diameter are theoretically deduced based upon Rowlinson’s TPT [37]-[39] but applied to steeply repulsive potentials by Heyes [209]. Then, some results of using those effective diameter expressions for different “soft-core” intermolecular potentials are presented. For the SWSS potential, the third-degree polynomial deduced from Rowlinson´s TPT modified by Heyes [209] is compared to the sixth-degree polynomial presented in eqn. (2.48) [165] - based upon the Barker and Henderson TPT- to model critical loci for three binary systems, asphaltene onset pressures (AOPs), bubblepoints (BPs), and reduced densities (\(\eta\)) for a real petroleum mixture. Finally, some conclusions are presented.

2.7.1 Deduction of other temperature-and density-dependent effective diameters.

The present section is focused to theoretically deduce temperature-and density-dependent effective diameters. Other two intermolecular potential models, besides Chen and Kreglewski´s SWSS [122], are used to include the soft-core (steepness) repulsion. The first one is the generalized Lennard-Jones potential, given as:
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\[ \phi(r) = \begin{cases} 4\epsilon \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^{n/2} & \text{if } r \leq \sigma \\ 0 & \text{if } r > \sigma \end{cases} \]  

(2.68)

Following Barker and Henderson [33, 34], the separation of the intermolecular potential into a repulsive and attractive part has been picked at \( r = \sigma \). In short, a repulsive part for \( r \leq \sigma \) and a perturbative (i.e., attractive) contribution for \( r > \sigma \). Naturally, Lennard-Jones intermolecular potential (LJ) is given when the steepness, \( n \), is equal to 12. Hence, different degrees (softness) of the repulsive wall can be obtained simply by varying \( n \). The other model is the inverse power (IP) potential. This is commonly used in TPTs [199, 209]. IP represents a “soft-sphere” totally repulsive with different degrees of steepness, \( n \). The IP potential is simply:

\[ \phi(r) = \begin{cases} \epsilon \left( \frac{\sigma}{r} \right)^n & \text{if } r \leq \sigma \\ 0 & \text{if } r > \sigma \end{cases} \]  

(2.69)

Following Tang [147], an effective diameter dependent on both density and temperature can be obtained into Barker and Henderson´s TPT framework by solving the equation:

\[ \int_0^\sigma y_{HS}(r)e^{-\beta\phi(r)}r^2dr - \int_0^\sigma y_{HS}(r)r^2dr = 0 \]  

(2.70)

As already presented, \( y_{HS}(r) \) means the cavity function for the reference pseudo-fluid made-up of hard spheres, and it is given by [147]:

\[ y_{HS}(r) = \begin{cases} -c_{HS}(r) & \text{if } r < \sigma_{HS} \\ g_{HS}(r) & \text{if } r \geq \sigma_{HS} \end{cases} \]  

(2.71)

In eqn. (2.71), the Percus-Yevick (PY) direct correlation function for hard spheres [41], \( c_{HS}(r) \), and the respective PY-RDF, \( g_{HS}(r) \), are usually found by solving the Ornstein-Zernike (OZ) integral equation around \( \sigma_{HS} \) [40, 127]. Hence, \( c_{HS}(r) \) is:

\[ c_{HS}(r) = \frac{\eta(1+2\eta)^2}{2(1-\eta)^4} \left( \frac{r}{\sigma_{HS}} \right)^3 + 6\eta \left( \frac{1+\eta/2}{1+\eta} \right)^2 \frac{r}{\sigma_{HS}} + \frac{(1+2\eta)^2}{(1-\eta)^4} \]  

(2.72)
In this section, Tang and Lu’s expression for $g_{HS}(r)$ is again used [176]:

$$
g_{HS}(r) = \frac{1+\eta/2}{(1-\eta)^2} \sigma_{HS} + \frac{1-5\eta-5\eta^2 r - \sigma_{HS}}{(1-\eta)^3} r + \frac{-3\eta+6\eta^2+21/2\eta^3 (r-\sigma_{HS})^2}{r\sigma_{HS}} \tag{2.73}
$$

This was the approach used in section 2.4 to deduce the density-and temperature-dependent effective diameter for PC-SAFT, given as a sixth-degree polynomial [165]: $\omega \sigma_{HS}^6 + \delta \sigma_{HS}^4 + \theta \sigma_{HS}^3 + \vartheta \sigma_{HS}^2 + \tau = 0$. Wherein the coefficients $\omega, \delta, \theta, \vartheta$ and $\tau$ depend upon density and temperature (see that section).

The two integrals in eqn. (2.70) must be solved by numerical integration if the GLJ or IP potentials are used for $\phi(r)$. For this purpose, in this work a forty-points Gauss-Legendre algorithm was chosen to find the respective $\sigma_{HS}$ at different $n$ and packing fraction values.

Apart from Tang’s focus on the framework of the Barker and Henderson TPT, Heyes [209] used a “softness” parameter ($\lambda$) into Rowlinson’s TPT to perform a Helmholtz energy expansion around $r = \sigma_{HS}$ (i.e., the contact condition). To author’s knowledge, Heyes was the first in applying Rowlinson’s approach “to steeply repulsive potentials very close to the hard-sphere limit” (see [209] for details). The final equation obtained is as follows [209]:

$$
\sum_{N=0}^{\infty} \frac{f_N(\sigma_{HS})}{N!} \left( \frac{-\sigma_{HS}^{N+1}}{N+1} + \int_0^\infty (r - \sigma_{HS})^N (1 - e^{-\beta \phi(r)}) dr \right) = 0 \tag{2.74}
$$

Wherein,

$$
f_N(\sigma_{HS}) = \frac{d^N}{dr^N} y_{HS}(r; \sigma_{HS}; \eta)|_{r=\sigma_{HS}} \tag{2.75}
$$

Heyes did not present a density-and temperature-dependent effective diameter expression obtained from eqn. (2.74). In fact, his work focused on using the basis case given by $N = 0$. The result for this case is the classical formula for the effective diameter given by Barker and Henderson [34], dependent upon temperature only:

$$
\sigma_{HS} = \int_0^\infty \left\{ 1 - e^{-\beta \phi(r)} \right\} dr \tag{2.76}
$$
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The difference between eqn. (2.76) and eqn. (2.39) (from Barker and Henderson TPT) is the upper limit in the integral, i.e., $\infty$ versus $\sigma$, respectively. In fact, for a repulsive potential, $\sigma \rightarrow \infty$ and eqn. (2.39) reduce to Rowlinson’s criteria [34].

In this section, eqn. (2.74) is used to explicitly deduce two expressions of effective diameter dependent on density and temperature. For this aim, at first the three terms in eqn. (2.74) are considered (i.e., $N = 0, 1, 2$). At contact, $y_{HS}(r; \sigma_{HS}; \eta)|_{r=\sigma_{HS}} = g_{HS}(r)$. Wherein eqn. (2.73) of Tang and Lu [176] is used for $g_{HS}(r)$. Then, eqn. (2.75) is expressed as:

$$f_N(\sigma_{HS}) = \frac{d^N}{dr^N} r^2 g_{HS}(r; \sigma_{HS}; \eta)|_{r=\sigma_{HS}}$$ (2.77)

Finally, by solving the derivatives in eqn. (2.77) for $N = 0, 1, 2$, and replacing the results into eqn. (2.74), the following cubic expression for a density-and temperature-dependent effective diameter is obtained as:

$$\bar{A} \sigma_{HS}^3 + \bar{B} \sigma_{HS}^2 + \bar{C} \sigma_{HS} + \bar{D} = 0$$ (2.78)

Here,

$$\bar{A} \equiv -\frac{1}{2} \alpha_0 + \frac{1}{6} \alpha_1 - \frac{1}{3} \alpha_2$$ (2.79)

$$\bar{B} \equiv \alpha_2 \cdot \int_0^\sigma E(r)dr$$ (2.80)

$$\bar{C} \equiv [\alpha_0 - \alpha_1 - 2\alpha_2] \int_0^\sigma r E(r)dr$$ (2.81)

$$\bar{D} \equiv [\alpha_1 + \alpha_2] \int_0^\sigma r^2 E(r)dr$$ (2.82)

$$E(r) \equiv 1 - e^{-\beta \phi(r)}$$ (2.83)

$$\alpha_0 \equiv \frac{1 + \eta/2}{(1-\eta)^2}, \quad \alpha_1 \equiv \frac{1-5\eta-5\eta^2}{(1-\eta)^3}, \quad \alpha_2 \equiv \frac{-3\eta+6\eta^2+21/2\eta^3}{(1-\eta)^4}$$ (2.84)

The integrals in eqns. (2.80) - (2.82) must be solved before using eqn. (2.78) to calculate the respective $\sigma_{HS}$ at a density and temperature given. Eqn. (2.78) can be evaluated analytically by applying Cardano’s formula, or numerically also by using, for instance, a Newton-Raphson type
routine. In this last case, eqn. (2.40) could be used as an initial guess. Again, for the GLJ and IP potentials, these three integrals must be solved numerically. On the contrary, for Chen and Kreglewski’s SWSS potential, these integrals are explicitly given here for \( N = 0, 1, \) and 2, ... as:

\[
\int_{0}^{\sigma} r^N \cdot E(r) \, dr = \frac{\sigma^{N+1}}{N+1} \cdot \left[ 1 - \left( 1 - \delta \right)^N \right] \cdot e^{-3\beta\epsilon} \tag{2.85}
\]

\( \delta \) is taken as 0.12 (i.e., the same value used in the original PC-SAFT). For \( N = 0 \), eqn. (2.85) reduces to eqn. (2.40) for PC-SAFT. Clearly, for Chen and Kreglewski’s SWSS potential, eqn. (2.78) appears simpler than eqn. (2.48), given as a result a sixth-degree polynomial. It is important to stress that if the reduced density tends to zero (i.e., \( \eta \rightarrow 0 \)), the effective diameters given by eqns. (2.70), and (2.78) depend upon temperature only. This fact is evident from eqn. (2.72) for \( c_{HS}(r) \), and eqn. (2.73) for \( g_{HS}(r) \). More clearly, when \( \eta \rightarrow 0 \) then \( c_{HS}(r) \rightarrow -1 \), and \( g_{HS}(r) \rightarrow 1 \). Thus, when \( \rho \rightarrow 0 \), then \( \sigma_{HS}(T, \rho) \rightarrow \sigma_{HS}(T) \). Hence, eqns. (1.7), (1.11), and (1.16) fulfill exactly the theoretical restriction that the second virial coefficient, \( B \), depends upon temperature and not on density. With \( B \) being again expressed by eqn. (2.66):

On the other hand, eqns. (2.74) and (2.77) can also be solved for \( N = 0, 1, 2, \) and 3, resulting in a fourth-degree polynomial given by:

\[
\bar{A}\sigma_{HS}^4 + \bar{B}\sigma_{HS}^2 + \bar{C}\sigma_{HS} + \bar{D} = 0 \tag{2.86}
\]

Wherein:

\[
\bar{A} \equiv -\frac{1}{2}\alpha_0 + \frac{1}{6}\alpha_1 - \frac{1}{12}\alpha_2 \tag{2.87}
\]

\[
\bar{B} \equiv \left[ \alpha_0 - \alpha_1 + \alpha_2 \right] \int_{0}^{\sigma} rE(r) \, dr \tag{2.88}
\]

\[
\bar{C} \equiv \left[ \alpha_1 - 2\alpha_2 \right] \int_{0}^{\sigma} r^2E(r) \, dr \tag{2.89}
\]

\[
\bar{D} \equiv \alpha_2 \int_{0}^{\sigma} r^3E(r) \, dr \tag{2.90}
\]

Here, \( E(r) \), and \( \alpha_0, \alpha_1 \), and \( \alpha_2 \) are given by eqns. (2.83) and (2.84), respectively. In fact, a fourth degree is the highest polynomial order obtained by combining Heyes’s approach with Tang and Lu’s
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mathematical expression for \( g_{HS}(r) \). Again, for Chen and Kreglewski’s SWSS potential, the integrals in eqn. (2.88) - (2.90) are given by eqn. (2.85).

Figure 2-33 presents a comparison of dimensionless effective diameters \( \sigma_{HS}^* \equiv \frac{\sigma_{HS}}{\sigma} \) versus reduced temperatures \( T^* \equiv \beta \epsilon \) calculated by using the third and fourth-degree polynomials, given by eqns. (2.78) and (2.86), respectively, at different reduced density values, \( \eta \). As shown, the numerical values overlap. Hence, the third-degree polynomial given by eqn. (2.78) is used in the rest of this work. To the best of author’s knowledge, it is the first time that Eqns. (2.78) and (2.86) are theoretically deduced.

Figure 2-33: Chen and Kreglewski’s SWSS potential. Heyes’s third-degree polynomial (continuous lines): — \( \eta = 0.1 \), — \( \eta = 0.3 \), — \( \eta = 0.5 \), — \( \eta = 0.6 \), — \( \eta = 0.7 \). Heyes’s fourth-degree polynomial (dashed lines): --- \( \eta = 0.1 \), --- \( \eta = 0.3 \), --- \( \eta = 0.5 \), --- \( \eta = 0.6 \), --- \( \eta = 0.7 \).

To be fair with Tang’s approach, eqn. 2.70 can also be solved at contact conditions. Thus, by using eqn. 2.73, eqn. 2.70 can be expressed as:

\[
\int_{\sigma-S_1}^{\sigma} g_{HS}(r) e^{-\beta \phi(r)} r^2 \, dr - \int_{\sigma_{HS}}^{\sigma} g_{HS}(r) r^2 \, dr = 0
\]  
(2.91)
Now, for Chen and Kreglewski’s SWSS potential, eqn. 2.91 is reduced to:

\[
\int_{\sigma - S_1}^\sigma g_{HS}(r)e^{-\beta \phi(r)}r^2 dr - \int_{\sigma_{HS}}^\sigma g_{HS}(r)r^2 dr = 0
\]  

(2.92)

Wherein \( S_1 \) is again 0.12\( \sigma \). Hence, a fourth-degree polynomial is obtained as:

\[
\Gamma \sigma_{HS}^4 + \xi \sigma_{HS}^2 + Y \sigma_{HS} + \Phi = 0
\]  

(2.93)

Wherein,

\[
\Gamma \equiv (A + B + C) \ast (1 + \text{EXPP})
\]  

(2.94)

\[
\xi \equiv -A \ast [(\sigma - S_1)^2 + \text{EXPP} \ast \sigma^2]
\]  

(2.95)

\[
Y \equiv -B \ast [(\sigma - S_1)^3 + \text{EXPP} \ast \sigma^3]
\]  

(2.96)

\[
\Phi \equiv -C \ast [(\sigma - S_1)^4 + \text{EXPP} \ast \sigma^4]
\]  

(2.97)

Here,

\[
A \equiv \frac{(\alpha_0 + \alpha_1 + \alpha_2)}{2}; \quad \xi \equiv \frac{(\alpha_1 - 2\alpha_2)}{3}; \quad C \equiv \frac{\alpha_2}{4}
\]  

(2.98)

\( \alpha_0, \alpha_1, \) and \( \alpha_2 \) are already given in eqn. 2.84.

\[
\text{EXPP} \equiv \frac{1-e^{-3\beta \varepsilon}}{e^{-3\beta \varepsilon}}
\]  

(2.99)

Eqn.2.93 obtained from Tang’s approach really produces the same effective diameters values as eqns. 2.78 and 2.86 form Heyes’s one (see figure 2-34). Nevertheless, due to its third-order polynomial condition, eqn. 2.78 continues to be the preferred model for PC-SAFT in calculating a density-and temperature-dependent effective diameter. Eqn. 2.93 has not be published in the literature and only is presented in this dissertation.
Figure 2-34: Chen and Kreglewski´s SWSS potential. Tang´s four-degree polynomial (continuous lines): — η = 0.1, — η = 0.3, — η = 0.5, — η = 0.6, — η = 0.7. Heyes´s fourth-degree polynomial (dashed lines): - - - η = 0.1, - - - η = 0.3, - - - η = 0.5, - - - η = 0.6, - - - η = 0.7.

2.7.2 Results and Discussion.

Figure 2-35 presents a comparison of dimensionless effective diameters versus reduced temperatures for the GLJ potential (i.e., eqn. (2.68)). Comparative calculations were performed by using eqns. (2.70) (Tang) and 2.78 (Heyes) for steepness values, n, of 10, 12, 18, and 36.
As seen in that figure, for this intermolecular potential, both approaches predict similar effective diameters for $\eta \geq 0.7$. If the steepness increases, the effective diameters for these two approaches are closer to each other. It is important to highlight that $n = 10$ should not be strictly considered as a “steep” potential, and the differences between these two approaches could be justified. This last value of steepness was included for completeness purposes. It is central to understand that a packing fraction of 0.7 is a very high value if it is considered that the phase diagram for the hard-sphere reference system used into the TPTs presents only a stable fluid branch from $\eta = 0$ up to the freezing point ($\eta \cong 0.492$), wherein a fluid-solid transition takes place. From the freezing point up to $\eta \cong 0.543$ occurs a co-existence between a solid phase and a liquid phase. But for higher $\eta$ values, only a (crystalline) solid exists up to the close-packing fraction ($\eta \cong 0.74$). In addition, as expressed by Robles et al. [198] “beyond the freezing point there is also a region of metastable fluid states that is
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supposed to end at the packing fraction $\eta \approx 0.58$, where a widely accepted glass transition occurs. The glass branch ends at $\eta \approx 0.64$, corresponding to the random close-packing of an amorphous solid". In fact, near the freezing line, the TPTs are usually less accurate. For instance, close to that line, the WCA TPT produces hard-sphere effective diameters so large that that reference fluid often lies in a metastable region [199]. Nonetheless, by using a “softer” potential and, additionally, an effective diameter depending on density (besides the temperature) the trend of obtaining metastable conditions is reduced because the density reduces the effective diameter. As stressed before, it is important to bear in mind that the most common TPTs were formulated for fluid phases under stable (isotropic) conditions [33-39], [99-104], [147], [199], [209].

Figure 2-36 depicts results for the IP potential. As noted, for this intermolecular potential the two approaches being compared exhibit minor concordance in the respective effective diameters, especially at higher packing fractions and for smaller steepness (“softer”) values. Like figure 2-35, Heyes´s approach tends to predict slightly lower effective diameters than Tang´s one. But this difference is reduced at ordinary (stable) packing fractions. For practical applications, these two models could be considered as equivalent.

Figure 2-37 exhibits the comparison between effective diameters given by the sixth-degree polynomial (i.e., eqn. (2.48)) from Tang and the cubic polynomial from Heyes, presented in eqn. 2.78, both models using Chen-Kreglewski´s SWSS potential.

As noted, from a practical viewpoint both models produce the same numerical results. This fact agrees with the results presented in figures 2-35 and 2-36, because the SWSS potential, used into EoS models like PC-SAFT, is really a steeply repulsive potential. Then, the phase-equilibrium calculations performed with PC-SAFT by using eqn. (2.48), and already reported in sections 2.4-2.6 (see also [165], [188], [192]) would be the same if the cubic polynomial given by eqn. (2.78) is utilized instead. Therefore, all these calculations will not be repeated here.
**Figure 2-36:** IP potential. Tang (continuous lines): $\eta = 0.1$, $\eta = 0.3$, $\eta = 0.5$, $\eta = 0.6$, $\eta = 0.7$. Heyes (dashed lines): $\eta = 0.1$, $\eta = 0.3$, $\eta = 0.5$, $\eta = 0.6$, $\eta = 0.7$. 

$n = 10$

$n = 12$

$n = 18$

$n = 36$

**Figure 2-37:** Chen and Kreglewski’s SWSS potential. Tang (continuous lines): $\eta = 0.1$, $\eta = 0.3$, $\eta = 0.5$, $\eta = 0.6$, $\eta = 0.7$. Heyes (dashed lines): $\eta = 0.1$, $\eta = 0.3$, $\eta = 0.5$, $\eta = 0.6$, $\eta = 0.7$. 

$n = 10$
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However, for completeness, figure 2-38 presents critical loci measured for the binary systems methane-propane, methane-pentane, and methane-decane [185], and the resulting predictions by using the two effective diameter polynomial models here compared. As can be seen, the critical loci predicted overlap.

**Figure 2-38:** Critical loci for three simple hydrocarbon binary systems: (a) CH₄-C₃H₈; (b) CH₄-C₅H₁₂; (c) CH₄-C₁₀H₂₂. Exp. data from [185]. Tang (continuous line): —. Heyes (dashed lines): ---.

Moreover, figure 2-39 compares asphaltene onset pressures (AOPs) and bubblepoints (BPs) calculated with PC-SAFT by using these two effective diameter models for a real petroleum reservoir fluid reported in [153] and modeled also in [165], [188], [192]. AOPs and BPs are liquid-liquid and liquid-vapor equilibria, respectively.
**Figure 2-39:** AOPs and BPs calculated with PC-SAFT. Chen and Kreglewski’s SWSS potential. Tang (continuous lines): —AOP, — BP. Heyes (dashed lines): --- AOP. --- BP. O Exp. AOP, Δ Exp. BP [153].

As noted, the respective curves of AOPs and BPs predicted by those two polynomials overlap. The same comparison is illustrated in figure 2-40 for the reduced densities, $\eta$, of the global- and asphaltene rich-phases present in equilibrium at the respective AOPs. Again, the overlap between the curves is evident. Notice that the overlap occurs even at very high-pressure conditions.

**Figure 2-40:** Reduced densities calculated with PC-SAFT. Chen and Kreglewski’s SWSS potential. Tang (continuous line): —. Heyes (dashed lines): ---.
2.7.3 Conclusions for section 2.7

For the first time, Heyes’s approach to Rowlinson’s TPT is used to theoretically deduce temperature- and density-dependent effective diameters. Both TPTs used in the present section, as formulated respectively by Tang and Heyes, predict similar density-and temperature-dependent effective diameters for steep repulsive potentials, and this concordance increases at lower packing fractions and higher steepness values. From a general viewpoint, these two approaches are exchangeable. Moreover, for Chen and Kreglewski’s SWSS potential, Heyes’s approach produced a cubic polynomial for the effective diameter that can be analytically solved. Thus, that expression could be introduced into based-molecular EoS models like PC-SAFT to perform phase equilibrium calculations, mainly for dense phases at low temperatures or high pressures. Conditions in which an effective diameter dependent upon both temperature and density is most relevant.

2.8 Tang´s hard-spheres radial distribution function versus Monte Carlo data. Effect on the temperature-and-density-dependent effective diameter from Heyes´s approach.

In this section, the hard-sphere RDF, $g_{HS}(r)$, of Tang and Lu [176], deduced by those researchers from the mean spherical approximation (MSA), and used throughout this thesis to deduce all the temperature-and density-dependent effective diameter expression, is tested against exact Monte Carlo (MC) data obtained by Largo [7] in the stable fluid region for hard spheres. Then, a new expression of RDF is obtained by fitting Largo´s MC data to a second-order polynomial, and it is used to deduce a new temperature-and density-dependent effective diameter based on Rowlinson´s TPT version applied by Heyes [37], [38], [39], [209]. The approach used here to obtain this new effective diameter is the same amply discussed in section 2.7.1. above.

Figures 2-41 to 2-49 presents the comparison of Tang and Lu´s RDF [176], see eqn. 2.73, against hard-sphere Largo´s MC simulation data [7] for $0.1 \leq \rho \sigma^3 \leq 0.9$ (i.e., $0.052 \leq \eta \leq 0.471$), and $1 \leq x \equiv \frac{r}{\sigma} \leq 1.21$. Wherein the continuous lines correspond to Tang´s RDF, unfilled circles are Largo´s hard-sphere MC data, and dotted lines represent the fitting of Largo´s MC data to a second-degree polynomial for different packing fraction data, $\eta$. 
Figure 2-41: Tang’s hard-sphere RDF versus Largo’s MC data ($\eta=0.052$) [7].

Figure 2-42: Tang’s hard-sphere RDF versus Largo’s MC data ($\eta=0.105$) [7].

\[
g_{ns} = -0.1003(\eta/r)^2 - 0.0526(\eta/r) + 1.2968 \\
R^2 = 0.9955 \text{ (MC data fitting)}
\]

\[
g_{ns} = 0.4255(\eta/r)^2 - 1.6214(\eta/r) + 2.5177 \\
R^2 = 0.9974 \text{ (MC data fitting)}
\]
Figure 2-43: Tang´s hard-sphere RDF versus Largo´s MC data (η=0.157) [7].

\[ g_{ns} = 1.0345 \left( \frac{r}{\sigma} \right)^2 - 3.5829 \left( \frac{r}{\sigma} \right) + 4.0883 \]
\[ R^2 = 0.9998 \text{ (MC data fitting)} \]

Figure 2-44: Tang´s hard-sphere RDF versus Largo´s MC data (η=0.209) [7].

\[ g_{ns} = 2.5568 \left( \frac{r}{\sigma} \right)^2 - 7.8514 \left( \frac{r}{\sigma} \right) + 7.1097 \]
\[ R^2 = 0.9999 \text{ (MC data fitting)} \]
Figure 2-45: Tang’s hard-sphere RDF versus Largo’s MC data (η=0.262) [7].

Figure 2-46: Tang’s hard-sphere RDF versus Largo’s MC data (η=0.314) [7].
Figure 2-47: Tang’s hard-sphere RDF versus Largo’s MC data ($\eta=0.367$) [7].

\[ g_{HS} = 21.399(x/\sigma)^2 - 55.457(x/\sigma) + 37.268 \]
\[ R^2 = 0.9998 \text{ (MC data fitting)} \]

Figure 2-48: Tang’s hard-sphere RDF versus Largo’s MC data ($\eta=0.419$) [7].

\[ g_{HS} = 38.868(x/\sigma)^2 - 97.885(x/\sigma) + 62.997 \]
\[ R^2 = 0.9995 \text{ (MC data fitting)} \]
Figure 2-49: Tang’s hard-sphere RDF versus Largo’s MC data ($\eta=0.471$) [7].

As can be seen from figures 2-41 to 2-49, Tang’s RDF deviates from MC data especially at high densities and for distances close to the contact value (i.e., for $x$ close to 1).

The new approach presented here is firstly to fit the Largo’s MC hard-sphere data to a second-order polynomial, for the range of $x$-values above mentioned, and for each packing fraction (dotted lines in figures 2-41 to 2-49). Then, the new analytical hard-sphere RDF is given in this thesis as:

$$g_{HS}(x) = \sigma_0 + \sigma_1 x + \sigma_2 x^2$$

Wherein $\sigma$ is the hard-sphere diameter. $\sigma_0$, $\sigma_1$, and $\sigma_2$ are parameters that depend on the packing fraction (i.e., reduced density). In this work, these parameters are exactly fitted by the following equations:

$$\sigma_0 (\eta) = 130117 \eta^6 - 176280 \eta^5 + 96114 \eta^4 - 25526 \eta^3 + 3503.7 \eta^2 - 223.06 \eta + 5.0943; R^2 = 1$$

(2.101)

$$\sigma_1 (\eta) = -295218 \eta^6 + 400475 \eta^5 - 218772 \eta^4 + 58148 \eta^3 - 8017.7 \eta^2 + 506.4 \eta - 11.69; R^2 = 1$$

(2.102)
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\[ \sigma_2 (\eta) = 167075 \eta^6 - 226985 \eta^5 + 124245 \eta^4 - 33054 \eta^3 + 4580.7 \eta^2 - 285.02 \eta + 7.6962; \quad R^2 = 1 \tag{2.103} \]

To the author’s knowledge, a simple analytical expression, such as that given by eqns. (2.100) - (2.103), to fit MC data of the hard-sphere RDF has not been published in the literature. In fact, for completeness, the complete set of Largo’s RDF MC data for \(0.1 \leq \rho \sigma^3 \leq 0.9\) (i.e., \(0.052 \leq \eta \leq 0.471\), and \(1 \leq x \equiv \frac{r}{\sigma} \leq 2.99\), was also fitted in this dissertation to a six-degree polynomial, and it is presented in Appendix D. That representation is relatively simple, and it could be very useful in the molecular theory of fluids if the hard-sphere concept is used as a starting point to obtain a most elaborated molecular model.

In this thesis, eqns. (2.100)- (2.103) are used with Heyes’s approach, amply discussed in section 2.7.1, to deduce a new temperature-and-density-dependent effective diameter. That mathematical expression is obtained by replacing eqn. (2.100) into eqns. (2.74), (2.75), and (2.77), giving, as a result, a fifth-degree polynomial for the effective diameter:

\[ \hat{A}\sigma_{HS}^5 + \hat{B}\sigma_{HS}^4 + \hat{C}\sigma_{HS}^3 + \hat{D}\sigma_{HS}^2 + \hat{E}\sigma_{HS} + \hat{F} = 0 \tag{2.104} \]

Wherein,

\[ \hat{A} \equiv -\frac{\sigma_2}{\sigma^2} \tag{2.105} \]

\[ \hat{B} \equiv -\frac{1}{2}\frac{\sigma_1}{\sigma^2} + 3\frac{\sigma_2}{\sigma^2} \int_0^\sigma E(r)dr \tag{2.106} \]

\[ \hat{C} \equiv -\frac{1}{3}\sigma_0 + \frac{\sigma_1}{\sigma} \int_0^\sigma E(r)dr - 8\frac{\sigma_2}{\sigma^2} \int_0^\sigma rE(r)dr \tag{2.107} \]

\[ \hat{D} \equiv -3\frac{\sigma_1}{\sigma} \int_0^\sigma rE(r)dr + 6\frac{\sigma_2}{\sigma^2} \int_0^\sigma r^2E(r)dr \tag{2.108} \]

\[ \hat{E} \equiv 3\frac{\sigma_2}{\sigma} \int_0^\sigma r^2E(r)dr \tag{2.109} \]

\[ \hat{F} \equiv \sigma_0 \int_0^\sigma r^2E(r)dr \tag{2.110} \]
$E(r)$ is given by eqn. (2.83). For Chen-Kreglewski’s SWSS potential, the integrals in eqns. (2.106) – (2.110) are, again, defined in eqn. (2.85). Obviously, eqns. (2.104) – (2.110) are applicable to other most complex intermolecular potential, but, as discussed for example in section 2.7, numerical methods are required to evaluate the integrals.

Figure 2-50 compares the reduced temperature-and density-dependent effective diameters, $\sigma_{HS}^* = \sigma_{HS}/\sigma$, calculated from eqn. (2.78) and (2.104), as a function of reduced temperature, $\tau \equiv kT/\epsilon$, and for different packing fractions, $\eta$ (i.e., reduced density). Eqn. (2.78) uses Tang’s hard-sphere RDF (i.e., eqn. 2.73), while (2.104) considers the RDF proposed in this thesis by fitting Largo’s hard-sphere RDF data obtained by Monte Carlo calculations (i.e., eqn. 2.100). As noted in that figure, these two effective diameter expressions give very similar values for the whole range of isotropic/stable hard-sphere fluid. Strictly speaking, eqn. (2.100) predicts slightly lower effective diameter values for the whole range of temperature and packing fractions. However, for light components (i.e., low densities) the effective diameters predicted by these two models are really the same. Then, comparisons are relevant only for heavy components at low temperatures.

**Figure 2-50:** Comparison of the reduced temperature-and density-dependent effective diameters, $\sigma_{HS}^* = \sigma_{HS}/\sigma$, calculated from eqn. (2.78) and (2.104), as a function of reduced temperature, $\tau \equiv kT/\epsilon$, for different packing fractions, $\eta$ (i.e., reduced density).
2.8.1 Results and Discussion.

Comparisons of AOP curves predicted by the effective diameter expressions given by the cubic polynomial in eqn. (2.78) and the fifth-degree polynomial presented in eqn. (2.104) are given for two reservoir fluids; hereafter called Fluid 1 [138] and Fluid 2 [153], respectively. For each fluid, different molecular weight values are assumed for the “asphaltene” component. Both effective diameter expressions are obtained in this thesis by using Heyes’ approach to Rowlinson’s TPT. In both cases, LK universal constants for PC-SAFT are used.

Figures 2-51 to 2-54 depicts the AOP curves predicted by these two effective diameter expressions for Fluid 1. As can be seen, eqn. (2.104) predicts slightly lower AOPs than eqn. (2.78). Nevertheless, from an engineering viewpoint, the differences appear no relevant. The asphaltene molecular weight values (MWasph) used for this fluid were 650, 700, 800, and 1000.

**Figure 2-51:** Fluid 1 (MWasph=650). Comparison of AOP curves predicted by eqns. (2.78) and (2.104). Eqn. (2.78).

![Graph showing AOP curves for Fluid 1 with MWasph = 650](image-url)
**Figure 2-52:** Fluid 1 (MWasph=700). Comparison of AOP curves predicted by eqns. (2.78) and (2.104). Eqn. (2.78).

**Figure 2-53:** Fluid 1 (MWasph=800). Comparison of AOP curves predicted by eqns. (2.78) and (2.104). Eqn. (2.78).
Figure 2-54: Fluid 1 (MW_{asph}=1000). Comparison of AOP curves predicted by eqns. (2.78) and (2.104). Eqn. (2.78).

Figures 2-55 to 2-58 presents the same analysis, but for Fluid 2. As noted in that figure, the behavior is completely equivalent to Fluid 1. Again, though eqn. (2.104) predicts lower AOPs at the same temperature than eqn. (2.78). From a practical point of view, the differences appear irrelevant. Then, Tang’s RDF seems like a good model to predict temperature-and density-dependent effective diameters. In addition, eqn. (2.78) is a cubic polynomial, instead of the fifth-degree polynomial given by eqn. (2.104). Obviously, eqn. (2.78) runs faster into a simulator, and, as discussed before, for Chen-Kreglewski SWSS potential the effective diameter can be found analytically.
**Figure 2-55:** Fluid 2. Comparison of AOP curves predicted by eqns. (2.78) and (2.104). MWasph = 650.

![Graph showing AOP curves for MWasph = 650.](image)

**Figure 2-56:** Fluid 2. Comparison of AOP curves predicted by eqns. (2.78) and (2.104). MWasph = 700.

![Graph showing AOP curves for MWasph = 700.](image)
Figure 2-57: Fluid 2. Comparison of AOP curves predicted by eqns. (2.78) and (2.104). MWasph = 800.

Figure 2-58: Fluid 2. Comparison of AOP curves predicted by eqns. (2.78) and (2.104). MWasph = 900.
2.8.2 Conclusions for section 2.8

A new hard-sphere RDF expression (i.e., eqn. 2.100) was obtained in this section by fitting Largo’s MC data. This expression was then used to deduce a temperature-and density-dependent effective diameter expression, resulting in a fifth-degree polynomial (eqn. 2.104). Comparison of this new expression of effective diameter with that given by using Tang’s RDF in eqn. (2.78) showed similar values of effective diameter per se, and similar predictions of AOP curves with PC-SAFT. The differences in AOP values occur at reduced temperatures. Both Tang’s RDF and the new hard-sphere RDF presented by fitting Largo’s MC data appear to be practical and simple hard-sphere RDF models to calculate effective diameters. Speaking strictly, the last one is most exact, and, to the author’s knowledge, a similar expression has not been published in the literature. Moreover, the RDF obtained in this thesis could be very useful in other topics related to the theory of molecular fluids. From a practical viewpoint, Tang’s RDF has the advantage of producing a cubic polynomial for the temperature-and density-dependent effective diameter in the framework of Heyes’s approach (i.e., eqn. 2.78) instead of a fifth-degree polynomial obtained by using the new RDF.

2.9 Role of the soft-core repulsion upon the prediction of characteristic curves with PC-SAFT.

The following material was already published by Cañas-Marín et al. (see reference [163]).

In this section, the role of the soft-core repulsion upon the capability of PC-SAFT of predicting coherent Brown’s ideal curves (Amagat, Boyle, and Charles) was analyzed. The soft-core repulsion is introduced by using two different theoretical approaches to define the effective diameter into the Barker and Henderson thermodynamic perturbation theory (TPT). Brown’s characteristic curves were predicted for seven pure components, representing spherical, planar, and non-spherical molecules. For all modeled components (i.e., independent of the molecular size) the soft-core repulsion included into the original effective diameter of PC-SAFT fails to predict physically coherent Amagat curves, and this original diameter should be used with caution to perform calculations at extreme conditions of temperature and pressure. On the contrary, the soft-core model resulting of combining Boltzmann factor criterion (BFC) approach and the generalized Lennard-Jones (GLJ) potential gives as a result a simple, analytical, and temperature-dependent effective diameter, that permits to trace physically coherent Brown’s characteristic curves with this equation of state (EoS). Finally, the BFC effective diameter is used to determine the effect of varying the
intermolecular potential steepness (or softness) upon Brown`s characteristic curves, producing Amagat envelopes that increases at higher steepness (i.e., less softness), while the contrary behavior is found for both the Boyle and Charles curves.

Brown [210] reported a group of curves, known as Brown`s characteristic (ideal) curves, representing thermodynamic states at which one thermodynamic property of a real pure fluid matches that of an ideal gas [211]. To predict physically reasonable Brown ideal curves, such as the Amagat (Joule inversion), Boyle, and Charles (Joule-Thompson inversion) ones, is challenging for any equation of state (EoS) intended to represent the thermodynamics of a real pure fluid at any condition on the P-T phase diagram.

The curves studied here are Brown's characteristic curves of first order, which are defined by the following criteria [124]:

\[
\left( \frac{\partial Z}{\partial T} \right)_V = 0 \quad (\text{Amagat}) \tag{2.111}
\]

\[
\left( \frac{\partial Z}{\partial V} \right)_T = 0 \quad (\text{Boyle}) \tag{2.112}
\]

\[
\left( \frac{\partial Z}{\partial P} \right)_T = 0 \quad (\text{Charles}) \tag{2.113}
\]

Where, \( Z, P \) and \( V \) represent the compressibility factor, the pressure, and the volume, respectively. Amagat curves cover pressures and temperatures usually out of the conditions experimentally accessible for most components. These ideal dome-shaped curves can have a maximum at pressures and temperatures of 100 to 200 times the critical pressure, and 20 times the critical temperature [124], [212], [214], and without having inflection points. Commonly, these curves start at very high temperatures, wherein the second virial coefficient has a maximum \( \left( \frac{dB}{dT} \right) = 0 \). For hydrogen, a substance of rapidly increasing technological importance, parts of the Amagat curve are experimentally accessible with standard autoclave technology [124]. For methane and some other components of the petroleum industry, these envelopes could be reached in deep reservoirs [213] with pressures above 100 MPa [213]. For any EoS, to trace physically significant Amagat curves represents a very demanding and important test [124]. In fact, Boshkova and Deiters [124] reported the failure of PC-SAFT [50] to predict a physically coherent Amagat curve for \( \text{H}_2 \), and argued that
this problem for \( \text{H}_2 \) could be related to the effective diameter originally used in this molecular based EoS. As shown in the present section, the failure of PC-SAFT is independent of the molecular size or shape. The same researchers presented, into the framework of the Weeks-Chandler-Andersen (WCA) TPT, an approach based on the calculation of a temperature-and density-dependent effective diameter to predict coherent Amagat curves with the simplified perturbed-hard-chain theory (SPHCT) equation of state. This last EoS also is a theoretically based model like PC-SAFT. This kind of focus of an effective diameter depending on both temperature and density has not an analytical solution, and then an iterative numerical procedure must be used to fine the effective diameter value. With this approach, an EoS such as SPHCT was recommended as a reliable tool for high pressure studies [124]. In fact, semi-empirical or theoretical EoS models usually fail because these Brown’s envelopes are related to soft-core repulsions [124], [163], that usually are not well represented in these models. Particularly, the reported failure of PC-SAFT to predict physically reasonable Amagat curves for the \( \text{H}_2 \) is directly related to an inadequate inclusion of the soft-core repulsion into the mathematical expression defining its original effective diameter in PC-SAFT [124], [163].

This section is organized as follows: first, the soft-core repulsion effect is introduced by using two different theoretical approaches to define the concept of effective diameter. The approach here denoted as “BFC” is explicitly deduced into the framework of Barker and Henderson’s TPT with the purpose of being coherent with PC-SAFT. Then, the role of the soft-core repulsion is studied by using these effective diameter expressions into PC-SAFT to predict Brown’s ideal curves for seven pure components: Ar, \( \text{N}_2 \), \( \text{H}_2 \), \( \text{CO}_2 \), \( \text{CH}_4 \), \( \text{C}_4 \text{H}_{10} \), and \( \text{C}_{10} \text{H}_{22} \), representing spherical, planar, and non-spherical molecules. Afterwards, BFC is used to study the impact of varying the steepness, \( n \), of the intermolecular potential upon the characteristic curves predicted by PC-SAFT. To the best of author’s knowledge, studies like this for PC-SAFT has not been published in the literature. Finally, some conclusions are presented.

### 2.9.1 Soft-core repulsion

As already amply discussed, Gross and Sadowski [50] derived PC-SAFT by using into Barker and Henderson’s effective diameter the soft-core repulsive part given by the square well square shoulder (SWSS) potential of Chen and Kreglewski [122]. However, this potential could be considered as the simpler model that includes a soft-core repulsion, represented by the square shoulder. The resulting expression for the original PC-SAFT effective diameter of a component \( i \) is then given by
The repulsive part in eqn. (2.68) is:

\[ u_0[r = d(T)] = \frac{\xi}{\beta} = \xi kT \]  

(2.114)

Where \( \xi \) is a parameter varying commonly between 0.5 and 1.5 [215]. Here, a value equal to 1.0 was used for this parameter because two molecules moving in a three-dimensional space need that their respective velocity vectors lie on the same plane [215]. \( \xi \) could also be used as an adjustable parameter [216], but in the present work the calculations are predictive, then a value equal to 1.0 is justified.
\[ u_0(r) = \left[ 4\varepsilon \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^{n/2} \right] \text{ if } r \leq \sigma \] (2.115)

Using eqn. (2.114) into (2.115), and by applying simple algebra,

\[ 4\varepsilon \beta \left[ \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^{n/2} \right] = \xi \Rightarrow \left[ \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^{n/2} \right] = \frac{\xi}{4\beta\varepsilon} \]

\[ \Rightarrow \left[ \left( \frac{\sigma}{r} \right)^{n/2} \right]^2 - \left( \frac{\sigma}{r} \right)^{n/2} = \frac{\xi}{4\beta\varepsilon} \] (2.116)

Eqn. (2.116) has the simple form:

\[ X^2 - X - C = 0 \] (2.117)

By solving this simple quadratic equation, the following expression is obtained:

\[ r = \sigma \left[ \frac{2}{1 \pm \sqrt{1 + \frac{\xi}{\beta\varepsilon}}} \right]^{2/n} \] (2.118)

Finally, for \( r = d(T) \):

\[ d(T) = \sigma \left[ \frac{2}{1 \pm \sqrt{1 + \frac{\xi}{\beta\varepsilon}}} \right]^{2/n} \] (2.119)

In eqn. (2.119) only the positive sign in the denominator has physical meaning. Thus,

\[ d(T) = \sigma \left[ \frac{2}{1 + \sqrt{1 + \frac{\xi}{\beta\varepsilon}}} \right]^{2/n} \text{ (BFC)} \] (2.120)

Eqn. (2.120) fulfills both theoretical limits (i.e., \( d(T) \rightarrow \sigma \) as \( T \rightarrow 0 \) and \( d(T) \rightarrow 0 \) as \( T \rightarrow \infty \)). If \( n \rightarrow \infty \), then \( d(T) \rightarrow \sigma \), which is the hard-sphere diameter, and it is independent of temperature.
Hence, the soft-core repulsion contribution is given in eqn. (2.120) by the term \( \left[ \frac{2}{1 + \sqrt{1 + \frac{\xi}{\beta \epsilon}}} \right]^{2/n} \), and the stepness can be varied by changing \( n \).

A similar expression to eqn. (2.120) but picked at \( r = 2^{1/6} \sigma \) was used by Silva et al. [216] to predict self-diffusion coefficients for Lennard-Jones fluids. This \( r \)-value of \( 2^{1/6} \sigma \) is valid for the WCA TPT but not for the Barker and Henderson theory, in which the PC-SAFT EoS was founded. In fact, Deiters et al. [217], [218] also used the BCF criterion into the WCA TPT to obtain EoS models, but the resulting models never achieved practical relevance. To the best of author’s knowledge, it is the first time that eqn. (2.120) is explicitly deduced into the framework of the Barker and Henderson theory to study the role of the soft-core repulsion on the performance of PC-SAFT to predict the above-mentioned Brown’s ideal curves.

Finally, Cotterman et al. [219] numerically solved the integral of Barker and Henderson (i.e., eqn. (2.39)) by using the Lennard-Jones (LJ) soft-core potential, instead of the simple square shoulder chosen by Gross and Sadowski [50]. The numerical results were correlated by those authors as a function of the reduced temperature, \( \tilde{T} \):

\[
d(\tilde{T}) = \sigma \frac{1 + 0.29770 \tilde{T}}{1 + 0.033163 \tilde{T} + 0.0010477 \tilde{T}^2}
\]

Eqn. (2.121) is considered as one of the best correlations to represent the Barker and Henderson diameter for the LJ potential and meets both theoretical limits [220]. This correlation is valid for \( 0 < \tilde{T} < 15 \). In fact, Tang et al. [147], [220], [221] used eqn. (2.121) to improve a TPT based on the mean spherical approximation (MSA) and found that a bad representation of the soft-core repulsion could spoil a TPT. Polishuk [222] also proposed to replace eqn. (2.40) of PC-SAFT by eqn. (2.121) to improve the performance of PC-SAFT for thermodynamic calculations. Furthermore, that researcher proposed eqn. (2.121) to predict coherent Amagat curves, because this expression, based upon the Lennard-Jones potential, has a softer repulsion than the square-shoulder model used originally by Gross and Sadowski [50]. However, unfortunately, Polishuk [222] did not report calculations of Brown’s ideal curves with PC-SAFT using that equation.
2.9.2 Results and Discussion

Figures 2-59 to 2-65 depict comparative results of Brown’s ideal curves predicted by PC-SAFT for Ar, N₂, H₂, CO₂, CH₄, C₄H₁₀, and C₁₀H₂₂, respectively. Here, reduced temperatures and pressures were used (i.e., $T/T_C$ and $P/P_C$). These figures clearly show that the soft-core repulsion model, given by the square-shoulder potential, and represented in the original PC-SAFT by eqn. (2.40) (panels A in all these figures), is not able to predict physically coherent Amagat curves. On the other hand, no problem is found in predicting the Boyle and Charles ones. In contrast, both Cotterman (panels B in all these figures) and BFC with $n = 12$ (panels C in all these figures) approaches, produce coherent Brown’s characteristic envelopes, with similar dome-shaped curves, for all the modeled substances. BFC commonly predicts Amagat curves extended towards higher temperatures than Cotterman, which means that BFC results in higher temperatures at which $dB/dT = 0$ than Cotterman. In contrast, Cotterman predicts higher maximum pressures. The similarity in shapes given by PC-SAFT for both BFC and Cotterman in those figures is coherent with the fact that these effective diameter models use the Lennard-Jones intermolecular potential to consider the soft-core repulsive wall. However, the differences in the predictions are mainly due to the distinct theoretical approaches followed to obtain the respective effective diameter mathematical expressions (i.e., eqn. (2.39) versus eqn. (2.114)). As explained above, the theoretical conceptions and simplifications used by Barker and Henderson are not the same to those supporting the BFC approach. The last one approach is simpler, theoretically based, and permits to obtain effective diameter expressions by easy algebraic manipulation. Additionally, BFC is completely analytical and does not require a numerical correlation.
Figure 2-59: Characteristic Curves for Ar predicted by PC-SAFT. (A) Original. (B) Cotterman. (C) BFC. — Amagat, ---- Charles, ⋅⋅ Boyle, ⋅⋅⋅ Tegeler et al. correlation [223].

(A)

(B)

(C)
Figure 2-60: Characteristic Curves for N$_2$ predicted by PC-SAFT. (A) Original. (B) Cotterman. (C) BFC. — Amagat, ---- Charles, ⋅ ⋅ ⋅ Boyle, ⋅ ⋅ ⋅ Span et al. correlation [224].
Figure 2-61: Characteristic Curves for $H_2$ predicted by PC-SAFT. (A) Original. (B) Cotterman. (C) BFC. — Amagat, ---- Charles, … Boyle.
**Figure 2-62:** Characteristic Curves for CO$_2$ predicted by PC-SAFT. (A) Original. (B) Cotterman. (C) BFC. — Amagat, ---- Charles, ·· Boyle, ·—· Span and Wagner correlation [225].
Figure 2-63: Characteristic Curves for CH$_4$ predicted by PC-SAFT. (A) Original. (B) Cotterman. (C) BFC. — Amagat, ---- Charles, ··· Boyle.
Figure 2-64: Characteristic Curves for \( \text{C}_4\text{H}_{10} \) predicted by PC-SAFT. (A) Original. (B) Cotterman. (C) BFC. — Amagat, ---- Charles, ‒‒ Boyle.
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**Figure 2-65:** Characteristic Curves for \( C_{10}H_{22} \) predicted by PC-SAFT. (A) Original. (B) Cotterman. (C) BFC. — Amagat, ---- Charles, ∙∙∙ Boyle.

![Characteristic Curves](image)

Figures 2-66 to 2-72 depict sensibilities of Brown’s ideal curves predicted by PC-SAFT for Ar, \( N_2 \), H\(_2\), CO\(_2\), CH\(_4\), C\(_4\)H\(_{10}\), and C\(_{10}\)H\(_{22}\), by varying the steepness, \( n \), into the BFC model. For this goal, \( n \)-values of 12, 18, 36, 54, and infinity, were used in eqn. (2.120). As can be seen, at higher \( n \)-values, representing a greater steepness (i.e., less softness), Amagat curves are displaced towards high pressures and temperatures, resulting in higher temperatures to obtain the condition where \( \frac{dB}{dT} = 0 \). At high pressures and temperatures, Amagat curves are more sensitive to the potential’s steepness because under these conditions the molecules spend most of the time at the soft repulsive branch of the intermolecular potential [226]. But, as expected, coherent Amagat curves were not possible of obtaining for \( n \) equal to infinity, which represents the hard-core limit. Additionally, problems to
predict Amagat curves with PC-SAFT were found for CO₂ at \( n \)-values of 36 and 54. A similar result occurs for C₄H₁₀ at \( n \)-value of 54, and for C₁₀H₂₂ at \( n \)-values of 18, 36 and 54. For this last component only the \( n \)-value equal to 12 (i.e., Lennard-Jones potential) produced a correct dome-shaped curve.

**Figure 2-66:** BFC. Characteristic Curves for Ar predicted by PC-SAFT. (A) Amagat. (B) Charles. (C) Boyle. \( \cdots n = 12, \quad \cdots n = 18, \quad \cdots n = 36, \quad \cdots n = 54; \quad \cdots n = \text{infinity}. \)
Figure 2-67: BFC. Characteristic Curves for N\textsubscript{2} predicted by PC-SAFT. (A) Amagat. (B) Charles. (C) Boyle. \( n = 12, \ldots, n = 18, \cdots n = 36, \ldots n = 54; \ldots n = \infty. \)
Figure 2-68: BFC. Characteristic Curves for H₂ predicted by PC-SAFT. (A) Amagat. (B) Charles. (C) Boyle. ⋅ ⋅ ⋅ \( n = 12 \), --- \( n = 18 \), — — — \( n = 36 \), – – – \( n = 54 \); — — \( n = \text{infinity} \).
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**Figure 2-69:** BFC. Characteristic Curves for CO₂ predicted by PC-SAFT. (A) Amagat. (B) Charles. (C) Boyle. ⋯ \( n = 12 \), ⋅ ⋅ ⋅ \( n = 18 \), ⋅ ⋅ ⋅ \( n = 36 \), ⋅ ⋅ ⋅ \( n = 54 \); ⋅ ⋅ ⋅ \( n = \) infinity.
Figure 2-70: BFC. Characteristic Curves for CH₄ predicted by PC-SAFT. (A) Amagat. (B) Charles. (C) Boyle. ∙∙∙ n = 12, ---- n = 18, —— n = 36, – – n = 54; — n = infinity.
Figure 2-71:  BFC. Characteristic Curves for \( \text{C}_4\text{H}_{10} \) predicted by PC-SAFT. (A) Amagat. (C) Charles. (C) Boyle. \( \cdots n = 12, \ldots \cdots \ldots \ldots n = 18, \ldots n = 36, \ldots \cdots n = 54; \ldots n = \text{infinity}. \)
**Figure 2-72:** BFC Characteristic Curves for C_{10}H_{22} predicted by PC-SAFT. (a) Amagat. (b) Charles. (c) Boyle. ⋅ ⋅ n = 12, ---- n = 18, — — n = 36, · · · n = 54; — n.

PC-SAFT with the BFC model always predicted a condition at which $\frac{dB}{dT} = 0$ for the seven components, and for all n-values, except for n equal to infinity. This behavior clearly is distinct to that found in figures 2-59 to 2-65 for the original PC-SAFT (i.e., panels A in figures 2-59 to 2-65), wherein it was impossible to obtain dome-shaped Amagat curves. Thus, the problems to obtain smooth dome-shaped Amagat curves for CO_{2}, C_{4}H_{10}, and C_{10}H_{22}, for some n-values, are numerical in nature and are not directly attributable to failures of the BFC model. Figure 2-65, panel A, presents a strange shape of Amagat curve for C_{10}H_{22} at low temperature, which could be due to an artificial second-critical point predicted by the original PC-SAFT, as was discussed by Polishuk et al. [182].
However, the important point to be highlighted here is that this strange behavior disappears by using a soft-core expression different to that used in the original PC-SAFT.

As was emphasized above, all the calculations here presented are completely predictive, because the goal in this work is to study the effect of the soft-repulsion upon the capability of PC-SAFT of predicting coherent Brown's ideal curves, especially the Amagat ones. For this reason, the original low-pressure and-temperature PC-SAFT parameters were used, although a parametric re-fitting step would be more advisable for practical calculations under extreme conditions of pressure and temperature [159]. With that in mind, figure 2-59 (Ar), figure 2-60 (N_2), and figure 2-62 (CO_2) also present Amagat curves obtained from empirical correlations published in the literature [223]-[225]. These Figures show that Amagat’s curves predicted by the Cotterman [219] expression and the BFC model compare well with the respective empirical correlations, being the BFC model closer than the Cotterman one to the data from those correlations. However, it is very important to stress that Amagat’s curves given by the empirical correlations (i.e., empirical EoS models) [223]-[225] at the highest temperatures really are estimations/extrapolations, because Amagat’s curves are out of the range experimentally accessible under those conditions [223]-[225]. Then, the comparisons between PC-SAFT and those correlations should be taken with caution. Parsafar and Izanloo (see Figure 7 in [211]) realized a similar comparison for Ar, N_2, and CO_2 among the Amagat curves predicted by other EoS models and the same empirical correlations here used [223]-[225].

Finally, as seen from figures 2-66 to 2-72, Boyle and Charles curves behave contrary to the Amagat ones, showing a shrinkage of the respective envelopes as n is increased. Notice that PC-SAFT has not problems in tracing the Boyle and Charles curves, but the Amagat curves are really a demanding test for this EoS. The success of predicting these curves depends heavily on the soft-repulsion model used. Note that eqn. (2.40) and eqn. (2.121) are obtained by using the same theorical approach (i.e., eqn. 2.39 of Barker and Henderson) to determine the soft-core (effective) diameters, but for eqn. (2.40) the softness given by the square shoulder repulsion from the SWSS potential is not enough to predict physically coherent Amagat curves.

As a matter of fact, eqn. (2.40), which is used originally for PC-SAFT, should be replaced by an expression such as BFC (i.e., eqn. (2.120)) for performing calculations of Amagat’s curves. Clearly, a temperature dependent effective diameter is enough for predicting physically reasonable Amagat curves with PC-SAFT, and then an effective diameter that depends on both temperature and density is not required for that purpose. Nevertheless, as explained before, a density-temperature dependent
effective diameter is a most rigorous approach, and, as already discussed in sections above, it is necessary for other kind of thermodynamic calculations, mainly at low temperatures, wherein the higher terms in the expansion given by the Barker and Henderson’s TPT are more important [33], [34], [147].

2.9.3 Conclusions for section 2.9

The role of the soft-core repulsion upon the prediction of the Brown’s characteristic (Amagat, Boyle, and Charles) curves with PC-SAFT was presented for seven pure components: Ar, N₂, H₂, CO₂, CH₄, C₄H₁₀, and C₁₀H₂₂, representing spherical, planar, and non-spherical components. To predict physically reasonable Amagat curves is really a demanding test for PC-SAFT, and the success depends heavily on the soft-repulsion model used to obtain the effective diameter expression. The soft-core potential in the original PC-SAFT cannot trace coherent Amagat curves. In contrast, both BFC and Cotterman models, based upon Lennard-Jones potential, were successful in achieving this goal. Finally, the Amagat curves showed an increment in temperatures and pressures at higher steepness, but a contrary behavior happened for the Boyle and Charles envelopes. The BFC model is analytical and simple, has theoretical basis, and predicts physically coherent dome shaped Amagat curves. This model is a good candidate to replace the approach used in the original PC-SAFT, particularly to perform calculations of Amagat curves. An effective diameter that depends on both temperature and density is not required for tracing this kind of Brown’s ideal curves.

2.10 The performance of the new second-order dispersive term combined with a hard-core repulsion to predict AOPs for reservoir fluids.

The second-order perturbation term deduced in this thesis (section 2.3) was used in combination with a hard-sphere diameter independent of the thermodynamic state. In other words, \( d = \sigma \). In the literature, it is common to find EoS models that use different approaches to consider the variation in the molecular diameters (or segments) with changes in the thermodynamic state. Some EoS models define \( d(T) = \sigma f(T, \rho) \) [124, 148, 165, 233], other EoS consider this diameter as depending on temperature only (i.e., \( d(T) = \sigma f(T) \)) [50, 105, 122, 138], and many other models simply assume that the diameter is independent of the thermodynamic state. In this last group, models such as the
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conventional cubic EoS models [68, 69], Perturbed Hard Chain theory (PHCT) [234], Simplified Perturbed Hard Chain theory (SPHCT) [235], SAFT-HS [236], SAFT-VR [110], Cubic Plus Association (CPA) [95], and, recently, Cubic Plus Chain (CPC) [237] can be considered as typical examples.

Then, in this section, the new second-order dispersion term developed in this thesis is used in combination with an “effective diameter” independent of temperature and density (i.e., \( d = \sigma \)), and the resulting model is used to model AOPs for several real reservoir fluids around the world.

From eqn. 2.14, the packing fraction is expressed simply as \( \eta = \frac{\pi d}{6} \sum x_i m_i \sigma_i^3 \). In other words, the “soft-core” diameter is replaced by the hard-cord diameter. The packing fraction really affects both the repulsion term and the dispersion contribution. Thus, eqn. 2.2 is here replaced by,

\[
\frac{A_0}{NkT} = \frac{A_{HS}}{NkT} = \frac{A_{hc}}{NkT} = \bar{m} \frac{A_{hs}}{NkT} - \sum x_i (m_i - 1) \ln \left( g_{ii}^{hs} \right)
\] (2.122)

Wherein the Helmholtz free energy for the reference fluid, \( \frac{A_0}{NkT} \), is exactly the energy of a chain formed by hard-spheres, \( \frac{A_{HS}}{NkT} \). Then, this chain is athermal.

By combining eqn. 2.122 with the new second-order dispersion given by eqn. 2-33, a Hard Sphere - PC-SAFT model is obtained (hereafter called HS-PC-SAFT-mod). Obviously, a HS-PC-SAFT version is also obtained by using eqn. 2.122 in combination with the original second-dispersion term given by Gross and Sadowski (i.e., eqn. 2.32).

Recently, Abutaqiya et al., [238] published four petroleum reservoir fluids from the Middle East (M13, M15, M30, and M36), and showed that the original PC-SAFT EoS is unable to reproduce the AOPs for these reservoir mixtures. Moreover, a cubic EoS as Peng-Robinson performed better than PC-SAFT for these specific fluids (see figure 9 in [238]). Then, these four fluids were modeled in the present thesis by using the original PC-SAFT, HS-PC-SAFT, and HS-PC-SAFT-mod.

Figure 2-73 depicts the comparison for the three EoS models for fluid M13, M15, M30, and M36.
As noted, the original PC-SAFT (black curves) is unable to reproduce the AOP experimental data, even though high asphaltene molecular weights of 3500, 5000, 6150, and 7000 were used to try to flatten the predicted AOP curves. In fact, the results here shown for the original PC-SAFT are similar to those reported by Abutaqiya et al. [238], who used molecular weights for the asphaltene component of 5900, 3006, 6298, and 7240. It is important to highlight that the strategy for characterizing the reservoir fluids used by Abutaqiya et al. [238] is different from the one used in this thesis. Then, the failure of the original PC-SAFT is independent of the characterization method used to describe the reservoir mixtures.

On the other hand, HS-PC-SAFT (green curves) performs better than the original PC-SAFT, but the performance deteriorates at lower temperatures. On the contrary, HS-PC-SAFT-mod (red curves)
behaves very well, and this last model has no problem in reproducing the experimental AOPs. Moreover, this model can predict AOPs at very low temperatures. In fact, molecular weights for the asphaltene component of 1550, 550, 1650, and 2000 for M15, M30, and M36, respectively, were required by HS-PC-SAFT-mod to reproduce these three fluids without difficulty. Moreover, the numerical stability shown by this model is excellent.

Figure 2-74 presents similar calculations for four fluids from Kuwait. Here called as K1 [151], K2 [186], K3 [151], and K4 [151].

Figure 2-74: Four fluids from Kuwait. K1, K2, K3, and K4. --- PC-SAFT (AOP), --- HS-PC-SAFT (AOP), --- HS-PC-SAFT-mod (AOP), ---- PC-SAFT (BP), ---- HS-PC-SAFT (BP), --- HS-PC-SAFT-mod (BP), ∆ Exp. BP, ○ Exp. AOP.
As noted, HS-PC-SAFT-mod (red curves) performs very well for these other four fluids and predicts “smooth” AOP curves. For this model, the asphaltene molecular weights for these fluids were 485, 700, 600, and 650, for fluids F1, F2, F3, and F4, respectively.

Figure 2-75 presents the comparative results for four fluids from the Gulf of Mexico (GoM): G1 [154], G2 [154], G3 [155], and G4 [155].

**Figure 2-75:** Four fluids from the Gulf of Mexico (GoM). G1, G2, G3, and G4 --- PC-SAFT (AOP), --- HS-PC-SAFT (AOP), --- HS-PC-SAFT-mod (AOP), ---- PC-SAFT (BP), ---- HS-PC-SAFT (BP), ---- HS-PC-SAFT-mod (BP), Δ Exp. BP, * Exp. AOP
Again, HS-PC-SAFT-mod (red curve) models the AOPs for these GoM fluids with excellent performance, even though the asphaltene content in the SARA analysis can be as high as 16 wt%, as is the case for fluid G3. Moreover, the asphaltene molecular weight used in HS-PC-SAFT-mod for this last fluid was 1600; while 5000 and 3500 were used for PC-SAFT, and HS-PC-SAFT, respectively, to try to improve the performance of these models, but the results were not satisfactory. The good numerical stability was again evidenced for the HS-PC-SAFT-mod.

Finally, figure 2-76 presents the same comparison for three fluids from South America: S1, S2, and S3.

**Figure 2-76:** Three fluids from South America. S1, S2, and S3. ____ PC-SAFT (AOP), _____ HS-PC-SAFT (AOP), _____ HS-PC-SAFT-mod (AOP), ---- PC-SAFT (BP), ---- HS-PC-SAFT (BP), ---- HS-PC-SAFT-mod (BP), ∆ Exp. BP, o Exp. AOP
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For these three fluids from South America, the results are similar, HS-PC-SAFT-mod performs excellent, and the numerical stability is very good.

2.10.1 Conclusions for section 2.10

In this section, a new thermodynamic model resultant of combining the new second-order dispersion term developed in section 2.3, and the concept of a hard-sphere diameter independent of the thermodynamic state was formulated and discussed (here called as HS-PC-SAFT-mod). Then, the resulting model was compared with the original PC-SAFT EoS, and also with the version of this EoS resultant of using the original second-order dispersion term in combination with the hard-sphere diameter independent on the thermodynamic state (i.e., HS-PC-SAFT) to model AOPs for fifteen petroleum fluids prone to precipitate asphaltenes from several assets around the world. The results show that the HS-PC-SAFT-mod here presented performs very well to models the AOPs, with excellent numerical stability. In addition, this model predicts AOPs at very low temperatures and requires asphaltene molecular weight values very much low than the other two models. HS-PC-SAFT-mod is really fast in convergence, and it is a serious candidate to be incorporated into an engineering simulator for flow assurance calculations.

2.11 Application to reservoir fluids prone to asphaltene precipitation

The main focus of this thesis was to model asphaltene onset pressures (AOPs) for petroleum reservoir fluids prone to precipitate this kind of dense organic material. This phenomenon represents one of the most difficult issues to be modeled and solved in the petroleum industry. In fact, one of the principal problems to develop thermodynamic models to predict the asphaltene precipitation from any reservoir fluid is the absence of a complete molecular characterization for the most polar/polarizable fraction, called generically “asphaltene” [156]. This “asphaltene” is commonly defined, in a simplified way, as a class of solubility [83], and represents the fraction from the reservoir fluid soluble in aromatic solvents by insoluble en n-alkanes [80, 84, 85]. Developments in the chemical/molecular comprehension for this “asphaltene” fraction, based on petroleomics, search to “reveal” the real identity of this “component” of the petroleum fluids [156]. These asphaltenes have the tendency of aggregation by changes mainly in pressure, temperature, and composition [85,
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The EoS models developed in this thesis, such as HS-PC-SAFT-mod and those with an effective diameter dependent on temperature and density, could be used as a basis to predict and regress experimental AOPs. To locate the AOP curves is fundamental to any EoS expected to model asphaltene precipitation because these curves represent the initial conditions for the precipitation, and perhaps the subsequent deposition, of asphaltic phases in a petroleum reservoir. Although asphaltene precipitation is a necessary condition for deposition, sometimes asphaltenes come out of the solution and do not adhere to the surfaces [158]. The topic of flow assurance related to asphaltene precipitation/deposition can represent huge losses in the production of hydrocarbons from petroleum reservoirs [239]. In offshore projects, “the cost of remediating an unexpected asphaltene problem is excessive. It is imperative that the behavior of asphaltenes in an offshore production system be understood in the design stage of the project. Proper control and remediation strategies must be built into the system from the beginning” [156]. For instance, Leontaritis et al. [240] reported that “in the Prinos field in the North Aegean Sea there were wells that, especially at the start of production, would completely cease flowing in a matter of a few days after an initial production rate of up to 3,000 BPD. The economic implications of this problem were tremendous considering the fact that a problem well workover cost could get as high as a quarter of a million dollars”. Also, in onshore assets the costs by each can be very high. Belhaj et al. [241] published that “several major onshore fields in Abu Dhabi are challenged with asphaltene deposition in their producing wells. One asphaltene clean-up operation using organic solvents and coiled tubing unit costs US $200,000. In addition, during the existence of the CO2 pilot project three asphaltene removal jobs were conducted. Asphaltene remediation techniques are very expensive with the potential impact on health and environment”. In deepwater projects, the costs are really impressive. For example, for a real field in the Gulf of Mexico, the asphaltene prevention/remediation costs were close to US $4.000.000 per year, and the production losses were calculated in US $54.000.000 per year [242].

For the above, to have EoS models with the capability of predicting/reproducing AOP curves represent a key tool in the general strategy of the flow assurance discipline to study scenarios involving asphaltene precipitation/deposition under changes in temperature, pressure, and composition [88-94].
3. Conclusions and recommendations

3.1 Conclusions

- For the first time, a modified Barker and Henderson’s second-order perturbation term was introduced into PC-SAFT EoS by suppressing its “non-correlated fluid shells” assumption. This modification produces a PC-SAFT version that predicts lower AOPs, MUCSTs, and CPs than the original EoS. In addition, this fact reduces the liquid-liquid region at the same temperature, increasing the isotropic fluid region. A new model, called HS-PC-SAFT-mod, was also formulated, and used to carry out AOP calculations for fluids around the world, showing excellent performance.

- For the first time, temperature-and density-effective diameter expressions were theoretically deduced and used with PC-SAFT EoS to predict AOPs, CPs, crossover temperatures, MUSTs, and HAOPs. These new expressions of effective diameter are polynomials and can be easily solved by a simple numerical routine.

- Globally, the results show that PC-SAFT with the new temperature-and density-dependent effective diameters substantially increase the isotropic fluid region, reducing the tendency of this EoS of predicting high densities, that fall within metastable states; in which, as well known, the TPTs fail. For simple systems, at ordinary conditions, the effect of density upon the effective diameter is generally irrelevant.

- For the first time, Heyes’s approach to Rowlinson’s TPT is used to theoretically deduce temperature-and density-dependent effective diameters. Both TPTs, as formulated respectively by Tang and Heyes, predict similar density-and temperature-dependent effective diameters for steep repulsive potentials, and this concordance increases at lower packing fractions and higher steepness values.
From a general viewpoint, the approaches by Tang and Heyes are exchangeable. Nevertheless, for Chen and Kreglewski’s SWSS potential, Heyes’s approach produced a simple cubic polynomial for the effective diameter that can be analytically solved. Thus, that expression could be introduced into based-molecular EoS models like PC-SAFT to perform phase equilibrium calculations, mainly for dense phases at low temperatures or high pressures. Conditions in which an effective diameter dependent upon both temperature and density is most relevant.

Two set of PC-SAFT universal constants and two effective diameter expressions were combined to predict different thermodynamic phase equilibria for simple and complex fluid mixtures. For simple mixtures, the variations in PC-SAFT universal constants or effective diameter expressions did not have a significant influence upon the predictions. Nevertheless, for complex mixtures characterized by denser fluids, the predicted effect on the liquid-liquid phase behavior is evident.

The PC-SAFT version given by the Liang-Kontogeorgis universal constants (LKUCs) plus a temperature-and density-dependent effective diameter, LK-PC-SAFT- d (T, ρ), generally predicted lower cloud-points and AOPs than the other versions used here, causing a significant reduction of the liquid-liquid region. On the contrary to the liquid-liquid equilibria, the liquid-vapor equilibria showed to be significatively insensitive to the PC-SAFT versions here studied.

The original PC-SAFT universal constants (GSUCs) should not be used due to their numerical drawbacks and the tendency of predicting densities belonging to metastable conditions.

LK-PC-SAFT- d (T, ρ) also generally predicts lower UAOPs and MUCST than the other combinations investigated. That combination produces the lowest densities for the global and incipient liquid phases at the AOPs for petroleum mixtures prone to precipitate asphaltenes. Moreover, LKUCs try to suppress or eliminate the predictions of HAOP curves. Hence, LK-PC-SAFT- d (T, ρ) increases the range of isotropic fluid conditions, in which the TPTs are expected to perform better. Phase behavior predictions with SAFT-type versions at packing fractions superior to η ≅ 0.492 should be considered with caution.

LK- PC- SAFT- d (T, ρ) predicts also the lowest LAOPs. Thus, this model produces the most shrunken asphaltene precipitation diagrams and reduces the pressure ranges in which the asphaltene precipitation occurs. Gross and Sadowski universal constants (GSUCs) should not be
used in modeling complex mixtures like petroleum ones because of their tendency of predict multiple fluid roots and metastable states.

- A temperature-and density-dependent effective diameter moves the predicted crossover temperatures towards lower values. On the contrary, these crossover temperatures are insensitive to changes in the universal constants of PC-SAFT.

- Both Tang’s RDF and the new hard-sphere RDF presented by fitting Largo’s MC data appear to be practical and simple hard-sphere RDF models to calculate effective diameters. Speaking strictly, the last one is most exact, and, to the author’s knowledge, a similar expression has not been published in the literature. Moreover, the RDF obtained in this thesis could be very useful in other topics related to the theory of molecular fluids. From a practical viewpoint, Tang’s RDF has the advantage of producing a cubic polynomial for the temperature-and density-dependent effective diameter in the framework of Heyes’s approach (i.e., eqn. 2.78) instead of a fifth-degree polynomial obtained by using the new RDF.

- To predict coherent Amagat curves are a challenge for PC-SAFT. The soft-core potential in the original PC-SAFT effective diameter is shown to be responsible for this failure. In contrast, temperature dependent effective diameter like BFC and Cotterman were successful in achieving this goal. Those two last models use the Lennard-Jones potential to introduce the soft-core repulsion.

- As demonstrated in this thesis, an effective diameter that depends on both temperature and density is not required for tracing coherent Amagat curves. Thus, the important point is to use an enoughly “soft-core” intermolecular potential into the effective diameter definition.

- The inclusion of most sophisticated “soft-core” repulsion potentials to improve the Amagat predictions with PC-SAFT could produce density-and temperature-dependent effective diameter expressions most complex, requiring solving numerical integrals to obtain the effective diameter for each segment or molecule. The last fact could be impractical for some time-demanding engineering calculations, for instance those related to petroleum reservoir simulators.
To change the universal constants in PC-SAFT did not improve its performance for predicting coherent Amagat curves. Because, as amply discussed in this dissertation, Amagat’s curves are mainly influenced by the “soft-core” repulsion included in the effective diameter. On the contrary, the universal constants in PC-SAFT are intimately related to the attractive contribution.

3.2 Recommendations

- As discussed in chapters 1 and 2, Gross and Sadowski chosen the “local compressibility approximation” from Barker and Henderson to develop PC-SAFT to define the second-order perturbation term (see eqn. 1.11). i.e.,

$$\beta A_2 = -\pi N p k T \int_0^\infty [u_1^*(r)]^2 \left( \frac{\partial \rho g_0}{\partial p} \right)_0 r^2 dr$$

Nonetheless, the “macroscopic compressibility approximation” is simpler because the compressibility term, $$\left( \frac{\partial \rho}{\partial p} \right)_0$$, is out of the integral (see eqn. 1.10). i.e.,

$$\beta A_2 = -\pi N p k T \left( \frac{\partial \rho}{\partial p} \right)_0 \int_0^\infty g_0(r)[u_1^*(r)]^2 r^2 dr$$

As emphasized by Barker and Henderson, any of those approaches could be used to define this perturbation term [33, 35]. Then, it would be very interesting to explore the development of a “modified PC-SAFT” by using the “macroscopic approximation”, because, in principle, that EoS could be numerically simpler and “faster” to run into a simulator.

- As was discussed before, the common assumption into the theoretically based EoS models, like PC-SAFT, is to take as reference system a “hard-sphere” or a “hard-sphere chain”. Nevertheless, other kind of “hard-core” geometry could be explored in the future. For instance, enough molecular simulation data exist for the RDF and EoS of a “hard-disk” [227]-[229] or their mixtures [230]-[232]. In fact, it could be very interesting to model some molecules as disks instead of spheres. For example, monomers of asphaltenes, caffeine, and so on. These molecules have aromatic and/or naphtenic rings, and a disk could be a picture most representative of their structure than a sphere [78].
A. Appendix: Levenberg-Marquardt (LM)

\[ m = (1 - \gamma)(0.0223MW + 0.751) + \gamma(0.0101MW + 1.7296) \]

\[ \sigma = (1 - \gamma)\left(4.1377 - \frac{20.1482}{MW}\right) + \gamma\left(4.6169 - \frac{93.90}{MW}\right) \]

\[ \frac{\varsigma}{\kappa} = (1 - \gamma)(0.00436MW + 283.93) + \gamma\left(508 - \frac{2344.82}{MW^{0.15}}\right) \]

\[ m = 1 \]

\[ (k_{ij})^{m+1} = x^m(k_{ij})^0 \]

\[ (\varsigma/\kappa)^{m+1} = \psi^m(\varsigma/\kappa)^0 \]

Bubblepoint & AOP fitted

LM ROUTINE

PC-SAFT parameters output
B. Appendix: Characterization Fluids 1-6 (Section 2.5) for four PC-SAFT models
### Table B1. Characterization Fluid 1 (Section 2.5) for four PC-SAFT models

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**GS-PC-SAFT**

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**GS-PC-SAFT dT & p**

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Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation
Table B3. Characterization Fluid 3 (Section 2.5) for four PC-SAFT models.

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<th>( \epsilon_{\text{ps}} / \text{K} )</th>
<th>Binary Interaction Coefficients</th>
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<td>1.206</td>
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<td>2.785</td>
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Table B6. Characterization Fluid 6 (Section 2.5) for four PC-SAFT models.

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C. Appendix: Characterization Fluids 1-6 (Section 2.6) for four PC-SAFT models
Table C1. Characterization Fluid 1 (Section 2.6) for four PC-SAFT models.

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**GS-PC-SAFT**

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Table C3. Characterization Fluid 3 (Section 2.6) for four PC-SAFT models.

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Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation.
Table C4. Characterization Fluid 4 (Section 2.6) for four PC-SAFT models.

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GS-PC-SAFT

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Development of an equation of state based on thermodynamic perturbation theory (TPT) for mixtures prone to asphaltene precipitation

Table C5. Characterization Fluid 5 (Section 2.6) for four PC-SAFT models.

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GS-PC-SAFT

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LK-PC-SAFT

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GS-PC-SAFT-d(T & ρ)

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LK-PC-SAFT-d(T & ρ)

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**Binary Interaction Coefficients**

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**Binary Interaction Coefficients**
D. Appendix: Largo’s MC data fitted in this thesis to a sixth-degree polynomial

Largo’s MC simulation data [7] of the hard-sphere RDF, $g_{HS}(x)$, for $0.1 \leq \rho \sigma^3 \leq 0.9$ (i.e., $0.052 \leq \eta \leq 0.471$), and $1 \leq x \equiv \frac{r}{\sigma} \leq 2.99$, are exactly fitted in this dissertation as follows:

$$g_{HS}(x) = \sigma_0 + \sigma_1 x^2 + \sigma_2 x^2 + \sigma_3 x^3 + \sigma_4 x^4 + \sigma_5 x^5 + \sigma_6 x^6$$ (D.1)

Wherein $\sigma$ is the hard-sphere diameter. $\sigma_0, \sigma_1, \sigma_2, \ldots \sigma_6$, are parameters that depend on the packing fraction (i.e., reduced density). In this work, these parameters are exactly fitted by the following equations:

$$\sigma_0 (\eta) = -1239.3\eta^6 + 90978\eta^5 - 52967\eta^4 + 18450\eta^3 - 2832.1\eta^2 + 288.31\eta - 8.7097; R^2 = 1$$ (D.2)

$$\sigma_1 (\eta) = 55389\eta^6 - 410223\eta^5 + 241263\eta^4 - 81507\eta^3 + 12724 \eta^2 - 1212.6\eta + 40.627; R^2 = 1$$ (D.3)

$$\sigma_2 (\eta) = -161214\eta^6 + 733550\eta^5 - 433864\eta^4 + 143872\eta^3 - 22625 \eta^2 + 2087.9\eta - 68.759; R^2 = 1$$ (D.4)

$$\sigma_3 (\eta) = 199261\eta^6 - 686398\eta^5 + 406601\eta^4 - 132839\eta^3 + 20918\eta^2 - 1885.6\eta + 60.872; R^2 = 1$$ (D.5)

$$\sigma_4 (\eta) = -115712\eta^6 + 343009\eta^5 - 203226\eta^4 + 65844\eta^3 - 10382\eta^2 + 921.77\eta - 29.341; R^2 = 1$$ (D.6)
Appendix D: Largo’s MC data fitted in this thesis to a sixth-degree polynomial

\[ \sigma_5(\eta) = 34118\eta^6 - 90189\eta^5 + 53355\eta^4 - 17145\eta^3 + 2702.5\eta^2 - 236.11\eta + 7.4204; \quad R^2 = 1 \]  \hspace{1cm} (D.6)

\[ \sigma_6(\eta) = -4033.4\eta^6 + 9759.1\eta^5 - 5764.2\eta^4 + 1837.6\eta^3 - 289.38\eta^2 + 24.845\eta - 0.7716; \quad R^2 = 1 \]  \hspace{1cm} (D.7)
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