RICE UNIVERSITY

Modeling of Asphaltene Precipitation and Arterial Deposition

by

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ABSTRACT

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The potential problem produced by asphaltene deposition during oil production has motivated the development of several experimental techniques and theoretical models, trying to understand and predict the asphaltene behavior. Despite the work devoted to understanding this subject, asphaltene deposition still represents a challenging unresolved problem.

Predicting asphaltene flow assurance issues requires the ability to model phase behavior of asphaltenes as a function of temperature, pressure, and composition. It has been previously shown that the Perturbed Chain form of the Statistical Associating Fluid Theory equation of state (PC-SAFT EOS) accurately predicts crude oil bubble point and density as well as asphaltene precipitation conditions. This approach has been used to examine the effects of gas injection, oil based mud contamination, and asphaltene polydispersity on the phase behavior of asphaltenes. In this work, a new application of the PC-SAFT EOS in studying the effect of carbon dioxide injection reveals an interesting dual effect of this compound in inducing or preventing asphaltene precipitation, depending on the operating conditions.

Novel tools for understanding and predicting properties of hydrocarbon and crude oil systems are also presented and discussed. These tools include the One-Third Rule –a
correlation between refractive index and mass density-, a revised solubility parameter modeling approach that includes an improved mixing rule for solubility parameters, and the development of a general method for modeling asphaltene stability.

The development of a simulation tool that simultaneously accounts for asphaltene precipitation, aggregation and deposition is also presented and discussed. The thermodynamic modeling using the PC-SAFT EOS is coupled with kinetic models and transport equations. The mechanism for asphaltene precipitation and deposition proposed in this work has been found to be consistent with various experiments and field observations. Furthermore, it also provides an explanation to some paradoxes, such as why some asphaltene precipitation inhibitors worsen asphaltene deposition or why strong asphaltene precipitants, such as propane, produce less amount of deposit.

The work presented in this dissertation will contribute in the development of a foundation for oil sample analysis and simulations that can predict the likelihood of asphaltene deposition in the newly found oil fields worldwide.
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Greek Symbols

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<tr>
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<tr>
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<td>axial distance, $= z/L$</td>
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Subscripts

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<td>dead oil</td>
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Chapter 1. Introduction

1.1 Research Motivation

Asphaltenes constitute a potential problem in oil production because of the tendency of this petroleum fraction to precipitate and deposit due to changes in temperature, pressure and composition. The ability to predict the occurrence and magnitude of asphaltene deposition in wellbores and flow lines is key in the flow assurance effort. The cost of installing and maintaining asphaltene mitigation equipment and chemicals is in the millions of dollars per year. Failure to anticipate asphaltene deposition can cost the operator in terms of remediation and production loss. Conversely, accurate prediction of deposition can enable differentiation between cases with substantially impaired production requiring well intervention from those with minimal or no wellbore deposition. This knowledge could save the expense of installing unnecessary equipment and injecting chemical inhibitors when they are not needed as well as helping the development of improved chemicals for prevention of wellbore deposition problems. As discoveries are made in deeper water, one trend is the increase in instability for asphaltenes in these crudes. Newer discoveries are giving indications that deposition in producer wellbores is likely and it is expected that these reservoir fluids will become the asphaltene production problems of the future.
1.2 Objectives

The aim of this study is to contribute to the understanding of asphaltene behavior in order to model and predict both the precipitation and deposition of this fraction in oil wellbores, in a wide range of pressures, temperatures and compositions. Although one of the main motivations of this work is to propose an effective model to understand and predict asphaltene deposition, this process cannot be separated from precipitation and aggregation mechanisms. Therefore, in a successful modeling approach all the different steps of asphaltene transport in the wellbore need to be taken into account simultaneously. Thus, efforts need to be made for understanding and quantifying both asphaltene precipitation and deposition.

Four main objectives have driven the work presented in this dissertation:

1. Verify and enhance current approaches and propose new alternatives in studying asphaltene phase behavior.

2. Develop a general method for modeling asphaltene stability.

3. Propose and validate a mechanism for asphaltene deposition in the wellbore.

4. Suggest appropriate algorithms to study and forecast the occurrence and magnitude of asphaltene deposition in the wellbore.
1.3 Thesis Structure

In this work, an updated overview of asphaltenes in the flow assurance context is provided. It is intended to offer a brief but yet comprehensive background on asphaltenes, its impact in oil production, and specifically the modeling approaches that can be used in order to analyze and predict asphaltene precipitation and deposition in the wellbore.

Chapter 2 offers a review on asphaltenes in crude oil systems. The definition of asphaltenes, its properties and impact in oil production, are presented and discussed.

Chapter 3 presents the theories of asphaltene stabilization, and justification of the solubility model approach used in this work. It also presents an overview of the previous work on modeling asphaltene phase behavior. An introduction to the Statistical Associating Fluid Theory equation of state is given as well as multiple examples of application in studying the effects on asphaltene phase behavior of pressure, temperature, composition and polydispersity. The special effect of carbon dioxide, which can both induce and prevent asphaltene precipitation, depending on the operating conditions, is discussed and explained based on thermodynamic analysis.

In Chapter 4 several novel models that can be used to study asphaltene stability are derived and explained. Examples of application are also provided. These models include the definition of the One-Third Rule that relates refractive index and mass density of hydrocarbon and crude oil systems. This correlation is based on the observation that the molar refractivity is approximately proportional to the molecular weight of a hydrocarbon molecule. The proportionality constant is approximately equal to one-third for hydrocarbons systems. The application of the One-Third rule in the calculation of
solubility parameters, and transport properties, as a function of the mass density is shown. A methodology to calculate solubility parameters as a function of pressure, temperature and composition is also presented and discussed in Chapter 4. This includes correlations derived from thermodynamics for the pressure and temperature dependence of cohesive energy and solubility parameters. Furthermore, a new mixing rule for solubility parameters is derived and compared with experimental data. Chapter 4 also includes the development and applications of general method for modeling asphaltene stability. By defining dimensionless parameters, the equilibrium curves of different multicomponent mixtures collapse onto one single curve. Universal plots for the bubble point and the onset of asphaltene precipitation have been obtained, which are in excellent agreement with results obtained from simulations. Extension of this model to mixtures containing dissolved gases, such as methane, CO$_2$ and ethane, is also included.

In Chapter 5 the mechanism that simultaneously accounts for the different steps of asphaltene transport in the wellbore is presented and discussed. The implementation of the model in a simulation tool is described. Some results are shown and the appropriate discussions are also included. The comparison with experimental data and field observations demonstrate good qualitatively agreement. Limitations of the model and experimental and field measurements that are needed to enhance the tool are pointed out.

In Chapter 6 another suspected condition affecting asphaltene deposition is explored; the potential effect of ferric ions inducing asphaltene precipitation at the water/oil interface is analyzed and initial results are shown.

Finally, in Chapter 7 conclusions and suggestions for future work are presented.
Chapter 2. Review of asphaltenes in crude oil systems

2.1 Oil Characterization

Compositional analysis of crude oils can be extremely complex due to the large number of components. It is believed that oil can contain more than 100,000 different molecules\(^1\). One simple analysis scheme widely used is to divide an oil sample into four different fractions: Saturate, Aromatic, Resin and Asphaltenes. This method called the SARA analysis started with the work done by Jewell et al.\(^2\) The saturate fraction is formed by nonpolar material including linear, branched and cyclic saturated hydrocarbons. Aromatics contain one or more aromatic rings, and are more polarizable. Resins and Asphaltenes have polar substituents. However, the difference between them is that asphaltenes are insoluble in an excess of heptane (or pentane), while resins aremiscible with these paraffinic solvents\(^3\). Figure 2.1 shows the classification of an oil according to the SARA analysis\(^4\).

![Separation scheme for SARA components](https://example.com/scheme.png)

\textbf{Figure 2.1.} Separation scheme for SARA components (ASTM D2007-80\(^5\)). Reproduced from Wang\(^4\)

Besides the clay-gel adsorption chromatography method, which is the basis of the
ASTM D2007-80⁵, there are at least two more approaches: The utilization of the high-pressure liquid chromatographic (HPLC), first introduced by Suatoni and Swab⁶, and the fastest separation method that uses a thin-layer chromatography with flame ionization detection (TLC-FID), first applied by Susuki according to the work published by Fan and Buckley³.

Unfortunately, an important disadvantage of the SARA analysis is that fraction measurements by different techniques and/or from different laboratories can show large differences³⁷. Despite this deficiency the SARA analysis is still widely used as a form of characterizing the oil and quantifying the amount of asphaltenes present.

### 2.2 Asphaltene definition, properties and its impact in oil production

Asphaltenes are a polydisperse mixture of the heaviest and most polarizable fraction of the oil. They are currently defined in terms of their solubility, being completely miscible in aromatic solvents, such as benzene, toluene or xylenes, but insoluble in light paraffinic solvents, such as n-pentane or n-heptane. Other strong asphaltenes precipitants are alcohols, water, and gases such as methane, nitrogen and CO₂. However, the latter, as it will be discussed in Section 3.4.6, can also prevent asphaltene precipitation depending on the operating conditions.

The word ‘asphaltene’ was coined by Boussingault in 1837 when he noticed that the distillation residue of some bitumens had asphalt-like properties⁸⁹.

Because of the limited definition of asphaltenes, which is based on its solubility and not by a specific chemical classification, there has been a lot of debate and problems
trying to identify and separate this fraction, as it was discussed in Section 2.1. The main problem is that different analytical techniques to separate and quantify asphaltenes might not produce comparable results as discussed by Fan and Buckley\(^3\). In fact, depending on the normal alkane used to precipitate asphaltenes, the material obtained may present a completely different appearance as it is shown in Figure 2.2. In this case asphaltene samples are separated from the same crude using two different normal alkanes. The sample shown in Figure 2.2(a) corresponds to asphaltenes obtained using normal pentane, whereas the Figure 2.2(b) illustrates the sample collected when normal heptane is used.

![Figure 2.2. Asphaltene samples precipitated from crude oil using \(n\)-pentane and \(n\)-heptane\(^{10}\).](image)

Despite the obvious differences in the separated samples, companies and laboratories use different normal alkanes (typically \(n\)-pentane or \(n\)-heptane) to separate and quantify asphaltenes. Thus, comparison of results from different laboratories or even different analytical procedures is meaningless and could lead to erroneous conclusions\(^3,7\).
It is important to keep in mind that asphaltenes are a polydisperse mixture, with a distribution of structures, molecular weights, and properties. Thus, depending on the alkane used a different section of that distribution is separated from the oil.

Asphaltene molecular weight and structure have also been subject to long term discussions and despite decades of research, the chemical composition and structure and their effect on the mechanisms of asphaltene stabilization are not thoroughly understood. Hydrocarbon complexity and atomic heterogeneity represent an enormous challenge in petroleomics*.\(^\text{11,12}\)

Various studies propose that asphaltenes are formed by atoms of carbon, hydrogen, nitrogen, oxygen and sulfur, as well as trace amounts of metallic elements such as vanadium and nickel\(^\text{9,13}\). Asphaltenes possess complex structures consisting of multiple aromatic rings\(^\text{14}\) (4-10 rings in typical virgin crude oil asphaltene molecules\(^\text{15,16}\)) and aliphatic side chains, with a carbon-hydrogen ratio of 1:1.2 with 40% of the carbon in aromatic structures and 90% of the hydrogen on saturated carbon\(^\text{15}\). In Figure 1.2.1 two different hypothetical asphaltene structures are shown.

Molecular weight of asphaltenes has been a very controversial topic as well\(^\text{16}\). The reason of this is that asphaltenes are known to aggregate even at low concentrations and in very good solvents such as toluene, leading to the formation of what have been called ‘nano-aggregates’\(^\text{17}\). These nano-aggregates are believed to be formed by stacking together about 6 to 8 asphaltene molecules\(^\text{17}\). The large molecular weights reported from

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* Petroleomics is the characterization of petroleum at the molecular level.
several techniques, such as Vapor Pressure Osmometry (VPO) or Size Exclusion Chromatography (SEC) are most likely due the formation of aggregates\textsuperscript{16}.

![Proposed asphaltene structures](image)

**Figure 2.3.** Proposed asphaltene structures for (a) Maya crude (Mexico)\textsuperscript{18}, and (b) 510C Residue of Venezuelan Crude\textsuperscript{19}.

Time-resolved fluorescence depolarization has been used to perform molecular diffusion measurements of asphaltenes, which have proven that asphaltene molecules are monomeric with relatively small average molecular weight of 750 Da and a range of 500-1000 Da\textsuperscript{20,21}. These values have been confirmed using other molecular diffusion measurements, including Taylor dispersion\textsuperscript{22}, nuclear magnetic resonance\textsuperscript{23} and fluorescence correlation spectroscopy\textsuperscript{24}.

These nano-aggregates can readily stick to one another and form bigger particles when the system is perturbed because of changes of pressure, temperature and composition. Reversibility of this process has been questioned, but it has been experimentally demonstrated\textsuperscript{25} that insoluble asphaltene particles can be readily dissolved in good solvents, such as toluene, under the effect of ultrasonic waves, which breaks the big aggregates down into small particles. Thus, redissolution of small aggregates is likely
to occur whereas redissolution of big particles could be a very slow process.

Asphaltene aggregation after addition of \( n \)-heptane can be observed in Figure 2.4. Asphaltene precipitation and aggregation are mechanism that may occur very slowly. Kinetic effects on asphaltene precipitation have been the subject of multiple studies\(^4,26\).

![50 μm](image)

**Figure 2.4.** Asphaltene precipitation and aggregation after addition of \( n \)-heptane\(^{27} \).

The study of the nature and behavior of asphaltenes is not only interesting, but it is also a way for elucidating the complex mechanism by which asphaltenes precipitate and deposit in the wellbore.

Arterial blockage in oil wellbores can occur as the result of the formation of different types of deposit. Waxes, gas hydrates and asphaltenes are only a few examples. Asphaltenes present a special challenge because, contrary to waxes and gas hydrates, they are not well characterized, form a non-crystalline structure and its deposition can occur even at relatively high temperatures.

Asphaltene deposition might reduce the oil flow in the wellbore producing loss in
revenue to a point that requires remediation. Intervention costs might range from USD 500,000 for an on-shore field to USD 3,000,000 or more for a deepwater well. These costs are without including the lost production that can be more than USD 1,000,000 per day.

A better understanding of the mechanisms by which asphaltenes disperse, precipitate and deposit is needed in order to improve the prediction and avoid the problems associated with them. Predicting asphaltene flow assurance issues requires the ability to model asphaltene phase behavior as a function of temperature, pressure, and composition. However, modeling phase behavior constitutes only one part of the solution. Additional efforts have to be made to elucidate the mechanisms of asphaltene deposition which can eventually lead to the development of improved experimental procedures and better predictive models that could differentiate between systems that precipitate and deposit and those that precipitate and do not form deposits in wellbores.
Chapter 3. Modeling Asphaltene Phase Behavior

3.1 Theories of Asphaltene Stabilization

Asphaltene stability in crude oil and the mechanisms of its precipitation have been subject of continuous investigation over many years. Two theories have been proposed to explain such phenomena. The first one is based on colloidal models, whereas in the second one solubility models are used. The idea of asphaltene colloidal particles stabilized by resins was first introduced by Nellensteyn. This concept was then refined by Pfeiffer and Saal. In the solubility theory (or molecular solution approach), asphaltenes are assumed to be part of a solution (oil). Asphaltene precipitation can be treated as liquid-liquid or solid-liquid equilibria. Resins and aromatics solubilize asphaltenes whereas saturates destabilize them. Examples of models based on the solubility approach are the Hirschberg model, the work of de Boer, Redelius, Park and Mansoori, Wiehe, Buckley and Wang, among others. Recent results suggest that the solubility model is more appropriate to study the stability of asphaltenes in crude oils. Using impedance analysis Goual has demonstrated that resins are unlikely to coat asphaltene nanoaggregates and therefore resins are not able to provide the steric stabilizing layer that the colloidal model proposes. Czarnecki has determined that the Hydrophilic-Lipophilic Balance (HLB), which provides an approximate measurement of polarity of surfactants, is negative for asphaltenes. Czarnecki concludes that asphaltenes are not polar, do not aggregate to form micelles, are not similar to surfactants, and do not stabilize water/oil emulsions. Hirasaki and Buckley have reported that for asphaltenes in crude oil systems it is polarizability (and not polar
interactions), which determines the asphaltene phase behavior. Recent results obtained by both experimental\textsuperscript{46} and molecular simulation schemes\textsuperscript{47} have validated this hypothesis. Thus, the solubility model is currently the most accepted theory for modeling asphaltene phase behavior. Among the solubility models, the thermodynamic modeling using the SAFT\textsuperscript{48-50} based equations of state have demonstrated excellent performance and predictive capabilities applied to a wide range of mixtures, including petroleum systems containing asphaltenes.

\section*{3.2 Previous work on modeling asphaltene phase behavior}

Previous studies of asphaltenes have relied on Flory-Huggins based models. Examples of such approaches include the Hirschberg model\textsuperscript{35}, de Boer plot\textsuperscript{51}, the ASIST method developed by Wang and Buckley\textsuperscript{52}, and the Yarranton et al. model\textsuperscript{53-55}. The advantage of a Flory-Huggins based approach is that the model is simple to apply and to interpret in terms of solubility parameters. These methods have been widely applied in the oil industry with success. However, a limitation of Flory-Huggins based models is that they do not explicitly include the effect of compressibility on phase behavior. This compressibility effect is essential to describing certain types of phase behavior commonly observed in systems with large size differences between molecules. In practice these theories require an equation of state to predict the effect of compressibility on the solubility parameter.

Equations of state can be more predictive since they directly include the effect of compressibility. Cubic equations of state (CEOS) are simple models that have been widely applied in industry. CEOS have been also applied in modeling asphaltene phase
behavior. Chung et al.\textsuperscript{56}, combined the Flory-Huggins model with the Peng-Robinson CEOS to model asphaltene solubility in oil. Burk et al.\textsuperscript{57}, obtained the Flory-Huggins model parameters from the Zudkevitch-Joffe-Redlich-Kwong CEOS. In the method proposed by Nghiem et al.\textsuperscript{58}, the C\textsubscript{31+} heavy end of crude oil is first divided into nonprecipitating and precipitating subfractions. Different interaction parameters are then assigned to reproduce experimental results. In another example, Akbarzadeh et al.\textsuperscript{59}, modified the Soave-Redlich-Kwong CEOS by adding an additional aggregation size parameter to asphaltenes. More recently, Nikookar, Omidkhah and Pazuki\textsuperscript{60-62}, have reported the development and application of a CEOS for modeling the asphaltene precipitation in crude oils.

However, the major limitation of CEOS is that they cannot describe adequately the phase behavior of mixtures of molecules with large size differences and they are unable to accurately calculate liquid densities. The reason for their poor prediction capability is that CEOS are typically fit to the critical point. Accurate modeling of liquid density is essential for an equation of state to predict liquid-liquid equilibria and their corresponding parameters, such as the solubility parameter, over a range of conditions. It has been found that CEOS that are fit to liquid phase density have better performance in reproducing phase behavior data.\textsuperscript{63}

A more modern equation of state is the Statistical Associating Fluid Theory (SAFT) family of models\textsuperscript{48-50,64}. This equation of state can accurately model mixtures of molecules of different sizes. Because it is based on statistical mechanics, SAFT can accurately predict the effects of temperature, pressure and composition on fluid phase properties. SAFT based equations of state have become important tools in predicting
polymer phase behavior to prevent fouling in polymer processing\textsuperscript{65}. We will focus our discussion particularly on the Perturbed Chain version of SAFT, developed by Gross and Sadowski\textsuperscript{64}. This version of SAFT accurately predicts the phase behavior of high molecular weight fluids similar to the large asphaltene molecules, and it is readily available in commercial simulators, such as Multiflash and VLXE.

3.3 The SAFT based modeling approach

The SAFT theory models a molecule as a chain of bonded spherical segments. The parameters for the model are physical. The model requires the number of segments in a chain molecule, the diameter or volume of a segment, and the van der Waals attraction between segments. These parameters are fit to saturated liquid densities and vapor pressures. These segments could represent methylene groups on a molecule, but in practice it is found that the fitted parameters for a segment represent about one and a half methylene groups. As expected, all three pure component parameters correlate with molecular weight within a homologous series. For example, the number of segments in a molecule correlates linearly with molecular weight within a homologous series, \textit{e.g.} alkanes and polynuclear aromatics. The segment-segment van der Waals attraction depends on molecular weight for small molecules but approaches a limiting value as the molecular weight increases. In modeling polyethylene, parameters can be estimated by extrapolating the correlations for the chain length, \textit{i.e.} number of segments, segment diameter, and segment-segment attraction energy for alkanes to the molecular weight of the polymer. Tables of pure component parameters are given by Gross and Sadowski\textsuperscript{64}, and Ting et al\textsuperscript{34}.
The SAFT equation of state can also predict the effect of association between molecules\textsuperscript{48-50,64}. The association term in SAFT is widely used to model systems containing alcohols and water. The association term has been adopted in other models. For example, the association term used in the cubic plus association equation of state\textsuperscript{66} is the SAFT association term\textsuperscript{48-50}. This term requires at least 2 additional parameters for each associating component. In modeling asphaltene precipitation we have not needed to include association to match the observed phase behavior.

The SAFT model has been applied to a wide range of systems by numerous academic groups and companies. Systems modeled range from alcohols to co-polymers, refrigerants to amphiphiles, and even electrolytes and ionic liquids. Although the theory was developed as a model for small associating molecules, the equation of state has seen its widest application for polymer solutions.

In the area of polymer solutions, the effects of size asymmetry, polydispersity, chain branching and functional groups on phase behavior predictions have been investigated\textsuperscript{65,67-71}. One of the algorithms developed by Jog and Chapman\textsuperscript{72} enables the efficient calculation of phase behavior for polydisperse polymer solutions with a large number of pseudocomponents without restriction on the polymer molecular weight distribution.\textsuperscript{72,73}

Polymer solutions and solutions containing oligomers are examples of mixtures with large size asymmetry that show similar phase behavior as observed in petroleum systems. As an example, consider a mixture of polystyrene, cyclohexane, and carbon dioxide shown in Figure 3.1.
Figure 3.1. Cloud-point curves and vapor-liquid equilibrium of the ternary system polystyrene (PS)-cyclohexane-carbon dioxide (PS: Mw = 101.4 kg/mol, Mw/Mn = 1.09; w_{PS} = 0.1 at 0% CO₂). Comparison of experimental data to PC-SAFT correlation results. The polymer is modeled as monodisperse (PS-cyclohexane, kij = 0.0075; PS-CO₂, kij = 0.195; cyclohexane-CO₂: kij = 0.13).

In this case the cyclohexane can be considered to be the "oil", polystyrene to be a large component similar to asphaltenes, and carbon dioxide is a precipitating agent. The system has been studied experimentally by de Loos, Bungert and Arlt and the results are reported in the literature\textsuperscript{74}. Gross and Sadowski have modeled this system with the PC-SAFT equation of state\textsuperscript{74}. New simulations for this system are reported in Figure 3.1.

In Figure 3.1, first consider the mixture with no carbon dioxide. The vapor pressure curve for cyclohexane is shown at the bottom. The nearly vertical phase boundary at about 20°C is an upper critical end point (UCEP) phase boundary. Below this temperature, the system splits into two phases. As the temperature rises above this boundary, the system moves from a region of two liquid phases to a single liquid phase.
This is typically explained to occur because at this phase boundary temperature the entropy gain from mixing just overcomes the enthalpically favored phase splitting.

There is another phase boundary as temperature is increased at constant pressure. This curve is a lower critical end point (LCEP) phase boundary. As the temperature is increased at constant pressure, the solvent expands (lowering the solubility parameter of the solvent) and becomes a poor solvent for the polymer. Prediction of this type of phase boundary requires an equation of state since it is the compressibility of the system that causes the phase splitting. The LCEP phase boundary usually occurs as you approach the critical temperature of the mixture since this is where the mixture is most compressible.

In Figure 3.1, considering the results at various amounts of carbon dioxide added to the system is like considering a live oil with increasing gas oil ratio or considering the effect of gas injection on the phase behavior of an oil. With greater amounts of carbon dioxide in the solvent, the bubble point curve for the solvent increases thus shifting the LCEP phase boundary to higher pressures and lower temperatures. At high enough CO\textsubscript{2} content the LCEP type phase boundary merges with the UCEP type phase boundary.

The points in Figure 3.1 show the experimental results of de Loos\textsuperscript{75}, Bungert\textsuperscript{76} and Saeki et al.\textsuperscript{77}. The curves show new calculations using a single set of temperature independent parameters fit by Gross and Sadowski using PC-SAFT. Agreement between the equation of state and the experimental data is notable for this system.

This system shows many qualitative similarities with the phase behavior reported for asphaltenes in crude oil. Similar to the polystyrene, asphaltenes are said to be stable at reservoir pressure but destabilize on depressurization. Also, interestingly, temperature
changes may result in either asphaltene precipitation or solubilization. For instance, it has been reported that in propane, asphaltenes become less soluble as temperature increases\(^7\). However, for titrations with heavier alkanes, \(e.g.\) C\(_5\)+, it has been reported that asphaltene stability increases with increasing temperature\(^7\). At a given temperature and pressure, increasing the gas content can destabilize asphaltenes. Each of these cases is analogous to the polystyrene system in Figure 3.1. The implication is that, similar to the polystyrene example, we can understand and predict (given equation of state parameters) the effect of temperature, pressure and composition on asphaltene phase behavior in crude oil\(^5\).

### 3.4 Asphaltene phase behavior modeling using the PC-SAFT EOS

#### 3.4.1 Oil characterization and the PC-SAFT EOS

As explained above, the PC-SAFT equation of state has three pure parameters for each non-associating component. To characterize an oil, the three parameters must be determined for each pseudo-component. A methodology has been developed to determine these parameters based on the stock tank oil density, the bubble point, SARA analysis of the oil, and gas chromatographic analysis providing the composition of the mixture\(^7\). Correlations for the three PC-SAFT parameters have been previously reported\(^7,8\) as a function of molecular weight for alkanes, benzene derivatives, and polynuclear aromatics.

This information about the oil is sufficient to fit parameters for each component except for the asphaltene component. The three PC-SAFT parameters for an asphaltene component are fit to measurements of asphaltene precipitation onset conditions. Such
precipitation onsets have been measured at ambient pressure by titrating with \( n \)-alkane precipitants or in high pressure measurements at a given gas composition. In the absence of a molecular weight distribution, asphaltenes can be treated as a monodisperse pseudocomponent. After fitting asphaltene parameters to the precipitation data, the PC-SAFT equation of state can predict the effect of temperature, pressure, and composition on asphaltene phase behavior. If no precipitation onset data is available for an oil, conditions for asphaltene precipitation can be predicted using asphaltene parameters fit to another oil. We have found that asphaltenes are well characterized using parameters for benzene derivatives. A detailed description of the method to determine pseudo-component parameters is given by Gonzalez\textsuperscript{79,80}.

3.4.2 Effect of Pressure

Operators have observed in the field that asphaltenes tend to plug over a range of pressures. For the wellbore, above or below a certain pressure range no deposition is observed. This behavior can be explained by analyzing the depressurization of the model oil composed by asphaltenes dissolved in toluene, presented in Figure 3.2. In this Figure, modified from Ting\textsuperscript{81}, the closed markers are measured bubble points, the open markers are measured asphaltene precipitation onset points (asphaltene stability boundary), and the curves are predictions of the PC-SAFT equation of state. At high pressure the asphaltenes are soluble in oil. However, during pressure depletion, the oil expands, reducing the oil solubility parameter, and becomes a poor solvent for asphaltene. At low enough pressure the asphaltene precipitation onset is reached and asphaltenes begin to precipitate. Upon further depressurization, the system arrives to its bubble point, where the light components, which are asphaltene precipitants, escape from
the liquid phase. As this happens, the solubility parameter of the oil increases until the oil becomes a better asphaltene solvent and the oil stabilizes again. Since this approach comprises an equilibrium model, the re-dissolution kinetics, which may play an important role, is not taken into account.

![Figure 3.2](image)

**Figure 3.2.** Asphaltene instability onsets (open symbols) and bubble points (filled symbols) for a model oil at two different temperatures. Lines represent the simulation results using PC-SAFT. Adapted from Ting.81

The same depressurization can be followed in a plot of solubility parameter35,82 as shown in **Figure 3.3**. The solubility parameter of the oil decreases as pressure is decreased to the bubble point. On further depressurization, the solubility parameter of the oil increases. It can be seen that along the asphaltene stability boundary, this system shows a nearly constant solubility parameter. This indicates, as shown in **Figure 3.3**, that asphaltenes are unstable below a certain solubility parameter of the oil as suggested by
Buckley and Hirasaki. This constant solubility parameter threshold has been used in some models of asphaltene stability. In further calculations using the PC-SAFT EOS, it has been found that the solubility parameter is not always constant along the asphaltene stability boundary. This result has been shown experimentally and explained using the Flory-Huggins equation.

![Figure 3.3](image)

**Figure 3.3.** Calculated solubility parameter during pressure depletion for the model live oil at 20.0°C with 0.143 mass fraction methane above the bubble point. Asphaltenes are unstable below the asphaltene instability line. Adapted from Ting.

### 3.4.3 Effect of Temperature

It has been previously mentioned that asphaltene solubility can either increase or decrease with increasing temperature. It has also been stated that the SAFT based equations of state are capable of predicting both the lower and upper critical solution temperatures that are present in complex systems. A lower critical end point temperature
phase transition can occur in systems with large size differences between molecules. In this case, an increase in temperature (at a fixed pressure) will result in a decrease in oil density and thus a decrease in solubility parameter resulting in the precipitation of asphaltenes. At lower temperatures, we can observe asphaltene precipitation with a decrease in temperature. Both of these behaviors have been observed experimentally\textsuperscript{83} as shown in Figure 3.4.

![Diagram illustrating asphaltene precipitation and bubble points for reservoir fluid A.](image)

**Figure 3.4.** Onset of asphaltene precipitation and bubble points for reservoir fluid A. Data from Jamaluddin et al.\textsuperscript{83} Curves correspond to simulations using the PC-SAFT EOS. Adapted from Gonzalez et al.\textsuperscript{84}

Furthermore, special temperature effects have been observed when CO\textsubscript{2} is added to an oil containing asphaltenes. It has been previously reported\textsuperscript{84} that CO\textsubscript{2} can destabilize or stabilize asphaltenes in an oil depending upon the temperature of the system.

It has been observed that, at temperatures below a certain crossover point, CO\textsubscript{2} can
act as an asphaltene precipitation inhibitor, whereas at temperatures above this point, CO₂ behaves as a strong asphaltene precipitant. This dual effect is not observed with other gases, such as nitrogen or methane. A more detailed analysis and discussion of this phenomenon is presented in Section 3.4.6 (Page 30).

3.4.4 Effect of Composition

The effect of compositional changes in live oils that may result in either asphaltene precipitation or solubilization has also been studied. Two examples are summarized here: the effect of oil-based mud contamination on asphaltene stability and the effect of gas injection.

Oil based mud (OBM) that is used to increase borehole stability during drilling can contaminate near wellbore reservoir fluids. An oil based mud can significantly modify the composition and predicted phase behavior of the asphaltene in the formation fluid causing wrong data interpretation⁸⁵. Since samples of the reservoir fluid that are submitted for laboratory analysis may be contaminated with oil based muds, the lab results must be corrected to remove the effect of the contamination. The extent of OBM contamination can be determined using chromatography. Since the OBM composition is known, the OBM free composition is calculated mathematically by subtracting the corresponding fraction. Simulations using the PC-SAFT EOS can be performed for the clean and the contaminated oil to describe to the effect of OBM contamination⁸⁰. Since the OBM is a precipitating agent for asphaltenes, we might expect that OBM contamination would increase the pressure at which asphaltenes start precipitating, but this is not necessarily the case. According to the results presented in Figure 3.5 for a live oil, fluid B, both the asphaltene precipitation onset and bubble point pressure decrease
when successive amounts of OBM are added to an original high asphaltene content sample. Both, the precipitation onset and the bubble point curves estimated by PC-SAFT, closely follow the experimental findings. Note that the gas-oil ratio (GOR) also decreases by the OBM addition. Although the OBM is a precipitant for asphaltenes, the OBM contamination dilutes the gaseous components of the oil that are stronger asphaltene precipitants. As the GOR decreases, the asphaltene precipitation onset pressure and bubble point pressure decrease. The correction for OBM contamination, which can be significant, as in the case of reservoir fluid C shown in Figure 3.6, requires an accurate equation of state model.

![Graph showing the effect of OBM contamination on asphaltene phase behavior.](image)

**Figure 3.5.** OBM contamination effect on asphaltene phase behavior. Adapted from Gonzalez.

The other compositional effect on asphaltene stability is due to gas injection. Gas injection has traditionally played an important role for oil recovery in oil field development. Injection of a gas that dissolves in oil allows the recovery of oil that would
otherwise be trapped in the tight pores of the rock.

The application of enriched or dry natural gas, CO₂ or N₂ flooding schemes to enhance oil recovery can induce destabilization and deposition of asphaltenes due to changes in composition.

Figure 3.6. Asphaltene precipitation behavior of reservoir fluid C, calculated with the PC-SAFT equation of state. Adapted from Gonzalez.²⁸

The asphaltene stability curve in a recombined oil as a function of pressure at different separator gas concentrations was determined in a previous work²⁸. The simulated results for the recombined oil reproduce the experimental data obtained in a PVT cell by Ting et al.²¹ at D.B. Robinson (Figure 3.7). Figure 3.8 shows a comparison of simulation results for nitrogen addition to a recombined oil with experimental depressurization data at reservoir temperature of 296°F from Jamaluddin et al.²³
Figure 3.7. SAFT-predicted and measured asphaltene instability onset and mixture bubble points for the recombined oil at 71°C. Adapted from Ting.\textsuperscript{81}

Figure 3.8. Addition of successive amounts of N\textsubscript{2} to reservoir Fluid A. Experimental data from Jamaluddin et al.\textsuperscript{83} Curves correspond to simulation results using the PC-SAFT equation of state.
The addition of 5, 10 and 20 mol% of nitrogen strongly increases the asphaltene instability onset. The difference between the asphaltene onset pressure and the bubble point pressure \((P_{\text{onset}} - P_{\text{bbp}})\) increases with the amount of injected nitrogen. The agreement between the simulated and the experimental data is excellent.

### 3.4.5 Effect of Polydispersity

Asphaltenes are a polydisperse class of components in the oil. Polydispersity can have a large affect on the phase behavior as well as on the deposition of asphaltenes. The effect of polydispersity can be seen by considering the example of a polymer solution.

Consider a plot of the cloud point pressure versus the mass fraction of a polymer for a polydisperse polymer in a solvent. The polymer molecular weight distribution is modeled using a few pseudo-components as illustrated in Figure 3.9. Using an algorithm developed by Jog et al.\(^{72}\), the phase behavior of this polydisperse polymer can efficiently be calculated. Data from de Loos\(^{86}\) for polyethylene are shown in Figure 3.9. These data were simulated assuming a monodisperse polymer as well as a polydisperse polymer. Higher polymer concentration, the cloud point pressure for a monodisperse polymer and a polydisperse polymer give nearly identical results. For the polydisperse polymer at concentrations above about 5%, the phase that precipitates (shown by the dashed shadow curve) is a light phase (polymer lean phase). Because the precipitating phase is polymer lean, the phase boundary depends primarily on the average molecular weight of the polymer, thus, the monodisperse result is similar to the polydisperse result. In crude oil systems, precipitation of such a light phase from a heavy oil has been observed in laboratory experiments\(^{87}\). For polymer concentrations typically less than about 5%, polydispersity changes the phase diagram dramatically. At these low polymer
concentrations, the phase that precipitates, shown by the shadow curve, is a heavy polymer rich phase. In this case, the phase boundary is determined by the highest polymer molecular weight components. As shown in Figure 3.9, a polydisperse system shows a dramatically higher cloud point pressure at low polymer concentration. The phase behavior of asphaltenes is expected to be qualitatively similar.

![Figure 3.9](image)

**Figure 3.9.** Cloud-point and shadow curves for poly(ethyleneoctene) + hexane at 450 K from experimental points and SAFT (curves). The dotted curve shows the composition of the incipient phase at the cloud point. Results for monodisperse and polydisperse polymers are included. Adapted from Jog et al. with experimental data taken from de Loos et al.

In Figure 3.10, the asphaltene component has been modeled as a mixture of three pseudocompents that mimic the incremental amount of asphaltene precipitated on 20 to 1 dilution of the oil with heptane, undecane, and pentadecane, respectively. From Figure 3.10 we can see that polydispersity also affects the amount of asphaltene precipitated. The figure shows the different precipitation profiles obtained for monodisperse versus...
polydisperse asphaltenes on titration with an alkane precipitant. For a monodisperse asphaltene, the amount of asphaltene that precipitates increases quickly upon addition of an alkane precipitant, beyond the precipitation onset condition. For polydisperse asphaltenes, the amount of asphaltene precipitated increases more slowly on adding a precipitant. As expected, asphaltene can re-dissolve at high enough dilution in a precipitant. The amount of dilution that is ‘high enough’ depends on the highest molecular weight components of the asphaltene fraction.

![Figure 3.10](image)

**Figure 3.10.** Solubility of monodisperse and polydisperse asphaltenes in model oil mixed with \( n \)-alkanes at 20°C and 1 bar. Reproduced from Vargas et al. 88

### 3.4.6 Modeling CO₂-induced asphaltene precipitation

Asphaltene precipitation onset pressure increases when 10 mol% of either, \( N_2 \) or methane, is added to the original fluid A, presented in **Figure 3.4**. A crossover of asphaltene precipitation onset with respect to the original fluid onset is observed after the addition of CO₂, according to **Figure 3.11**.
Figure 3.11. Fluid A phase behavior after addition of (a) methane, (b) N\textsubscript{2} and (c) CO\textsubscript{2}. The solid black line corresponds to the original live oil fluid A. Experimental data from Jamaluddin et al.\textsuperscript{83} Reproduced from Gonzalez et al.\textsuperscript{84}
Figure 3.12. Addition of successive amounts of (a) methane, (b) N₂ and (c) CO₂ to reservoir Fluid A at two different temperatures. Exp. data from Jamaluddin et al.⁸³; lines represent simulations using the PC-SAFT EOS. From Gonzalez et al.⁸⁴
Below the temperature crossover, around 200 °F, the addition of CO₂ increases asphaltene stability in the crude oil. Above this temperature, the asphaltene solubility decreases and the onset pressure goes to a minimum and increases at higher temperatures. Addition of 20 mol% of CO₂ clearly shows this behavior as presented in Figure 3.11.

The addition of consecutives amounts of N₂ to fluid A was also measured experimentally. Simulations using the PC-SAFT EOS at two different temperatures, below and above the crossover point, confirm the special behavior for CO₂, according to Figure 3.12. Whereas the addition of methane and N₂ increases the onset point pressure of a mixture at any temperature in the range studied, for CO₂ this behavior is opposite at temperatures below the crossover point.

In order to elucidate this phenomenon and provide an explanation of this special behavior for CO₂, a thermodynamic analysis of a model oil, based in the concept of the Solubility Parameter is proposed. According to Hildebrand, two materials with similar solubility parameter gain sufficient energy on mutual dispersion to permit mixing.

In order to calculate the solubility parameters of the species involved, including the CO₂, and explain the effect of the solubility parameters in the stability of the mixture we utilize a model oil. This oil was originally studied and characterized by Ting et al. The dead oil is composed by 1 g of asphaltene / 100 mL of toluene. The asphaltene molecular weight and specific gravity where found to be 1700 g/mol (for a pre-aggregated asphaltene) and 1.16, respectively. The PC-SAFT parameters for asphaltene were tuned to reproduce experimental data: \( \sigma = 4.05 \text{ Å}, \ \varphi/k = 349.8 \text{ K} \) and \( m = 75 \). For pure components these parameters are available in the literature. The model live oil was
obtained by mixing 16.9 wt% of methane with the balance amount of dead oil. The binary interaction parameter \((k_{ij})\) for the pair methane-toluene was obtained from binary VLE data and it was found to be \(k_{C1-Tol} = 0.023\).

**Figure 3.13** shows good agreement between the simulation results and the experimental data for both the bubble point curve and the asphaltene precipitation onset for the model live oil described above.

![Figure 3.13. P-T diagram for model live oil. Experimental data versus simulation results. Reproduced from Gonzalez et al.](image)

After addition of a certain amount of CO\(_2\) a change in the corresponding PT diagram is observed, according to **Figure 3.14**. In this example, CO\(_2\) is added arbitrarily to the live oil to a final concentration of 30.5 wt% of CO\(_2\). Due to this addition, the oil becomes stable at any pressure at temperatures below 80\(^\circ\)F. In this example, the crossover temperature is about 300\(^\circ\)F. This means that if CO\(_2\) is added at a temperature below
300°F the asphaltene becomes more stable, whereas the opposite behavior is obtained for temperatures above the crossover point.

As it was previously stated, this special behavior for CO₂ can be explained in terms of the solubility parameter concept. The solubility parameter for asphaltene, oil, CO₂ and methane were calculated at the onset pressure as a function of temperature using the PC-SAFT EOS. The results are plotted in Figure 3.15. According to simulation results, the addition of CO₂ at temperatures below 300°F increases the solubility parameter of the oil, and due to its increasing proximity with the solubility parameter of the asphaltene, the mixture becomes more stable. In the other hand, at temperatures above 300°F, the solubility parameter of the oil decreases with the increasing amount of CO₂ added. In this case the oil becomes unstable and the asphaltene readily precipitates. The solubility

![Figure 3.14. Comparison between the original live oil and the live oil after the addition of CO₂ (red line). The oil becomes more stable at temperatures below 300°F and less stable above this temperature. Reproduced from Gonzalez et al.](image)
parameter of methane is always lower than the solubility parameter of the oil, therefore
the injection of methane increases the oil instability at any temperature. For this reason
CO₂ can act as an inhibitor or promoter of asphaltene precipitation, depending on the
temperature of the system, whereas methane is always a strong precipitant agent.

![Graph showing solubility parameters vs temperature]

**Figure 3.15.** Onset solubility parameters for different species as a function of
temperature. Reproduced from Gonzalez et al.²⁴

### 3.5 Chapter Summary

In this chapter the effects of temperature, pressure, and composition on asphaltene
phase behavior have been analyzed. Examples of each case have been presented based
on experimental data and modeling using the PC-SAFT equation of state. The emphasis
has been to provide a physical explanation of the phase behavior and to relate the phase
behavior to that of analogue mixtures with large size asymmetry. In most cases,
asphaltene stability in crude oils can be related to changes in solubility parameter of the
crude oil under changing conditions of temperature, pressure, and composition. The PC-SAFT equation of state has been shown to accurately model the phase stability of asphaltenes in crude oil over a wide range of conditions and for a variety of cases including reservoir depressurization, oil based mud contamination, and gas addition. This enables the model to predict asphaltene behavior at reservoir conditions based on data at ambient conditions.
Chapter 4. Improved models for studying asphaltene stability

4.1 Definition and application of the One-Third Rule

Both density and refractive index are important properties of crude oils that are routinely monitored, most of the time independently. Mass density (typically reported as API gravity) not only determines if a crude oil is light or heavy, but is also an important input parameter for experimental determination of interfacial tension, viscosity and other transport properties. Additionally, mass density is an input parameter in reservoir and wellbore simulators. Thus, an accurate determination of the mass density of crude oils is essential. Refractive index, $n$, is another property of great importance, which can give information about the intermolecular interactions in a system. In the particular case of hydrocarbon and crude oil systems, where polar interactions are weak, intermolecular attractions are determined by the polarizability that can be directly related to the refractive index through the Lorentz-Lorenz equation.

\[
\alpha = \left( \frac{3}{4\pi N_A} \right) R_m
\]  

(4.1)

\[
\alpha = \left( \frac{3}{4\pi N_A} \right) \left( \frac{n^2 - 1}{n^2 + 2} \right)^\nu
\]  

(4.2)

where: $\alpha$ is the electronic polarizability, $R_m$ is the molar refractivity, $N_A$ is the Avogadro’s number, $n$ is refractive index at the frequency of the sodium-D line, and $\nu$ is the molar volume.

Hirasaki and Buckley\textsuperscript{41} have reported that for asphaltenes in crude oil systems it is polarizability (and not polar interactions), which determines the asphaltene phase behavior. These observations are in good agreement with simulation results\textsuperscript{34,80,81,84,88,90}. 

A method based on refractive index measurements to determine asphaltene stability has been proposed and successfully implemented by Wang and Buckley.\(^{44}\)

There are several correlations that have been reported in the literature that relate the solubility parameter as well as transport properties, such as viscosity, diffusivity, thermal conductivity and heat capacity with the refractive index.\(^{44,91,92}\)

Therefore, refractive index and density measurements, can give important information about the phase behavior and transport properties of petroleum systems. Furthermore, as it has been recognized in previous independent works, density and refractive index are strongly correlated.\(^{93-97}\) The objective of this work is to provide a practical method for taking advantage of this correlation in the analysis of data and prediction of properties of hydrocarbon and crude oil systems.

### 4.1.1 Definition of the One-Third Rule

Molar refractivity of different families of pure hydrocarbons can be correlated to their molecular weight, according to Figure 4.1.\(^{97}\) The relationship between these two properties is obtained from the Lorentz-Lorenz model, where the molar refractivity is a function of the refractive index, \(n\), the molecular weight, \(MW\), and the mass density, \(\rho\), according to Eq. (4.3).

\[
R_m = \left( \frac{n^2 - 1}{n^2 + 2} \right) \frac{MW}{\rho} = F_{RI} \frac{MW}{\rho} \tag{4.3}
\]
Figure 4.1. Molar refractivity as a function of the molecular weight for different pure hydrocarbons. A common slope equal to about one-third is obtained.

From Figure 4.1 it can be readily concluded that molar refractivity is approximately proportional to molecular weight for a wide range of hydrocarbons with a proportionality constant equal to about one-third. This result implies that the function of the refractive index, $F_{RI}$, divided by the mass density, $\rho$, is a constant approximately equal to one-third for all the different tested substances. The name “One-Third” rule is used as an easy way to remember an approximate value for this relationship. This ratio does not necessarily hold for all the substances, as we will see in the following sections. However, in many cases, in the absence of more accurate data, the value of one-third can be used with very good results.

To exemplify the broad coverage of this relationship, consider the comparison between two substances: $n$-heptane and naphthalene. The former is transparent liquid at
ambient conditions with a linear molecular structure and possesses a mass density of 0.6837 g/cm$^3$ and refractive index of 1.3878, at 20°C$^98$; the latter is a crystalline white solid with the structure of two fused benzene rings; at 20°C its mass density is 1.0253 g/cm$^3$ and its refractive index is 1.6230$^98$. Despite the very different appearance, structure and physical properties, as illustrated in Table 4.1, both substances have almost the same value of the ratio $F_{RI}/\rho$. Note that this ratio is not exactly equal to one-third but it is very close to this value.

**Table 4.1.** Comparison of physical properties of $n$-heptane and naphthalene. Despite the difference of appearance, and physical properties, the ratio $F_{RI}/\rho$ is about the same in both cases.

<table>
<thead>
<tr>
<th></th>
<th>n-heptane</th>
<th>naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$, g/cm$^3$</td>
<td>0.6837</td>
<td>1.0253</td>
</tr>
<tr>
<td>$n$</td>
<td>1.3878</td>
<td>1.6230</td>
</tr>
<tr>
<td>$\left(\frac{n^2-1}{n^2+2}\right) \frac{1}{\rho}$</td>
<td>0.345</td>
<td>0.344</td>
</tr>
</tbody>
</table>

Data from: CRC Handbook of Chemistry and Physics$^98$.

Good agreement is also obtained when we apply the one-third rule to petroleum systems. Wang and Buckley reported information of refractive indices and mass densities for 12 different crude oils$^{44}$. The ratio of $F_{RI}/\rho$ for the different oils is presented in Figure 4.2. The wide range of API gravities, ranging from 9.9 to 41.3, assures the broad application of the One-Third rule in crude oil systems. Note that for the lightest crude oil
(Lagrange), the ratio $F_{RI}/\rho$ is slightly over the value of one-third. For the rest of the studied samples, the agreement is remarkable.

\[
\left( \frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{\rho}
\]

![Figure 4.2](image)

**Figure 4.2.** Validation of the one-third rule for 12 crude oil samples, pure toluene, and $\alpha$-methyl naphthalene. Experimental data were from Wang and Buckley.\(^{44}\)

In order to offer a physical interpretation of the One-Third rule, the following analysis is proposed. In Eq. (4.3), the ratio $MW/\rho$ represents the apparent molar volume of the fluid, whereas $R_{m}$ the actual volume occupied by molecules per unit mol. Therefore, the function of refractive index, $F_{RI}$, constitutes the fraction of fluid occupied by the molecules.

A different way of writing Eq. (4.3) is by explicitly defining a molecular mass density, $\rho^{\circ}$, that turns out to be approximately equal to 3 g/cm$^3$ for hydrocarbons and crude oil systems, according to Eq. (4.4).
\[
\left(\frac{n^2 - 1}{n^2 + 2}\right) \frac{1}{\rho} = \frac{R_m}{MW} = \frac{1}{\rho^o} \approx \frac{1}{3}
\]  

(4.4)

where \(\rho^o\) is the mass density of a molecule.

In other words, the value of one-third represents the inverse of the density of a hydrocarbon molecule. This value is about the same for many pure hydrocarbon substances and mixtures. However, as we pointed out previously the one-third value does not necessary apply to all the components. For light and very heavy hydrocarbons there is a deviation with respect the one-third value. Table 4.2 shows the values of \(F_{RI}/\rho\) for several pure hydrocarbons.

According to Table 4.2, the ratio \(F_{RI}/\rho\) is, strictly speaking, a function of the mass density. For low densities the value \(F_{RI}/\rho\) increases, as the density decreases. This explains why in Figure 4.2, the lighter crude oils are underestimated using a constant value of one-third. Data for \(F_{RI}/\rho\) and mass densities reported on Table 4.2, were correlated and Eq. (4.5) was obtained:

\[
\frac{F_{RI}}{\rho} = \frac{1}{\rho^o} = 0.5054 - 0.3951\rho + 0.2314\rho^2
\]  

(4.5)

Eq. (4.5) is known as the Lorentz-Lorenz expansion\(^{93}\), and the parameters 0.5054, -0.3951 and 0.2314 are the first three refractivity virial coefficients at 20°C, which have been fit to the data shown on Table 4.2.
Table 4.2. FRI / $\rho$ values for aliphatic, aromatic and polyaromatic hydrocarbons at 20°C.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$MW$ g/mol</th>
<th>$n$</th>
<th>$\rho$ g/cm$^3$</th>
<th>$\frac{F_{RI}}{\rho} = \frac{1}{\rho/\rho^0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aliphatic Alkanes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>16.04</td>
<td>1.1926</td>
<td>0.3026$^b$</td>
<td>0.408</td>
</tr>
<tr>
<td>Ethane</td>
<td>30.07</td>
<td>1.2594</td>
<td>0.4358$^b$</td>
<td>0.375</td>
</tr>
<tr>
<td>Propane</td>
<td>44.10</td>
<td>1.3016</td>
<td>0.5188$^b$</td>
<td>0.362</td>
</tr>
<tr>
<td>Butane</td>
<td>58.12</td>
<td>1.3308</td>
<td>0.5788</td>
<td>0.353</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>72.15</td>
<td>1.3575</td>
<td>0.6262</td>
<td>0.350</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>86.18</td>
<td>1.3749</td>
<td>0.6548</td>
<td>0.350</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>100.20</td>
<td>1.3878</td>
<td>0.6837</td>
<td>0.345</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>128.26</td>
<td>1.4054</td>
<td>0.7176</td>
<td>0.342</td>
</tr>
<tr>
<td>n-Decane</td>
<td>142.28</td>
<td>1.4102</td>
<td>0.7300</td>
<td>0.340</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>170.34</td>
<td>1.4216</td>
<td>0.7487</td>
<td>0.339</td>
</tr>
<tr>
<td>n-Tridecane</td>
<td>184.37</td>
<td>1.4256</td>
<td>0.7564</td>
<td>0.338</td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>198.39</td>
<td>1.4290</td>
<td>0.7628</td>
<td>0.338</td>
</tr>
<tr>
<td>n-Pentadecane</td>
<td>210.40</td>
<td>1.4389</td>
<td>0.7764</td>
<td>0.339</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>226.45</td>
<td>1.4345</td>
<td>0.7733</td>
<td>0.337</td>
</tr>
<tr>
<td>n-Heptadecane</td>
<td>238.46</td>
<td>1.4432</td>
<td>0.7852</td>
<td>0.338</td>
</tr>
<tr>
<td>n-Octadecane</td>
<td>254.50</td>
<td>1.4390</td>
<td>0.7768</td>
<td>0.339</td>
</tr>
<tr>
<td>n-Nonadecane</td>
<td>268.53</td>
<td>1.4409</td>
<td>0.7855</td>
<td>0.336</td>
</tr>
<tr>
<td>n-Eicosane</td>
<td>282.50</td>
<td>1.4425</td>
<td>0.7886</td>
<td>0.336</td>
</tr>
<tr>
<td><strong>Aromatic Alkanes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>1.5011</td>
<td>0.8765</td>
<td>0.336</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.14</td>
<td>1.4961</td>
<td>0.8669</td>
<td>0.337</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>106.17</td>
<td>1.4959</td>
<td>0.8670</td>
<td>0.337</td>
</tr>
<tr>
<td>Propylbenzene</td>
<td>120.19</td>
<td>1.4920</td>
<td>0.8620</td>
<td>0.337</td>
</tr>
<tr>
<td>Butylbenzene</td>
<td>134.22</td>
<td>1.4898</td>
<td>0.8601</td>
<td>0.336</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>106.17</td>
<td>1.4972</td>
<td>0.8642</td>
<td>0.339</td>
</tr>
<tr>
<td>Heptylbenzene</td>
<td>176.30</td>
<td>1.4865</td>
<td>0.8567</td>
<td>0.335</td>
</tr>
<tr>
<td><strong>Poly-nuclear Aromatic Alkanes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>128.17</td>
<td>1.6230</td>
<td>1.0253</td>
<td>0.344</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>142.20</td>
<td>1.6170</td>
<td>1.0202</td>
<td>0.343</td>
</tr>
<tr>
<td>Nonylnaphthalene</td>
<td>254.41</td>
<td>1.5477</td>
<td>0.9371</td>
<td>0.339</td>
</tr>
</tbody>
</table>

Data from CRC Handbook of Chemistry and Physics$^{98}$.  
$^a$ Estimated using Eq. (4.2), with molecular polarizabilities from Miller$^{99}$ and molar volumes from Barton$^{100}$.  
$^b$ Estimated with values of molar volume from Barton$^{100}$. 

As an example consider the information reported in Figure 4.3 that shows notable agreement of the one-third rule (assuming $F_{RI}/\rho = 1/3$) compared to experimental data of seven crude oils in a temperature range of 10 to 70°C. Thus, although both mass density and refractive index are functions of temperature, the ratio $F_{RI}/\rho$ is nearly constant in this temperature range.

![Figure 4.3. Validation of the one-third rule in a wide range of temperatures for different crude oils. Experimental data were taken from Wang\textsuperscript{101}.

With this result we can be confident that the One-Third rule can be successfully applied in correlating density and refractive index, for pure substances and mixtures, over a wide range of operating conditions.

The rediscovery and extension of this relationship, proposed originally for pure substances by Bykov\textsuperscript{102}, offers the possibility of its practical application to real crude oil systems.
4.1.2 Applications of the One-Third Rule

4.1.2.1 Data Consistency Test

A very straightforward application of the One-Third rule is a consistency test for experimental measurements of refractive index and mass density, when both values are obtained independently. Even in its simplest form, assuming that $F_{RI} / \rho = 1/3$, it can be easily recognized when an experimental measurement is not consistent.

Figure 4.4 shows the results of a consistency test applied to over two hundred crude oil samples $^{101}$. For most of the cases the ratio $F_{RI} / \rho$ is about 1/3.

![Figure 4.4](image)

Figure 4.4. Consistency test for refractive index and mass density measurements of over 200 crude oil samples $^{101}$. Ratio $F_{RI} / \rho$ is about 1/3 for most of the tested samples.

Another example of how the One-Third rule can be useful in determining data consistency is when we analyze data from the CRC handbook of Chemistry and Physics $^{98}$. It reports for $n$-undecane a refractive index of 1.4398 and a mass density of 0.7402 g/cm$^3$, which gives an experimental value of $F_{RI} / \rho = 0.356$. According to Eq.
(4.5) the expected value would be $F_{Ri}/\rho = 0.3395$. It turns out that the reported refractive
index is incorrect.

A refractive index of $n = 1.4167$ is estimated using $F_{Ri}/\rho = 0.3395$. An experimental
value of $n = 1.4171$ is reported in the literature. Thus, by using the above procedure it
is possible not only to identify data inconsistency, but we can also estimate the correct
value of refractive index.

**4.1.2.2 Interpolation/Extrapolation of Data**

Refractive index and density data are frequently reported at ambient conditions. However, for practical applications sometimes it is desirable to know the refractive index
at other temperatures. This is possible if we have information of mass density at ambient
temperature and at the desired temperature. Because $F_{Ri}/\rho$ can be assumed independent
of temperature, Eq. (4.6) can be readily obtained:

$$F_{Ri}(T) = F_{Ri}(T_0) \frac{\rho(T)}{\rho(T_0)}$$

(4.6)

where $T$ and $T_0$ represent the desired temperature and the reference temperature, respectively.

As an example consider the case of $n$-nonadecane, where information about mass
density and refractive index are reported at 35°C. At this temperature, $n = 1.4356$ and $\rho =
0.7752 \text{ g/cm}^3$. The refractive index at 70°C is 1.4210. With this information, by
applying equation (4.6) we readily obtain that the density at 70°C should be 0.7524
$\text{g/cm}^3$. The reported value is 0.7521 $\text{g/cm}^3$.

Now let us assume that we only know information about the mass density at ambient
temperature and the desired temperature. From Table 4.2, density of \( n \)-nonadecane at 20°C is 0.7855 g/cm\(^3\). Using Eq. (4.5) we obtain \( F_{RI}/\rho = 0.3376 \). Using density at 70°C (0.7521 g/cm\(^3\))\(^{104} \) we get the refractive index, \( n = 1.4216 \) (absolute error = +0.0006). Agreement is remarkable considering that no information about refractive index at any temperature was used. Note that if the density value at 35°C was used, instead of the value at 20°C, a refractive index of \( n = 1.4220 \) would be obtained. As it was previously pointed out the reason of the increase in error is due to the fact that equation (4.5) was fit to experimental data at 20°C.

4.1.2.3 Refractive Index from an Equation of State

The One-Third rule can also be applied for estimating the refractive index from values of mass density obtained from an equation of state. For this calculation it is necessary to use an equation of state capable of reproducing accurate values of liquid mass density. We have previously reported the successful application of the Perturbed Chain version of the Statistical Associating Fluid Theory (PC-SAFT) equation of state in predicting liquid properties, including mass density, and the phase behavior of crude oil systems.\(^{88} \) Figure 4.5 shows the comparison between experimental values of refractive indices and the results obtained by simulation using the PC-SAFT equation of state combined with the One-Third rule. The solid line is assuming \( F_{RI}/\rho = 1/3 \) whereas the dashed line is obtained with Eq. (4.5). Note that for heavy hydrocarbons the approximation of \( F_{RI}/\rho = 1/3 \) is good enough. However, this approximation is not as good for lighter hydrocarbons. In such cases, Eq. (4.5) should be employed.
Figure 4.5. Estimation of refractive index using a combination of PC-SAFT and the one-third rule. The continuous line was obtained with \( F_{R_I}/\rho = 1/3 \) and the dashed line with Eq. (4.5). Refractive indices are from the CRC handbook of Chemistry and Physics \(^{98} \) for butane and heavier hydrocarbons, and for methane, ethane and propane refractive indices are calculated using Eq. (4.2) with molecular polarizabilities from Miller \(^{99} \) and molar volumes from Barton \(^{100} \).

4.1.2.4 Solubility Parameter Calculation

Accurate calculation of solubility parameters is of great importance in modeling complex systems such as those composed by polymers or asphaltenic crude oils, using a regular solution theory based models. Examples of application to crude oil systems are numerous \(^{28,35,41,89} \). Wang and Buckley \(^{44} \) reported a correlation between the solubility parameter and the function of refractive index, \( F_{RI} \), at ambient conditions:

\[
\delta = 52.042 F_{RI} + 2.904 \tag{4.7}
\]

where \( \delta \) is units of MPa\(^{0.5} \).

The One-Third rule can now be applied to estimate solubility parameters of liquid hydrocarbons or crude oil systems as a function of their mass densities at ambient temperature. Note that although \( F_{RI}/\rho = 1/3 \) can be used as a rough approximation, for a
more accurate calculation it may be preferable to use Eq. (4.5). Incorporating Eq. (4.5) into Eq. (4.7) we obtain:

\[ \delta = 2.904 + 26.302 \rho - 20.5618 \rho^2 + 12.0425 \rho^3 \]  

(4.8)

where \( \delta \) is units of MPa\(^{0.5} \) and \( \rho \) is in units of g/cm\(^3 \).

Note that Eq. (4.8) is intended to be valid only for liquid hydrocarbons at ambient conditions.

As an example consider the cases of \( n \)-hexane and toluene, which according to Table 4.2, have densities of 0.6548 and 0.8669 g/cm\(^3 \), respectively. Using equation (4.8), the solubility parameter for \( n \)-hexane is 14.7 MPa\(^{0.5} \) and for toluene is 18.1 MPa\(^{0.5} \) at ambient conditions, which are in good agreement with values reported in the literature.\(^{100} \)

Prediction of solubility parameters at ambient conditions is useful. However, it is necessary to extend the calculation of solubility parameters to other conditions of pressure and temperature. The corresponding equations can be derived from thermodynamic relationships, as presented in Section 4.2 (Page 51).

### 4.1.2.5 Transport Properties Prediction

Riazi\(^ {91,92,105} \) has reported that a general model for calculating transport properties, such as viscosity (\( \mu \)), diffusivity (\( D \)), and thermal conductivity (\( k \)), has the form presented in Eq. (4.9):

\[ \theta_r = A \left( \frac{1}{F_{RI}} - 1 \right) + B \]  

(4.9)
where $\theta_r$ is a transport property in the form of $1/\mu$, $1/k$ or $D$, at the same temperature as $F_{RI}$. Constants A and B for various hydrocarbons are given by Riazi et al\textsuperscript{105,106}.

Combining Eqs. (4.6) and (4.9) we obtain:

$$\theta_r (T) = A \left( \frac{1}{F_{RI} (T_0)/\rho (T_0)} \cdot \frac{1}{\rho (T)} - 1 \right) + B$$  \hspace{1cm} (4.10)

where the term $F_{RI} (T_0)/\rho (T_0) = 0.5142 - 0.4176 \rho (T_0) + 0.2454 \left[ \rho (T_0) \right]^2$, according to equation (4.5).

For the heat capacity, Riazi\textsuperscript{92} proposed Eq. (4.11):

$$C_P = A_i \left( \frac{F_{RI}}{1 - F_{RI}} \right) + B_i \hspace{1cm} (4.11)$$

where $A_i$ and $B_i$ have been determined for pure hydrocarbons from various groups, and they are independent of temperature. Riazi also presented correlations for these constants as a function of molecular weight for different homologous series.

Similarly to Eq. (4.10), Eq. (4.11) can also be expressed in terms of mass densities, by using Eqs. (4.5) and (4.6).

\subsection*{4.2 Calculation of solubility parameters as a function of pressure, temperature and composition}

The cohesive energy, $e$, is defined as the negative value of the residual internal energy, $-u^{res}$, and can be calculated as the product of the molar volume, $v$, and the solubility parameter squared, $\delta^2$. 
According to Eq. (4.12), the cohesive energy can be readily calculated using an equation of state, such as PC-SAFT, by obtaining the internal energies of the liquid at the pressure and temperature of interest, and the internal energy of a gas at the same temperature but for $P \rightarrow 0$, i.e. internal energy of an ideal gas.

4.2.1 Pressure dependence of the Solubility Parameter

The pressure dependence of the cohesive energy and the solubility parameter can be derived from thermodynamic relationships.

The pressure dependence of the cohesive energy, $e$, of a pure component is given by Eq. (4.14):

$$
\left( \frac{\partial e}{\partial P} \right)_T = -\left( \frac{\partial u^{\text{res}}}{\partial P} \right)_T = T \left( \frac{\partial v}{\partial T} \right)_p + P \left( \frac{\partial v}{\partial P} \right)_T
$$

(4.14)

The thermal expansion, $\alpha_p$, and the isothermal compressibility, $\kappa_T$, are defined according to Eqs. (4.15) and (4.16), respectively.

$$
\alpha_p = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p
$$

(4.15)

$$
\kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T
$$

(4.16)

For small finite differences in pressure and temperature, $\alpha_p$ and $\kappa_T$ can be assumed to be constant, i.e. we can get average values $\overline{\alpha_p}$ and $\overline{\kappa_T}$ in that interval and Eq. (4.14) can be integrated to obtain Eq. (4.17):
\[ e(P,T) = e_0(P_0,T) + \left( \frac{1 - T \alpha_p}{\kappa_T} \right) (v - v_0) + P v - P_0 v_0 \]  

(4.17)

where: \( v \) and \( v_0 \) are evaluated at \( P \) and \( P_0 \), respectively.

Similarly, for the solubility parameter, Eq. (4.18) can be derived:

\[ \delta^2(P,T) = P + \frac{\rho_0(P_0,T)}{\rho(P,T)} \left[ \delta_0^2(P_0,T) - P_0 \right] + \left( \frac{1 - T \alpha_p}{\kappa_T} \right) \left( 1 - \frac{\rho_0}{\rho} \right) \]  

(4.18)

Or in terms of mass density, \( \rho \):

\[ \delta^2(P,T) = P + \frac{\rho(P,T)}{\rho_0(P_0,T)} \left[ \delta_0^2(P_0,T) - P_0 \right] + \left( \frac{1 - T \alpha_p}{\kappa_T} \right) \left( 1 - \frac{\rho(P,T)}{\rho_0(P_0,T)} \right) \]  

(4.19)

where \( \rho \) and \( \rho_0 \) are the mass densities evaluated at actual conditions \((P, T)\) and reference conditions \((P_0, T)\), respectively; \( \alpha_p \) is the thermal expansion and \( \kappa_T \) is the isothermal compressibility, which are defined according to Eqs. (4.20) and (4.21), respectively.

\[ \alpha_p = -\frac{1}{\rho} \frac{\partial \rho}{\partial T} \]  

(4.20)

\[ \kappa_T = \frac{1}{\rho} \frac{\partial \rho}{\partial P} \]  

(4.21)

Using Eq. (4.19), the solubility parameter of a liquid can be calculated at a given \( P \), starting from a known solubility parameter value at a reference pressure, \( P_0 \), and values of mass density as a function of pressure, in the range of interest. Solubility parameters at reference condition, \( \delta_0 \), can be obtained from the literature\(^{100} \) or, alternatively, they can be estimated using Eq. (4.8) at ambient pressure, \( P_0 = 1 \) bar. If the pressure range is wide, it can be split into several small intervals, and use successive calculations. At every interval, the corresponding values of \( \alpha_p \) and \( \kappa_T \) are calculated.

The procedure described above was implemented for the calculation of the solubility
parameter of \( n \)-hexane and benzene as a function of pressure. Solubility parameters at ambient pressure were obtained from Barton\(^{100} \). Density data were obtained from the National Institute of Standards and Technology (NIST) database\(^{107} \). Figure 4.6 shows the excellent agreement between successive calculations using Eq. (4.19) and molecular simulation data reported by Rai et al\(^{108} \).

![Figure 4.6](image)

**Figure 4.6.** Comparison between proposed model (continuous lines) and data\(^{108} \) (open markers) for the solubility parameters of benzene and hexane, as a function of the pressure.

### 4.2.2 Temperature dependence of the Solubility Parameter

The temperature dependence of solubility parameter shown in Eq. (4.22) can also be derived from thermodynamic relationships.

\[
\delta^2 (P,T) = \delta^2_0 (P,T_0) \exp[-\alpha_p (T - T_0)] + \frac{C_v \cdot \rho_0 (P,T_0)}{MW \cdot \alpha_p} \left( \exp[-\alpha_p (T - T_0)] - 1 \right) \quad (4.22)
\]

where \( \rho_0 \) is the mass densities evaluated at reference conditions \( (P, T_0) \), respectively; \( \alpha_p \) is the thermal expansion and it is defined according to equation (4.20); \( C_v \) is the heat
capacity at constant volume; and \( MW \) is the molecular weight.

Eq. (4.22) can be simplified as we identify that the first term value is much greater than the second term. We can drop the second term and obtain Eq. (4.23):

\[
\delta^2 (P, T) = \delta^2_0 (P, T_0) \exp[-\alpha_P (T - T_0)]
\] (4.23)

Note that Eq. (4.23) is equivalent to the expression reported by Hildebrand and Scott\textsuperscript{89} for the calculation of the temperature dependence of the solubility parameter.

In Eq. (4.23), once again, the value of solubility parameter at the reference condition, e.g. \( T = 20^\circ\text{C} \), can be calculated using Eq. (4.8). Values of mass density to estimate the thermal expansion, \( \alpha_P \), can be obtained from the NIST database\textsuperscript{107}. When the temperature range is wide, it can be split into several small intervals, and use successive calculations. At every interval, the corresponding values of \( \alpha_P \) are calculated.

With these analyses we conclude that the solubility parameter at any pressure and temperature can be estimated based solely on data of mass density at the pressures and temperatures of interest, using Eqs. (4.8), (4.19), and (4.23).

4.2.3 New Mixing Rule for Solubility Parameters

The current expression used to calculate the solubility parameter of a mixture, \( \delta_{mix} \), from the solubility parameter of the pure constituents is given by Eq. (4.24):

\[
\delta_{mix} = \sum_i \phi_i \delta_i
\] (4.24)

where: \( \phi \) is the volume fraction and \( \delta \) is the solubility parameter of the pure component \( i \).

This equation is an extension of the Scatchard-Hildebrand Regular Solution Theory to
mixtures containing polymers and solvents. The interaction energy of two different molecules is estimated assuming a geometric mean for the cohesive energy\textsuperscript{109}. However, even at that time, it was well known that this was an approximate result. The interaction energy density is, in general, less than or equal to the geometric mean, a result demonstrated by London\textsuperscript{110}.

This mixing rule offers a simple and accurate enough method for estimating the solubility parameters of mixtures containing liquids. However, as it was originally recognized by Hildebrand et al.\textsuperscript{111}, the presence of dissolved gases requires a special treatment. At that time, the effective volume and solubility parameter for hypothetical liquid-like dissolved gases were fit, assuming that the same mixing rule held. Even though this is a procedure that even in current references is followed\textsuperscript{100}, it has been known that the geometric mean for intermolecular forces becomes increasingly poor as the difference in size between different molecules increases\textsuperscript{112}.

A different approach can be followed starting from the definition of the cohesive energy and the molar volume of the mixture in terms of the partial molar properties of the constituents, according to Eqs. (4.25) and (4.26).

\[
e_{\text{mix}} = \sum_i x_i \tilde{e}_i \tag{4.25}
\]

\[
v_{\text{mix}} = \sum_i x_i \tilde{v}_i \tag{4.26}
\]

where: \(x_i\) is the mol fraction of component \(i\), and \(\tilde{e}_i\) and \(\tilde{v}_i\) are the partial molar cohesive energy and the partial molar volume of component \(i\), respectively.

By combining the definition of the solubility parameter with Eqs. (4.25) and (4.26), a
A quadratic mixing rule for the solubility parameter can be readily obtained.

\[
\delta_{\text{mix}}^2 = \sum \hat{\phi}_i \hat{\delta}_i^2
\]  

(4.27)

where: \( \hat{\phi}_i = \frac{x_i \bar{v}_i}{v_{\text{mix}}} \) and \( \hat{\delta}_i^2 = \frac{\bar{e}_i}{\bar{v}_i} \).

Eq. (4.27) represents an exact relationship to calculate the solubility parameter of the mixture. However, it is difficult to calculate the partial molar properties of the components and certain assumptions need to be made. Effective molar volumes and cohesive energies can be proposed for this effect.

The mixing rule proposed in this work has been validated for the system n-heptane/alpha-methyl naphtalene and is reported in Figure 4.7. Experimental data has been reported by Wang.

![Figure 4.7](image.png)

**Figure 4.7.** Comparison between the old mixing rule and the new mixing rule proposed in this work, with experimental data from Wang.
From **Figure 4.7** it is clear that the new mixing rule provides a better estimate for the solubility parameter of the mixture.

Several simulations were performed using the PC-SAFT EOS, and the results led to two important conclusions: (1) The two mixing rules give similar results for mixtures formed by similar liquids. (2) The new mixing rule is in excellent agreement with the simulation results, even for mixtures containing dissolved gases. In this case the difference with the old mixing rule was observed to be a maximum. A more detailed discussion of this analysis is presented in Appendix A.

The effectiveness of the new mixing rule depends on the accuracy of the values of partial molar properties of the different components. In some cases effective values can be used, however it may be necessary to obtain correlations for these partial molar properties as a function of composition. An approach to correlate the cohesive energy at the bubble point or asphaltene precipitation onset is proposed in the next section.

### 4.3 Development of a general method for modeling asphaltene stability

#### 4.3.1 Universal Curves for Bubble Point and Asphaltene Precipitation Onset

The correlations presented in Section 4.2 are useful in estimating the solubility parameters of a mixture as a function of pressure, temperature and composition. These tools can be applied to the analysis of petroleum systems in order to obtain a general method for modeling the phase behavior. For instance, relationships between the solubility parameters, cohesive energy, pressure and composition, at fixed temperature,
along the bubble point and onset of asphaltene precipitation curves can be readily obtained.

Although an extensive experimental database for the phase behavior of multiple crude oil systems is desirable to validate the proposed models, the time and cost are prohibitive. Alternatively, computer simulations using reliable equations of state, such as PC-SAFT, can be successfully applied to represent the systems of interest. The PC-SAFT EOS has been effectively utilized for modeling the bubble point, and onset of asphaltene precipitation in multiple cases, considering, for example, the effect of oil-based mud\textsuperscript{80}, gas injection\textsuperscript{90}, commingling of oils\textsuperscript{79}, and CO\textsubscript{2}-induced asphaltene precipitation\textsuperscript{84}.

In this study, a model dead oil composed by 1 g of \(n\)-C\textsubscript{7} precipitated asphaltene in 100 mL of toluene, is used. Several asphaltene precipitants can be proposed to study their effect on the onset of asphaltene precipitation, and ultimately, to elucidate a universal method for modeling the asphaltene instability.

This model oil mixed with methane was previously studied and characterized by Ting\textsuperscript{81}. In Figure 3.2 it is presented the comparison between experimental data and simulation results using the PC-SAFT EOS. PC-SAFT parameters and binary interaction parameters have been previously reported\textsuperscript{64,81,90}. The agreement is very good even assuming that asphaltenes are a monodisperse fraction. The good quantitative agreement between simulations and experimental data gives confidence in the effectiveness of the PC-SAFT EOS in the prediction of the phase behavior of crude oil systems, when no other experimental data is available.

As it can be observed from conventional pressure-composition (\(P-x\)) diagrams for
asphaltene stability, there is a different set of curves with no apparent relationship between them, for different asphaltene precipitants.

A different approach is now proposed in which, instead of a $P$-$x$ diagram, a cohesive energy – composition $(e-x)$ diagram is used. Because of the lack of reported data in the literature, and the prohibitive cost of performing extensive experimental measurements, the cohesive energy of a mixture of the model dead oil containing different asphaltene precipitants is calculated using the PC-SAFT EOS.

It has been found that the cohesive energy behaves linearly as a function of the asphaltene precipitant content, along a coexistence curve, e.g. bubble point or precipitation onset. Figure 4.8(a) reports the simulation results for the bubble point curve at a fixed temperature of 65°C of different mixtures as a function of the precipitant mole fraction. The corresponding trend lines are also included to emphasize the linearity obtained. Because the cohesive energies are normalized with respect the cohesive energy of dead oil, a common intercept equal to unity is obtained. Furthermore, the slope of each straight line is related to the cohesive energy of the corresponding precipitant, as it is shown in Figure 4.8(a). With the intercept and slope obtained from this analysis, a universal curve for the bubble point can be constructed as it is shown in Figure 4.9.

Figure 4.8(b) presents the simulation results for the asphaltene precipitation onset. The bubble point curves are shown in a light color as a reference. The corresponding trend lines are also shown. These straight lines converge to a single intercept that corresponds to the energy of incipient asphaltene precipitation for the model dead oil. This energy is a hypothetical value that can not be measured or calculated directly, but it can be estimated by extrapolation. In this particular case, for the model oil and the
temperature studied, the value is 0.86. The mathematical procedure to calculate this common intercept based on the method of minimum squares is presented in Appendix B. This value is of great importance because it defines the stability of the oil. The oil is less stable as this intercept increases, i.e. less amount of precipitant or pressure depletion is required to induce asphaltene precipitation.

The mathematical procedure to calculate this common intercept based on the method of minimum squares is presented in Appendix B.

This value is of great importance because it defines the stability of the oil. The oil is less stable as this intercept increases, i.e. less amount of precipitant or pressure depletion is required to induce asphaltene precipitation.

\[ \frac{v_{\text{mix}}}{v_{\text{do}}} \delta^2 = 0.86 \]

\[ v_{\text{p}} \delta^2, \text{kJ} \]

**Figure 4.8.** Simulation results using the PC-SAFT EOS for (a) Bubble point, and (b) Onset of asphaltene precipitation, for a mixture containing a model dead oil and multiple asphaltene precipitants. The slopes of the different straight lines are related to the effective cohesive energy of the precipitant used, evaluated at the corresponding conditions.
Figure 4.8(b) presents the simulation results for the asphaltene precipitation onset. The bubble point curves are shown in a light color as a reference. The corresponding trend lines are also shown. These straight lines converge to a single intercept that corresponds to the energy of incipient asphaltene precipitation for the model dead oil. This energy is a hypothetical value that can not be measured or calculated directly, but it can be estimated by extrapolation. In this particular case, for the model oil and the temperature studied, the value is 0.86. The mathematical procedure to calculate this common intercept based on the method of minimum squares is presented in Appendix B. This value is of great importance because it defines the stability of the oil. The oil is less stable as this intercept increases, i.e. less amount of precipitant or pressure depletion is required to induce asphaltene precipitation.

This analysis leads to general equations for the bubble point and onset of asphaltene precipitation, Eqs. (4.28) and (4.29), respectively:

\[
\frac{v_{mix} \delta^2_{mix}}{v_{do} \delta^2_{do}} = \frac{1}{v_{do} \delta^2_{do}} \left[(v_p \delta^2_p - v_{do} \delta^2_{do}) \cdot x_p + v_{do} \delta^2_{do}\right] \tag{4.28}
\]

\[
\frac{v_{mix} \delta^2_{mix}}{v_{do} \delta^2_{do}} = \frac{1}{v_{do} \delta^2_{do}} \left[(v_p \delta^2_p - v_{do} \delta^2_{do})_{onset} \cdot x_p + (v_{do} \delta^2_{do})_{onset}\right] \tag{4.29}
\]

where the subindex onset refers to the effective cohesive energy of the dead oil and the pure precipitants along the precipitation onset curve. Because this condition is associated to very extreme pressures, these parameters may need to be extrapolated in the practice.

Eqs. (4.28) and (4.29) can be rearranged to obtain the form:

\[
\delta^2_{mix} = \frac{v_p x_p}{v_{mix}} \delta^2_p + \frac{v_{do} \left(1-x_p\right)}{v_{mix}} \delta^2_{do} = \phi_p \delta^2_p + \phi_{do} \delta^2_{do} \tag{4.30}
\]
for either the bubble point of the precipitation onset.

Eq. (4.30) corresponds to a mixing rule of a pseudo-binary mixture that is consistent with the new mixing rule proposed in Section 4.2.3 (Page 55), i.e. Eq. (4.27), if we recall that the volumes and cohesive energies in Eqs. (4.28) and (4.29) are effective or apparent values.

In Figure 4.9, the master curves for the bubble point and the onset of asphaltene precipitation, represented by Eqs. (4.28) and (4.29), are compared with the simulation results using the PC-SAFT EOS. The different phases, and stability and instability regions are detailed.

From these results we learned that the simple models described by Eqs (4.28) and (4.29), and consequently, the new mixing rule for the solubility parameters, are consistent and in excellent agreement with the results predicted by the PC-SAFT EOS. Therefore, the proposed models are very promising in providing new alternatives for characterizing the asphaltene stability of a crude oil, and modeling the phase behavior. An extension for its practical application and the proposed procedure for experimental analysis are now addressed.
4.3.2 Application of the General Method for Modeling Asphaltene Stability

The insights that have been found from the proposed models and the thermodynamic analysis using the PC-SAFT EOS, lead to the definition of a new approach for characterizing the crude oil and describing its phase behavior, with a few data points.

The cohesive energy of a system, $e_{mix}$, can be assumed to be a linear function of the precipitant mole fraction along the coexistence curve, i.e. bubble point or asphaltene precipitation curves.

As presented in Section 4.2 (Page 51), the cohesive energy is the negative of the residual internal energy of the mixture, $-u_{mix}^{res}$, and can be estimated from the solubility
parameter, $\delta_{\text{mix}}$, and the molar volume, $v_{\text{mix}}$, according to Eq. (4.31).

\[ e_{\text{mix}} = -u_{\text{mix}}^{\text{residual}} = v_{\text{mix}} \delta_{\text{mix}}^2 \]  

(4.31)

The solubility parameter can be estimated from refractive index measurements, as it was previously presented, using Eq. (4.7).

\[ \delta = 52.042 F_{RI} + 2.904 \]  

(4.7)

Where $\delta$ is in units of MPa$^{0.5}$.

If no refractive index measurements are available, a good estimation for the solubility parameter can be obtained from mass density, by using Eq. (4.8).

\[ \delta = 2.9041 + 26.7600 \rho - 21.2327 \rho^2 + 2.7711 \rho^3 \]  

(4.8)

where $\delta$ is in units of MPa$^{0.5}$ and $\rho$ is in units of g/cm$^3$.

A sketch of the application of the general model for modeling asphaltene stability at a constant temperature $T$ is presented in Figure 4.10.

The numbers in Figure 4.10(a), (c) and (d) correspond to the steps in constructing the curves, given that data about the cohesive energies of dead oil, asphaltene precipitant or mixtures are known at bubble point and precipitation onset conditions.

The cohesive energy can be calculated either from refractive index or mass density, using Eqs. (4.31), (4.7) and (4.8). Values of cohesive energy can be extrapolated from ambient conditions measurements to high pressure using Eq. (4.17).
Figure 4.10. Application of the general method for modeling asphaltene stability. (a) The bubble point can be determined by the cohesive energy density of dead oil and pure precipitant, at the corresponding conditions. (b) Using the relationships for the cohesive energy as a function of pressure, Eq. (4.32), it is possible to determine the P-x curve. (c) The cohesive energy of incipient precipitation (point 3) can be obtained by extrapolating the precipitation onset curves using different precipitants. (d) With the common intercept and at least one precipitation onset, with the precipitant of interest, it is possible to define the cohesive energy along the onset of asphaltene precipitation. Similarly, a P-x curve can be obtained.

For the bubble point curve several data points along the coexistence curve are required, according to Figure 4.10(a). One point can be the cohesive energy of the dead oil at its saturation pressure. This value is used to normalize all the cohesive energies. The normalized cohesive energy of the dead oil at its saturation pressure is represented by point 1 in Figure 4.10(a). If the asphaltene precipitant is liquid at low or moderate pressures, and the experimental measurement is feasible, this is taken as the second data point (point 2). Otherwise any measurement along the bubble point curve is useful.
Obviously, the more data points obtained the better. However, for description purposes, we will keep the figures as simple as possible with the fewest number of data points. The straight line drawn represents the bubble point curve for that particular system (line 3).

The P-x diagram, Figure 4.10(b), can be recovered by solving Eq. (4.17) for \( P \):

\[
P = P_0 \frac{v_0}{v} + \frac{e(P, T) - e_0 (P_0, T)}{v} + \left(1 - \frac{T \alpha}{K_T}\right) \left(\frac{v_0}{v} - 1\right)
\]

(4.32)

The asphaltene precipitation onset requires one additional step, as described in Figure 4.10(c). Because the cohesive energy of incipient precipitation cannot be measured directly, this value can be determined by measuring at least three data points along the precipitation onset curve with one single asphaltene precipitant. The set of points is represented with number 1 in Figure 4.10(c). Alternatively, measurements with a second asphaltene precipitants can also be used (set number 2).

The cohesive energy of incipient precipitation (point 3) can be obtained by extrapolating the precipitation onset curves with the different precipitants. This is the common intercept described in Section 4.3.1.

Then, the precipitation onset curve can be drawn by measuring a few data points with the asphaltene precipitant of interest, according to Figure 4.10(d). Finally, if desired, the pressure-composition curve can be recovered by applying Eq. (4.32) with the variables evaluated at the corresponding conditions.

The stability test of a sample of crude oil under given conditions can be readily performed by locating the cohesive energy density in the corresponding phase diagram. For instance, for the model oil described in Section 4.3.1, the phase diagram obtained
from simulation results is shown in Figure 4.11.

As expected, there is a region of asphaltene stability, at high pressure that also corresponds to a high cohesive energy. If we deplete pressure, the cohesive energy of the mixture decreases and at some point the asphaltene precipitation onset is reached. Upon further depletion the system arrives to its bubble point. At this condition the methane comes out from the liquid phase, the oil becomes more stable, and the cohesive energy of the remaining liquid phase starts to increase again.

![Stability diagram for a model dead oil and methane at 65°C. Circles correspond to simulation data, and the lines to the expressions for bubble point and precipitation onset proposed in this work.](image)

**Figure 4.11.** Stability diagram for a model dead oil and methane at 65°C. Circles correspond to simulation data, and the lines to the expressions for bubble point and precipitation onset proposed in this work.

The analysis is similar to the corresponding pressure-composition diagram. However, because of the linear trend between the cohesive energy and the mole fraction of asphaltene precipitant, using this new approach, the experimental data can be easily extrapolated to forecast the behavior at other compositions. Furthermore, the cohesive energy of incipient precipitation is a characteristic value of a dead oil, at a given temperature, that can be used as a common point for estimating the precipitation onset
curve, regardless of the asphaltene precipitant involved.

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The method presented in this work is promising in offering good prediction capabilities of asphaltene stability in crude oils.

4.4 Chapter Summary

Important progress has been made in developing a general method for modeling asphaltene stability under a wide range of conditions. New equations are presented that contribute in the calculation of important variables such as the solubility parameter and the cohesive energy of a mixture and its components.

A new correlation, named the One-Third rule, can relate the refractive index and the mass density of a crude oil, over a wide range of temperatures and pressures. An extension for the estimation of the solubility parameter as a function of the mass density was also presented.

The effect of pressure over the solubility parameter and the cohesive energy was derived from thermodynamic relationships. The equation obtained is in excellent
agreement with data reported in literature. This equation is capable of relating the cohesive energy of a mixture with pressure along a coexistence curve, i.e. bubble point or precipitation onset.

A new mixing rule for solubility parameters was derived and proposed as an alternative to handle systems containing dissolved gases. Although, the current and the new mixing rules predict the same behavior for systems containing normal liquids, it is well known that the current mixing rule becomes increasingly poor as the difference in size between molecules increases. This is the case where the mixing rule proposed in this work should be especially valuable.

In order to find a general method for modeling the phase behavior of crude oils containing asphaltenes, mixtures of model oil and different asphaltene precipitants were studied. Because of the prohibitive costs and technical difficulties of performing extensive experiments, a simulation approach using the PC-SAFT EOS was adopted. This equation of state has demonstrated its ability to successfully modeling the phase behavior of petroleum systems. From simulation results, it was found that the cohesive energy of a mixture, normalized with respect the cohesive energy of dead oil, follows a linear trend with respect the mole fraction of asphaltene precipitant, along a coexistence curve. Furthermore, the slopes of such lines are related to the cohesive energies of the dead oil and the corresponding precipitant. The precipitation onset curves of the different mixtures converge to a single point when no asphaltene precipitant is present. This hypothetical value is characteristic of a dead oil at a given temperature, and can be used to estimate the onset of asphaltene precipitation curve when any asphaltene precipitant is added.
From this analysis, master equations for the bubble point and the onset of asphaltene precipitation were obtained, which are in excellent agreement with the simulation results. Moreover, these relationships can be readily derived from the new mixing rule proposed in this work.

A procedure for applying these findings in modeling any particular system was also discussed. By exploiting the linear behavior of the cohesive energy/composition relationship, a few data points are required to obtain the curves for bubble point and onset of asphaltene precipitation. In this way, the framework for future experimental analysis is established.
Chapter 5. Development of an Asphaltene Deposition Simulator

The objective of chapter is to provide a macroscopic modeling approach for understanding how asphaltenes are transported in a wellbore, including different phenomena, such as precipitation, advection, aggregation and deposition. The creation of a computer program based on this modeling approach is also described. It is also intended to provide an explanation to some paradoxes, such as why some asphaltene precipitation inhibitors worsen asphaltene deposition or why strong asphaltene precipitants, such as propane, produce less amount of deposit. Preliminary results obtained with this new simulation tool have been qualitatively validated with experimental work and field observations.

5.1 Proposed mechanism for asphaltene transport in the wellbore

Transport of asphaltenes in the wellbore may follow a multistep process including precipitation, aggregation, advection and deposition. The mechanism is summarized in Figure 5.1. At reservoir conditions asphaltenes are soluble in oil. However, during pressure depletion, the oil expands, reducing the oil solubility parameter, and becomes a poor solvent for asphaltene. At low enough pressure the asphaltene precipitation onset is reached and asphaltenes begin to precipitate at a certain rate. According to the mechanism, asphaltene precipitation leads to the formation of the first asphaltene particles, represented in Figure 5.1, as dark circles. These particles, that we will call micro-aggregates, can stick to one another undergoing an aggregation process, forming bigger particles or they can follow a diffusion mechanism to the surface of the tubing, where they stick and build up a deposit. Additionally both small and big particles are
transported upwards by the moving fluid, in a process known as advection.

Figure 5.1. Proposed mechanism for asphaltene transport in the wellbore.

The rate of asphaltene precipitation can be modeled as a pseudo-first order reaction in a tubular system, where the rate of precipitation is proportional to the difference between the actual concentration of asphaltene in the oil and the concentration of asphaltene at equilibrium, according to Eq (5.1).

\[
\frac{dF_A}{dV} = +r_p = k_p \left( C_A^\ast - C_A^{eq} \right)
\]  

(5.1)

where \( F_A \) is the rate at which the micro-aggregates are formed in units of mass per unit time, \( V \) is the system volume, \( r_p \) is the precipitation rate in units of mass per unit time and unit volume, \( k_p \) is the specific precipitation rate constant, \( C_A^\ast \) is the actual concentration
of asphaltenes in the oil and $C_A^{eq}$, the concentration of asphaltenes in the oil at equilibrium, at the given operating conditions.

In other words, the precipitation rate is determined by the degree of supersaturation, i.e. the greater the supersaturation degree of asphaltenes in the crude oil, the quicker the precipitation rate. When the supersaturation degree is zero, the system is right at the onset of asphaltene precipitation. According to the model, a negative supersaturation implies that the system is undersaturated and redissolution of micro-aggregates is possible. Reversibility of precipitated asphaltene has been a subject of extensive discussion. However, it seems a reasonable assumption that the small particles can be redissolved more rapidly than big particles. In fact, it has been experimentally demonstrated that insoluble asphaltene particles can be readily dissolved under the effect of ultrasonic waves, which breaks the big aggregates down into small particles. Thus, redissolution of micro-aggregates is likely to occur whereas redissolution of big particles could be neglected, at least in the timeframe of interest. A condition where redissolution of micro-aggregates can occur is when the system pressure falls below the bubble point pressure, where the light components, which are asphaltene precipitants, come out of the liquid phase. As this happens, the solubility parameter of the oil increases until the oil becomes a better asphaltene solvent. All the remaining micro-aggregates are readily redissolved. Big aggregates remain, as they are redissolved much more slowly. In our model, the big aggregates are assumed to be insoluble.

Eq (5.1) can be solved to get a final expression for the asphaltene precipitation rate:

$$r_p = k_p \left(C^*_0 - C_A^{eq}\right) \exp(-k_p \tau)$$  

(5.2)
where \( r_p \) is the precipitation rate, \( k_p \) the precipitation rate constant, \( C_0^* \) the concentration of asphaltenes in solution at inlet conditions, \( C_A^{eq} \), the concentration of dissolved asphaltenes at equilibrium, and \( \tau \) is space time. In this particular case, \( \tau \) is calculated as

\[
\tau = \frac{z}{\langle v_z \rangle} \quad (5.3)
\]

where \( \tau \) is the time in which the fluid travels a distance \( z \) at an average velocity \( \langle v_z \rangle \).

The micro-aggregates formed from precipitation can continue the aggregation process, diffuse both in axial and radial directions, deposit at the surface of the pipe or travel along with the fluid. In our model, axial diffusion is neglected, as the transport in that direction is assumed to be dominated by the advection term.

Diffusion and advection are modeled using the traditional equations of mass transport. The aggregation and deposition steps are modeled using a pseudo-first order reaction, according to Eqs (5.4) and (5.5).

\[
-r_A = k_A C_A \quad (5.4)
\]

\[
-r_D = k_D C_A \quad (5.5)
\]

where \( r_A \) and \( r_D \) are the rates of asphaltene aggregation and deposition, respectively, and \( k_A \) and \( k_D \) are the corresponding rate constants.

All these phenomena can be incorporated into a mathematical model that tracks the transport of micro-aggregates. The material balance in transient state for these particles is represented by Eq. (5.6).
\[
\frac{\partial C_A}{\partial t} = -v_z \frac{\partial C_A}{\partial z} + 1 \frac{\partial}{\partial r} \left( D \cdot r \cdot \frac{\partial C_A}{\partial r} \right) - \frac{k_A C_A^{m_A}}{k_p \left( C_0 - C_A^{eq} \right)} \exp \left( -k_p \frac{z}{v_z} \right)
\]

(5.6)

subjected to the following boundary and initial conditions:

- **BC1**: \( \frac{\partial C_A}{\partial r} = 0 \) \at \( r = 0 \) \forall \( z \)
- **BC2**: \( C_A = C_0 \) \at \( z = 0 \) \forall \( r \)
- **BC3**: \( D \frac{\partial C_A}{\partial r} = -k_D C_A^{m_D} \) \at \( r = R \) \forall \( z \)
- **IC**: \( C_A = C_0 \) \at \( t = 0 \) \forall \( r, z \)

where \( C_A \) is the concentration of micro-aggregates, \( t \) is the time, \( v_z \) velocity of the fluid, \( z \) the axial distance, \( R \) is the radial distance, \( R \) is the radius, \( D \) is the diffusion coefficient, \( C_0 \) is the concentration of micro-aggregates at inlet conditions, \( C_A^{eq} \) is the concentration of dissolved asphaltenes at equilibrium, \( k_A \) and \( k_p \) the aggregation and precipitation rate constants, respectively. \( m_A \) and \( m_D \) represent the reaction orders for aggregation and deposition, respectively. Because no information was available to determine reaction orders \( m_A \) and \( m_D \), they were assumed to be equal to one for simplicity. As more information becomes available, orders \( m_A \) and \( m_D \) can be adjusted accordingly.

Boundary condition 3, BC3, represents the deposition of asphaltenes.

The velocity of the fluid, \( v_z \), is a function of radius for laminar flow. For flow in a circular pipe:

\[
v_z = v_z(r) = 2 \left( v_z \right) \left( 1 - \left( \frac{r}{R} \right)^2 \right)
\]

Velocity can be assumed constant and equal to the average velocity, \( \left\langle v_z \right\rangle \), in turbulent regime (except at \( R = R_0 \), where \( v_z = 0 \)).
Eq. (5.6) can be expressed in dimensionless form letting $\psi = C_A/C_0^*$, $\theta = t(v_z)/L$, $\zeta = z/L$ and $\eta = r/R$ to obtain Eq. (5.7): 

$$\frac{\partial \psi}{\partial \theta} = 2(\eta^2 - 1) \frac{\partial \psi}{\partial \zeta} + \left( \frac{L}{Pe} \eta \frac{1}{\partial \eta} \right) \left( \eta \frac{\partial \psi}{\partial \eta} \right) - Da_A \psi + Da_p (1 - \psi^{eq}) \exp(-Da_p \zeta)
$$

subjected to the boundary conditions in the corresponding dimensionless form:

- **BC1**: $\frac{\partial \psi}{\partial \eta} = 0$ at $\eta = 0 \forall \zeta$
- **BC2**: $\psi = \psi_0$ at $\zeta = 0 \forall \eta$
- **BC3**: $\frac{\partial \psi}{\partial \eta} = -Da_p \psi$ at $\eta = 1 \forall \zeta$
- **IC**: $\psi = \psi_0$ at $\theta = 0 \forall \eta, \zeta$

Transformation of the partial differential equation into a dimensionless form yields to the definition of dimensionless variables: $Pe$, the Péclet number, and $Da_A$, $Da_P$, $Da_D$, the Damköhler numbers of aggregation, precipitation and deposition, respectively.

$Pe = \frac{v_z R}{D}$, $Da_p = \frac{k_p L}{v_z}$, $Da_A = \frac{k_A L}{v_z}$, $Da_D = \frac{k_D R}{D}$.

If $m_A$ and $m_D$ were different than one: $Da_A = \frac{k_A (C_0^*)^{m_A-1} L}{v_z}$, $Da_D = \frac{k_D (C_0^*)^{m_D-1} R}{D}$.

Péclet number physically represents the ratio:

$$Pe = \frac{\text{Rate of transport by advection}}{\text{Rate of transport by diffusion}}$$

Damköhler numbers represents the ratios:

$$Da_p = \frac{\text{Rate of production of microaggregates by precipitation}}{\text{Rate of transport of microaggregates by advection}}$$

$$Da_A = \frac{\text{Rate of consumption of microaggregates by aggregation}}{\text{Rate of transport of microaggregates by advection}}$$

$$Da_D = \frac{\text{Rate of consumption of microaggregates by deposition}}{\text{Rate of transport of microaggregates by diffusion}}$$
The current stage of the deposition model considers an isothermal system with simple micro-aggregate units, which are assumed to be the entities that could stick to the surface and form a deposit, neglecting bigger aggregates. It has been shown, both experimentally\textsuperscript{114} and by molecular simulations\textsuperscript{115}, that the bigger the aggregates the less suitable they are for deposition. The extension of the current mechanism to include aggregates of bigger size is possible and may be pursued in the future.

A distinction between precipitation and aggregation is also important in the proposed model. Although at first the mechanism of both phenomena could be assumed identical, it has been shown experimentally that this might not be the case. Kraiwattanawong et al.\textsuperscript{116} have reported that none of the asphaltene chemical inhibitors that they tested in their study prevented the phase separation of asphaltenes, but some of them did slow or stop flocculation and growth. The assumption of two distinct steps of phase separation and particle growth seems reasonable.

5.2 Model implementation and simulator structure

The proposed model has been implemented both in transient and steady state forms. The systems studied are at two different scales: wellbore and capillary. The objective of simulating asphaltene deposition in a capillary system is to obtain a better understanding of the variables affecting the process. New experiments can be proposed based on this new knowledge. A conventional numerical technique of finite differences has been used for solving the partial differential equation in dimensionless form with the corresponding boundary conditions. A detailed description of the solution can be found in Appendix D.

A parametric study has been conducted, where the effect of the different parameters
of the model are tested. Furthermore, the effect of temperature on asphaltene precipitation/aggregation/deposition has also been analyzed. For this purpose, typical Arrhenius functional forms for the temperature dependence of reaction rates and viscosity, and the Wilke and Chang\textsuperscript{117} model for diffusion coefficient have been assumed. Simulation results are then compared with experimental and field observations.

The simulator structure is represented by Figure 5.2. Input variables are shown in the left hand side. Operation variables such as pressure and temperature, flow rate and system geometry are needed, as well as the characterization of oil and asphaltenes. The method for obtaining the PC-SAFT parameters for oil fractions and asphaltenes has been previously described by Gonzalez\textsuperscript{79,80}. Additionally the rates of precipitation, aggregation and deposition are needed, in order to define the corresponding dimensionless numbers of the model. Alternatively, deposition profiles can be matched by tuning the values of unknown variables. The thermodynamic modeling using the PC-SAFT EOS for estimating the asphaltene stability is performed in the commercial software VLXE. Because the native language of VLXE, written in C++, is different than the deposition simulator, written in Fortran, a translating interface had to be coded. This interface allows the operation of both simulators in their native languages, and live interaction, as well as the flexibility of future individual upgrades without affecting the performance of the assembled simulation tool. VLXE is used to calculate the concentration of asphaltenes at equilibrium (asphaltene solubility), which along with the actual concentration of asphaltenes in the oil, determines the supersaturation degree and consequently, the precipitation rate, according to Eq.(5.2).
Figure 5.2. Simulator structure including, input parameters, and interface for thermodynamic modeling.

The thermodynamic calculations performed in VLXE are reported and stored in the form of a look-up table, which is the input file to the deposition simulator. Therefore, the deposition simulator is not restricted to be operated in connection with VLXE. Other commercial simulators can be used to generate the look-up table containing the information of asphaltene solubility at different operation conditions. Alternatively, a multiphase flash algorithm can be coded following the procedure described in Appendix C. The look-up table approach is used instead of a fully compositional simulator to reduce the computational time necessary to perform the calculations.

5.3 Results and Discussion

Simulations have been performed, and a mechanism that explains the competition between asphaltene aggregation and deposition has been identified. This competition follows directly from the mechanism of formation and consumption of micro-aggregates described in the previous section. If conditions are favorable for enhancing aggregation,
the amount of available micro-aggregates decreases rapidly, diminishing the deposition rate, and vice versa. Most of the asphaltene precipitation inhibitors act as asphaltene dispersants, decreasing the population of big aggregates and thus, enhancing the permanence of micro-aggregates. Consequently, asphaltene deposition could be promoted. Therefore, this competing phenomenon explains why some asphaltene dispersants actually worsen the deposition problem, as it has been confirmed recently.

Another interesting experimental observation has been reported while conducting capillary tests. When asphaltenic crude oil is pre-mixed with an asphaltene precipitant, and after some time the mixture is flown through the capillary, no deposition is seen. In order to observe deposition, the oil has to be mixed with an asphaltene precipitant and fed to the capillary immediately. The explanation of this experimental observation can also be drawn from the proposed mechanism. In the former case, aggregation of asphaltene micro-aggregates was undertaken, depleting the population of the simplest and smallest particles, and thus, preventing deposition. In the latter case, both aggregation and deposition can take place, due to the existence of micro-aggregates along the capillary tube.

Additionally, the unexpected poor deposition produced by strong asphaltene precipitants, such as propane, can also be explained in terms of the given mechanism. The addition of a strong asphaltene precipitant rapidly increases the supersaturation degree and consequently the precipitation occurs quickly. As the concentration of micro-aggregates in the bulk of the fluid rapidly increases, the aggregation process that can take place at any point of the system is favored over deposition that can occur only at the boundary layer.
The temperature effect has also been studied. The preliminary results show that in a capillary, as temperature increases, the asphaltene deposition flux increases towards the capillary inlet, and it rapidly decreases towards the outlet. This behavior is in good agreement with experimental data obtained from capillary experiments. The comparison is shown in Figure 5.3.

![Figure 5.3](image)

**Figure 5.3.** Sensitivity analysis of Damköhler number of precipitation: Effect on asphaltene deposition flux. A comparison with experimental data from Wang and Buckley\textsuperscript{101} is presented.

Furthermore, it has been obtained that at lower temperatures, the amount deposited not only decreases but it is also more uniform. It was found that there is a temperature at which asphaltene deposition is maximum, according to Figure 5.4.
Figure 5.4. Simulation results of the temperature effect on deposition, in a capillary system.

Beyond that temperature asphaltene deposition flux decreases and finally stops. This is an expected behavior, as we can anticipate from a typical asphaltenic crude oil phase diagram shown in Figure 3.4 (Page 23), where data from Jamaludin et al.\textsuperscript{83} for asphaltene precipitation are compared with simulation results\textsuperscript{84,88}, using the PC-SAFT EOS. Asphaltene precipitation, and consequentially deposition, stops because at temperatures above the UCEP (Upper Critical End Point) boundary, asphaltenes become stable in crude oil. However, the model also predicts that at very high temperatures, above the LCEP (Lower Critical End Point) boundary, asphaltenes become unstable again and form a deposit. This is more likely to happen inside heat exchangers, at a later stage of the refining process, and not in the wellbore.

Wellbore simulations were also performed, where the objective was to study the flexibility of the model to match the reported measurements of the Hassi-Messaoud field\textsuperscript{119}. Different combinations of parameter values were tested and the qualitative
agreement obtained is acceptable, as it can be seen in Figure 5.5.

\[ \zeta = \frac{r}{L} \\
\eta = \frac{r}{R} \]

**Figure 5.5.** Comparison of simulation results on deposition profiles with field measurements of the Hassi-Messaoud field\(^{119}\).

There are two ways of obtaining the appropriate parameter values: one is by matching one by one the different terms of the model (precipitation, aggregation, and deposition rates) against the corresponding experimental data. Because this information is not typically available, the alternative is to tune the parameter values simultaneously to match a deposition profile and the data that might be available.

### 5.4 Chapter Summary

A macroscopic approach for providing insight into the mechanism of transport of asphaltenes in the wellbore has been presented. A complex multi-step process that includes precipitation, aggregation, advection and deposition of asphaltenes has been
coded in a simulation tool, and the results obtained have been validated with experimental data and field observations.

A competing phenomenon between aggregation and deposition has been identified. Such a mechanism is useful in providing an explanation for interesting paradoxes including the adverse effect of some asphaltene precipitation inhibitors on asphaltene deposition, and the poor deposition obtained when strong asphaltene precipitants are used, among others.

Simulations of capillary systems have also been performed. The effect of temperature on the deposition rate has been studied at fixed pressure, and the first results in this area have been obtained. Asphaltene deposition may or may not be uniform along the capillary depending on the temperature, keeping all the other variables constant. As the temperature increases the amount deposited towards the capillary inlet increases, but it reduces elsewhere. After reaching a maximum at a certain temperature, deposition decreases as temperature increases, because we approach the upper critical end point boundary, above which asphaltene is stable in the oil.

The simulation results obtained in a wellbore system, while performing a sensitivity analysis of the model parameters, are comparable with those reported from the Hassi-Messaoud field.

Although, fine tuning of the different parameters of the model is still necessary, the ideas behind the development of this asphaltene deposition simulator should contribute significantly to understanding and predicting asphaltene precipitation and deposition under reservoir conditions.
Chapter 6. Other suspected condition affecting asphaltene precipitation

6.1 Potential effect of Fe(III) ion inducing asphaltene precipitation

Preliminary results suggest that the presence of water containing ferric ions in CO₂ flooding production wells could have an important effect in inducing precipitation of asphaltenes at the water/oil interface and possibly in increasing arterial deposition.

This section describes the background, field observations and initial experiments that support this idea. However, further studies are necessary to verify this hypothesis and quantify the tendency of asphaltene precipitation and deposition attributed to the presence of iron ions.

During a site visit to an on-shore field in Colorado it was identified that the asphaltene deposits collected from the tubing above the electric submersible pump (ESP) contained certain particles of yellow and red color, as it is shown in Figure 6.1. This color is characteristic of ferric oxides / hydroxides. This supposition was later confirmed with elemental analysis.

Because ferric ions in aqueous solutions are good flocculants of organic matter, the iron could have favored the precipitation and agglomeration of asphaltene particles. Different authors have reported that ferric chloride is an excellent flocculant for organic matter in water systems, at pH of 5.5, especially for aromatic hydrocarbons containing hydroxyl and carboxylic groups.
6.1.1 Suspected activity of ferric ions in the wellbore

Ferric ions could be present in the wellbore as a result of:

1) injection of formation water with naturally dissolved iron
2) corrosion of pipes, and
3) gradual dissolution of iron bearing minerals such siderite, pyrrhotite, pyrite, hematite, and ferrite.

The problem is aggravated in CO₂ flooding producing wells, where the low pH produced by the carbonic acid increases corrosion and dissolution of iron minerals.

Ferric ion can be a strong oxidant, capable of dissolving metallic iron:

\[ 2Fe^{3+}(aq) + Fe^0(aq) \rightarrow 3Fe^{2+}(aq) \]  \hspace{1cm} (6.1)

then ferrous ion is readily oxidize at low pH according to the following reaction:
Corrosion of pipes due to this autocatalytic reaction is itself an important problem that needs to be addressed. Additionally, the presence of ferric ions has been previously identified to induce asphaltic sludge formation in the presence of acid\textsuperscript{123}. This phenomenon has been reported with crudes of Western Canada such as Beaverhill Lake crude, crudes of Alaska and California, the San Andres crudes of West Texas, and the Smackover crudes of Mississippi, among others. Although some work has been devoted to the identification and description of this problem during acid stimulation treatments\textsuperscript{123-125}, not much attention has been dedicated to understanding the effect of iron ions themselves on asphaltene precipitation and aggregation.

### 6.1.2 Interfacial precipitation of asphaltenes

Initial experiments using a pendant drop apparatus have been carried out to verify the formation of asphaltene aggregates at the interface of water/oil systems.

Asphaltenes were extracted from a crude oil from Gulf of Mexico, following standard procedures. A model oil containing 1 g of asphaltenes / 100 mL toluene was prepared, as well as solutions of ferric chloride (0.05 g FeCl\textsubscript{3}·6H\textsubscript{2}O / 100 mL) and sodium chloride (synthetic brine, 10 g NaCl / 100 mL).

Multiple experiments were carried out using the model oil and the different aqueous solutions. In this case the former is the light fluid and the latter the heavy one.

A droplet of model oil was formed using an inverted needle, submerged in a cell containing the aqueous phase, as it is shown in Figure 6.2. The droplet was left in contact
with the aqueous phase for variable amount of time (1, 10, 60, and 180 minutes). After this time the oil was withdrawn carefully to shrink the droplet and observe the formation of a film at the water / oil interface.

![Diagram of pendant drop apparatus](image)

**Figure 6.2.** Pendant drop apparatus for measuring interfacial properties of water / oil systems.

### 6.1.3 Preliminary results

A film, presumably of asphaltenes, was formed at the water / oil interface. Although this film was observed in all the cases, it was qualitatively appreciated that the film formed more rapidly in the presence of ferric ion. In fact, it was observed that in that case the film starts to form immediately upon formation of the oil droplet.

The progression of the oil droplet shrinking reveals the formation of a film in presence of ferric ion, according to **Figure 6.3.**
Figure 6.3. Progression of droplet shrinking upon oil withdrawal. The formation of a film is observed.

After completely withdrawing the liquid and collapsing the film, the oil is re-injected, as it is shown in Figure 6.4.

Figure 6.4. Progression of oil reinjection after oil withdrawal.

6.1.4 Conclusions and Proposed Work

The presence of iron oxide / hydroxide particles trapped in the asphaltene deposits observed in the field, the well-known properties of ferric ions to flocculate aromatic components, and the qualitatively observations using a pendant drop apparatus technique justify the need of exploring this subject in deeper and more quantitative detail.

Systematic studies using an Oscillating Pendant Drop apparatus (OPDA) are proposed. The idea is to use different aqueous phases, i.e. brine, ferric chloride at
different pH values, distilled water, with real crude oils and model oils, to quantify the effect of iron ions forming an asphaltene layer at the water / oil interface. The formation of asphaltene layers as a function of time can be studied using the OPDA. These studies could provide useful information about the kinetic of formation of this film under the different conditions, as well as some of its physical properties.

Additionally, experiments can be proposed to study the effect of ferric ions in increasing the deposition tendency of asphaltenes. For example, experiments can be designed to quantify the corrosion produced by ferric ions at different conditions, as well as potential alteration of the wettability of the metallic surfaces. Important insight into the mechanism of asphaltene deposition could be obtained.
Chapter 7. Conclusions and Recommendations

7.1 Conclusions

Important progress has been made in developing tools for the analysis and quantification of asphaltene precipitation and deposition in the wellbore during oil production operations.

In Chapter 1 it was stated that this research has been motivated by four main objectives, which have been successfully addressed, according to the developments and results described below:

1. Verify and enhance current approaches and propose new alternatives in studying asphaltene phase behavior.

The methods for modeling asphaltene phase behavior using the Flory-Huggins based models can be enhanced by considering the compressibility effects on the solubility parameter calculation. Correlations for the pressure and temperature dependence of the solubility parameter, as well as an improved mixing rule for solubility parameters have been developed and validated using molecular simulations and experimental data (Section 4.2). The new mixing rule for solubility parameters was derived as an alternative to handle systems containing dissolved gases or components with high disparity of solubility parameter values. Although, the current and the new mixing rules predict about the same behavior for systems containing liquids, it is well known that the current mixing rule becomes increasingly poor as the difference in size between molecules increases. This is the case where the new mixing rule is expected to offer superior performance.
The analysis of phase stability using the solubility parameter approach is valuable even when other modeling techniques are employed, as it was shown in Section 3.4.6 in the analysis of CO$_2$ induced asphaltene precipitation. In this example, the PC-SAFT EOS was used for modeling asphaltene phase behavior. However, the explanation of the dual effect of CO$_2$, which is able to induce or prevent asphaltene precipitation depending on the operating conditions, was explained based on the compressibility of CO$_2$ at high pressure and its effect on the solubility parameter.

Another important contribution has been the development of a new correlation, named the One-Third Rule, which can relate the refractive index and the mass density of a hydrocarbon system, over a wide range of temperatures and pressures. It offers the possibility of evaluating the consistency of data, or its interpolation and extrapolation, as well as the calculation the solubility parameter and transport properties.

2. Develop a general method for modeling asphaltene stability.

Important progress has been made in the development of a general method for modeling the phase behavior of crude oils containing asphaltenes. Because a prohibitive cost and technical difficulties of performing extensive experimental work at high pressures and temperatures, a simulation approach using the PC-SAFT EOS has been proposed to generate pseudo data that can be used to study these systems. This equation of state has demonstrated its ability to accurately predict crude oil bubble point and density as well as asphaltene precipitation conditions. From simulation results, it was identified that the cohesive energy of a mixture is a linear function of the molar fraction of the asphaltene precipitant or mixture of precipitants involved. Furthermore, the slopes
of these linear functions are related to the cohesive energy of the dead oil and the corresponding precipitant. Interestingly, the precipitation onset curves of the different mixtures studied converge to a single intercept in the limit of zero mole fraction of precipitant. This hypothetical value, which offers a new alternative to establish the tendency of an oil to precipitate asphaltenes, is characteristic of a dead oil at a given temperature, and can be used to estimate the onset of asphaltene precipitation for any given precipitant or mixture. A procedure for applying this development in modeling any particular system was also proposed. By exploiting the linear behavior of the cohesive energy and composition relationships, instead of the traditional pressure versus composition curves, a few data points are needed to obtain curves for bubble point and onset of asphaltene precipitation.

3. Propose and validate a mechanism for asphaltene deposition in the wellbore.

A macroscopic approach for providing insight into the transport of asphaltenes in the wellbore has been presented and discussed. Section 5.1 shows the development of a complex multi-step mechanism that includes precipitation, aggregation, advection and deposition of asphaltenes. The main assumption of this model is that the micro-aggregates, formed during the precipitation of asphaltenes, are small particles that can stick to one another undergoing an aggregation process, forming bigger particles or they can follow a diffusion mechanism to the surface of the tubing, where they stick and build up a deposit. It is assumed that bigger particles have a negligible tendency to deposit. This idea was later validated with experimental evidence and molecular simulations performed by other groups, as discussed in Section 5.1. A competing phenomenon
between aggregation and deposition has been identified. This competition follows directly from the mechanism of formation and consumption of micro-aggregates. If conditions are favorable for enhancing aggregation, the amount of available micro-aggregates decreases rapidly, diminishing the deposition rate, and vice versa. The proposed mechanism is useful in providing an explanation for interesting paradoxes including the adverse effect of some asphaltene precipitation inhibitors on asphaltene deposition, and the poor deposition obtained when strong asphaltene precipitants are used, among others, as it was explained in Section 5.1.

4. Suggest appropriate algorithms to study and forecast the occurrence and magnitude of asphaltene deposition in the wellbore.

The mechanism proposed for asphaltene transport in the wellbore has been translated into a mathematical model that represents the material balance of micro-aggregates in the wellbore. A computer program solves the partial differential equation subjected to boundary conditions that include the formation of asphaltene deposit using an appropriate numerical scheme. A finite difference method has been implemented. The physical domain is divided into several cylindrical elements where the pressure and temperature are assumed to be constant. Then using a look up table, which is created using a thermodynamic modeling tool, at the corresponding pressure and temperature, the concentration of asphaltenes at equilibrium conditions are determined. The supersaturation degree, which is the difference between the actual concentration of asphaltenes and the concentration at equilibrium, determines the rate of precipitation. The rate of precipitation is equal to the rate at which the micro-aggregates are formed. A
kinetic term is employed for modeling the aggregation and deposition rates and for simplicity a pseudo-first order reaction is assumed in both cases. By bringing the isothermal model into a dimensionless form, four parameters are obtained: a Péclet number, and three Damkhöler numbers (precipitation, aggregation and deposition). The mathematical model can be solved using the computer program for a given set of dimensionless numbers to obtain the deposition flux both in transient and steady states. Comparison can be made with experimental or field data.

Simulations of capillary systems have also been performed. The objective of these simulations is to obtain a better understanding of the variables affecting the process. New experiments can be proposed based on this new knowledge. The effect of temperature on the deposition rate has been studied, and the first results in this area have been obtained. Asphaltene deposition may or may not be uniform along the capillary depending on the temperature, keeping all the other variables constant. As the temperature increases the amount deposited towards the capillary inlet increases, but it reduces elsewhere. After reaching a maximum at a certain temperature, deposition decreases as temperature increases, because we approach the upper critical end point boundary, above which asphaltene is stable in the oil. There is no experimental evidence yet to support these results, but different research groups have shown interest in performing these measurements. In the near future it would be possible to validate these results and extend the simulation schemes to the wellbores where temperature might play an important role as well.

The simulation results obtained in a wellbore system, while performing a sensitivity analysis of the model parameters, are comparable with those reported from the Hassi-
Messaoud field.

The simulations performed suggest that asphaltene polydispersity play a significant role defining the deposition profile.

Although, fine tuning of the different parameters of the model is still necessary, the ideas behind the development of this asphaltene deposition simulator should contribute significantly to understanding and predicting asphaltene precipitation and deposition under reservoir conditions.

Another important contribution of this research project is the identification of the effect of water containing ferric ions that can potentially induced asphaltene precipitation at the water-oil interface. Preliminary results suggest that the presence of water containing ferric ions in CO₂ flooding production wells could have an important effect in inducing precipitation of asphaltenes at the water/oil interface and possibly in increasing arterial deposition. Chapter 6 presented the background, field observations and initial experiments that support this idea. The presence of iron oxide / hydroxide particles trapped in the asphaltene deposits observed in the field, the well-known properties of ferric ions to flocculate aromatic components, and the preliminary experiments using a pendant drop apparatus justify the need of exploring this subject in a deeper and more quantitative way.
7.2 Recommendations

Results presented in this dissertation are encouraging and lead to the establishment of several recommendations for future work:

1. Investigation of effect of asphaltene polydispersity on deposition flux

Most of the time, for simplicity, asphaltenes are assumed to be monodisperse for modeling and simulation purposes. However, according to the information presented in Sections 3.4.5 and 5.3 polydispersity of asphaltenes may play a determinant role not only in defining its precipitation tendency, amount precipitated, and rate of precipitation, but it also affects dramatically the deposition flux obtained from the simulations. It is recommended to include asphaltenes as a polydispersed distribution. As more data becomes available for deposition rates, from experimental work, field measurements or molecular simulations, it would be possible to compare the data against the simulation results using monodisperse and polydispersed asphaltenes and quantify this effect.

2. Validation of the dual action of CO₂ as asphaltene precipitant and inhibitor

The simulation results shown in Section 3.4.6 for the peculiar effect of CO₂ in inducing or preventing asphaltene precipitation, depending on the pressure and temperature of the field, has been at least qualitatively validated by field observations. However, quantitative data was unavailable at the moment of elaborating this analysis. As more information becomes available it would be interesting to extend the simulation methods described in this work to other cases of crude oils containing asphaltenes that are put in contact with CO₂. The simulation results can also provide an indication of the
pressures and temperatures that should be employed in the laboratory to observe the increase or decrease in the stability of asphaltenes due to CO$_2$ addition.

3. Application of the One-Third rule to relate the mass density of the oil with its tendency to precipitate asphaltenes

According to the work presented in Section 4.3 the cohesive energies or the solubility parameters of the oil, precipitants and asphaltenes can be used to determine the tendency of the crude oil to precipitate asphaltenes. It was also shown in Section 4.1.2.4 that the One-Third Rule can be used to calculate the solubility parameter as a function of the mass density at room temperature and then use the correlation for the temperature dependence to calculate the solubility parameter at any temperature. Thus, it would be possible by using density data at different temperatures to estimate the solubility parameters of the oil and precipitants and estimate the tendency of the crude oil to precipitate asphaltenes at any temperature. Furthermore, it has been proposed and validated against experimental data and molecular simulations, that the phase behavior of asphaltenes can be explained based solely on van der Waals interactions, and that the polar interactions and hydrogen-bonding can be neglected. The implication then is that the phase behavior is dominated by the polarizability of the asphaltene molecules, which can be determined experimentally using refractive index measurements. However, because the One-Third Rule offers a relationship between refractive index and mass density, it could be possible, in principle, to calculate the polarizability of asphaltenes, and the crude oil based on their respective mass densities. If the dispersion forces are related to the polarizability of the molecules, it might be possible to quantify such forces
based on simple determinations of the mass density at the different conditions. In other words, it seems reasonable to propose a procedure to calculate the tendency of a given crude oil to precipitate asphaltenes, based on the values of density at a given temperature and pressure. Information about density of crude oil containing different amounts of asphaltene precipitant at different pressures and temperatures are necessary to perform this analysis. The experiments might not be easy to perform, but simulation schemes using the PC-SAFT EOS might be adopted to help in the definition of the experimental protocols.

4. Validation of the new mixing rule with dissolved gases

The new mixing rule for solubility parameters presented in Section 4.2.3 was proposed as an alternative to handle systems containing dissolved gases. Although, the current and the new mixing rules predict about the same behavior for systems containing liquids, it is well known that the current mixing rule becomes increasingly poor as the difference in size between molecules increases. Unfortunately, no data were found for systems containing hydrocarbon and dissolved gases. Experimental determination of density of a system containing different proportions of a liquid hydrocarbon and a dissolved non-polar gas would be useful to validate the new mixing rule. The calculation of the effective solubility parameter of the gas will require the determination of its partial molar volume. Equations for the temperature and pressure dependence of the solubility parameter described in Section 4.2 may be useful to estimate the solubility parameter of the components starting from the reported values at ambient conditions. It is important to emphasize that the reported values for solubility parameters of gases might not be correct,
as they are based on a mixing rule that it is suspected to be wrong for such systems.

5. Extension of the general method for modeling asphaltene stability in crude oils

Section 4.3 presented the development of a general method for modeling asphaltene precipitation in a model system containing asphaltenes in toluene at a fixed temperature. The procedure can be extended to study crude oil systems with different precipitants and mixture of precipitants at different temperatures. The insight obtained from studying the model oil is expected to be valid for more complex systems. However, it is necessary to carry out both simulations and experiments to validate this idea. Correlations for the temperature and pressure dependence of the solubility parameters, as well as the mixing rule proposed in Section 4.2 may useful tools for this study. Measurements of density of the mixture at different compositions, temperatures and pressures would be very useful to obtain experimental validation of this method.

6. Study of ferric ions effect inducing asphaltene precipitation at the water-oil interface and potential stabilization of emulsions

The presence of iron oxide / hydroxide particles trapped in the asphaltene deposits observed in the field, the well-known properties of ferric ions to flocculate aromatic components, and the qualitatively observations using a pendant drop apparatus technique justify the need of exploring this subject in deeper and more quantitative detail.

Systematic studies using an Oscillating Pendant Drop apparatus (OPDA) are proposed. The idea is to use different aqueous phases, i.e. brine, ferric chloride at different pH values, distilled water, with real crude oils and model oils, to quantify the
effect of iron ions forming an asphaltene layer at the water/oil interface. The formation of asphaltene layers as a function of time can be studied using the OPDA. These studies could provide useful information about the kinetics of formation of this film under the different conditions, as well as some of its physical properties.

Additionally, experiments can be proposed to study the effect of ferric ions in increasing the deposition tendency of asphaltenes. For example, experiments can be designed to quantify the corrosion produced by ferric ions at different conditions, as well as potential alteration of the wettability of the metallic surfaces. Important insight into the mechanism of asphaltene deposition could be obtained.

It is also possible that by a similar mechanism, the presence of ferric ions in the water phase may stabilize emulsions. Experiments can be designed accordingly to verify this hypothesis and propose alternatives to minimize the negative impact of ions in the water phase.

7. Enhancement of the deposition simulator and validation against experimental and field data

The simulation tool described in this work can be enhanced by incorporating energy and hydrodynamic models. The former consists in an energy balance over the entire domain, which can be discretized similarly to what was done to solve the material balance for micro-aggregates. The dimensionless energy equation will lead to new dimensionless numbers Nusselt and Prandtl that will have to be defined for the given systems either through appropriate correlations or by fitting the parameters to known experimental or field measurements. Heat capacity and thermal conductivity of the crude
oil could be estimated using the One-Third Rule described in Section 4.1.2.5. It would be also interesting to explore the possibility of incorporating a computational fluid mechanic scheme to account for the hydrodynamic forces affecting the advection, diffusion and deposition of asphaltene particles.

As it was previously pointed out, one simplification of the model was to assume that only monomers can stick to the wall, whereas bigger aggregates were neglected. This detail can also be addressed in a future development to include a distribution of particles being adsorbed at the boundary layer.

One more additional component to be considered is the aging of the deposit that has been observed in the field. Apparently the soft deposit initially formed, that possibly includes oil trapped in the asphaltene structure, matures over time, squeezing light components out and leading to the formation of a more rigid structure that becomes more difficult to remove by mechanical methods.

And ultimately it would be necessary to relate the model parameters to thermodynamic and transport properties of the oil and asphaltenes both in solution and deposited, as well as the characteristics of the reservoir, wellbore and operating conditions. More experimental data to calculate the kinetic rates of asphaltene precipitation, aggregation and deposition may become available in the near future, enabling the determination of such correlations.
The results presented in this dissertation are promising in offering new alternatives to model asphaltene precipitation and deposition. Multiple lessons have been learned and the simulation results, validated with experimental data and field observations, provide insight into the mechanism of asphaltene transport in the wellbore. This knowledge would contribute in the development of experimental procedures and simulation schemes that could predict the likelihood of asphaltene deposition in the newly found oil fields worldwide.
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Appendix A. New Mixing Rule for Solubility Parameters

If we assume that a mixture is ideal, i.e. the energy and volume of mixing are equal to zero, then the internal energy and volume of the mixture, can be calculated as:

\[ u_{\text{mix}} = \sum_i x_i u_i \]  
(A.1)

\[ v_{\text{mix}} = \sum_i x_i v_i \]  
(A.2)

where \( x_i \) is the molar fraction, \( u \) is the residual internal energy and \( v \) is the molar volume.

In the other hand, we know that according to the definition of the solubility parameter, applied to the mixture:

\[ -u_{\text{mix}} = v_{\text{mix}} \delta_{\text{mix}}^2 \]  
(A.3)

Substituting Eqs. (A.1) and (A.2) into Eq. (A.3), and simplifying, we get:

\[ \frac{\sum x_i u_i}{v_{\text{mix}}} = \sum_i \frac{x_i v_i}{v_{\text{mix}}} \left(\frac{-u_i}{v_i}\right) = \sum_i \phi \delta_i^2 \]  
(A.4)

\[ \delta_{\text{mix}}^2 = \sum_i \phi \delta_i^2 \]  
(A.5)

where: \( \phi_i = x_i \frac{v_i}{v_{\text{mix}}} \) is the volume fraction of component \( i \).

It has been generally accepted that the mixing rule for solubility parameters can be expressed as:

\[ \delta_{\text{mix}} = \sum_i \phi \delta_i \]  
(A.6)
If the mixture is non-ideal then we can utilize the partial molar properties of the components, in the following way:

\[ u_{\text{mix}} = \sum x_i \tilde{u}_i \]  \hspace{1cm} (A.7)

\[ v_{\text{mix}} = \sum x_i \tilde{v}_i \]  \hspace{1cm} (A.8)

\[ -u_{\text{mix}} = v_{\text{mix}} \delta_{\text{mix}}^2 \]  \hspace{1cm} (A.9)

\[ \delta_{\text{mix}}^2 = \frac{-\sum x_i \tilde{u}_i}{v_{\text{mix}}} = \sum x_i \tilde{v}_i \left( \frac{-\tilde{u}_i}{\tilde{v}_i} \right) \]  \hspace{1cm} (A.10)

\[ \delta_{\text{mix}}^2 = \sum \tilde{\phi}_i \tilde{\delta}_i^2 \]  \hspace{1cm} (A.11)

where: \( \tilde{\phi}_i = x_i \frac{\tilde{v}_i}{v_{\text{mix}}} \) is the partial volume fraction of component \( i \), and \( \tilde{\delta}_i \) is the partial molar solubility parameter of component \( i \).

The following example illustrates the validation of new mixing rule, Eq. (A.11), and compare the results obtained with the old mixing rule, Eq. (A.6).

Consider the case of a mixture of ethane/heptane/toluene at 40°C (313.15 K) and 40 atm. Under these conditions the mixture with less than 60% mol of ethane is a subcooled liquid. Liquid-like properties of ethane can be calculated under these conditions, i.e. contribution of ethane to the liquid mixture properties. Partial or apparent values of volume and cohesive energy can be used for the estimation of solubility parameters. This procedure can readily be extended to more complex mixtures, such as asphaltene crude oils containing light components.
Let us say that the objective is to calculate the liquid-like solubility parameter of ethane from a mixture of toluene-heptane-ethane @ 40°C and 40 atm for different compositions.

Different experimental schemes can be applied for determining the solubility parameter of the mixture, as well as its volume, and cohesive energy. However, because these measurements are difficult to perform, require very high pressures and therefore imply a very expensive operation, one alternative is to generate pseudo-data using a reliable modeling approach. It has been shown that the SAFT based models have been successfully applied in modeling the phase behavior of hydrocarbon and crude oil systems. This approach is particularly accurate for the determination of liquid properties, such as density. The calculations are performed using PC-SAFT EOS in Multiflash®. The PC-SAFT parameters for the three components are already defined in the properties database of the program, and where taken from the original reference by Gross and Sadowski\textsuperscript{64}. A binary interaction parameter, $k_{ij}$, between the ethane/toluene is considered equal to 0.015\textsuperscript{82} whereas between ethane/heptane and heptane/toluene no interaction parameter is considered. Table A.1 shows simulation results for mixtures with six different compositions, M1 to M6. Values of internal energy and molar volume of the mixture have been obtained. The solubility parameter of the mixture is also calculated using Eq. (A.3).

Using the data from Table A.1 and assuming ideal mixing, the cohesive energy and molar volume of ethane were calculated, using Eqs. (A.1) and (A.2). The results are shown in Table A.2. Additionally, the solubility parameter of ethane can also be
calculated using three different approaches: (1) from the definition, $\delta_i = \sqrt{-u_i/v_i}$; (2) from Eq. (A.6), the old mixing rule; and, (3) from Eq. (A.11), the new mixing rule. The numbers in last three columns correspond to each one of these approaches.

**Table A.1.** Internal energy, molar volume and solubility parameter using PC-SAFT EOS at 40°C and 40 atm, for different compositions of a mixture containing ethane/heptane/toluene. The corresponding values for toluene and heptane as pure substances are also provided.

<table>
<thead>
<tr>
<th>Substance</th>
<th>% mol</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
<th>Toluene</th>
<th>Heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>10%</td>
<td>M1</td>
<td>M2</td>
<td>M3</td>
<td>M4</td>
<td>M5</td>
<td>M6</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>Heptane</td>
<td>30%</td>
<td>M3</td>
<td>M4</td>
<td>M5</td>
<td>M1</td>
<td>M2</td>
<td>M3</td>
<td>0%</td>
<td>100%</td>
</tr>
<tr>
<td>Ethane</td>
<td>60%</td>
<td>M5</td>
<td>M6</td>
<td>M1</td>
<td>M2</td>
<td>M3</td>
<td>M4</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>$u$(J/mol)</td>
<td>-18588</td>
<td>-18864</td>
<td>-31276</td>
<td>-26098</td>
<td>-26807</td>
<td>-31709</td>
<td>-34966</td>
<td>-33452</td>
<td></td>
</tr>
<tr>
<td>$v$(cm$^3$/mol)</td>
<td>99.0</td>
<td>89.5</td>
<td>129.8</td>
<td>122.1</td>
<td>100.5</td>
<td>117.2</td>
<td>109.3</td>
<td>150.6</td>
<td></td>
</tr>
<tr>
<td>$\delta$(MPa$^{0.5}$)</td>
<td>13.7</td>
<td>14.5</td>
<td>15.5</td>
<td>14.6</td>
<td>16.3</td>
<td>16.4</td>
<td>17.9</td>
<td>14.9</td>
<td></td>
</tr>
</tbody>
</table>

From the results shown in **Table A.2** it is clear that the assumption of ideal mixing is not consistent with the prediction of the PC-SAFT EOS. The reason is that both the internal energy and the molar volume are strongly dependent of the composition of the mixture (temperature and pressure are fixed, in 40°C and 40 atm, respectively). But the results obtained using the first and third approaches are identical, as expected.

**Table A.2.** Internal energy, molar volume and solubility parameter for ethane, calculated indirectly assuming ideal mixing, from data in Table 3.1.1, using three different approaches: (1) from the definition, $\delta_i = \sqrt{-u_i/v_i}$; (2) from Eq. (A.6), the old mixing rule; and, (3) from Eq. (A.11), the new mixing rule.

<table>
<thead>
<tr>
<th>$u_{Ethane}$</th>
<th>$v_{Ethane}$</th>
<th>$\delta_{Ethane}$ (1)</th>
<th>$\delta_{Ethane}$ (2)</th>
<th>$\delta_{Ethane}$ (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-8425</td>
<td>71.43</td>
<td>10.86</td>
<td>11.37</td>
<td>10.86</td>
</tr>
<tr>
<td>-8381</td>
<td>69.38</td>
<td>10.99</td>
<td>11.73</td>
<td>10.99</td>
</tr>
<tr>
<td>-7147</td>
<td>65.98</td>
<td>10.41</td>
<td>12.31</td>
<td>10.41</td>
</tr>
<tr>
<td>-8434</td>
<td>69.42</td>
<td>11.02</td>
<td>11.67</td>
<td>11.02</td>
</tr>
<tr>
<td>-8274</td>
<td>66.13</td>
<td>11.19</td>
<td>12.29</td>
<td>11.19</td>
</tr>
<tr>
<td>-6936</td>
<td>64.32</td>
<td>10.38</td>
<td>12.65</td>
<td>10.38</td>
</tr>
</tbody>
</table>

| avg          | -7933        | 67.78                  | 10.81                  | 12.00                  | 10.81                  |
| stdev        | 696.14       | 2.70                   | 0.34                   | 0.49                   | 0.34                   |
| %stdev       | 8.78         | 3.99                   | 3.11                   | 4.05                   | 3.11                   |
The non-ideality of the mixture in the calculation of its solubility parameter is now studied. In this analysis the same mixture of ethane/heptane/toluene at 40°C and 40 atm is simulated. It is important to recall that under these conditions the mixture remains in a subcooled form even at high concentrations of ethane, i.e. ~60% mol.

The first step is to conceptually split the ternary mixture into three binary mixtures. Volume and cohesive energy are calculated as a function of composition. For all the simulations the PC-SAFT EOS is used. The interaction parameter of 0.015 for ethane-toluene is also considered, and the interactions between ethane-heptane, toluene-heptane are neglected.

In Figure A.1 the change in the molar volume of the binary mixtures with respect the composition can be observed. The markers represent the results obtained from the simulation and the solid black lines the linear trend fit. For the mixture of heptane and toluene it is clear that the volume of mixing is negliglve. For the case of ethane we find a discrepancy since the molar volume of pure ethane predicted from the two mixtures is different, *i.e.* 73.05 and 68.25 cm$^3$/mol, with heptane and toluene, respectively.

To force these two lines to intercept at the same point at $x_1 = 1.0$, a regression analysis is performed. A quadratic regression is used and the difference between the two intercepts is included in the error function to be minimized. The result of the regression is shown in dashed lines in Figure A.1 for both mixtures. According to this analysis the molar volume of pure ethane is ~75.2 cm$^3$/mol.
Figure A.1. Molar volume of binary mixtures including ethane/toluene/heptane at 40°C and 40 atm. Markers represent the data obtained from the PC-SAFT simulation. Solid black lines the linear trends fitted and the dashed color lines a quadratic regression with common intercept point as a constraint.

The conclusion is that in terms of volume, the pair toluene-heptane can be assumed to form an ideal mixture whereas ethane-toluene and ethane-heptane form non-ideal mixtures. Therefore, the general equation for the molar volume of the ternary mixture can be proposed as:

$$v_{mix} = \alpha_0 x_E^2 + \alpha_1 x_E + v_H x_H + v_T x_T$$  \hspace{1cm} (A.12)

where: $\alpha_0$ and $\alpha_1$ are constants, $v_H$ and $v_T$ are the molar volumes of heptane and toluene, respectively and $x_i$ is the mol fraction of component $i$.

The values of $\alpha_0$ and $\alpha_1$ are correlated to the simulation data, so that for the ternary mixture at 40°C and 40 atm:

$$v_{mix} = 9.0974 x_E^2 + 66.1183 x_E + 150.6485 x_H + 109.3376 x_T$$  \hspace{1cm} (A.13)

where: $v_{mix}$ is in cm$^3$/mol.
From Eq. (A.13) an equation for the partial molar volume of ethane can be derived as:

\[
\bar{v}_E = \frac{\partial (n_{mx} v_{mx})}{\partial n_E} = 18.1947 x_E - 9.0974 x_E^2 + 66.1183 \tag{A.14}
\]

Note that since there is no excess volume for the pair toluene-heptane, the partial molar volume of ethane is independent of the toluene and heptane mol fractions. Figure A.2 shows the change of the partial molar volume of ethane with respect its mol fraction in the mixture.

Figure A.2. Partial molar volume of ethane in a mixture of ethane/toluene/heptane at 40°C and 40 atm as function of the ethane mol fraction and independent of the ratio of toluene/heptane.

Therefore the molar volume of the mixture can be calculated as:

\[
v_{mx} = \bar{v}_E x_E + v_H x_H + v_T x_T \tag{A.15}
\]

In Figure A.3 molar volumes of different mixtures calculated with the PC-SAFT EOS are compared with the volumes calculated using Eqs. (A.13) and (A.15). The
agreement is very good, especially when the molar volumes are greater than 90 cm$^3$/mol.

**Figure A.3.** Comparison between the volume of the mixture calculated from the partial molar volume of ethane as a function of its concentration and the volume obtained from the simulation.

**Figure A.4.** Residual internal energy of binary mixtures including ethane/toluene/heptane at 40°C and 40 atm. Markers represent the data obtained from the PC-SAFT simulation. From these data we can conclude that the excess residual energy for the three binary mixtures is negligible.

A similar analysis and procedure can be implemented to calculate the cohesive energy of the mixture. In **Figure A.4** it is shown how the residual internal energy for the three binary mixtures follows a linear trend.
Thus, it can be readily conclude that a single value for the residual internal energy of ethane is enough to accurately predict the energy of the mixture. The partial internal energy of pure ethane is fit from the simulation data to the value of -8,345.95 J/mol. The residual internal energy for the ternary mixture can be calculated using Eq. (A.16):

\[ u_{mix} = -8345.95x_E - 33452.5x_H - 34966.1x_T \]  \hspace{1cm} (A.16)

From its definition the partial molar solubility parameter for ethane can be calculated as:\n
\[ \delta_E = \sqrt{-\frac{u_E}{\bar{v}_E}} \]. Therefore:

\[ \bar{\delta}_E = \sqrt{\frac{8345.95}{18.1947x_E - 9.0974x_E^2 + 66.1183}} \]  \hspace{1cm} (A.17)

And again the discrepancies between the old and the new mixing rules can be tested.

\[ \delta_{mix} = \sum_i \phi_i \delta_i \]  \hspace{1cm} (A.6)

\[ \delta_{mix}^2 = \sum_i \phi_i \delta_i^2 \]  \hspace{1cm} (A.11)

The results are shown in Table A.3. For six different mixtures the PC-SAFT EOS in Multiflash provides the volume and residual internal energy, so that the solubility parameter of the mixture can be obtained. Two different ways to calculate this property are used: first, the Regular Solution Theory in which the excess volume is assumed to be equal to zero and \( \delta_{mix} \) is calculated using Eq. (A.6). In this case the solubility parameter of ethane is constant and evaluated at \( x_E = 1.0 \); and second, with the procedure proposed in this work, in which we take into account the excess volume, Eq. (A.17), and \( \delta_{mix} \) is
Table A.3. Solubility parameter calculation using the Regular Solution Theory (RST) and the new approach proposed in this work. The columns labeled as PC-SAFT show the results obtained from the simulations.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Mole fraction</th>
<th>Molar volume of the mixture, cm³/mol</th>
<th>Residual Internal Energy, J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
<td>Heptane</td>
<td>Ethane</td>
</tr>
<tr>
<td>M1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>M2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>M3</td>
<td>0.3</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>M4</td>
<td>0.1</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>M5</td>
<td>0.6</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>M6</td>
<td>0.6</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Volume Fraction</th>
<th>Volume Fraction, RST (*)</th>
<th>} v̇ E = Eq (A.14)</th>
<th>RST (**)</th>
<th>AAPD (%)</th>
<th>RST (**)</th>
<th>AAPD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
<td>Heptane</td>
<td>Ethane</td>
<td>Toluene</td>
<td>Heptane</td>
<td>Ethane</td>
<td>Eq (A.14)</td>
</tr>
<tr>
<td>M1</td>
<td>0.109</td>
<td>0.450</td>
<td>0.441</td>
<td>0.108</td>
<td>0.446</td>
<td>0.446</td>
<td>73.8</td>
</tr>
<tr>
<td>M2</td>
<td>0.356</td>
<td>0.164</td>
<td>0.480</td>
<td>0.353</td>
<td>0.162</td>
<td>0.485</td>
<td>73.8</td>
</tr>
<tr>
<td>M3</td>
<td>0.252</td>
<td>0.695</td>
<td>0.052</td>
<td>0.251</td>
<td>0.692</td>
<td>0.058</td>
<td>67.8</td>
</tr>
<tr>
<td>M4</td>
<td>0.089</td>
<td>0.738</td>
<td>0.173</td>
<td>0.088</td>
<td>0.730</td>
<td>0.182</td>
<td>70.8</td>
</tr>
<tr>
<td>M5</td>
<td>0.644</td>
<td>0.148</td>
<td>0.208</td>
<td>0.635</td>
<td>0.146</td>
<td>0.219</td>
<td>70.8</td>
</tr>
<tr>
<td>M6</td>
<td>0.558</td>
<td>0.384</td>
<td>0.058</td>
<td>0.554</td>
<td>0.382</td>
<td>0.064</td>
<td>67.8</td>
</tr>
</tbody>
</table>

RST: Regular Solution Theory

\( v_{mix} = \sum_i x_i v_i \), \( v_E = v_{mix} v_E \) = 75.2 cm³/mol

\( \phi_i = \frac{x_i}{v} \)

\( \delta_{E, RST} = \sqrt{-\frac{\partial U}{v_E}} = \text{constant} \)

New mixing rule error

Old mixing rule error
calculated using Eq. (A.11), recalling that the partial molar volume fraction is defined as:

$$\phi_i = x_i \frac{\bar{v}_i}{v_{mix}}$$

where: $v_{mix} = \bar{v}_E x_E + \bar{v}_H x_H + \bar{v}_T x_T$, and $\bar{v}_E = \frac{\partial(n_m v_{mx})}{\partial n_E} = 18.1947x_E - 9.0974x_E^2 + 66.1183$

According to the results presented in Table A.3 the method proposed in this work predicts more accurately the results obtained from the simulation, than the Regular Solution Theory. The excess volume that is usually neglected is actually very important in the calculation of the properties of the mixture. The partial molar volume of ethane in a mixture of ethane/toluene/heptane at 40°C and 40 atm changes from 66.1 to 75.2 cm$^3$/mol (from 0 to 100% ethane). The corresponding solubility parameter goes from 11.24 to 10.53 MPa$^{0.5}$ at the same pressure and temperature.

This dramatic change of the partial molar volume of ethane affects not only its solubility parameter but the volume fraction and its contribution to the solubility parameter of the mixture.

We observe that the method shown in this work reduces in almost an 80% the average error in the prediction of the solubility parameter of the mixture, with respect the Regular Solution Theory.

Now we can extend our analysis to the study of a model oil containing asphaltenes. The system is composed by a mixture of stock tank oil (STO) and precipitant. The STO composition is 1 g of asphaltene / 100 mL toluene. The precipitant used are methane, ethane, propane, butane, pentane, hexane and heptane. The simulation is performed for
different mole fractions of precipitant using the PC-SAFT EOS in the Multiflash® Platform.

For the asphaltene:

Physical properties: MW = 4000 g/mol\*, sp. gr. = 1.16

PC-SAFT parameters: \( \varepsilon/k = 350.8 \) K, \( \sigma = 4.05 \) Å and \( m = 80 \)

\* Molecular Weight of a pre-aggregate asphaltenes

The temperature is 77°F.

The mixture is simulated under different mol fractions of precipitant, while the ratio of asphaltene/toluene is hold constant. The cohesive energy is properly correlated with a constant value of cohesive energy of the precipitant, i.e. the cohesive energy of the precipitant is independent of the composition, whereas the volume of the precipitant is a strong function of the composition-pressure along the onset curve. The partial molar volume is properly correlated using a quadratic polynomial.

Table A.4 shows the differences between the calculated values using PC-SAFT EOS, and the values reported by Barton\textsuperscript{100} and Prausnitz\textsuperscript{112}.

Table A.4. Comparison between the results obtained from the simulation using PC-SAFT EOS, and the reported values by Barton\textsuperscript{100} and Prausnitz\textsuperscript{112} for solubility parameters, molar volume and cohesive energy for different light hydrocarbons at 25°C.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Solubility parameter</th>
<th>Volume</th>
<th>Cohesive Energy Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Barton</td>
<td>Prausnitz</td>
</tr>
<tr>
<td>Methane</td>
<td>6.9</td>
<td>9.6</td>
<td>11.6</td>
</tr>
<tr>
<td>Ethane</td>
<td>10.6</td>
<td>11.6</td>
<td>13.5</td>
</tr>
<tr>
<td>Propane</td>
<td>12.5</td>
<td>12.7</td>
<td>NA</td>
</tr>
<tr>
<td>Butane</td>
<td>13.6</td>
<td>13.5</td>
<td>NA</td>
</tr>
<tr>
<td>Pentane</td>
<td>14.2</td>
<td>14.3</td>
<td>NA</td>
</tr>
<tr>
<td>Hexane</td>
<td>14.7</td>
<td>14.8</td>
<td>NA</td>
</tr>
<tr>
<td>Heptane</td>
<td>15.0</td>
<td>15.2</td>
<td>NA</td>
</tr>
</tbody>
</table>
The first important observation is the substantial difference between the solubility parameter values of methane and ethane reported by Barton\textsuperscript{100} and Prausnitz\textsuperscript{112}. Even though Barton\textsuperscript{100} refers to the work done by Prausnitz\textsuperscript{112} when reporting the values of solubility parameters for methane and ethane, the values of solubility parameter in both references are different.

\textbf{Figure A.5} shows the comparison between the simulation and the values reported by Barton\textsuperscript{100} for the solubility parameter. The former is represented by the solid lines, whereas the latter correspond to the dashed lines. We observe that for the ethane and the heavier precipitants in one point of the onset curve the agreement is good. For the case of methane the two lines are always very distant to each other.

\textbf{Figure A.5.} Solubility parameter comparison between the simulation (solid lines) and the values from Barton\textsuperscript{100} (dashed lines).
It is important to notice that the values reported in the literature for dissolved gases were obtained by fitting their parameters (molar volume and solubility parameter) to satisfy the old mixing rule\textsuperscript{112}. According to the procedure proposed by Prausnitz\textsuperscript{112} the solubility parameter of dissolved gases is calculated from Eq. (A.18):

\[
\frac{1}{x_2} = \frac{f_{L}^{\text{pure},2}}{f_2^G} \exp \left[ \frac{v_2^L (\delta_2 - \delta_{\text{mix}})^2}{RT} \right]
\]

(A.18)

where: \( f_{L}^{\text{pure},2} \) is the fugacity of (hypothetical) pure liquid solute, and \( \delta_{\text{mix}} \) is the solubility parameter of the mixture, calculated as: \( \delta_{\text{mix}} = \sum \phi_i \delta_i \).

Eq (A.18) assumes that Regular Solution Theory is valid for this system (excess volume and excess entropy are assumed to be equal to zero). This assumption could be incorrect for mixtures in which the components are very different in size and shape. Eq. (A.18) also assumes that the linear mixing rule is valid for systems containing gases. However, even at that time, it was well known that the assumption made by the old mixing rule, of using geometric mean to calculate the interaction energy, was a poor approximation when gases were present. This was result demonstrated by London\textsuperscript{110}.

The agreement between the results obtained from the simulation using PC-SAFT and those reported by Barton\textsuperscript{100} is good enough for the propane and the heavier precipitants, according to Figure A.5. But even though the partial molar volume of methane predicted by PC-SAFT is similar to the value reported in the literature\textsuperscript{100}, the maximum percent difference between the corresponding solubility parameter is almost 40%.

The application of the new mixing rule and comparison against the old mixing rule can be extended to petroleum systems. In this example a model oil composed by toluene
and asphaltene is used. These two components are grouped in one single pseudo-component, a model stock tank oil (STO). The mixture of interest is STO + precipitant. The composition of the STO is constant: 1 g asphaltene / 100 mL toluene.

Applying the old mixing rule for the solubility parameter it is obtained that:

\[
\delta_{mx} = \frac{\phi_{asph} \delta_{asph} + \phi_{tol} \delta_{tol}}{\phi_{STO}} + \phi_p \delta_p \tag{A.19}
\]

\[
\delta_{mx} = \phi_{STO} \delta_{STO} + \phi_p \delta_p \tag{A.20}
\]

\[
\delta_{mx} = \delta_{STO} + (\delta_p - \delta_{STO}) \phi_p \tag{A.21}
\]

where: \(\delta\) and \(\phi\) are the solubility parameter and the volume fraction, respectively. Thus, knowing the values for the solubility parameter of the STO and the precipitant it is possible to predict the solubility parameter of the mixture for any composition of precipitant.

In Figure A.6 the solid lines correspond to the Eq. (A.21) for the different mixtures whereas the dashed lines represent the data obtained from the simulation. As we can see the application of the old mixing rule fails to predict the simulation results for dissolved gases, e.g. methane, ethane, propane and butane. For precipitants with a lower vapor pressure the prediction is much better, e.g. hexane, heptane.
If the new mixing rule is used, Eqs. (A.22) and (A.23) can be readily obtained.

\[
\delta_{mx} = \phi_{asph} \delta_{asph}^2 + \phi_{vol} \delta_{vol}^2 + \phi_p \delta_p^2 + \phi_{sto} \delta_{sto}^2
\]  
(A.22)

\[
\delta_{mx} = \delta_{sto}^2 + \left( \delta_p^2 - \delta_{sto}^2 \right) \phi_p
\]  
(A.23)

In Figure A.7 the solid lines are the prediction of Eq. (A.23) whereas the dashed lines correspond to the data obtained from simulations using PC-SAFT. In this case the predictions are more accurate even for the dissolved gases.
Figure A.7. Comparison of the new mixing rule, $\delta_{mx}^2 = \sum_i \phi_i \delta_i^2$ (solid lines), against the results from simulations using the PC-SAFT EOS (dashed lines).

It is important to mention that the error in Figure A.7 is being amplified, compared with the results shown in Figure A.6, because Figure A.7 shows the square of the solubility parameter. Solubility parameter can be calculated instead, according to Eq. (A.24):

$$\delta_{mx} = \sqrt{\delta_{STO}^2 + (\delta_p^2 - \delta_{STO}^2) \phi_p}$$  \hspace{1cm} (A.24)

The normalized solubility parameter of the mixture is shown in Figure A.8 Error! Reference source not found., where it can be seen that the new mixing rule agrees with the results obtained from the simulation.
Figure A.8. Theoretical calculation for the solubility parameter of a mixture developed from the new mixing rule, $\delta_{mx} = \sqrt{\sum \phi_i \delta_i^2}$ (solid lines) compared with the results obtained from the simulation (dashed lines). The labels correspond to the precipitant used in each case, *i.e.*, $C_1$: methane, $C_2$: ethane...

From the results presented in this section it can be concluded that the new mixing rule that weights the square of the partial solubility parameter, instead of the solubility parameter, provides a better agreement with respect the results obtained from the simulation using PC-SAFT EOS.
Appendix B. Multi-linear regression with common intercept

In Section 4.3 the analysis of the bubble point and asphaltene precipitation onset for a model oil composed by asphaltene in toluene and various precipitants was presented. This study, based on diagrams of cohesive energy versus mole fraction of the precipitant, was proposed as alternative to the traditional phase diagrams of pressure versus composition. The advantage of using the cohesive energy is that the bubble point and asphaltene precipitation onset curves of mixtures of dead oil and different precipitants are straight lines and can be related to the cohesive energies of the dead oil and the precipitant at the conditions of interest.

Figure B.1 presents the simulation results for the cohesive energy of mixtures at the onset of asphaltene precipitation.

![Figure B.1. Simulation results using the PC-SAFT EOS for onsets of asphaltene precipitation, for a mixture containing a model dead oil and multiple asphaltene precipitants.](image)

The corresponding trend lines are also shown in Figure B.1 to emphasize the linearity obtained. These straight lines converge to a single intercept that corresponds to the energy of incipient asphaltene precipitation for the model dead oil. In this case the common intercept is 0.86. This normalized cohesive
energy is a hypothetical value that can not be measured or calculated directly, but it can be estimated by extrapolation. This common intercept can be defined as a degree of how undersaturated is the dead oil with respect the asphaltene: At increasing value of the intercept, the dead oil becomes more unstable.

An optimization algorithm was applied using the least-square method in order to obtain this common intercept. The squared error function is defined as:

\[
\text{error}^2 = \sum_{k=1}^{p} \sum_{i=1}^{n_k} (m_k x_{ki} + b - y_{ki})^2
\]

(B.25)

where: \( m_k \) is the slope which best fit the set of data \( k \); \( b \) is the common intercept; \( p \) the total number of data sets, i.e. number of precipitants tested; and \( n_k \) is the number of data pairs \((x_{ki}, y_{ki})\) in set \( k \).

By minimizing the squared error to obtain the optimal values of \( m_1, m_2, \ldots, m_p \) and \( b \):

\[
\frac{\partial \text{error}^2}{\partial b} = 2 \sum_{k=1}^{p} \sum_{i=1}^{n_k} (m_k x_{ki} + b - y_{ki}) = 0 \quad \Rightarrow \quad b N + m_1 \sum_{i=1}^{n_1} x_{i1} + m_2 \sum_{i=1}^{n_2} x_{i2} + \ldots + m_p \sum_{i=1}^{n_p} x_{ip} = \sum_{k=1}^{p} \sum_{i=1}^{n_k} y_{ki}
\]

\[
\frac{\partial \text{error}^2}{\partial m_1} = 2 \sum_{i=1}^{n_1} (m_1 x_{i1} + b - y_{i1}) (x_{i1}) = 0 \quad \Rightarrow \quad b \sum_{i=1}^{n_1} x_{i1} + m_1 \sum_{i=1}^{n_1} x_{i1}^2 = \sum_{i=1}^{n_1} x_{i1} y_{i1}
\]

\[
\frac{\partial \text{error}^2}{\partial m_2} = 2 \sum_{i=1}^{n_2} (m_2 x_{i2} + b - y_{i2}) (x_{i2}) = 0 \quad \Rightarrow \quad b \sum_{i=1}^{n_2} x_{i2} + m_2 \sum_{i=1}^{n_2} x_{i2}^2 = \sum_{i=1}^{n_2} x_{i2} y_{i2}
\]

\[
\vdots
\]

\[
\frac{\partial \text{error}^2}{\partial m_p} = 2 \sum_{i=1}^{n_p} (m_p x_{pi} + b - y_{pi}) (x_{pi}) = 0 \quad \Rightarrow \quad b \sum_{i=1}^{n_p} x_{pi} + m_p \sum_{i=1}^{n_p} x_{pi}^2 = \sum_{i=1}^{n_p} x_{pi} y_{pi}
\]

where \( N \) is the total number of data pairs (energy vs. composition) in the system.

In matrix notation:
In this case:

$$x \equiv x_p$$

$$y \equiv \frac{v_{mix} \delta_{mix}^2}{v_{do} \delta_{do}^2}$$

(B.3)

By solving the linear system of equations shown in Eq. (B.3) the optimal values for the slope of the different mixtures and the common intercept are obtained.
Appendix C. Algorithm for Multiphase Flash Calculations

Introduction

In connection with oil production processes, phase equilibrium calculations where multiple phases are present is a typical simulation problem. In this section, a robust and efficient algorithm to perform multiphase flash calculations is presented. An example is provided and the computer code is included. In this example a cubic EOS is used. However, it can be adapted to use other equations of state, such as the PC-SAFT EOS.

Methodology

A multiphase isothermal flash is proposed, following the methodology developed by Michelsen\textsuperscript{126-129}, in which the minimization of the Gibbs energy at equilibrium, can also be satisfied by minimizing the objective function $Q$:

$$Q = \sum_{j=1}^{F} \beta_j - \sum_{i=1}^{C} z_i \ln E_i$$

(C.1)

where: $\beta_j$ is the fraction of phase $j$ in equilibrium, $z_i$ is the overall composition of substance $i$ in the system, and $E$ is defined as:

$$E_i = \frac{\sum_{k=1}^{F} \beta_k}{\phi_{ik}}$$

(C.2)

where $\phi_{ik}$ is the fugacity coefficient of component $i$ in the phase $j$.

The minimum of $Q$ is subject to values of $\beta_j$ such that,

$$\frac{\partial Q}{\partial \beta_j} = 0, \quad \beta_j \geq 0 \quad \text{or} \quad \frac{\partial Q}{\partial \beta_j} > 0, \quad \beta_j = 0$$

(C.3)
The gradient of \( Q \), \( g_j \), is defined as:

\[
g_j = \frac{\partial Q}{\partial \beta_j} = 1 - \sum_{i=1}^{C} \frac{z_i}{E_i \hat{\phi}_j}
\]

The Hessian matrix is defined as:

\[
H_{jk} = \frac{\partial^2 Q}{\partial \beta_j \partial \beta_k} = \sum_{i=1}^{C} \frac{z_i^2}{E_i^2 \hat{\phi}_i \hat{\phi}_k}
\]

and at the solution, it can be verified that,

\[
y_{ij} = \frac{z_i}{E_i \hat{\phi}_{ij}}
\]

One additional difficulty that the program needs to address is the possibility of addition or removal of phases during the iterative solution. Instead of modifying the dimensions of the gradient and Hessian vectors during the calculations, the corresponding elements of the gradient vector and Hessian matrix are replaced by zeros, and with 1 on the Hessian diagonal.

Figure C.1 and Figure C.2 show a flow chart for the computational procedure of this multiphase flash algorithm. The complete code is included at the end of this Appendix.

The dominant eigenvalue method proposed by Crowe and Nishio\(^{130}\) is also adopted to accelerate the convergence, as suggested by Michelsen\(^{127,129,131}\)
**Multiphase Flash Routine**

- **z**: overall composition
- **P**: pressure
- **T**: temperature
- **CP**: critical properties

Calculate:

- \( \ln K_i^{\text{Wilson}} \), \( \ln \phi_{i,j}^0 \)
- \( \beta_j \), \( \beta A_j \)
- \( y_{i,j} \)

Calculate:

- \( E \) and \( Q \)

**Update:**

\( \ln \phi_{i,j}^0 \leftarrow \ln \phi_{i,j} \)

**Error:**

\[ \sum_{i,j} (\ln \phi_{i,j} - \ln \phi_{i,j}^0) \]

**Figure C.1.** Flowchart of Main Program for Multiphase Flash calculations.

**Calculate:**

- \( \beta_j \), \( \beta A_j \), \( y_{i,j} \)
- \( z_i, \ln \phi_{i,j}^0, E_i \)

**Calculate:**

- \( g_i, g_{\text{copy}}, H_{j_k} \)

**Solve:** \( \Delta \beta_j : H \Delta \beta + g = 0 \)

**Calculate:**

- \( E_{\text{new}} \) and \( Q_{\text{new}} \)

**Figure C.2.** Routine for phase fraction calculation assuming constant fugacity coefficients.
Example

The problem was tested with a system composed by ethane (20 mole%), propane (50 mole%), n-butane (20 mole%) and water (10 mole%), at T = 280 K, P = 0.5 MPa.

For this system, the equilibrium constants used for initialize the simulation were the Wilson K-factors\textsuperscript{128,129}, modified for the components that were present at low concentrations. For instance, the equilibrium constants for the water present in the organic phase and the hydrocarbons present in the aqueous phase were set to be hundred times greater than the Wilson K-values. The reason of modifying the equilibrium constants in this way is to assure a good estimate for the fugacity coefficients of highly diluted components. As we can expect, the activity coefficient for such components in the component-lean phase is very high at infinite dilution.

As initial estimate gases are assumed to behave ideally:

\[
\ln \hat{\phi}_{i,Y} = 0
\]  \hspace{1cm} (C.7)

And from the definition of the equilibrium constant, K:

\[
\ln K_i = \ln \hat{\phi}_{i,L} - \ln \hat{\phi}_{i,Y} = \ln \hat{\phi}_{i,L}
\]  \hspace{1cm} (C.8)

And by definition:

\[
\ln \hat{\phi}_{i,L} = \ln \phi_{i,L} + \ln \gamma_{i,L}
\]  \hspace{1cm} (C.9)

where: \( \hat{\phi}_{i,L} \) is the fugacity coefficient of component \( i \), in the liquid mixture; \( \phi_{i,L} \) is the fugacity coefficient as a pure component at the same pressure and temperature and \( \gamma_{i,L} \) is the activity coefficient.
Due to the non-ideality of hydrocarbon-water systems, it is expected that the activity coefficient of water in the organic phase, i.e. at infinite dilution, is much greater than unity.

Another alternative for obtaining good estimates for the activity coefficients would be the Henry’s Law constants. But this would require additional information that might not be readily available.

The results of the simulation are reported in Table C.1.

**Table C.1.** Compositions and phase fractions for the hydrocarbon-water system at 280 K and 0.5 MPa.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Feed</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.2</td>
<td>0.2883</td>
<td>0.0656</td>
<td>0.0000</td>
</tr>
<tr>
<td>Propane</td>
<td>0.5</td>
<td>0.5775</td>
<td>0.5020</td>
<td>0.0000</td>
</tr>
<tr>
<td>Butane</td>
<td>0.2</td>
<td>0.1329</td>
<td>0.4323</td>
<td>0.0000</td>
</tr>
<tr>
<td>Water</td>
<td>0.1</td>
<td>0.0013</td>
<td>0.0001</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase Frac</th>
<th>Z mix</th>
<th>Vapor</th>
<th>Liquid 1</th>
<th>Liquid 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6328</td>
<td>0.2681</td>
<td>0.0991</td>
<td></td>
</tr>
<tr>
<td>0.9195</td>
<td>0.0206</td>
<td>0.0051</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values obtained both for the phase fractions and the compositions of the components in all the phases agree with the Multiphase Flash Program provided by Michelsen and Mollerup at the Tie-Line Tech website\(^{132}\).

A total of four iterations were necessary to converge the system, assuming as initial estimate that all the phases existed in an equimolar phase fraction, i.e. $\beta_1 = \beta_2 = \beta_3 = 1/3$.

Four iterations were also required if just one phase was assumed to be present. The result was invariant with respect of which phase was initially assumed to be present.

When an additional component was added to the system, e.g. methane, the number of
iterations also remained invariant. The results of the modified system upon addition of methane are presented in Table C.2.

Effects of temperature and pressure on numerical stability and convergence were also studied for this modified system. For values of T = 280±15K and P = 0.5±0.3 MPa there was no change in the number of iterations. However, for a T = 295 K, as the pressure was increased, more iterations were needed to converge to the solution because the system was approaching its critical region. The vapor phase disappeared when a pressure of 2.75 MPa or greater was applied. A maximum of iterations was reached close to a pressure of 4.22 MPa. Figure C.3 shows the number of iterations for different system pressures.

Table C.2. Compositions and phase fractions for the modified system at 280 K and 0.5 MPa.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Feed</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.1</td>
<td>0.1457</td>
<td>0.0053</td>
<td>0.0000</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.1</td>
<td>0.1373</td>
<td>0.0311</td>
<td>0.0000</td>
</tr>
<tr>
<td>Propane</td>
<td>0.5</td>
<td>0.5735</td>
<td>0.4985</td>
<td>0.0000</td>
</tr>
<tr>
<td>Butane</td>
<td>0.2</td>
<td>0.1422</td>
<td>0.4650</td>
<td>0.0000</td>
</tr>
<tr>
<td>Water</td>
<td>0.1</td>
<td>0.0014</td>
<td>0.0001</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

| Phase Frac | 1    | 0.6782   | 0.2228   | 0.0991   |
| Z mix      | 0.9198 | 0.0208   | 0.0051   |
| Vapor      |      |      |         | 0.0991   |
| Liquid 1   |      |      |         | 0.0208   |
| Liquid 2   |      |      |         | 0.0051   |
Figure C.3. Number of Iterations required versus the system pressure, at T = 295 K.

Summary

A multiphase flash algorithm was coded and optimized in order to simulate a system composed by hydrocarbons and water. The results obtained were consistent with other available resources, and an analysis of the performance of the program when components, pressure or temperature are changed, was also presented.

The applications of this program for the analysis of highly non-ideal systems, forming multiple phases are very numerous. The results obtained so far, in terms of numerical robustness, computational time, and flexibility (addition of components and potential phases) are very promising in offering a tool to analyze complex systems.
FORTRAN Code

Program Multiphase
! PT Multiphase Flash Program
! Created by: Francisco M. Vargas
! January 2009
! This program performs calculations to find the number of phases,
! phase fraction, and composition of the components in all the phases,
! for a given P and T.
! The program uses the Rachford-Rice equation. For numerical solution a
! Newton-Raphson method (successive substitution) and accelerated
! convergence using the Dominant Eigenvalue Method are implemented.

Implicit double precision (a-h,o-z)
Dimension z(5), fug(5,3)
Dimension list(5)
Dimension pc(5), tc(5), omega(5), ictyp(5)
Double Precision lnK(5), t, beta(3)
Double Precision E(5), g(3), h(3,3), gcory(3), w(3)
Double Precision alpha0(3), betanew(3), Enew(5)
Double Precision compositions(5,4)
Double Precision compositionsDEM(5,4)
Double Precision fugt(5), fugp(5), fugx(15,5), aux(13)
Double Precision fugnew(5,3), zmix(3)
Double Precision fugnewDEM(5,3)
Double Precision fugstored(15,3)
Double Precision d1(15), d2(15), fugDEM(5,3)
Double Precision betaDEM(3)
Double Precision phasel, phase2, phase3, phase1DEM, phase2DEM,
phase3DEM
Double Precision feed, fugfeed(5)
Double Precision lambda
Integer counter, countDEM, countStored, countrestore
Logical betaexists(3), converged, betaexistsDEM(3)

Character name(5)*7

ncomp=5       ! number of components
neq=0         ! 0: SRK, 1: PR
nphase=3      ! maximum number of phases

! Definition of the components
! (numbers correspond to the INDAT -EOS- Database)
list(1)=1
list(2)=2
list(3)=3
list(4)=5
list(5)=12

! Overall (feed) composition
z(1)=0.1d0
z(2)=0.10d0
z(3)=0.50d0
z(4)=0.20d0
z(5)=0.10d0
! Component Name
name(1) = 'Methane'
name(2) = 'Ethane'
name(3) = 'Propane'
name(4) = 'Butane'
name(5) = 'H2O'

! INPUT DATA

\[
t=295 \text{d0} \\
p=2.75 \text{d0} \\
\text{improved} = 0
\]

\[
\text{error} = 1. \\
\text{tolerance} = 1. \text{d}-5
\]

\[
\text{beta} = 1.0/3. \\
\text{betaexists} = .true.
\]

!(Assumption: All the phases exist initially)

Call Initialization(ncomp,neq,list,p,t,fug)

countDEM = 0
iter = 0

Do while (error.gt.tolerance)
iter = iter + 1

Call EQcalculation(beta,fug,z,E,Q,nphase)

Call MultiphaseFlash(z,fug,E,Q,beta,betaexists,compositions,nphase)

TERMO routine calculates fugacity coefficients, and thermodynamic
derivatives, using SRK and PR EOS
This routine is not provided here.

Do k = 1,nphase
Call termo(4,0,iconl,t,p,zmix(k),compositions(:,k+l),fugnew(:,k),fugt,fugp,fugx,aux)
End do

error = 0.

Do i = 1,5
Do k = 1,nphase
error = error + abs(fugnew(i,k) - fug(i,k))
End do
End do

fug = fugnew

! Improved = 1, corresponds to the Dominant Eigenvalue Method
If (improved.eq.1) then
betaexistsDEM = betaexists
countDEM = countDEM + 1
countStored = 0
    Do k = 1, nphase
    Do i = 1, 5
        countStored = countStored + 1
        ! We store ln(\Theta_i) for the 5 components in phase 1, phase 2 and phase 3
        ! in one single column. Then we repeat this "storage" for three consecutive successive
        ! substitutions
        ! countStored is a counter from 1 to 15 total fugacities
        ! countDEM counts from 1 to 3 successive substitutions
        ! i is an index for the number of components
        ! k is an index for the number of phases
        fugstored(countStored, CountDEM) = fug(i, k)
    End do
    End if

! If we have stored 3 successive substitutions we calculate the dominant
eigenvalue method and estimate the
! converged value after an infinite number of iterations
If ((countDEM.eq.3).and.(improved.eq.1)) then
    countDEM = 0
! d1 is dk, d2 is dk+1
    d2sum = 0.
    dprod = 0.
    Do j = 1, 15
        d1(j) = fugstored(j, 2) - fugstored(j, 1)
        d2(j) = fugstored(j, 3) - fugstored(j, 2)
        d2sum = d2sum + d2(j)**2
        dprod = dprod + d1(j)*d2(j)
    End do
! Lambda is the Dominant Eigenvalue Method
    lambda = d2sum/dprod
    countrestore = 0
    Do k=1, nphase
        Do i = 1, 5
            countrestore = countrestore + 1
            fugDEM(i, k) = fugstored(countrestore, 3) + d2(countrestore)*lambda/(1.-lambda)
        End do
    End do
    End do

betaDEM = beta
betaexistsDEM = betaexists
Call EQcalculation(betaDEM, fugDEM, z, E, Q, nphase)
Call MultiphaseFlash(z, fugDEM, E, Q, betaDEM, betaexistsDEM, compositionsDEM, nphase)
Do k = l,nphase
  Call termo(4,0,iconl,t,p,zmix(k),compositionsDEM(:,:k+1),fugnewDEM(:,k),fugt,
  fugp,fugx,aux)
End do

Call termo(4,0,iconl,t,p,zmixfeed,z,fugfeed,fugt,fugp,fugx,aux)
dGRT = 0.
dGRTDEM = 0.
phasel = 0.
phase2 = 0.
phase3 = 0.
feed = 0.
phaselDEM = 0.
phase2DEM = 0.
phase3DEM = 0.

Do i = 1,5
  phasel = phasel + compositions(i,2)*beta(1)*(log(compositions(i,2))+fug(i,1))
  phase2 = phase2 + compositions(i,3)*beta(2)*(log(compositions(i,3))+fug(i,2))
  phase3 = phase3 + compositions(i,4)*beta(3)*(log(compositions(i,4))+fug(i,3))
  feed = feed + compositions(i,1)*(log(compositions(i,1))+fugfeed(i))
  phaselDEM = phaselDEM + compositionsDEM(i,2)*betaDEM(1)*(log(compositionsDEM(i,2))+fugnewDEM(i,
  1))
  phase2DEM = phase2DEM + compositionsDEM(i,3)*betaDEM(2)*(log(compositionsDEM(i,3))+fugnewDEM(i,
  2))
  phase3DEM = phase3DEM + compositionsDEM(i,4)*betaDEM(3)*(log(compositionsDEM(i,4))+fugnewDEM(i,
  3))
End do

dGRT = phasel + phase2 + phase3 - feed
dGRTDEM = phaselDEM + phase2DEM + phase3DEM - feed

If ((dGRTDEM-dGRT).lt.0) then
  fug = fugnewDEM
  beta = betaDEM
  compositions = compositionsDEM
End if
End if
End do

Write(*,50) " T = ", t, " K; P = ", p, " MPa"
Write(*,*) "Phase Fraction = "
Write(*,80) " ",(beta(k),k=1,3)
Write(*,*) "Compressibility Factor = 

Write(*,80) "",(zmix(k),k=1,3)
Write (*,*),"Subst Feed Phase 1 Phase 2 Phase 3"
Do i =1,5
   Write(*,80) name(i),(compositions(i,k),k=1,4)
End do

50 Format (a,f6.2,a,f5.2,a)
80 Format(a, 5e12.4)
100 Format(5e12.4)

Write(*,*)
Write(*,444) "Total number of iterations = ", iter

End Program

!====================================================================

Subroutine Initialization(ncomp,neq,list,p,t,fug)

Implicit Double Precision (a-h,o-z)
Dimension list(5),tc(5), pc(5), omega(5), fug(5,3)
Double precision lnK(5)
Dimension ictyp(5)

Call indat (ncomp, neq, list)
! indat is a routine that initializes the recollection of critical
properties. This routine is not provided here.

Do i = 1,5
   Call getcr(i,tc(i),pc(i),omega(i),ictyp(i))
! getcr is a routine that assigns the critical properties from a
database. This routine is not provided here.
End do

Do i = 1,5
   lnK(i) = log(Pc(i)/P) + 5.373*(1+omega(i))*(1.-Tc(i)/T)
End do

! beta1: vapor phase, beta2: hydrocarbon phase, beta3: water phase
! we assume that the vapor phase is an ideal gas (for initialization).
! ln(phiV) = 0. for all the components
! ln(Ki) = ln(phil) for both liquid phases. Exceptions are hydrocarbons in
! the water phase
! and water in the hydrocarbon phase.
! for the hydrocarbon-rich phase: lnKH2O = lnKwilson + 4.6 (KH2O =
100*Kwilson)
! for the water-rich phase: lnKhydrocarbons = lnKwilson + 4.6 (KHC =
100*Kwilson)

fug(:,1)=0.
fug(:,2)=lnK
fug(:,3)=lnK

! correction of lnK for hydrocarbons and water, in the water-rich and organic-rich phases, respectively.
! still, lnphiL = lnK (updated values of K)
fug(5,2)=lnK(5)+4.6       ! component 5: water, phase 2: organic-rich phase
fug(1:4,3)=lnK(1:4)+4.6   ! component 1-3: organics, phase 3: water-rich phase

Return
End Subroutine

! ==============================================================

Subroutine
MultiphaseFlash(z,fug,E,Q,beta,betaexists,compositions,nphase)

Implicit double precision (a-h,o-z)
Dimension z(5), fug(5,3)
Double precision beta(3)
Double precision E(5), g(3), h(3,3), gcop(3), w(3)
Double precision alpha0(3), betanew(3), Enew(5)
Double precision compositions(5,4)

Integer counter,nphase

Logical betaexists(3), converged

converged = .false.

Do while (.not.converged)
error = 1.
tolerance = 1.d-10
iter = 0
itermax = 100

Do while ((error.gt.tolerance).and.(iter.lt.itermax))

iter = iter + 1

Do k = 1, nphase
  Do i = 1,5
    g(k) = g(k) + z(i)/(E(i)*exp(fug(i,k))
  End do

End do

Do k = 1, nphase
  Do l = 1, nphase
    Do i = 1, 5
\[ h(k,l) = h(k,l) + \frac{z(i)}{(E(i)^{**2}\exp(fug(i,l))\exp(fug(i,k)))} \]

End do
End do

Do j = 1, nphase
  If (.not. betaexists(j)) then
    g(j) = 0.
    Do k = 1, 3
      h(j,k) = 0.
      h(k,j) = 0.
    End do
    h(j,j) = 1.
  End if
End do

Call gauss(H,-g,nphase,w)

! write(*,100) (w(j),j=1,3)

Do k = 1, nphase
  If(abs(w(k)).gt.0) then
    alpha0(k) = -beta(k)/w(k)
    If (alpha0(k).le.0) alpha0(k) = 1000
  Else
    alpha0(k) = 1000
  End if
End do

alpha0used = min(alpha0(1), alpha0(2), alpha0(3))
If (alpha0used.gt.1.) alpha0used = 1.

difference = 1.
epsilon = 1.d-10
counter = 0

Do while (difference.gt.epsilon)
  counter = counter + 1
  Do k = 1, nphase
    betanew(k) = beta(k) + alpha0used*w(k)*(0.5**(counter-1))
    If (betanew(k).lt.0) betanew(k)=0.d0
  End do

Call EEqcalculation(betanew,fug,z,Enew,Qnew,nphase)

difference = Qnew - Q

End do

Q = Qnew
E = Enew
beta = betanew

Do i=1,nphase
If (beta(i).lt.1d-10) then
  beta(i) = 0d0
  betaexists(i) = .false.
End if
End do

error = 0.

Do k = 1,nphase
  error = error + abs(w(k))
End do

End do

converged=.true.

Do k = 1,nphase
  If (.not.betaexists(k)) then
    If (gcopy(k).le.0) then
      If (abs(gcopy(k)-min(gcopy(1),gcopy(2),gcopy(3))).lt.tolerance) then
        betaexists(k) = .true.
        converged = .false.
      End if
    End if
  End if
End if
End do

! Calculate compositions of the different phases
compositions(:, 1) = z

Do i = 1,5
  Do k = 1,nphase
    compositions(i,k+1) = z(i)/(E(i)*exp(fug(i,k)))
  End do
End do

100 Format(5el2.4)

Return
End Subroutine

! ==========================================================================

Subroutine EQcalculation(beta,fug,z,E,Q,nphase)
! Calculation of E and Q

Implicit Double Precision (a-h,o-z)

Dimension beta(3), fug(5,3), z(5), E(5)

! E is a vector of length C (number of components)
E=0.
Do i =1,5 ! loop over the number of components
   Do k =1,nphase ! loop over the number of phases
      E(i) = E(i) + beta(k)/exp(fug(i,k))
   End do
End do

Qphase = 0.
Do k = 1,nphase ! loop over the number of phases to calculate the
phase-dependent term of Q
   Qphase = Qphase + beta(k)
End do

Qcomp = 0.
Do i = 1, 5 ! loop over the number of components to calculate the
component-dependent term of Q
   Qcomp = Qcomp + z(i)*log(E(i))
End do

Q = Qphase - Qcomp

Return
End Subroutine

! ====================================================================
! Solution of the linear system of Equations (Gauss Elimination)

Subroutine gauss(A,b,n,xs)
! In order to solve the linear system of equations that arise from
! a Guass-Elimination method is used.
Double Precision A(n,n), b(n), xs(n), AB(n,n+l)
Double precision max, rowmax(n+l), sum
Integer kmax

! Augmented Matrix AB = [A|b]
Do i = 1,n
   Do j = 1,n
      AB(i,j) = A(i,j)
   End do
   AB(i,n+l) = b(i)
End do

Do j = 1,n
   max = 0.
   kmax = 1
! Partial pivoting
   Do k = j,n
      If (abs(AB(k,j)).gt.max) then
         max = abs(AB(k,j))
         kmax = k
      End if
   End do
\begin{verbatim}
  Do k = l, n+1
    rowmax(k) = AB(kmax, k)
    AB(kmax, k) = AB(j, k)
    AB(j, k) = rowmax(k)
  End do

  ! Gauss elimination (Triangulation)
  Do i = j+1, n
    Do k = n+1, 1, -1
      AB(i, k) = AB(i, k) - AB(i, j)/AB(j, j) * AB(j, k)
    End do
  End do

  ! Back substitution

  xs(n) = AB(n, n+1)/AB(n, n)
  Do j = n-1, 1, -1
    sum = 0.
    Do k = j+1, n
      sum = sum + AB(j, k) * xs(k)
    End do
    xs(j) = (AB(j, n+1) - sum)/AB(j, j)
  End do

  Return

End

! Notation:
! A: Matrix of coefficients Ax=b
! xs: Vector of solutions
! b: Vector of independent terms
! AB: Augmented matrix: [A|b]
! max: maximum absolute value in the column
! kmax: position of the max value
! rowmax: row that contains the maximum element in the column
! sum: the sum of the aij*xj for j.ne.i
\end{verbatim}
Appendix D. PDE Solution Using Finite Difference Method

Eq. (5.7) in Section 5.1 is a partial differential equation (PDE) that represents the isothermal transport in transient state of asphaltene micro-aggregates in the wellbore, in dimensionless form, due to precipitation, aggregation, deposition, advection and diffusion mechanisms.

\[
\frac{\partial \psi}{\partial \eta} = -2(1-\eta^2) \frac{\partial \psi}{\partial \zeta} + \left( \frac{L}{R} \right) \frac{1}{\eta} \frac{1}{Pe} \left( \frac{\eta}{\partial \eta} \frac{\partial \psi}{\partial \eta} \right) - Da_A \psi + Da_P \left( 1 - \psi^{eq} \right) \exp \left( - Da_P \zeta \right)
\]

(5.7)

where: \( \psi = \frac{C_A}{C_0} \), \( \theta = t \left( \frac{v_z}{L} \right) \), \( \zeta = z/L \) and \( \eta = r/R \).

and \( Pe = \frac{\langle v_z \rangle R}{D} \), \( Da_p = \frac{k_p L}{\langle v_z \rangle} \), \( Da_A = \frac{k_A C_0^{m_A-1} L}{\langle v_z \rangle} \), \( Da_D = \frac{k_D C_0^{m_D-1} R}{D} \).

subjected to the boundary and initial conditions, in dimensionless form:

\( BC_1: \frac{\partial \psi}{\partial \eta} = 0 \) at \( \eta = 0 \ \forall \ \zeta \)

\( BC_2: \psi = \psi_0 \) at \( \zeta = 0 \ \forall \ \eta \)

\( BC_3: \frac{\partial \psi}{\partial \eta} = - Da_D \psi^{m_D} \) at \( \eta = 1 \ \forall \ \zeta \), \( IC: \psi = \psi_0 \) at \( \theta = 0 \ \forall \ \eta, \zeta \)

Additionally, the diffusion term can be expanded as:

\[\left( \frac{L}{R} \right) \frac{1}{Pe} \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \eta \cdot \frac{\partial \psi}{\partial \eta} \right) = \left( \frac{L}{R} \right) \frac{1}{Pe} \left( \frac{\partial^2 \psi}{\partial \eta^2} + \frac{1}{\eta} \frac{\partial \psi}{\partial \eta} \right)\]

(D.1)

Eq. (5.7) can be solved using Finite Difference Method (FDM).

A rectangular mesh is created in the domain of interest, formed by \( r = [0,R] \) and \( z = [0,L] \) or, in dimensionless variables, \( \eta = [0,1] \) and \( \zeta = [0,1] \), according to Figure D.1

\( \eta = 0 \) corresponds to the center of the tube and \( \zeta = 0 \) represents the tube inlet.

\( n_r \) points are used in \( r \)-direction and \( n_z \) points are used in \( z \)-direction, giving a total of \( n_r n_z \) grid points. The corresponding linear system of equations has a dimension of \( n_r n_z \times n_r n_z \).
For the k-point in the mesh, Eq. (5.7) is discretized in $\theta$, $\eta$ and $\zeta$ directions, as:

\[
\frac{\psi_k^{\theta+1} - \psi_k^\theta}{\Delta \theta} + \left(1 - \eta_k^2\right) \frac{\psi_k^{\eta+1} - \psi_k^{\eta-1}}{\Delta \zeta} - \frac{L}{R} \frac{1}{Pe} \left( \frac{\psi_{k+\eta}^{\theta+1} - 2\psi_{k}^{\theta+1} + \psi_{k-\eta}^{\theta+1}}{\Delta \eta^2} + \frac{1}{\eta_k} \frac{\psi_{k+\eta}^{\theta+1} - \psi_{k-\eta}^{\theta+1}}{2\Delta \eta} \right) + Da_\theta \psi_k^{\theta+1} = p^\theta
\]

(D.2)

where: $\Delta \eta$ and $\Delta \zeta$ are the grid sizes in $r$ and $z$ directions, respectively, $\Delta \theta$ is the time step, and $p$ is the rate of precipitation, $p = Da_\eta \left(1 - \psi^{eq}\right) \exp\left(-Da_p \zeta\right)$.

An implicit method is adopted to discretize $\theta$.

Note that although $R$ is strictly speaking a function of time, because the deposition of asphaltenes reduces the effective radius for transport of oil, it is assumed that at initial stages deposition does not affect the radius considerably. The algorithm can be modified incorporating variable $R$ as a function of time.

The final system of linear equations has the following form:

\[
\mathbf{Q}\psi = \mathbf{z}
\]

(D.3)
where: $\Omega$ is a matrix of coefficients of dimension $n_r n_z \times n_r n_z$. $\psi$ is a vector that contains the solution of the problem (dimension $n_r n_z \times I$) for time $\theta+1$, and $\xi$ is a vector that contains the independent variables (dimension $n_r n_z \times I$)

All the elements of matrix $\Omega$ and vector $\xi$ are initialized: $\Omega = 0$ and $\xi = 0$.

Discretization is now applied to the different points in the mesh.

1) For the bottom side ($\zeta = 0$):

Second boundary condition, BC$_2$, is applied:

$$BC_2: \quad \psi = \psi_0 \quad \text{at} \quad \zeta = 0 \quad \forall \eta$$

For $k = 1$ to $(n_r-1)n_z + 1$ step $n_z$

$$\Omega_{kk} = 1$$

$$\xi_k = \psi_0$$

2) For the left side ($\eta = 0$):

First boundary condition, BC$_1$, is applied:

$$BC_1: \quad \frac{\partial \psi}{\partial \eta} = 0 \quad \text{at} \quad \eta = 0 \quad \forall \zeta$$

$$\frac{\psi^{\theta+1}_{k+n_z} - \psi^{\theta+1}_{k-n_z}}{2\Delta \eta} = 0 \quad \Rightarrow \quad \psi^{\theta+1}_{k+n_z} = \psi^{\theta+1}_{k-n_z} \quad \text{... Substituting in Eq. (D.2):}$$

For $k = 2$ to $n_z - 1$:

$$\frac{\psi^{\theta+1}_{k} - \psi^{\theta}_{k}}{\Delta \theta} + \left(1 - \frac{\eta_k^2}{\Delta \zeta}\right) \frac{\psi^{\theta+1}_{k+1} - \psi^{\theta+1}_{k-1}}{\Delta \zeta} + \frac{L}{R} \frac{2 \left( \frac{\psi^{\theta+1}_{k+n_z} - \psi^{\theta+1}_{k-n_z}}{\Delta \eta^2} \right) + D_{a1} \psi^{\theta+1}_{k}}{\Delta \theta} = p_k^{\theta}$$

$$\left( - \frac{1 - \eta_k^2}{\Delta \zeta} \psi_{k-1} + \frac{1}{\Delta \theta} \left( \frac{1}{R} \frac{2}{Pe} \frac{1}{\Delta \eta^2} + D_{a1} \right) \psi_k + \frac{1 - \eta_k^2}{\Delta \zeta} \psi_{k+1} - \frac{L}{R} \frac{2}{Pe} \frac{1}{\Delta \eta^2} \psi_{k+n_z} \right)^{\theta+1} = \left( p_k + \frac{\psi_k}{\Delta \theta} \right)^{\theta}$$

(D.4)
3) For the upper-left corner ($\eta = 0, \zeta = 1$):

First boundary condition, $BC_1$, is applied:

$$BC_1: \frac{\partial \psi}{\partial \eta} = 0 \text{ at } \eta = 0 \quad \forall \zeta$$

\[ \frac{\psi_{k+1}^{\theta+1} - \psi_{k-1}^{\theta+1}}{2\Delta \zeta} = 0 \implies \psi_{k+1}^{\theta+1} = \psi_{k-1}^{\theta+1} \quad \text{and:} \]

using the backwards difference approximation in $z$-direction:

$$\frac{\partial \psi}{\partial \zeta} \approx \frac{\psi_{k-2}^{\theta+1} - 4\psi_{k-1}^{\theta+1} + 3\psi_{k}^{\theta+1}}{2\Delta \zeta} \quad \text{... Substituting in Eq. (D.2):}$$

For $k = n_z$:

\[ \left( \frac{1}{\Delta \zeta} - 4 \frac{\eta_i}{\Delta \zeta} + \frac{3}{\Delta \zeta} \right) \psi_{k-1}^{\theta+1} + \left( \frac{1}{\Delta \theta} \right) - 3 \left( \frac{1}{\Delta \theta} \right) + \left( \frac{L}{R} \right) \frac{2}{\text{Pe}} \frac{1}{\Delta \eta^2} + Da_{\zeta} \psi_{k-n_z}^{\theta+1} = \left( \frac{L}{R} \right) \frac{1}{\text{Pe}} \frac{1}{\Delta \eta^2} \psi_{k+n_z}^{\theta+1} = \left( p_{k} + \frac{\psi_{k}^{\theta}}{\Delta \theta} \right) \]

(D.5)

4) For the upper side ($\zeta = 1$):

Using the backwards difference approximation in $z$-direction:

$$\frac{\partial \psi}{\partial \zeta} \approx \frac{\psi_{k-2}^{\theta+1} - 4\psi_{k-1}^{\theta+1} + 3\psi_{k}^{\theta+1}}{2\Delta \zeta} \quad \text{... Substituting in Eq. (D.2):}$$

For $k = 2 \cdot n_z$ to $(n_x - 1) \cdot n_z$ step $n_z$:

\[ \left( \frac{1}{\Delta \zeta} - 4 \frac{\eta_i}{\Delta \zeta} + \frac{3}{\Delta \zeta} \right) \psi_{k-2}^{\theta+1} + \left( \frac{1}{\Delta \theta} \right) - 3 \left( \frac{1}{\Delta \theta} \right) + \left( \frac{L}{R} \right) \frac{2}{\text{Pe}} \frac{1}{\Delta \eta^2} + Da_{\zeta} \psi_{k-n_z}^{\theta+1} = \left( p_{k} + \frac{\psi_{k}^{\theta}}{\Delta \theta} \right) \]

(D.6)
5) For the upper-right corner (η = 1, ζ = 1):

Third boundary condition, BC3, is applied:

\[
BC_3: \frac{\partial \psi}{\partial \eta} = -Da_{D}\psi \text{ at } \eta = 1 \ \forall \ \zeta
\]

\[
\frac{\psi^{\theta+1}_{k+n_\zeta} - \psi^{\theta+1}_{k-n_\zeta}}{2\Delta \eta} = -Da_{D}\psi^{\theta+1}_k \Rightarrow \psi^{\theta+1}_{k+n_\zeta} = \psi^{\theta+1}_{k-n_\zeta} - 2Da_{D}\psi^{\theta+1}_k \Delta \eta
\]

And using the backwards difference approximation in z-direction:

\[
\frac{\partial \psi}{\partial \zeta} \approx \frac{\psi_{k-2} - 4\psi_{k-1} + 3\psi_k}{2\Delta z} \quad \text{... Substituting in Eq. (D.2): For } k = n_r n_z:
\]

\[
\frac{\psi^{\theta+1}_k - \psi^{\theta}_k}{\Delta \theta} + (1-\eta_k^2)\frac{\psi^{\theta+1}_{k-1} - 4\psi^{\theta+1}_{k-1} + 3\psi^{\theta+1}_k}{\Delta \zeta} - \left(\frac{L}{R}\right) \frac{2}{Pe} \left(\frac{\psi^{\theta+1}_{k-n_\zeta} - (1+\Delta \zeta Da_{D})\psi^{\theta+1}_k - 1}{\eta_k} Da_{D}\psi^{\theta+1}_k\right)
\]

\[
+ Da_{A}\psi^{\theta+1}_k = p^{\theta}_k
\]

\[
\left(\frac{L}{R}\right) \frac{2}{Pe} \left(\frac{1}{\Delta \eta^2}\right)\psi_{k-n_\zeta} - \frac{(1-\eta_k^2)}{\Delta \zeta} \psi_{k-2} - 4 \frac{(1-\eta_k^2)}{\Delta \zeta} \psi_{k-1} + \left(1 + \frac{1}{\Delta \theta} + 3 \frac{(1-\eta_k^2)}{\Delta \zeta} + \left(\frac{L}{R}\right) \frac{2}{Pe} \left(\frac{1+\Delta \eta Da_{D}}{\Delta \eta^2} + \frac{1}{\eta_k} Da_{D}\right) + Da_{A}\right) \psi_{k}^{\theta+1}
\]

\[
= \left(p_k + \frac{\psi_k^{\theta}}{\Delta \theta}\right)^\theta
\]

(D.7)

6) For the right side (η = 1):

Third boundary condition, BC3, is applied:

\[
BC_3: \frac{\partial \psi}{\partial \eta} = -Da_{D}\psi \text{ at } \eta = 1 \ \forall \ \zeta
\]

\[
\frac{\psi^{\theta+1}_{k+n_\zeta} - \psi^{\theta+1}_{k-n_\zeta}}{2\Delta \eta} = -Da_{D}\psi^{\theta+1}_k \Rightarrow \psi^{\theta+1}_{k+n_\zeta} = \psi^{\theta+1}_{k-n_\zeta} - 2Da_{D}\psi^{\theta+1}_k \Delta \eta
\]

Note that the advection term vanishes at η = 1 because \(v(1) = 0\)

Substituting in Eq. (D.2): For \(k = (n_r - 1)n_z + 2\) to \(n_r n_z - 1\)

\[
\frac{\psi^{\theta+1}_k - \psi^{\theta}_k}{\Delta \theta} - \left(\frac{L}{R}\right) \frac{2}{Pe} \left(\frac{\psi^{\theta+1}_{k-n_\zeta} - (1+\Delta \eta Da_{D})\psi^{\theta+1}_k - Da_{D}\psi^{\theta+1}_k}{\Delta \eta^2}\right) + Da_{A}\psi^{\theta+1}_k = p^{\theta}_k
\]

\[
\left(\frac{L}{R}\right) \frac{2}{Pe} \left(\frac{1}{\Delta \eta^2}\right)\psi_{k-n_\zeta} + \left(\frac{1}{\Delta \theta} + \left(\frac{L}{R}\right) \frac{2}{Pe} \left(\frac{1+\Delta \eta Da_{D}}{\Delta \eta^2} + Da_{D}\right) + Da_{A}\right) \psi_{k}^{\theta+1} = \left(p_k + \frac{\psi_k^{\theta}}{\Delta \theta}\right)^\theta
\]

(D.8)
7) For the interior points:

For \( k_x = 2, n_t - 1 \)

For \( k = (k_x - 1) \cdot n_z + 2 \) step \( k_x \cdot n_z + 1 \)

\[
\frac{\psi_k^{\theta+1} - \psi_k^\theta}{\Delta \theta} + (1 - \eta_k^2) \frac{\psi_{k+1}^{\theta+1} - \psi_{k-1}^{\theta+1}}{\Delta \zeta} = \left( \frac{L}{R} \right) \frac{1}{Pe} \left( \frac{1}{\Delta \eta^2} - \frac{1}{\eta_k} \frac{1}{2 \Delta \eta} \right) \psi_{k-n} - \left( \frac{1 - \eta_k^2}{\Delta \zeta} \right) \psi_{k-1} + \left( \frac{1}{\Delta \theta} + \frac{L}{R} \right) \frac{1}{Pe} \frac{1}{\Delta \eta^2} + D_{a_k} \psi_{k+n}^{\theta+1} = p_k^\theta
\]

\[
\begin{pmatrix}
\left( \frac{L}{R} \right) \frac{1}{Pe} \left( \frac{1}{\Delta \eta^2} - \frac{1}{\eta_k} \frac{1}{2 \Delta \eta} \right) \psi_{k-n} - \left( \frac{1 - \eta_k^2}{\Delta \zeta} \right) \psi_{k-1} + \left( \frac{1}{\Delta \theta} + \frac{L}{R} \right) \frac{1}{Pe} \frac{1}{\Delta \eta^2} + D_{a_k} \\
+ \left( \frac{1 - \eta_k^2}{\Delta \zeta} \right) \psi_{k+n}^\theta
\end{pmatrix} = \left( p_k + \frac{\psi_k^\theta}{\Delta \theta} \right) \psi_{k+1}^\theta
\]

(D.9)

\( p_k \) is used to represent the precipitation rate at the grid point \( k \), which is changing along the tube: \( p_k = Da_i (1 - \psi_{eq}^\theta) \exp \left( -Da_i \zeta_k^\theta \right) \).

It is important to mention that Eq. (5.7) describes the transport of micro-aggregates under laminar regime (capillary experiments). For wellbore simulations the dimensionless radius \( \eta \) in the advective term (not in the diffusion term) becomes equal to \( 1/\sqrt{2} \). Thus, the advective term in Eq. (5.7) becomes simply \( \frac{\partial \psi}{\partial \zeta} \).

Advective terms of Eqs. (D.4)–(D.7) and (D.9) have to be updated accordingly.
Eq. (5.7) can be re-arranged, dropping the accumulation term, to obtain the steady state version of the model under laminar flow:

\[
2\left(1-\eta^2\right)\frac{\partial \psi}{\partial \zeta} = \left(\frac{L}{R}\right) \frac{1}{\eta} \frac{1}{Pe} \frac{\partial}{\partial \eta} \left(\eta \cdot \frac{\partial \psi}{\partial \eta}\right) - Da_A \psi + Da_p \left(1-\psi^{eq}\right) \exp\left(-Da_p \zeta\right)
\]

where: \( \psi = C_A/C_0 \), \( \zeta = z/L \) and \( \eta = r/R \).

and \( Pe = \frac{\langle v_z \rangle R}{D} \), \( Da_p = k_p L \), \( Da_A = \frac{k_A C_0^{n_A-1} L}{\langle v_z \rangle} \), \( Da_d = \frac{k_d C_0^{n_d-1} R}{D} \).

With the boundary conditions, in dimensionless form:

BC1: \( \frac{\partial \psi}{\partial \eta} = 0 \) at \( \eta = 0 \) \( \forall \zeta \)

BC2: \( \psi = \psi_0 \) at \( \zeta = 0 \) \( \forall \eta \)

BC3: \( \frac{\partial \psi}{\partial \eta} = -Da_d \psi^{n_d} \) at \( \eta = 1 \) \( \forall \zeta \)

Discretization for the steady state version can be readily obtained from Eqs. (D.4)-(D.9):

1) For the bottom side (\( \zeta = 0 \)):

For k = 1 to \((n_r-1)n_z + 1\) step \(n_z\)

\[
\Omega_{kk} = 1
\]

\[
\xi_k = \psi_0
\]

2) For the left side (\( \eta = 0 \)):

For k = 2 to \(n_x - 1\):

\[
-\frac{\left(1-\eta_k^2\right)}{\Delta \zeta} \psi_{k-1} + \left(\frac{L}{R}\right) \frac{2}{Pe \Delta \eta^2} + Da_A \psi_k + \frac{\left(1-\eta_k^2\right)}{\Delta \zeta} \psi_{k+1} = \frac{L}{Pe \Delta \eta^2} \psi_{k+n_x} = p_k
\]

3) For the upper-left corner (\( \eta = 0 \), \( \zeta = 1 \)):

For k = \(n_x\):

\[
-\frac{\left(1-\eta_k^2\right)}{\Delta \zeta} \psi_{k-2} - 4\frac{\left(1-\eta_k^2\right)}{\Delta \zeta} \psi_{k-1} + \left(3\frac{\left(1-\eta_k^2\right)}{\Delta \zeta} + \left(\frac{L}{R}\right) \frac{2}{Pe \Delta \eta^2} + Da_A \right) \psi_k - \frac{L}{Pe \Delta \eta^2} \psi_{k+n_x} = p_k
\]
4) For the upper side ($\zeta = 1$):

For $k = 2 \cdot n_z$ to $(n_r - 1) \cdot n_z$ step $n_z$:

\[
\left( \frac{L}{R} \right) \frac{2}{Pe} \left( \frac{1}{\eta_z^2} - \frac{1}{\eta_z} \right) \psi_{k-n_z} - \frac{(1-\eta_z^2)}{\Delta \zeta} \psi_{k-2} - 4 \frac{(1-\eta_z^2)}{\Delta \zeta} \psi_{k-1} \\
+ \left( 3 \frac{(1-\eta_z^2)}{\Delta \zeta} + \left( \frac{L}{R} \right) \frac{2}{Pe} \frac{1}{\eta_z^2} + Da_A \right) \psi_k - \left( \frac{L}{R} \right) \frac{1}{Pe} \left( \frac{1}{\eta_z^2} + \frac{1}{\eta_z} \right) \psi_{k+n_z} = p_k 
\]  

(D.12)

5) For the upper-right corner ($\eta = 1, \zeta = 1$):

For $k = n_r \cdot n_z$ :

\[
\left( \frac{L}{R} \right) \frac{2}{Pe} \left( \frac{1}{\Delta \zeta} \right) \psi_{k-n_z} - \frac{(1-\eta_z^2)}{\Delta \zeta} \psi_{k-2} - 4 \frac{(1-\eta_z^2)}{\Delta \zeta} \psi_{k-1} \\
+ \left( 3 \frac{(1-\eta_z^2)}{\Delta \zeta} + \left( \frac{L}{R} \right) \frac{2}{Pe} \left( \frac{1+\Delta \eta Da_D}{\Delta \zeta^2} + \frac{1}{\eta_z} \right) Da_D + Da_A \right) \psi_k = p_k 
\]  

(D.13)

6) For the right side ($\eta = 1$):

For $k = (n_r - 1) \cdot n_z + 2$ to $n_r \cdot n_z - 1$

\[
\left( \frac{L}{R} \right) \frac{2}{Pe} \left( \frac{1}{\Delta \zeta} \right) \psi_{k-n_z} + \left( \frac{L}{R} \right) \frac{2}{Pe} \left( \frac{1+\Delta \eta Da_D}{\Delta \zeta^2} + Da_D \right) \psi_k = p_k 
\]  

(D.14)

7) For the interior points:

For $k_x = 2, n_r - 1$

For $k = (k_x - 1) \cdot n_z + 2$ step $k_x \cdot n_z + 1$

\[
-\left( \frac{L}{R} \right) \frac{1}{Pe} \left( \frac{1}{\eta_z^2} - \frac{1}{\eta_z} \right) \psi_{k-n_z} - \frac{(1-\eta_z^2)}{\Delta \zeta} \psi_{k-1} + \left( \frac{L}{R} \right) \frac{2}{Pe} \frac{1}{\eta_z^2} \psi_k \\
+ \left( \frac{1-\eta_z^2}{\Delta \zeta} \psi_{k+1} - \left( \frac{L}{R} \right) \frac{1}{Pe} \left( \frac{1}{\eta_z^2} + \frac{1}{\eta_z} \right) \psi_{k+n_z} = p_k 
\]  

(D.15)

Eqs. (D.10)–(D.15) represent the model under laminar flow. Similarly to the transient model, for wellbore simulations the dimensionless radius $\eta$ in the advective term (not in the diffusion term) becomes equal to $1/\sqrt{2}$.

Advective terms of Eqs. (D.4)–(D.7) and (D.9) have to be updated accordingly.
To avoid the need of manually changing the advective term when switching from turbulent to laminar regimes and vice versa, a new binary variable $\lambda$ is introduced.

\[
Advection = \left[ \lambda + 2(1 - \lambda)(1 - \eta^2) \right] \frac{\partial \psi}{\partial \zeta} \tag{D.16}
\]

where $\lambda$ is a binary variable that is equal to one for turbulent flow and zero for laminar flow.

Discretization of the PDE can be modified accordingly for both transient and steady state versions of the model. For example, the general model (applicable for both capillary and wellbore simulations) for the steady state version can be discretized in the following way, with $\lambda = 0$ for capillary simulations and $\lambda = 1$ for wellbore simulations:

1) For the bottom side ($\zeta = 0$):

For $k = 1$ to $(n_r-1) \cdot n_z + 1$ step $n_z$

\[
\Omega_{kk} = 1
\]

\[
\xi_k = \psi_0
\]

2) For the left side ($\eta = 0$):

For $k = 2$ to $n_z - 1$:

\[
\frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2\Delta \eta} \psi_{k-1} + \left( \frac{L}{R} \frac{2}{Pe \Delta \eta^2} + Da_{x} \right) \psi_k + \frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2\Delta \eta} \psi_{k+1} - \left( \frac{L}{R} \frac{2}{Pe \Delta \eta^2} \right) \psi_{k+n_z} = p_k
\]  

(D.17)

3) For the upper-left corner ($\eta = 0$, $\zeta = 1$):

For $k = n_z$:

\[
\frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2\Delta \eta} \psi_{k-1} - \frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2\Delta \eta} \psi_{k+1}
\]

\[
+ \left( \frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2\Delta \eta} + \left( \frac{L}{R} \frac{2}{Pe \Delta \eta^2} + Da_{x} \right) \right) \psi_k - \left( \frac{L}{R} \frac{2}{Pe \Delta \eta^2} \right) \psi_{k+n_z} = p_k
\]

(D.18)
4) For the upper side (ζ = 1):

For k = 2 \cdot n_x \text{ to } (n_r - 1) \cdot n_x \text{ step } n_x:

\[
\left( \frac{L}{R} \right) \frac{2}{P e} \left( \frac{1}{\Delta \eta^2} - \frac{1}{\eta_k} \right) \psi_{k-n_x} = \frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2 \Delta \eta} \psi_{k-2} - 4 \frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2 \Delta \eta} \psi_{k-1}
\]

\[
+ \left( \frac{3}{2 \Delta \eta} \right) \psi_{k-n_x} = p_k
\]

(D.19)

5) For the upper-right corner (η = 1, ζ = 1):

For k = n_r \cdot n_x:

\[
\left( \frac{L}{R} \right) \frac{2}{P e} \left( \frac{1}{\Delta \eta^2} \right) \psi_{k-n_x} = \frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2 \Delta \eta} \psi_{k-2} - 4 \frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2 \Delta \eta} \psi_{k-1}
\]

\[
+ \left( \frac{3}{2 \Delta \eta} \right) \psi_{k-n_x} = p_k
\]

(D.20)

6) For the right side (η = 1):

For k = (n_r - 1) \cdot n_x + 2 \text{ to } n_r \cdot n_x - 1

\[
\left( \frac{L}{R} \right) \frac{2}{P e} \left( \frac{1}{\Delta \eta^2} \right) \psi_{k-n_x} + \left( \frac{L}{R} \right) \frac{2}{P e} \left( \frac{1 + \Delta \eta D a_D}{\Delta \eta^2} \right) \psi_k = p_k
\]

(D.21)

7) For the interior points:

For k_x = 2, n_r - 1

For k = (k_x - 1) \cdot n_x + 2 \text{ step } k_x \cdot n_x + 1

\[
- \left( \frac{L}{R} \right) \frac{1}{P e} \left( \frac{1}{\Delta \eta^2} - \frac{1}{\eta_k} \right) \psi_{k-n_x} = \frac{\lambda + 2(1 - \lambda)(1 - \eta^2)}{2 \Delta \eta} \psi_{k-2} + \left( \frac{L}{R} \right) \frac{1}{P e} \frac{1}{\eta_k} \psi_{k-1}
\]

\[
+ \left( \frac{3}{2 \Delta \eta} \right) \psi_{k-n_x} = p_k
\]

(D.22)
After solving Eq. (5.7), the dimensionless deposition flux, $j_A$, can be calculated according to Eq. (D.23):

$$j_A = \frac{RJ_A}{DC_0^*} = \left( \frac{\partial \psi}{\partial \eta} \right)_{\eta=1} = -Da_D \left( \psi \right)_{\eta=1}$$

where: $j_A$ is the dimensionless deposition flux, $R$ is the tube radius, $J_A$ is the deposition flux in units of mass per unit time and per unit area, $D$ is the diffusion coefficient, $C_0^*$ is the concentration of dissolved asphaltenes at inlet conditions (used to normalize all the concentrations in the model), $\psi$ is the normalized concentration of micro-aggregates $= C_A / C_0^*$, $\eta$ is the normalized radius $= r/R$, and $Da_D$ is the Damköhler number of deposition.

Besides the difference on the flow regime, discussed above, another important difference between capillary experiments and wellbore flow is that in the former the pressure drop is negligible, and because experiments are typically done at constant temperature, it can be assumed that the solubility of asphaltenes along the capillary is constant, i.e. $\psi^{eq} = $ constant. In this case the precipitation rate at grid point $k$ becomes:

$$p_k = Da_p \left( 1 - \psi^{eq} \right) \exp \left( -Da_p \zeta_k \right)$$

where $\psi^{eq}$ is the normalized concentration of dissolved asphaltenes at equilibrium, which can be evaluated at inlet conditions.

In the wellbore, because of the pressure drop, $\psi^{eq}$ changes with $\zeta$. $\psi^{eq}$ is clearly a strong function of temperature as well, but in this analysis the temperature is assumed to be constant. The incorporation of the energy equation to account for non-isothermal operations is of great importance and it is recommended as one of the most important task in improving and extending the modeling approaches described on this dissertation.