BUBBLE POINT SUPPRESSION IN UNCONVENTIONAL LIQUIDS RICH RESERVOIRS AND ITS IMPACT ON OIL PRODUCTION

by

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ABSTRACT

The average pore size in producing unconventional, liquids-rich reservoirs is estimated to be less than 100 nm. At this nano-pore scale, capillary and surface disjoining force interactions, such as van der Waals, structural, and adsorption, affect the phase behavior that is not considered to be significantly, different than in conventional reservoirs. In this dissertation, a comprehensive discussion of the thermodynamics required to model phase behavior of unconventional, liquidsrich reservoirs is presented. Three oil compositions from different unconventional reservoirs are used to generate results.

The impact of confinement manifests itself in the form of reduction of the liquid pressure at which the first gas bubble forms when compared to the bulk fluid measurements in PVT cells. It is shown that the suppression of the bubble-point pressure impacts the saturated portion of the liquid formation volume factor and extends the undersaturated portion of the curve. The equilibrium gas composition is different for each supersaturation level and the gas is composed of lighter components as the supersaturation, i.e., the bubble-point suppression, increases. The minimum radius of the pore that is required to form a specified size bubble is also investigated and the range of pore sizes required under different assumptions is reported.

The impact of this phase behavior deviation on the flow of confined fluids is investigated using a black-oil simulator, COZSim, which evaluates gas and oil fluid properties at corresponding phase pressures. The simulator was independently developed in a DOE project with the capability to incorporate the findings of this research. The results of the analysis show that there is a difference in gas production and gas saturation distribution in the reservoir with and without the confinement impact on the PVT properties. The produced GOR is lower when the confinement is considered due to the bubble-point suppression. These results indicate that the use of bulk fluid measurements in modeling and predicting the performances of nano-porous unconventional reservoirs may result in significant underestimation of the reservoir potential.

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CHAPTER 1

INTRODUCTION

This research is a Doctor of Philosophy study that was conducted at the Marathon Center of Excellence for Reservoir Studies (MCERS) in the Petroleum Engineering Department of Colorado School of Mines.

The objective of this research is to improve our understanding of fluid flow in unconventional reservoirs by focusing on the bubble-point pressure behavior in nanopores. A two-tier approach was used. First, the bubble-point pressure was determined in the presence of capillary and surface forces in nano-pores. Second, the impact of the confined PVT behavior on reservoir flow was investigated using numerical simulation.

The bubble-point suppression was quantified and its impact on the formation volume factor, gas composition at bubble point, was investigated and the minimum pore size required to form a stable gas bubble was analyzed.

Evaluating fluid behavior (PVT) at different gas and oil pressures and including the impact of bubble-point suppression in confined environments have an impact on the predicted flow behavior. The nano-pore PVT behavior was quantified using a DOE^{*}/NETL^{**} black-oil simulator called COZSim (Ozgen 2012). COZSim is a simulator with a modified black-oil formulation that can evaluate the PVT properties of oil and gas at corresponding phase pressures (Ozgen, 2012). The simulator's input and source code was modified (by third-party software developers) to include the excess suppression. Correlations to quantify the excess suppression value as a function of the bulk PVT properties and capillary pressure were generated and input into the simulator.

^{*}DOE = Department of Energy

^{**}NETL= National Energy Technology Labs

In this introduction the organization of the dissertation, motivation, hypotheses, objectives, phases and the method of this research is presented.

1.1 Organization of the Dissertation

This dissertation explains the motivation, background, methodology, and objectives of the study.

The presentation of the dissertation is divided into seven chapters:

Chapter 1, introduction, includes motivation, background, objective, and research methodology.

Chapter 2 presents a review of the literature, relevant to the conduct of this research.

Chapter 3 introduces the concepts used to model the phase behavior in nano-pore environment.

Chapter 4 discusses the modeling of hydrocarbon phase behavior in nano-pores, and provides PVT data for fluid samples from three unconventional reservoirs.

Chapter 5 presents correlations generated to quantify the bubble-point suppression of the bubble point pressure in nano-pores as a function of bulk black-oil PVT properties and capillary pressure.

Chapter 6 demonstrates the impact of confined nano-pore space on the phase behavior of reservoir fluids and the resulting effects on reservoir performance..

Chapter 7 summarizes the conclusions and recommendations of the research with comments on its potential extensions.

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1.2 Motivation of Research

In recent years, gas and oil production from resource rocks has become an important portion of our hydrocarbon production mix. Advances in drilling and completion technologies including horizontal wells and hydraulic fracturing have made it possible to exploit unconventional resources. Despite the recent technological advances that have enabled us to exploit ultra-tight, unconventional resources, hydrocarbon fluid properties and flow mechanisms in these ultra-tight porous media are poorly understood. The problem may be phrased as, what happens when the size of the pores reduces down to the size of the building blocks of the fluids? Or, as Huber et al. (2007) put it, "... to what extend macroscopically determined wetting properties or values of fluid parameters, such as the viscosity, or the surface tension, accurately describe the flow of liquids in such extreme spatial confinement?"

In the oil industry, the conventional, laboratory-based PVT analyses are designed to characterize the bulk fluid behavior without the consideration of spatial confinement. Conversely, studies in the area of nanotechnology have shown that the behavior of fluids under confinement deviates from that of bulk fluids because of the increased effect of capillary, structural, electrostatic, van der Waals, and adsorptive forces. The elevated interaction among the molecules of the fluid plus the influence of pore walls on the molecules may change the apparent physical properties of the fluid, such as the critical pressure and temperature, density, viscosity, surface tension, etc. (Kanda et al., 2004, Chen et al., 2008, Singh et al., 2009, Moore et al., 2010, Travalloni et al., 2010a,2010b, and Sapmanee, 2011).

Therefore, for the characterization of hydrocarbon reservoir fluids, the data that are obtained from PVT cells or test tubes do not reflect the capillary pressure discontinuities in the reservoirs. In this respect, PVT measurements represent a simplification due to the negligible effect of capillary pressure and surface forces. This simplification may be valid for the large pore radii of conventional reservoirs. However, its validity becomes questionable when the pore sizes drop down to the level of a few nanometers in unconventional reservoirs.

The exploitation of oil from nano-pore rocks is relatively new and the observed production data only covers a relatively short period of time to properly model these reservoirs. The understanding of the flow mechanisms that govern three-phase flow is limited. For example, conventional wisdom and numerical modeling efforts indicate that there must be a change in the reservoir behavior around the bubble-point pressure and the GOR should increase. Field observations from unconventional reservoirs, however, are not always aligned with these expectations. In some cases, despite a considerable drop in bottomhole pressure below bubble point, no significant increase in GOR is observed. This phenomenon is sometimes called "gas blockage"in the industry.

The motivation of this study is to contribute to the efforts in improving our modeling and prediction capabilities for nano-porous unconventional reservoirs. This motivation is justified by the increased effort reported in the petroleum engineering literature to explore, adopt, and enhance the exiting knowledge about phase-behavior in confinement, develop correlations and new approaches to incorporate the effects of pore proximity into unconventional reservoir simulation. It must be emphasized that the whole set of similar concepts can be discussed in the context of condensate reservoirs where the main issue is the impact of confinement on dew point pressure. However this research focuses on oil behavior only.

1.3 Hypotheses

This research has originated from our observations of production behavior in unconventional liquids-rich reservoirs through bubble point. Unlike conventional systems, a discernible increase in GOR is usually not observed in these unconventional systems. Based on this observation it has been hypothesized that the thermodynamics of nano-porous systems could display unconventional behavior. This general hypothesis has been divided into the following individual hypotheses of which the investigation has setup the scope of the research.

The main hypotheses of this research are itemized below:

Hypothesis 1: Based on the existing knowledge of bubble formation in porous media, the impact of capillary pressure on bubble-point pressure could be significant. It must be possible to incorporate the impact of capillary pressure on PVT behavior and bubble formation mechanisms in nano-pore rocks.

Hypothesis 2: The GOR behavior of the wells that produce from nano-pore rocks cannot be explained by conventional PVT and flow mechanisms. It must be possible to characterize the conditions required for gas formation in nano-pore rocks.

Hypothesis 3: The gas bubble formation in heterogeneous porous media under the influence of capillary pressure should have an impact on composition of gas in different pore sizes, which should lead to concentration gradients in porous media. **Hypothesis 4**: The phase behavior in confined environment should have an impact on flow in porous media. Although this impact may be considered under the realm of a compositional formulation, it must be possible to incorporate the phase behavior changes into a black-oil simulator to quantify the impact on flow.

1.4 Objectives

The purpose of this research is to improve our understanding of fluid flow in modeling unconventional oil reservoirs by focusing on the bubble-point pressure behavior in nano-pore flow medium. The most important expectation from this research is an improved description of fluid phase behavior in nano-pore reservoirs.

The objectives are:

- 1. Present a comprehensive discussion of hydrocarbon multi-component thermodynamics, which is required in modeling multiphase flow in unconventional, liquids-rich reservoirs.
- Assess the impact of ignoring capillary pressure and surface disjoining forces (like Van der Waals) on the phase behavior of fluid mixtures in conventional reservoirs.
- 3. Quantify bubble-point in the presence of surface and capillary forces and present its implications on the other reservoir fluid properties, such as the formation volume factor and gas composition.
- 4. Determine the minimum pore size to accommodate a stable bubble in vaporliquid equilibrium (VLE).

5. Conduct reservoir modeling to study the impact of confinement on fluid behavior using a third-party black-oil simulator.

1.5 Phases of the Research

This research has consisted of exploratory, constructive, and verification phases:

Exploratory Phase: In the exploratory phase, the problem was defined, including

- (i) the statement of the hypotheses,
- (ii) investigation of existing knowledge and data,
- (iii) definition of the specific objectives and the boundaries of the research, and
- (iv) selection of the research methods.

Constructive Phase: During the constructive phase,

- (i) A computational code that determines VLE and calculates the bubble-point pressure conditions, formation volume factor, and vapor and liquid volumes at the bubble point under the effect of capillary and surface forces was developed in FORTRAN 90.
- (ii) Correlations necessary to quantify the excess suppression as an input to the simulator were generated as a function of bulk PVT properties and capillary pressure using best-fit algorithms in Excel. These correlations were used as input into a black-oil simulator to incorporate the confined phase behavior.
- (iii) A numerical simulator, which evaluates the PVT properties at different phase pressures, was utilized to demonstrate the impact of confined phase behavior on flow.

Verification Phase: The final phase of the research has comprised:

- (i) the verification of the numerical VLE models using field data, and
- (ii) interpretation of the results to verify the validity of the initial hypotheses.

1.6 Method of Study

Field data from three unconventional shale plays were used in the verification of the phase behavior calculations. Results were analyzed and interpreted to determine the effects of confinement in unconventional oil reservoirs. The impact of confined phase behavior on flow was also demonstrated using example simulation data sets. Two models were utilized in the constructive phase; the first model is developed to study phase behavior under capillary and surface forces, the second model is taken from a DOE/NETL work and modified to incorporate the effect of bubble-point suppression in black oil formulation.

The first model enables the investigation of the phase behavior in confinement when capillary and surface forces are included. The vapor-liquid equilibrium (VLE) calculations are extended to account for capillary and surface van der Waals forces that exist in nano-pores. This yields gas and oil pressures separated by capillary pressure and van der Waals forces when the first gas bubble appears. The idea of having a stable initial gas bubble was adopted from the nucleation theory (Yortsos, 1997). Hence, the bubble generation through nucleation was not modeled. Three oil samples from unconventional, liquids-rich reservoirs were used to generate practical results. For these three samples, we investigated the relative contribution of capillary and surface van der Waals forces on supersaturation, the pore size that is required to accommodate a stable bubble of different sizes, and the impact of bubble size on the suppression of the bubble-point pressure. To demonstrate the outcome in practical terms, the results were presented in terms of their impact on bubble-point pressure and formation volume factor calculations. Given a fluid composition and temperature, the model calculates oil PVT properties, such as bubble-point pressure and formation volume factor, B_0 , in addition to the composition of the phases at different bubble-point pressures. The computational code was written in FORTRAN 90.

The second model incorporates the phase behavior in confinement in a simulation model, COZSim, independently developed by NITEC (Ozgen, 2012). COZSim has a modified black-oil formulation that evaluates the PVT properties of oil and gas at different pressures. The simulator has a variable bubble point formulation. Because of the effect of pore proximity, it is necessary to work with three different pressures in nanoporous oil reservoirs; the system (or bulk) pressure, oil pressure, and gas pressure. The bulk pressure is the hypothetical pressure that exists under the assumptions of the PVT measurements. The capillary pressure and surface forces separate oil and gas pressures. Although the capillary pressure can be computed from the interfacial tension and pore geometry data, excess suppression needs to be known to compute the difference of the fluid pressures in confinement from the PVT determined bubble-point pressure. This requires the knowledge of the amount of excess suppression. Correlations were generated using the MS Excel regression algorithms to quantify excess suppression as a function of bulk PVT properties.

CHAPTER 2

LITERATURE REVIEW

Commercial compositional simulators usually use a cubic equation of state (EOS) to calculate phase behavior of the hydrocarbon fluids. For example, Eclipse implements a generalized cubic EOS formulation described by Martin (1973). This generalized EOS can be converted to Peng-Robinson, Redlich-Kwong, Soave-Redlich-Kwong, and Zudkevitch-Joffe-Redlich-Kwong EOS by using appropriate coefficients. The EOS parameters are generally determined by the calibration of the model to the laboratory measurements, such as Constant Composition Expansion (CCE), Constant Volume Depletion (CVD), and Differential Liberation (DL), and separator tests. These tests are performed in PVT cells without consideration of the porous media effects. Similarly, black-oil simulators use the tabulated values of fluid properties that are measured under laboratory conditions in PVT cells.

In 1989, Whitson and Søreide solved the VLE calculations including the effect of capillary pressure. Their calculations showed a change in oil and gas compositions when the flash calculations were performed under the effect of capillary pressure. Similarly, Zarragoicoechea and Kuz (2003) documented the difference in phase behavior of confined fluids when compared to bulk fluids. They showed that to properly account for the behavior of confined fluids, the critical properties of the components must be altered as a function of the ratio of the molecule size to the pore size. In another study, Zhang and Wang (2006) showed the critical-point shift due to confinement and they investigated the impact of the change in wall fluid interaction. Sapmanee (2011) recently used the critical-point shift approach to generate phase diagrams for a gas condensate sample in a

nano-porous formation. He also demonstrated the shift in the phase diagram due to confinement. Recently, Travalloni et al. (2010a, 2010b) used an extension of the generalized van der Waals theory to include the impact of confinement on equation of state (EOS) calculations.

Vanderlick et al. (1989) developed an exact statistical mechanical solution, which can be used to investigate the thermodynamic properties of fluids confined to micropores using hard rod mixtures. In a similar approach, Corti and Debenedetti (1997) used to extend the pressure equation from Helmholtz free energy by adding a pressure component for the constrained system. In this case the total pressure is the combination of $P_{ideal}+P_{virial}+P_{constraint}$. It should be noted that, in common EOS applications, only the ideal and the virial portions of the pressure equation is solved.

Abu Al-Rub and Datta (1998) developed a generalized Clasius-Clayperon equation in the presence of external forces starting from the general energy balance equation for multi-component descriptions. They considered a multi component system with a spherical interface. Similarly, a multi-component, non-ideal-formulation version of the Kelvin equation, which is commonly used to determine the saturation pressure of pure fluids for curved interfaces, is available (Saphiro and Stenby, 1997) in Chemical Engineering literature. Saphiro and Stenby (2001) also investigated the condensate phase behavior using flash calculations under capillary pressure using fugacity coefficients and successive substitution. They reported the differences in phase envelope when the capillary forces are included. However, the use of these formulations in the oil and gas industry is not common. By using the Kelvin equation for pure fluids, Udell (1982) showed that the equilibrium liquid-phase pressure in small pores might be significantly lower than the bulk fluid saturation pressure. He assumed that for the gas bubble to form and to be stable in a pore (confined space), its size must be smaller than or equal to the size of the pore; otherwise, the gas bubble would collapse. The difference between the bulk-fluid saturation pressure and the equilibrium liquid-phase pressure is defined as supersaturation. The smaller the bubble size, the larger the supersaturation at phase equilibrium. This is because of the extra energy cost associated with the capillary and surface effects (Coussy 2011).

Bauget and Lenormand (2002) argued that, in the existence of capillary forces, the classical thermodynamic behavior is not sufficient to explain gas bubble formation in porous medium. They indicated that, when capillary forces are considered, the classical thermodynamic approach requires very high supersaturation values that are typically not observed in conventional hydrocarbon reservoirs.

The nucleation theory, which describes the bubble nucleus formation due to thermal fluctuations below the bubble-point pressure (Wilt, 1989), has been used to explain bubble formation in porous medium. Two types of nucleation have been considered in the literature. Homogenous nucleation, which does not require the presence of solid surfaces, and heterogeneous nucleation, which requires either nucleated or preexisting bubbles in the crevices of the pore space to stabilize the gas bubble (Yorstos and Parlar, 1989, Yortsos, 1997, Tsimpanogiannis and Yortsos, 2001, and Jones et al., 1999). Yorstos and Parlar (1989) proposed that a critical supersaturation is reached when the gas-liquid interface at the active nucleation site overcomes the capillary barrier and discussed the effects of various parameters on gas growth. Tsimpanogiannis and Yortsos (2001) developed a continuum model and showed that the critical gas saturation depends on the nucleation sites and characteristics.

A detailed discussion of gas bubble formation in porous media can be found in the study of Bauget and Lenormand (2002). In this work it is concluded that the most viable gas bubble formation mechanism that is consistent with field and laboratory observations is the heterogeneous nucleation with pre-existing bubbles. Based on experimental results, El Yousifi et al. (1997) concluded that pre-existing bubbles trapped in the crevices are released when the capillary pressure at the cavity is overcome. They measured the supersaturation values experimentally. Supersaturation values up to 420 psi were also reported by Bora et al. (2000) in micromodels. Scherpenisse et al. (1994) and Kamath and Boyer (1995) measured supersaturation in their core experiments. Kamath and Boyer (1995) also observed that there was a significant difference between the critical gas saturation values calculated through pressure depletion versus gas injection procedure. They attributed the difference to the impact of capillary forces on gas-bubble growth during depletion.

Recently Meyer et al. (2009) postulated that the existence of a stable bubble must be related to the capillary forces between the fluids as well as the van der Waals forces between the surface and the fluid. Surface forces can be defined as the extra force exerted by the fluid film to be stable (Fenwick 1997). Electrostatic, van der Waals and adsorption are the surface fluid interactions that are the most relevant to the porous medium (Scovazzo and Todd, 2001).

Until recently, the literature on the application of numerical simulation to unconventional oil reservoirs was very limited. Cipolla et al. (2010) used numerical simulation as a tool to evaluate unconventional gas reservoirs. They introduced a simulation model that utilized logarithmic gridding around wells and very fine gridding to represent fractures. Chaudhary et al. (2011) used a similar approach to model oil production from Eagle Ford Shale. They conducted a very detailed sensitivity analysis on variety of reservoir parameters and investigated the impact of each parameter on the ultimate recovery. Wang and Liu (2011) used a coarse dual-porosity simulation model for an Eagle Ford oil well and obtained a reasonable history match. Recently Whitson and Sunjerga (2012) investigated the discrepancy of the measured and observed fluid behavior in liquids-rich shale reservoirs using reservoir simulation. They recommended using a regressed EOS generated to match the produced fluid properties rather than actual measurements to be used in simulation models. They also investigated the impact of different simulation parameters on the calculated GOR and/or OGR. All the studies above used commercial simulators.

CHAPTER 3

BACKGROUND AND GAS PHASE FORMATION IN POROUS MEDIA

This chapter presents a summary of the existing knowledge of the phase behavior and its modifications for the confined environment.

3.1 Classical Thermodynamics – Phase Behavior in Unconfined Space

A phase is a part of a system that is uniform in physical and chemical properties. Multiple phases can coexists when they are in equilibrium (Ahmed, 2007). Phase equilibria have been of great interest as it describes the behavior of fluids in nature including the hydrocarbons that we extract from the reservoirs. In broadest sense, thermodynamics of phase equilibria concerns with energy transformation from one form to the other and the change of the physical properties of the matter as a result of this process. In petroleum industry, thermodynamics of phase equilibria address the question "under given temperature and pressure and mass of components what are the amounts and composition of phases that result?" (Kovscek, 1996).

3.1.1 Fundamental Relationships of Thermodynamics

Phase behavior descriptions start with the definition of free energy. Gibbs free energy, which is also called as free enthalpy of a fluid is written as (Coussy, 2010)

$$dG = Vdp - SdT + \sum_{i} \mu_{i} dN_{i}, \qquad (3.1)$$

where

G: Gibbs free energy

V: volume,m³

p: pressure, bar

S: entropy, joule/K

T: temperature, K

 μ : chemical potential, joule/mole

N: number of moles

i: component

For a component in a mixture to be in equilibrium with the same component in another mixture, their chemical potentials should be equal at a given a temperature and pressure. The equilibrium condition of a mixture is given as

$$\mu_i = \mu'_i, \tag{3.2}$$

where

 μ_i : chemical potential of component i in mixture 1

 μ_i' : chemical potential of component i in mixture 2

While solving the equilibrium, it is common to use the convenient variable fugacity introduced by Lewis in 1901. Lewis proposed an expression for Gibbs free energy for a non-ideal fluid as follows:

$$dG_i = RTd \ln f_i . aga{3.3}$$

This expression is the definition of fugacity of component i in a closed single-phase system and f_i is a function called fugacity. Eq. 3.3 is at constant temperature. If we write the Gibbs free energy equation for an ideal system, the equation would be

$$dG_i = RTd \ln P. \tag{3.4}$$

As fugacity in Eq. 3.3 is substituted in place of pressure in Eq. 3.4, its units should be pressure as well.

At constant pressure and temperature, it can be shown that

$$G_i = \mu_i, \tag{3.5}$$

and

$$dG_i = d\mu_i = RTd \, lnf_i.$$

Since the chemical potentials should be equal at equilibrium, this rule translates that, at equilibrium, the fugacity values should be equal as well; that is,

$$\mu_i^{\alpha} = \mu_i^{\beta} \longrightarrow f_i^{\alpha} = f_i^{\beta}, \qquad (3.6)$$

where α and β are the phases.

For a multi component system the same equivalency still holds. For a multi component system, a dimensionless ratio called fugacity coefficient is derived from the following equation at constant pressure and mole fraction (x_i) :

$$ln\frac{f_i}{x_iP} = -\frac{1}{RT} \int_0^P \Delta V_i' dP, \qquad (3.7)$$

where $\Delta V'_i$ is the residual partial volume which is a measure of deviation from the Ideal Gas Law.

From this equation, the fugacity coefficient is defined as (Kovscek, 1996, and Ahmed, 2007)

$$\phi_i = \frac{f_i}{x_i P} \,. \tag{3.8}$$

3.1.2 Flash Calculations and Equation of States

In a multi-component system, the equilibrium ratio is defined as the ratio of the mole fraction component in vapor (gas) phase to mole fraction of the component in liquid phase (Ahmed, 2007, and Lake, 1989). It is formulated as

$$K_i = \frac{y_i}{x_i},\tag{3.9}$$

where

K_i: equilibrium ratio, commonly called K-value for component i

y_i: vapor mole fraction of component i

x_i: liquid mole fraction of component i

To perform volumetric and compositional calculations, the phase-equilibrium relationships are commonly used as part of the flash calculations. Flash calculations are performed to determine the liquid and gas mole fractions of each component, liquid and gas mole ratios, and properties of a fluid with a given composition when the temperature and/or pressure conditions change. The following relationships that are based on K-values are the basis of the flash calculations:

$$n = n_l + n_v.$$
 (3.10)
If N=1.0, then
 $1 = n_l + n_v$ (3.11)

and

$$x_i n_l + y_i n_v = z_i. aga{3.12}$$

Using the definition of K-value,

$$x_i = \frac{z_i}{n_l + n_\nu K_i} \tag{3.13}$$

and

$$y_i = \frac{z_i K_i}{n_l + n_\nu K_i}.$$
(3.14)

Here, n represents number of moles and subscripts l and v represent the liquid and vapor phases.

Note that total mole fraction of the components, total gas mole fractions of the components and the total liquid mole fractions of the components should equal to unity; that is,

$$\sum_{i} z_i = 1, \tag{3.15}$$

$$\sum_{i} y_i = 1, \tag{3.16}$$

and

$$\sum_{i} x_i = 1. \tag{3.17}$$

Therefore,

$$\sum_{i} \frac{z_{i}K_{i}}{n_{l}+n_{\nu}K_{i}} - \sum_{i} \frac{z_{i}}{n_{l}+n_{\nu}K_{i}} = 0.$$
(3.18)

Rearranging this equation provides the following function that is used to solve the vapor mole fraction in flash calculations:

$$f(n_{\nu}) = \sum_{i} \frac{z_{i}(K_{i}-1)}{n_{\nu}(K_{i}-1)+1} = 0.$$
(3.19)

This equation can be solved by the Newton-Rhapson iterative procedure.

To start the flash calculations, an estimation of the K-value is necessary. For this estimation, the following correlation developed by Wilson (1968) is commonly used:

$$K_{i} = \frac{P_{cri}}{P} exp\left[5.37\left(1 + \omega_{i}\left(1 - \frac{T_{cri}}{T}\right)\right)\right],\tag{3.20}$$

where P_{cri} , T_{cri} and ω_i are the critical temperature, critical pressure, and accentric factor of component i respectively. In the same equation P represents the system pressure.

As stated earlier, for a system to be in equilibrium, the fugacity of each component in each phase should be equal. This condition should be satisfied by the flash calculations as follows:

$$f_i^l = f_i^v \,. \tag{3.21}$$

The fugacity coefficient defined previously can be related to the K-value in equilibrium:

$$K_{i} = \frac{\left[\frac{f_{i}^{l}}{x_{i}P}\right]}{\left[\frac{f_{i}^{v}}{y_{i}P}\right]} = \frac{\phi_{i}^{l}}{\phi_{i}^{v}}.$$
(3.22)

The general form of the fugacity coefficient equation is written as follows:

$$ln\phi_{i} = \frac{b_{i}}{b}(Z-1) - \ln(Z-B^{*}) + \frac{A^{*}}{B^{*}(u^{2}-4\omega)^{1/2}} \left(\frac{b_{i}}{b} - \partial i\right) ln[A],$$
(3.23)

$$A = \frac{2z + B^*(u + (u^2 - 4\omega)^{1/2})}{2z + B^*(u - (u^2 - 4\omega)^{1/2})},$$
(3.24)

$$A^* = \frac{aP}{R^2 T^2},$$
(3.25)

$$B^* = \frac{bP}{RT},\tag{3.26}$$

$$\frac{b_i}{b} = \frac{T_{cri}/P_{cri}}{\sum_j y_j T_{crj}/P_{crj}},\tag{3.27}$$

and

$$\partial_i = \frac{2a_i^{1/2}}{a} \sum_j y_j a_j^{1/2} \left(1 - K_{ij} \right).$$
(3.28)

If K_{ij} is equal to zero then

$$\partial_i = 2 \left(\frac{a_i}{a}\right)^{1/2}.\tag{3.29}$$

The z factor is calculated by finding the roots of the EOS used. The fugacity of each phase is then calculated. This procedure is iterative and repeated until the fugacities of liquid and gas for each component are equal or, more precisely, when the difference is less than the tolerance of convergence specified.

Cubic EOS is commonly used in petroleum industry to solve the PVT relationship of the non-ideal fluid mixtures. The EOS is solved for the z factor and used in the flash calculations. The general form of the cubic EOS is as follows:

$$Z^{3} - (1 + B^{*} - uB^{*})Z^{2} + (A^{*} + wB^{*^{2}} - uB^{*} - uB^{*^{2}})Z - A^{*}B^{*} - wB^{*^{2}} - wB^{*^{3}}$$
(3.30)

$$A^* = \frac{a^P}{R^2 T^2}$$
(3.31)

$$B^* = \frac{bP}{RT} \tag{3.32}$$

The parameters for the most commonly used EOS are given in Table 3.1.

Equation	u	w	b	a
Van der Waals	0	0	RT _{cr} /8P _{cr}	$\frac{2T}{64}R^2T_{cr}^2/P_{cr}$
Redlich-Kwong (RK)	1	0	0.08664 <i>RT_{cr}/P_{cr}</i>	$\frac{0.42748R^2T_{cr}^{2.5}}{P_{cr}T^{1/2}}$
Soave-Redlich-Kwong (SRK)	1	0	0.08664 <i>RT_{cr}/P_{cr}</i>	$\frac{0.42748R^2T_{cr}^2(1+f_w(1-T_r^{1/2}))^2}{P_{cr}}$
Peng-Robinson (PR)	2	-1	$\frac{0.0778RT_{cr}}{P_{cr}}$	$\frac{0.45724R^2T_{cr}^2}{P_{cr}}\left(1+f_w(1-T_r^{1/2})\right)^2$

Tab	le 3	.1-	Cubic	EOS	parameters
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For the SRK EOS:

$$f_w = 0.48508 + 1.5119\omega - 0.1561\omega^2, \tag{3.33}$$
and for the PR EOS:

$$f_w = 0.37464 + 1.54226\omega - 0.26992\omega^2, \tag{3.34}$$

where ω is the accentric factor.

Three roots of the equation of state provide the z factor. The details of the root calculation of a cubic equation are provided in Ahmed (2007).

It should be noted that volume corrections are necessary especially for the liquid phase. The following relationships are used to modify the z factor using volume shift.

$$V_{corr}^{l} = V_{L} - \sum_{i} x_{i} c_{i}, \qquad (3.35)$$

$$V_{corr}^{\nu} = V_{\nu} - \sum_{i} y c_{i}. \tag{3.36}$$

where

$$c_i = S_{pi}b_i. aga{3.37}$$

Here S_{pi} is the shift parameter of each component and b_i is the covolume as specified in Table 3.1 for each EOS.

3.1.3 Conditions for Bubble Point and Dew Point

The VLE calculations are used to solve parameters that are necessary to describe the flow in the reservoirs. Two of these parameters that are interesting to reservoir engineers are the dew-point and bubble-point pressures. Phase diagrams are widely used to define the phase behavior of fluids (Figure 3.1). Phase diagrams which are also commonly called P-T diagrams depict the behavior of a certain fluid composition at different temperatures and pressures. The phase envelope which is the set of saturation pressures at different temperatures defines the two phase region where gas and liquid phases can coexist. Outside the phase envelope the fluid is in single phase based on the temperature. The cricondenbar and cricondentherm represent the highest pressure and temperature points on the phase envelope.

Critical point where the phases cannot be defined divides the phase envelope into bubble point and dew point curves. At lower temperatures to the left of the critical point, fluid is in liquid phase (oil) and at high temperatures on the right of the critical point, the fluid is in vapor phase (gas). As the pressure reduces at the same temperature like during depletion, the reservoir fluid if originally in single phase hits the bubble point or the dew point curve and transitions into the two phase region.



Figure 3.1- A Typical Phase Diagram (Fan et al., 2005)

The dew-point pressure is defined as the pressure at which an infinitesimal quantity of liquid is in equilibrium with gas phase in the system. Based on this assumption that the total number of moles approximates to the number of moles in gas phase, Eqs. 3.10 through 3.18 can be used to derive the conditions at the dew point as follows:

$$\sum_{i} \frac{z_i}{\kappa_i} = 1. \tag{3.38}$$

The bubble-point pressure is defined as the pressure at which an infinitesimal quantity of gas is in equilibrium with liquid phase in the system. Assuming that the total number of moles is approximately equal to the total number of moles in liquid phase, the conditions at the bubble point can be obtained from Eqs. 3.10 through 3.18 as follows:

$$\sum_{i} (z_i K_i) = 1. \tag{3.39}$$

3.2 Classical Thermodynamics for Confined Fluids

3.2.1 Fundamental Relationships for Confined Fluids

Kelvin equation has long been used to describe the VLE at a curved interface for pure fluids. Udell (1982) used Kelvin equation to describe the bubble formation in a pore. For single-component systems, mechanical and chemical equilibrium conditions should be met for the gas bubble to be stable. The criteria for the collapse or growth of a gas bubble can be written as

$$P_g = P_l + \frac{2\sigma}{r_b},\tag{3.40}$$

where r_b is the radius of the bubble, σ is the interfacial tension, P_g and P_l are the gas- and liquid-phase pressures, respectively. Similarly, the capillary pressure in a porous medium is expressed as

$$P_g = P_l + \frac{2\sigma}{r_e},\tag{3.41}$$

where r_e is the equivalent pore radius given by $(\cos \theta)/r$ with θ and r representing the contact angle and the pore radius. Based on Eqs. 3.40 and 3.41, all bubbles that form will collapse unless $r_b \leq r_e$.

Udell (1982) provided the following equation to calculate the degree of liquid supersaturation which is the difference between the measured saturation pressure and the actual saturation pressure:

$$P_{vo} = RT\rho_l ln \frac{P_{vo}}{P_l + \frac{2\sigma}{r_e}},\tag{3.42}$$

where P_{vo} is the saturation pressure, P_l is the liquid pressure at saturated conditions, R is the universal gas constant, and T is the temperature. He showed that liquid-pressurelowering could be significant for smaller r_e values for water (for example, at 100°C, water liquid-pressure becomes negative when r_e is less than 1 micrometer). He also concluded that in pores with radii less than 0.1 micrometer, evaporation and condensation would probably be an adsorption controlled phenomenon. Figure 3.2 shows the liquidpressure lowering for different pore sizes.



Figure 3.2- Liquid pressure-lowering as a function of pore radius (Udell, 1982).

Hsieh and Ramey (1983) reached a similar conclusion for vapor. Considering the forces of attraction between the liquid and solid surfaces, they concluded that vapor pressure is lower than what is calculated by the real-gas law due to adsorption. Hsieh and Ramey presented the following equation for the actual vapor pressure in porous media.

$$P = P' \frac{\tilde{A}\delta_s}{V} (\rho_2 - \rho_1) ZRT.$$
(3.43)

In Eq. 3.43, P is the actual pressure of the container, P' is the pressure calculated by the real-gas law and the rest of the right-hand side is the desorption component. In the desorption component of Eq. 3.43, \tilde{A} is the total surface area inside the container, δ_s is the range of surface forces, ρ_1 is the density of gas molecules not affected by surface forces.

Hsieh and Ramey (1983) also developed an equation to estimate the critical radius of curvature below which the adsorption becomes dominant. This critical radius can be calculated by the following equation:

$$\ln\left(\frac{P_{vo}}{P}\right) = \frac{2\sigma_o V_l}{RT} \left(\frac{1}{\bar{r} + 2\delta_{con}}\right). \tag{3.44}$$

In this equation, P_{vo} is vapor saturation pressure, σ_o is the liquid gas interfacial tension, V_1 is the volume of the container, \bar{r} is the mean radius of curvature, and δ_{con} is a specific constant for a given fluid (in the order of 10^{-8} cm).

Saphiro and Stenby (1997) generalized the Kelvin equation for a multicomponent non-ideal mixture and obtained the generalization of Kelvin equation in the following form.

$$\frac{P_c}{P_d} = \frac{V_{vl}(P_d, y)}{V_l(y)} Z_{av}(y) ln X - X + 1.$$
(3.45)

In this equation, P_c is the capillary pressure, P_d is the dew point pressure, V_{v1} is the mixture volume, V_1 is the liquid volume, y is the molar fraction of vapor, Z_{av} is the average z factor, and X is the relative pressure, which is the ratio of the vapor pressure to the dew point pressure. Using this approach, they showed that it was possible to quantify the phase behavior without using flash calculations.

Saphiro and Stenby (2001) also modeled VLE for condensates under capillary pressure difference where phase pressures are not equal. They modified the flash calculations and solved it using successive substitution based on the following relation.

$$z_{i}^{l} = \frac{y_{i} P_{g} \phi_{i}^{g}}{\phi_{i}^{l} P_{l}},$$
(3.46)

where z is the mole fraction, P is the pressure \emptyset is the fugacity coefficient and i, l, and g represent the component index, liquid phase, and gas phase, respectively.

Whitson and Søeride (1989) performed the flash calculations including capillary pressure for a volatile oil sample in Ekofisk field. For the sample they analyzed, they showed that the capillary forces could be ignored for pore radii as small as 0.05 microns.

Abu Al-Rub and Datta (1998) investigated the impact of long-range surface forces on the phase behavior and developed a theory that accounts for the effect of surface forces exerted by the solid as well as due to the curvature of the vapor-liquid interface. They wrote the generalized internal energy for a multicomponent system with spherical interface in the presence of external force field (Figure 3.3) as follows:

$$dE = TdS + P_{\alpha}\theta R_{\alpha}^{2}dR_{\alpha} - P\theta R_{\beta}^{2}dR_{\beta} + \sigma d\theta + \sum_{i}^{n}\psi dn_{i}.$$
(3.47)

In this equation, E is the internal energy, T is the temperature, S is the entropy, P_{α} and P_{β} are the α - and β -phase pressures, θ is the angle, and $\theta R_{\alpha}^2 dR_{\alpha}$ and $\theta R_{\beta}^2 dR_{\beta}$ are the work terms, dV_{α} and dV_{β} , in the energy equation (PdV term) respectively.



Figure 3.3 - Phase Equilibrium with spherical interface (Abu Al-Rub and Datta, 1982).

Abu Al-Rub and Datta (1998) extended the Kelvin equation in the presence of external forces as follows:

$$ln\left(\frac{P}{P_{\nu}^{\infty}}\right) = C^{E} - \frac{\Delta H_{\nu l}^{E}}{RT} - \frac{2\sigma V_{l}}{RT}.$$
(3.48)

Here

P_v^r: vapor pressure over a curved interface under external forces

 P_v^{∞} : vapor pressure for a flat interface in the absence of surface forces.

C^E: equation constant in presence of surface forces

 ΔH_{vl}^{E} : Excess enthalpy due to surface forces

3.2.2 Alternative Phase Behavior Models for Confined Fluids

Alternative approaches to model the fluid behavior in constrained environments using an equation of state are available in the literature. In this section, two of these approaches will be discussed.

The first approach is based on the solution of hard rod fluid using statistical mechanics. Vanderlick and Davis (1989) proposed that using statistical mechanics of hard rod mixtures, the fluid behavior of confined fluids could be studied. Using this method, they showed that the pore-averaged mole fraction of a component in a binary mixture changes as a function of the pore width (or separation distance). As the separation distance becomes large, the mole fraction approaches the mole fraction at the bulk (unconfined) conditions, x_1^b (Figure 3.4). Similar trends can be seen in Figure 3.5 for the disjoining pressure, which is defined as the difference between the pore pressure and the bulk pressure. Figure 3.5 shows the results for six different bulk mole fractions.



Figure 3.4 – Pore average mole fraction as a function of the separation distance

(Vanderlick and Davis, 1989).



Figure 3.5 – Disjoining pressure as a function of the separation distance (Vanderlick and Davis, 1989).

Corti and Debenedetti (1997) used a similar approach to that of Vanderlick and Davis (1989). They extended the pressure equation from Helmholtz free energy by adding a pressure component for the constraint system. In this case the total pressure is

the combination of $P_{ideal}+P_{virial}+P_{constraint}$. Using this approach they were able to model the metastable state of the superheated conditions. They showed that fluids could exist at negative pressures when constraint is introduced unlike the unconstrained system, which cannot exist in negative pressures. Figure 3.6 shows the pressure behavior as a function of the density of the hot rod fluids, ρa (number of hard rod fluids times the hard rod length) for different severity of the constraint l (the length of the system)



Figure 3.6 – Equation of state evaluation as a function of different severity of constraint, 1. (Corti and Debenedetti, 1998)

Using the constraint equation of state that they developed, Corti and Debenedetti (1997) generated phase envelopes for different severity of constraints. They showed that

phase envelopes are different for different constraint levels and phase transition cannot occur outside the phase envelopes calculated for each severity of constraint (Figure 3.7).



Figure 3.7 – Density, temperature projection of the phase diagram for different severity of constraint. In this figure ρ_r and T_r are the reduced density and temperature respectively. (Corti and Debenedetti, 1998)

The second alternative approach is based on an extension of the van der Waals equation of state. Travalloni et al. (2010) extended the van der Waals equation of state to include confinement impact using the configuration depicted in Figure 3.8. In Figure 3.7, Region I is considered beyond the attractive field of the pore wall; therefore, only molecule to molecule interactions are considered in this region. Region II represents the area that the molecules are affected by the pore wall such that molecule to molecule and wall to molecule interactions are considered. This region's width is represented by width of the molecule-wall interaction, δ_p . Region III represents the inaccessible area to mass centers of the fluid molecules and its width is equal to the half of the sphere-shaped molecule diameter, $\sigma_{dia}/2$.



Figure 3.8 – Region inside a cylindrical pore, defined by the molecule-wall interaction

(Travalloni, 2010)

The extended van der Waals equation is given by Travalloni et al. (2010) as

follows:

$$P = \frac{RT}{v - b_p} - \frac{a_p}{v^2} - \theta_g \frac{a_p}{v^2} \left(1 - \frac{b_p}{v}\right)^{\theta_g - 1} \left(1 - F_{pr}\right) \left(RT \left(1 - exp \left(-\frac{N_{av}\varepsilon_p}{RT}\right)\right) - N_{av}\varepsilon_p\right).$$
(3.49)

Here,

$$a_p = \sum_{i=1}^{NC} \sum_{j=1}^{NC} \left(z_i z_j \sqrt{a_i a_j} \left(1 - \frac{2}{5} \frac{\sigma_{dia,ij}}{r_p} \right) \right), \tag{3.50}$$

$$b_p = \sum_{i=1}^{NC} z_i b_{p,i}, \tag{3.51}$$

and

$$b_{p,i} = \frac{N_{av}}{\rho_{max,i}}.$$
(3.52)

In the Eq. 3.50, R is the universal gas constant, T is the temperature in K, v is the average molar volume in m³/mol, θ_g is the geometric term, which is a function of r_p , δ_p and $\sigma_{dia}/2$, N_{av} is the Avagadro number, ε_p is the energy parameter of the attractive interaction between two fluid molecules, ρ_{max} is the molecular density of the packed fluid modified by confinement, and F_{pr} is the value of the fraction of the confined fluid molecules subjected to the attractive field of the pore walls for random distribution of the fluid molecules inside the pores.

3.3 Nucleation

There are two steps to gas formation in porous media. One is the formation and release of the gas bubble through nucleation and the other is the bubble growth through mass transfer (Yorstos, 1997). Nucleation is defined as the bubble nucleus formation due to the thermal fluctuations below the bubble-point pressure (Wilt, 1989). Two types of nucleation is considered in literature, homogenous nucleation which does not require solid surfaces and heterogeneous nucleation that requires either nucleated or pre-existing bubbles in the crevices of the pore space to stabilize the gas bubble (Yorstos and Parlar, 1989). The appearance of bubbles is a random process and the rate of the nucleation is defined as (El Yousfi et al., 1997)

$$J = 2N_{mol} \left(\frac{2\sigma}{\pi mB}\right)^{1/2} \exp\left(-\frac{16\pi\sigma^3}{3kT\Delta P^2}\right) \quad , \tag{3.53}$$

where, J is the rate of nucleation (number of bubbles per unit time and unit volume of liquid), N_{mol} is the number of molecules per unit volume, m is the mass of a molecule, kT is thermal energy, σ is the interfacial tension, B is a parameter close to 2/3, ΔP is the difference between the equilibrium pressure and the actual pressure.

The stability of the bubble depends on its radius. If the radius of the bubble is large enough to overcome the capillary pressure, the bubble will grow otherwise the bubble will collapse. The most important parameter in this case that controls the collapse or the growth of the bubble is the supersaturation. Supersaturation (Eqn 3.54) is defined as the difference between the equilibrium pressure and the liquid pressure to form a stable bubble. However the supersaturation necessary to generate a stable bubble for homogenous nucleation is very high to justify the actual performance observed by the experimental studies (Bauget and Lenormand, 2002, El Yousfi et al., 1997).

$$\Delta P = P_b - P_l \tag{3.54}$$

Heterogenous nucleation was deemed necessary to have a stable bubble for the low supersaturation values observed (Jones et al., 1992). In this case a correction factor is added to the nucleation equation to compensate for the activation energy reduction due to the wettability and contact angle however this theory is not sufficient to explain the observations if gas nuclei formation is required for gas bubble formation.

The more popular approach that has been shown to be valid by experiments is the pre-existing bubbles in the conical cavities of the porous medium (Yorstos and Parlar, 1989, Bauget and Lenormand, 2002, and Meyer et al., 2009). In this case the bubble is assumed to be trapped in the non-liquid wet crevices due to the balance created between

the gas and the liquid chemical potential by the adjustment of gas liquid curvature due to the crevice geometry and wettability conditions. Bauget and Lenormand (2002) have the best explanation of this phenomenon as seen in the Figure 3.9.



Figure 3.9 - Stabilization of a gas bubble in pore crevices (Bauget and Lenormand, 2002).

The existence of supersaturation threshold has been observed experimentally by El Yousfi et al. (1997), Scherpenisse et al. (1994), Bora et al. (2000), Kamath and Boyer (1995), and Firoozabadi and Kashchiev (1996) on variety of experiments. The supersaturation threshold shows that there is a maximum bubble size and no nucleation can occur below this supersaturation value. As Kamath and Boyer (1995) declared in their work, the degree of supersaturation increases as the capillary forces increase.

Kamath and Boyer (1995) measured up to 75 psi supersaturation values in their core experiments. Bora et al. (2000) reported up to 420 psi supersaturation pressure in their micro-model experiments for heavy oil. They could not observe any population of bubbles less than 2 micrometer in size. Scherpenisse et al. (1994) reported up to 98 psi supersaturation in their core experiments and the maximum gas saturation achieved for their core sample was 3%.

Tsimpanogiannis and Yortsos (2001) sketched the nucleation cavity as shown in Figure 3.9. If a conical geometry is assumed, the configuration of the gas bubble in the cavity can be simplified as in Figure 3.11.



Figure 3.10 - Schematic of nucleation cavity in a host pore (Tsimpanogiannis and

Yortsos, 2001).



Figure 3.11 - Gas bubble entrapped in a conical cavity (Meyer et al., 2009).

3.4 Surface Forces

Surface disjoining forces can be defined as the extra force exerted by the fluid film to be stable (Fenwick, 1997). It is created by the anisotropy of tangential and normal components of the pressure at the fluid interface (Derjaguin and Churaev, 1987). While the normal component is constant and balances the mechanical forces, the tangential component is not constant and leads to concept of surface disjoining forces (Scovazzo and Todd, 2001).

The simplest case to describe surface disjoining forces is for flat-plate geometry. There are three types of surface forces relevant in porous media: The van der Waals interaction, electrostatic interaction and solute/pore-wall adsorption interaction. The equations of these interactions for flat plate configuration are provided below (Scovazzo and Todd, 2001):

Surface disjoining forces due to the van der Waals interactions is given by:

$$\Pi_{\nu dw} = -\frac{A}{6\pi z_o^3},$$
(3.55)

where

 Π_{vdw} : flat-plate van der Waals interaction, Pa

A: Hamaker constant, J

 z_o : fluid thickness, m

Surface disjoining forces due to electrostatic interaction is given by:

$$\Pi_e = Dexp(-\kappa z_0), \tag{3.56}$$

where

 Π_e : flat-plate electrostatic interaction, Pa

$$D = (64n_{ion}kT)tanz_o^2 \left[\frac{z_s se\psi}{4kT} \right]$$
(3.57)

with

 n_{ion} : ion number density, ions/m³

k: Boltzman constant, J/K

z_o: fluid thickness , m

T: absolute temperature, K

z_s: solute charge number, valence

e: the electron charge, C

 ψ : electrostatic surface potential, V

 κ : Debye-Hückel reciprocal length, m⁻¹

And the surface disjoining forces due to solute/pore wall interaction is given by:

$$\Pi_s = 2C_{\infty}A_0/\nu(z_o - \delta)^3$$
(3.58)

In Eq. 3.58,

 Π_s : flat-plate solute/pore wall adsorption interaction, Pa

 C_{∞} : bulk solute concentration, mol/mol

 A_0 : solute-water interaction constant, J-m³

v: molecular volume, m³/mol

zo: fluid thickness, m

 δ : minimum solute approach distance, m

In this study only the van der Waals interactions were utilized in modeling efforts. The derivations of van der Waals forces are available for different fluid surface interface configurations. Below are some examples of these configurations and the equations associated with them:

For a slit-pore geometry for configuration in Figure 3.6a Eqn. 3.55 can be rewritten as,

$$\Pi = -\frac{A_{132}}{6\pi z_o^3} \tag{3.59}$$

and for a spherical particle near a surface (Figure 3.6b), the contributions from surface van der Waals forces are given by,

$$\Pi = \frac{F}{A_s}.$$
(3.60)

In Eq. 3.60,

$$\mathbf{F} = -\frac{A_{132}\mathbf{d}}{12z_0^2},\tag{3.61}$$

 A_s is the surface area, d represent the diameter of the spherical particle, and z_o is the distance to the surface, fluid thickness (Figure 3.12).



Figure 3.12 - Configurations of a particle near a surface (Ahmadi, 2002).

In Eqs. 3.59 and 3.61, A_{132} is the Hamaker constant between two phases (1 and 2) in a given medium (3). As an example, the phases can be gaseous (1) and solid (2) and the medium can be oil (3). The Hamaker constant can be calculated from the following relation using Lifshitz theory (Prieve and Russel, 1988):

$$A_{132} = \frac{3}{4} \mathrm{kT} \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3\mathrm{hv}_e}{8\sqrt{2}} \frac{(\mathrm{n}_{r_1}^2 - \mathrm{n}_{r_3}^2)(\mathrm{n}_{r_2}^2 - \mathrm{n}_{r_3}^2)}{\sqrt{(\mathrm{n}_{r_1}^2 + \mathrm{n}_{r_3}^2)} \sqrt{(\mathrm{n}_{r_2}^2 + \mathrm{n}_{r_3}^2)} \left\{ \sqrt{(\mathrm{n}_{r_1}^2 + \mathrm{n}_{r_3}^2)} + \sqrt{(\mathrm{n}_{r_2}^2 + \mathrm{n}_{r_3}^2)} \right\}},$$
(3.62)

where h is the Plank's constant, k is the Boltzman constant, T is temperature, v_e is the adsorption frequency, ϵ is the dielectric constant, and n_r is the refractive index.

In our evaluations, the parameters that were used to calculate the Hamaker constant are extracted from the literature and are given in Table 3.2.

Table 3.2 - The parameters used to calculate Hamaker constant. (Material Characteristics,

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Parameter	Fluid		Surface
	Gas	Oil	Dolomite
Refractive index, n _r	1.000443	1.47	1.68
Dielectric constant,	1.000944	2.15	9.10

In most studies, capillary forces are the main driver that controls the stable bubble size and the nucleation process. Recently, Meyer et al. (2009) proposed that the existence of a stable bubble is related to the capillary forces between the fluids as well as the Van der Waals forces between the surface and the fluid (Van der Waal forces are referred to as disjoining pressure in this study). They defined the pressure balance as the summation of the capillary and surface forces as in Eq. 3.63. More discussion on this equation is provided in Chapter 4.

$$P_g - P_l = \frac{2\sigma}{r} + \Pi_{total},\tag{3.63}$$

where

$$\Pi_{VdW}(r,TH) = \frac{1}{6\pi} \left(\frac{A_{wgs}}{8(r-TH)^3} - \frac{A_{swg}}{8(r-TH)^3} + \frac{A_{swg}}{8r^3} \right),$$
(3.64)

for the configuration depicted in Figure 3.13.



Figure 3.13 - Configuration used in Eq. 3.61 (Meyer et al. 2009).

According to Meyer et al. (2009), if we assume that the disjoining pressure compensates the capillary pressure, the initial radius of a gas bubble can be calculated from the following relation:

$$\frac{2\sigma}{R_0} = \Pi_{\text{total}}(r, \text{TH}). \tag{3.65}$$

In Eq. 3.62,

r: distance from cavity to the middle of the cavity (Figure 3.8)

TH: film thickness (if water wet)

R₀: initial radius of the stable bubble

As shown in Figure 3.14, for an example set of parameters, Meyer et al. (2009) showed that the equilibrium between the disjoining pressure (Van der Waals forces) and the capillary pressure might be found at 7 nanometers.



Figure 3.14 - Disjoining and capillary pressure vs. radius (Meyer et al., 2009).

CHAPTER 4

MODELING OF HYDROCARBON PHASE BEHAVIOR IN NANO-PORES

This chapter summarizes the modeling approach used while analyzing the impact of capillary pressure and surface forces on phase behavior in pore confinement with an emphasis on bubble point.

4.1 Model Approach

Cubic equations of state (EOS) formulations are widely used in the modeling of phase behavior of oil and gas reservoir fluids. The EOS parameters are tuned to replicate various types of PVT tests performed in laboratories and then the resulting EOS is used in reservoir modeling applications such as numerical simulation and estimation of reserves. Since the laboratory PVT measurements provide bulk fluid properties (without the capillary effects), the EOS that is tuned to laboratory PVT data neglects the porous media (confinement) effects.

Unlike the conventional oil and gas reservoirs, the pore sizes of unconventional reservoirs can be quite small. Pore-throat and pore-size distributions of a typical sample from Barnett mudstone are shown in Figures 4.1 and 4.2. As can be observed from Figure 4.1, the mode value of the pore-throat size can be estimated as 12.5 nm. Similarly, the mode of the pore size can be estimated as 50 nm, while noting that the data may be truncated at the lower end. In either case, the pore size is too small when compared to conventional reservoirs, and warrants investigation of the impact of capillary and surface forces on vapor-liquid-equilibrium.



Figure 4.1 - The distribution of pore-throat diameter in Barnett mudstone (Bruner and





Figure 4.2 - The pore-body diameter distribution in Barnett mudstone (Bruner and Smosna, 2011)

The classical approach to solve VLE using cubic EOS formulations uses a single system pressure. This ignores the phase pressure differences due to capillary and other forces present in the porous medium. When the capillary forces are considered, the phase pressures are not equal and the difference is given by the following Laplace's equation:

$$p_g - p_l = \frac{2\sigma}{r}.$$
(4.1)

In this equation, r is the radius of curvature, P_g is the gaseous phase pressure, and P_l is the liquid phase pressure, assuming that the liquid is the wetting phase. The interfacial tension denoted by σ in Eq. 4.1 can be described by the Macleod-Sugden formulation (Lee and Chien, 1984):

$$\sigma = \left[\sum_{i} \text{PCH}_{i} \left(\rho_{l}^{m} x_{i} - \rho_{g}^{m} y_{i}\right)\right]^{4}, \tag{4.2}$$

where, PCH_i is parachor, ρ_l^m is liquid molar density, ρ_g^m is gas molar density, x_i and y_i are mole fractions in liquid and gaseous phases, respectively, and i is the component index.

When the surface forces are included, the difference in phase pressures can be represented in the following form:

$$P_g - P_l = \frac{2\sigma}{r} + \Pi, \tag{4.3}$$

where Π is the contribution from the surface forces. Although Π may contain structural, electrostatic, and adsorptive forces, for simplicity, we will only include the van der Waals forces in our calculations. An example of computation of the van der Waals for a slit-pore

geometry (Fig. 3.11a) and a spherical particle near a surface (Fig. 3.11b) has been given in Section 3.4.

The Peng Robinson Equation of State (PR EOS) is commonly used in modeling PVT behavior. In our approach, we utilized the PR EOS and modified the VLE calculations to include the capillary and surface forces. Specifically, the VLE calculations were modified to account for the different pressures of the liquid and gaseous phases that can no longer be represented by a single system pressure. In the VLE calculations, a capillary-corrected K value is defined as follows:

$$K_{ci} = K_i \frac{P_l}{P_g}$$
(4.4)

where

$$K_i = \frac{\phi_i^l}{\phi_i^g} \tag{4.5}$$

and ϕ_i^l and ϕ_i^g are the fugacity coefficients of components in liquid and gaseous phases, respectively. In our approach, the component fugacities in the gaseous and liquid phases were computed by using the individual phase pressures. Eqn. 4.3 was used to represent the difference between the gaseous and the liquid phase pressures for a given radius of the first stable gas bubble. The bubble-point pressure was calculated through the adaptation of the capillary-corrected K-value definition. Stenby and Saphiro (2001) used a similar approach to investigate the liquid drop formation in gas condensate systems. At the bubble-point pressure, since the liquid phase composition can be assumed to be identical to the overall composition (z_i), the following equality was assumed to hold.

The procedure can be summarized by the flow diagram in Fig. 4.3.



Figure 4.3 – Flow diagram of the procedure used.

4.2 Impact of Confinement

The bubble-point suppression values with reference to the bulk-fluid (unconfined) behavior (EOS without capillary pressure, P_c) were calculated for different gas-bubble radii to determine the impact of capillary and surface forces as a function of radius. The impact of the bubble-point suppression on fluid expansion was investigated by examining

the oil formation volume factor. The change in gas-phase composition at different suppression levels was analyzed.

Calculations were performed by using EOS parameters obtained outside of this research for three different liquids-rich, unconventional reservoir fluids. In the rest of this work they will be referred as Sample1, Sample 2 and Sample 3. Sample 1 is a high-GOR oil at low reservoir temperature. Sample 2 is a low-GOR oil at high reservoir temperature. Sample 3 is also a high-GOR oil but at a very high reservoir temperature. Conventional PVT-cell measurements were used to calibrate the EOS parameters that represent the bulk-fluid conditions (i.e. $P_c=0$). These tuned EOS parameters were used in the remaining calculations.

4.2.1 Impact of Surface Forces

Surface forces were included in the calculations for three different configurations. In the first configuration, the gas bubble was assumed to be contacting the surface directly on both sides. The Hamaker constant was calculated using the solid-gas-solid configuration (A_{132} in Eq. 3.59 is A_{SGS}). The slit-pore geometry was used in these calculations (Figure 3.11a) where the separation distance, z_0 , was set to be equal to the bubble diameter, d. In the second configuration, the gas bubble was assumed to be separated from the solid surface by a thin ($4^{\circ}A$) layer of oil film. The Hamaker constant was calculated using solid-oil-gas properties (A_{132} in Eq. 3.61 is A_{SOG}). In the third configuration, gas was assumed to be stuck on the solid surface and surrounded by oil. In this final case, the Hamaker constant was calculated using solid-gas-oil configuration

 $(A_{132} \text{ in Eq. 3.9 is } A_{SGO})$. The separation distance, z_o , was set to be equal to the gasbubble diameter, d.

Our calculations indicated that, for the cases that were considered, the contribution of the surface forces was small compared to the capillary forces. For the first and third configurations, the calculated Hamaker constant was positive indicating the presence of attractive forces. For the second configuration, the calculated Hamaker constant was negative indicating the presence of repulsive forces.

By using the third configuration that is described above, Figures 4.4 and 4.5 show the relative contributions of the capillary and the van der Waals forces for oil Samples 2 and 3, respectively. The calculated contributions by using the first and the third configurations yield similar results. For both samples, the contribution of the surface van der Waals forces increases inversely with the radius of the bubble. It remains to be small, however, when compared to capillary forces. The relative contribution of the surface forces is higher for Sample 3 (Figure 4.5) due to the low interfacial tension that reduces the capillary forces. The trends that are shown in Figures 4.4 and 4.5 indicate that the surface forces may become dominant at much smaller radius. As shown by Meyer et al. (2009), for example, if the gas is trapped in a conical wedge in the pore, the surface force contribution can be much higher and may exceed the capillary pressure.



Figure 4.4 - Comparison of the contributions from capillary and surface forces for oil

sample 2.



Figure 4.5- Comparison of the contributions from capillary and surface forces for oil

sample 3.

Figure 4.6 shows the capillary and van der Waals force contributions for the second configuration, in which the Hamaker constant was negative (repulsive). In this case, the surface van der Waals forces are additive to the capillary forces, and amplify the bubble-point suppression. Even though the magnitude of the van der Waals forces is higher, their trend with respect to bubble radius is similar to the capillary forces. This suggests that the capillary forces will always dominate in this configuration.



Figure 4.6 - Comparison of the contributions from capillary and surface forces for oil sample 2.

It should be noted that only the surface van der Waals forces were included in the above calculations and the values of the Hamaker parameters required for the fluids and the pore surface were obtained from literature sources. The actual measurements for the fluids and the surfaces involved in field applications will improve the computation of Hamaker constant and yield more accurate results. The above results, however, should provide a good initial estimate for the effect of the surface forces on phase behavior in confinement.

4.2.2 Phase Diagram Shift and Suppression of Bubble Point

Based on the conclusions that were reached in the previous section, for the remainder of this work the impact of surface forces were ignored. For a 10-nm bubble size, Figures 4.7, 4.8 and 4.9 compare a portion of the phase diagrams of oil Samples 1, 2 and 3, respectively. The curves depict the two-phase region boundaries for the bulk ($P_c=0$) and the confined ($P_c>0$) fluid cases. Consistent with classical approaches, for the bulk fluid calculations, at the bubble point, the gaseous and the liquid phase pressures overlap. For the confined fluid calculations, the bubble point pressure equals the liquid phase pressure, while the gaseous phase pressure (not shown) will be higher by the value of the capillary pressure. As can be seen in these figures, the calculated bubble-point pressures are significantly suppressed when the capillary pressure is included in the calculations. Sample 3 has the smallest suppression for the same bubble size due to its lower interfacial tension.



Figure 4.7 - Portion of the phase diagram for oil Sample 1.



Figure 4.8 - Portion of the phase diagram for oil Sample 2.



Figure 4.9 - Portion of the phase diagram for oil Sample 3.

While the above calculations reflect a bubble size of 10 nm, the following calculations reflect the sensitivity of bubble-point suppression to the size of the gas bubble. Figure 4.10 shows the impact of different bubble size (hence, P_c) on the bubble-point pressure for oil Sample 3. When compared to the bulk fluid calculations, a gas bubble with a radius of 10 nm shows an average impact of 4 bars, which is larger than the corresponding capillary pressure value (1.30 bars). A gas bubble radius of 1 nm (P_c =28.7 bars) yields a bubble-point suppression of 81 bars. Similar results can be seen for oil Sample 1 in Figure 4.11. However, due to low bulk fluid bubble-point pressures and its high interfacial tension, the suppression could not be calculated for oil Sample 2 for the 1-nm radius bubble (the suppression was too high).


Figure 4.10 - Comparison of bubble-point suppression for different bubble radii for oil

Sample 3.



Figure 4.11 - Comparison of bubble-point suppression for different bubble radii for oil

Sample 1.

The excess suppression can be explained by examining the equilibrium chemical potential for different equilibrium conditions. Figure 4.12 (Udell 1982) shows the chemical potential vs. pressure for a pure component system. In this figure, the ABCDEF line represents the gas phase while the JLMNO line represents the liquid phase. At the same system pressure, the chemical potentials of liquid and gas phases are equal at the overlapping points D and L. At different pressures, the equilibrium point shifts to P_g for gas and P₁ for liquid. The difference between the points D and L and P_g is the excess suppression that is observed in the calculations. The difference between P_g and P₁ is the capillary pressure.



Figure 4.12 - Comparison of chemical potentials of liquid and gas phases in equilibrium (Modified from Udell, 1982).

4.2.3 Estimate of Oil Volume in Equilibrium with the First Bubble

Unless we assume that the initial gas bubble somehow occupies the entire pore space, it must reside within the pore with some oil. By combining the VLE calculations with material balance, the volume of oil that can be in equilibrium with the initial gas bubble can be calculated. This calculation requires the knowledge of the total mole fraction of the gaseous phase. In the following calculations, we assumed that the gaseous phase is infinitesimal at the bubble-point, and its mole fraction is 10⁻⁵ and used the procedure provided below.



Figure 4.13 – Procedure used to calculate the liquid gas bubble size.

Figure 4.14 shows the radius of the oil phase that is in equilibrium with the initial gas bubbles of different sizes. Even for a closed system, if the pore size is greater than or equal to the oil phase radius, one can assume that the initial gas bubble can be stable. Given the infinitesimal gas phase assumption described above, for pore sizes that are

smaller than the oil phase radius, it can be stated that the gas bubble may not form unless the oil can somehow expand into the neighboring pores. As can be seen in Figure 4.14, a 1-nm radius gas bubble will have to be in equilibrium with 37-nm radius liquid (denoted by an arrow). This indicates that, for the liquid and gas phases to be in equilibrium, a 1nm radius gas bubble can form in pores that are larger than 37 nm in radius. Similarly, a gas bubble with 10-nm radius can form in pores that are over 200-nm radius.



Figure 4.14 - Comparison of the calculated liquid radii that is in equilibrium with gas for various bubble sizes.

4.2.4 Impact on Gas Composition

Another implication of having different gaseous and liquid phase pressures at bubble point is that the equilibrium gaseous phase composition at bubble point must change with pressure suppression. The gaseous phase contains lighter components as the bubble-point suppression increases. Figure 4.15 shows the C1 and C7+ mole fractions of the gaseous phase for different levels of supersaturation.



Figure 4.15 - Comparison of the calculated liquid radii that is in equilibrium with gas for various bubble sizes.

Having different gas compositions (at bubble point) in different size pores will impact the growth of gas bubble and the flow due to diffusion. In general, diffusion is considered to be a slow process and is neglected in conventional reservoirs where fluid velocities are higher and dominated by Darcy flow. In unconventional reservoirs, however, the fluid velocity is significantly lower (due to nano-Darcy permeability), Darcy-flow contribution is small, and the contribution of diffusion becomes more significant. Because the objective of this paper is to discuss the phase behavior, we defer the discussion of diffusive flow in liquids-rich reservoirs to a subsequent paper. We should note, however, that, as explained above, the heterogeneity of the pore size distribution is one of the important reasons for concentration gradients causing diffusive flow in unconventional, liquids-rich reservoirs.

4.2.5 Impact on Formation Volume Factor

To assess another implication of the bubble-point suppression, we also calculated the oil formation volume factor as a function of liquid pressure. Figures 4.16 through 4.18 show the pressure versus oil formation volume factor for the bulk-fluid ($P_c=0$) and confined-fluid ($P_c > 0$) cases for the three oil samples. For oil Sample 3, the formation volume factor could not be calculated at low saturation pressures, and thus the dashedline portion of the curve in Figure 4.16 was estimated by extrapolation.

The undersaturated portion of the B_o curve was extended to the suppressed bubble point pressure. Extending the undersaturated portion of the B_o curve immpacts the reserve calculations as these calculations are based on the difference between the initial B_o and the B_o at the bubble point. The extension provides higher reserves.



Figure 4.16 - Formation volume factor vs. pressure with and without capillary pressure



impact for Sample 1.

Figure 4.17 - Formation volume factor vs. pressure with and without capillary pressure

impact for Sample 2.



Figure 4.18 - Formation volume factor vs. pressure with and without capillary pressure impact for Sample 3 (the dashed curve indicates extrapolation).

4.3 Conclusions

The results presented in this chapter show that the capillary discontinuities and surface forces in confinement of the nano-pores of liquids-rich reservoirs cause significant deviation from the conventional phase behavior. The bubble-point pressure is suppressed in nano-scale pores and the suppression amount is a function of the bubble radius and the interfacial tension. In general, higher capillary pressures (that is, the smaller bubble radius) result in higher bubble-point-pressure suppression.

The contribution of the surface forces on phase behavior depends on the configuration of the fluids within the confinement, pore geometry, and the mineralogical content of the pore surface. For the particular examples considered in this paper, the

contribution of the surface forces was small. However, the results also showed an increasing trend with decreasing pore radius and increasing pore surface-to-volume ratio that indicate the possibility of more significant surface forces. Other geometries and mineralogical properties of the solid surface may increase the contribution of the surface forces, yet they were not considered in this paper.

We also show that the VLE condition for the first gas bubble places significant restrictions on the pore sizes where the gas bubble can form in a closed system. If we assume that the pore size that is required for the VLE is the sum of the liquid and gas volumes; as the first stable bubble size is increased, then the pore size that is required to contain the equilibrium oil and gas increases. For a 1-nm-radius bubble to exist, the required pore size was calculated to be approximately 38 nm. For larger gas bubble radii, the required pore size quickly exceeds the common range of pore sizes that are observed in liquids-rich unconventional reservoirs.

The equilibrium gas composition at bubble point differs for different suppression values. The equilibrium gas is composed of lighter components as the bubble-point suppression increases. Having differing gas compositions (at the bubble point) in different size pores should impact the gas phase growth and may cause flow due to diffusion. Diffusive flow is a welcome addition to conventional Darcy flow in nano-pore systems.

Finally, for the samples that were studied, we quantified the impact of bubblepoint suppression on the formation volume factor. We showed that for a confined fluid $(P_c>0)$, the undersaturated portion of the formation volume factor versus pressure

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relationship extended into the lower pressure range, when compared with that for the bulk fluid ($P_c=0$). This observation alters the fluid expansion and positively impacts the performances of liquids-rich reservoirs.

CHAPTER 5

CORRELATION FOR EXCESS SUPPRESSION

This chapter presents correlations generated as part of this study to quantify the excess suppression so that the black-oil simulation formulation can handle the confinement impact on the fluid behavior.

5.1 Background

Black-oil simulators are widely used to model the flow in oil and gas reservoirs. They are preferred over the compositional simulators due to simplicity, availability of black-oil data through correlations and the faster run times that can be achieved. The reservoir simulators that are commonly used in the industry evaluate the fluid properties at a single system pressure. COZSim, which is a DOE/NETL-funded extended black-oil simulator, is capable of evaluating gas and liquid fluid properties at their corresponding pressures. However due to the black-oil formulation it is not possible to perform the VLE calculations within the simulator to calculate the total bubble-point suppression due to confinement.

As shown in the previous chapters, the magnitude of the bubble-point suppression is more than the capillary pressure; the additional suppression is called the excess suppression in this study (Figure 4.13). In order to properly include the total suppression, the source code of the simulator was modified by NITEC, which has the IP rights to COZSim.

5.2 Modeling Approach

One important step before the black-oil simulator can be used for modeling confinement impact on phase behavior is to quantify the suppression as a function of bulk PVT properties, which are available from either lab measurements or through correlations. For this purpose, flash calculations were performed to obtain oil compositions at different saturation pressures for bulk conditions. The resulting oil compositions were then used to calculate the suppressed bubble-point pressures as a function of bubble radii. In other words the procedure described to find the bubble-point suppression in Chapter 4 repeated for a series of compositions corresponding to different bulk saturation (bubble-point) pressures.

Different bulk and confined properties, such as solution gas oil ratio, formation volume factor, oil density, interfacial tension, and molecular weight, were also calculated during the process. All of these properties were tabulated and cross-plotted to find the best relationship to correlate the excess suppression as a function of bulk PVT properties and capillary pressure. These calculations were performed for the three unconventional fluid samples that were used previously to calculate the confinement impact. The use of three different samples provided a good range of fluid properties for a more comprehensive analysis. Tables 5.1 through 5.3 tabulate the compositions for different samples at different saturation pressures. As can be seen in these tables, a wide range of compositions was covered for each sample.

Psat (bar)	180	170	160	150	125	100	75	50	25	10
Comp1	0.0113049620	0.0111313950	0.0109344360	0.0107107540	0.0100076250	0.0090324832	0.0076739588	0.0057845088	0.0032077879	0.0013186453
Comp2	0.3704224000	0.3552736000	0.3395463000	0.3232123000	0.2795198000	0.2313904000	0.1784973000	0.1208872000	0.0596670100	0.0228024010
Comp3	0.1369665000	0.1374115000	0.1377704000	0.1380116000	0.1377994000	0.1354856000	0.1288776000	0.1132410000	0.0776876360	0.0376008260
Comp4	0.0936434420	0.0957649420	0.0979992620	0.1003511000	0.1067694000	0.1139489000	0.1216438000	0.1285489000	0.1267700000	0.0975155310
Comp5	0.3876626000	0.4004185000	0.4137496000	0.4277142000	0.4659037000	0.5101426000	0.5633073000	0.6315384000	0.7326676000	0.8407626000

Table 5.1 – Fluid compositions at different saturation pressures for Sample 1.

Table 5.2 – Fluid compositions at different saturation pressures for Sample 2.

Psat (bar)	240	230	220	210	200	190	180	170	160	150	140	130	120	110	100	90
Comp1	0.0094728144	0.0089648189	0.0084646195	0.0079709301	0.0074837948	0.0070035630	0.0065308791	0.0060662980	0.0056103617	0.0051635792	0.0047264746	0.0042994996	0.0038831299	0.0034778225	0.0030840919	0.0027024939
Comp2	0.4102309000	0.3978274000	0.3851902000	0.3722133000	0.3588399000	0.3450296000	0.3307569000	0.3159986000	0.3007348000	0.2849481000	0.2686264000	0.5217578000	0.2343375000	0.2163636000	0.1978450000	0.1787992000
Comp3	0.2523504000	0.2538840000	0.2549186000	0.2562986000	0.2576926000	0.2590648000	0.2603759000	0.2615793000	0.2626189000	0.2634244000	0.2639072000	0.2639539000	0.2634175000	0.2621059000	0.2597668000	0.2560633000
Comp4	0.1605640000	0.1657335000	0.1710398000	0.1765366000	0.1822586000	0.1882357000	0.1944945000	0.2010642000	0.2079774000	0.2152719000	0.2229915000	0.2311907000	0.2399357000	0.2493103000	0.2594197000	0.2703999000
Comp5	0.1386654000	0.1440506000	0.1494335000	0.1548938000	0.1604793000	0.1662277000	0.1721707000	0.1783409000	0.1847740000	0.1915108000	0.1985981000	0.2060940000	0.2140691000	0.2226141000	0.2318433000	0.2414907900
Comp6	0.0287462080	0.0298652330	0.0309832170	0.0321167820	0.0332759400	0.0344685500	0.0357012080	0.0369807410	0.0383145810	0.0397112030	0.0411803460	0.0427340830	0.0443871020	0.0461581910	0.0480710940	0.0501571860

Table 5.3 – Fluid compositions at different saturation pressures for Sample 3.

Psat (bar)	70	65	60	55	50	40	30	20
Comp1	0.0297783410	0.0262582660	0.0229764800	0.0199280050	0.0171062290	0.0121099570	0.0079197101	0.0044827908
Comp2	0.0014898655	0.0014637711	0.0014313362	0.0013913736	0.0013424705	0.0012108195	0.0010193121	0.0007478063
Comp3	0.1614601000	0.1521489000	0.1421970000	0.1316215000	0.1204512000	0.0965058280	0.0708986370	0.0446228530
Comp4	0.0855261980	0.0847559050	0.0837051350	0.0823074650	0.0804782730	0.0750595110	0.0661439970	0.0516301840
Comp5	0.0886638980	0.0892666390	0.0897736850	0.0901465860	0.0903279860	0.0897511990	0.0867718090	0.0782227590
Comp6	0.0177167410	0.0179459900	0.0181752760	0.0184010940	0.0186180880	0.0189875080	0.0191329270	0.0185834190
Comp7	0.0565760960	0.0574011950	0.0582419220	0.0590911770	0.0599374140	0.0615341780	0.0626685990	0.0621000490
Comp8	0.0198662690	0.0202163700	0.0205821660	0.0209648330	0.0213642620	0.0222100950	0.0230889770	0.0238224790
Comp9	0.0304079890	0.0309622180	0.0315443050	0.0321558710	0.0327983830	0.0341796540	0.0356727650	0.0370973680
Comp10	0.0413012650	0.0421293710	0.0430074860	0.0439413860	0.0449381660	0.0471595940	0.0497832780	0.0529765750
Comp11	0.4672133000	0.4774522000	0.4883683000	0.5000507000	0.5126375000	0.5412917000	0.5769000000	0.6257137000

Once the compositions were determined, the suppressed bubble-point pressures in confinement for different gas bubble radii were calculated for each composition. It was not possible to cover the whole range of radii for all the compositions. The suppression was larger than the bulk bubble-point pressure for the small radii thus could not be calculated. Tables 5.4 through 5.6 show the bulk and confined properties calculated for the fluid Samples 1, 2 and 3.

Bulk Properties					Confined Properties							
Psat,		Во,	oil surface density,	Rs,	Pliq (Psat),			ift,		Excess supression,		
bar	MW	Vres/Vsurf	gr-mol/cm3	cm3/cm3	bar	Pgas, bar	r, cm	dynes/cm	Pc, bar	bar		
180	98.1748	1.445505	0.869155	137.6468	174.9200	177.5338	2.00E-06	2.6100	2.6138	2.4662		
180	98.1748	1.445505	0.869155	137.6468	169.6442	174.9950	1.00E-06	2.6700	5.3508	5.0050		
180	98.1748	1.445505	0.869155	137.6468	158.4854	169.7167	5.00E-07	2.8090	11.2313	10.2833		
180	98.1748	1.445505	0.869155	137.6468	142.2941	162.2610	3.00E-07	2.9960	19.9669	17.7390		
180	98.1748	1.445505	0.869155	137.6468	120.0294	152.3814	2.00E-07	3.2358	32.3520	27.6186		
150	106.1888	1.381157	0.868137	113.1981	143.7107	147.4339	2.00E-06	3.7240	3.7232	2.5661		
150	106.1888	1.381157	0.868137	113.1981	137.1967	144.8124	1.00E-06	3.8080	7.6157	5.1876		
150	106.1888	1.381157	0.868137	113.1981	123.5380	139.4315	5.00E-07	3.9751	15.8935	10.5685		
150	106.1888	1.381157	0.868137	113.1981	104.0417	132.0091	3.00E-07	4.1958	27.9674	17.9909		
170	100.7291	1.423795	0.868838	129.3473	164.5409	167.4858	2.00E-06	2.9465	2.9449	2.5142		
170	100.7291	1.423795	0.868838	129.3473	158.8680	164.9033	1.00E-06	3.0179	6.0353	5.0967		
170	100.7291	1.423795	0.868838	129.3473	146.9059	159.5545	5.00E-07	3.1640	12.6486	10.4455		
170	100.7291	1.423795	0.868838	129.3473	129.6295	152.0526	3.00E-07	3.3644	22.4231	17.9474		
170	100.7291	1.423795	0.868838	129.3473	106.1184	142.2430	2.00E-07	3.6156	36.1246	27.7570		
160	103.3969	1.402350	0.868492	121.2015	154.1367	157.4521	2.00E-06	3.3170	3.3154	2.5479		
160	103.3969	1.402350	0.868492	121.2015	148.0522	154.8409	1.00E-06	3.3946	6.7887	5.1591		
160	103.3969	1.402350	0.868492	121.2015	135.2562	149.4568	5.00E-07	3.5520	14.2006	10.5432		
160	103.3969	1.402350	0.868492	121.2015	116.8770	141.9656	3.00E-07	3.7641	25.0886	18.0344		
160	103.3969	1.402350	0.868492	121.2015	113.4510	140.5992	2.80E-07	3.8018	27.1482	19.4008		
125	113.8023	1.328834	0.867149	93.69869	117.5465	122.4682	2.00E-06	4.9217	4.9217	2.5318		
125	113.8023	1.328834	0.867149	93.69869	109.8740	119.9054	1.00E-06	5.0159	10.0314	5.0946		
125	113.8023	1.328834	0.867149	93.69869	101.3885	117.1203	6.50E-07	5.1135	15.7318	7.8797		

Table 5.4 - Bulk and confined fluid properties of Sample 1.

Bulk P	roperties	;			Confined Properties							
Psat, bai	MW	Bo, Vres/Vsurf	oil surface density, gr-mol/cm3	Rs, cm3/cm3	Pliq (Psat), bar	Pgas, bar	r, cm	ift, dynes/cm	Pc, bar	Excess supression, bar		
7	0 124.60406	1.266311	0.734729	62.33742	62.6333	68.4687	2.00E-06	5.8355	5.8354	1.5313		
7	0 124.60406	1.266311	0.734729	62.33742	60.1706	67.9617	1.50E-06	5.8435	7.7911	2.0383		
7	0 124.60406	1.266311	0.734729	62.33742	55.2371	66.9527	1.00E-06	5.8581	11.7156	3.0473		
7	0 124.60406	1.266311	0.734729	62.33742	40.4154	63.9751	5.00E-07	5.8904	23.5597	6.0249		
7	0 124.60406	1.266311	0.734729	62.33742	20.7639	60.1409	3.00E-07	5.9066	39.3771	9.8591		
f	5 126.8538	1.254800	0.734509	58.56951	57.4140	63.5149	2.00E-06	6.1010	6.1009	1.4851		
e	126.8538	1.254800	0.734509	58.56951	54.8888	63.0321	1.50E-06	6.1076	8.1433	1.9679		
e	126.8538	1.254800	0.734509	58.56951	49.8338	62.0723	1.00E-06	6.1195	12.2385	2.9277		
e	126.8538	1.254800	0.734509	58.56951	34.6754	59.2466	5.00E-07	6.1431	24.5712	5.7534		
f	126.8538	1.254800	0.734509	58.56951	14.6408	55.6222	3.00E-07	6.1469	40.9814	9.3778		
f	129.2083	1.242914	0.734283	54.72312	52.2390	58.6157	2.00E-06	6.3767	6.3767	1.3843		
e	0 129.2083	1.242914	0.734283	54.72312	49.6491	58.1583	1.50E-06	6.3820	8.5092	1.8418		
e	129.2083	1.242914	0.734283	54.72312	44.4684	57.2500	1.00E-06	6.3909	12.7816	2.7500		
e	129.2083	1.242914	0.734283	54.72312	28.9614	54.5823	5.00E-07	6.4053	25.6209	5.4177		
e	129.2083	1.242914	0.734283	54.72312	8.5321	51.1745	3.00E-07	6.3960	42.6424	8.8255		
5	5 131.7204	1.230593	0.734042	50.78792	47.0271	53.6962	2.00E-06	6.6691	6.6691	1.3038		
5	5 131.7204	1.230593	0.734042	50.78792	44.3692	53.2661	1.50E-06	6.6727	8.8968	1.7339		
5	5 131.7204	1.230593	0.734042	50.78792	39.0566	52.4127	1.00E-06	6.6781	13.3562	2.5873		
5	5 131.7204	1.230593	0.734042	50.78792	23.1852	49.9126	5.00E-07		26.7275	5.0874		
Ę	5 131.7204	1.230593	0.734042	50.78792	2.3539	46.7337	3.00E-07		44.3798	8.2663		

Table 5.5 - Bulk and confined fluid properties of Sample 2.

Bulk Pro	operties		•	Confined Properties							
			oil surface		_		_			Excess	
		Во,	density,	Rs,	Pliq (Psat),			ift,		supression,	
Psat, bar	MW	Vres/Vsurf	gr-mol/cm3	cm3/cm3	bar	Pgas, bar	r, cm	dynes/cm	Pc, bar	bar	
240	76.2249	1.760271	0.808609	208.3033	237.9570	238.6279	2.00E-06	0.6710	0.6709	1.3721	
240	76.2249	1.760271	0.808609	208.3033	235.6644	237.0794	1.00E-06	0.7080	2 1416	2.9206	
240	76.2249	1.760271	0.808609	208.3033	230.3333	227.7377	3.00E-07	0.8973	5.9779	12,2623	
240	76.2249	1.760271	0.808609	208.3033	208.6046	219.0678	2.00E-07	1.0471	10.4632	20.9322	
240	76.2249	1.760271	0.808609	208.3033	155.7335	185.9863	1.00E-07	1.5132	30.2528	54.0137	
230	78.2181	1.725699	0.808638	196.6919	227.6581	228.5063	2.00E-06	0.8483	0.8482	1.4937	
230	78.2181	1.725699	0.808638	196.6919	224.9313	226.7119	1.00E-06	0.8908	1.7806	3.2881	
230	78.2181	1.725699	0.808638	196.6919	218.7515	222.6680	5.00E-07	0.9796	3.9165	7.3320	
230	78.2181	1.725699	0.808638	196.6919	209.0057	216.3707	3.00E-07	1.1053	7.3650	13.6293	
230	78.2181	1.725699	0.808638	196.6919	194.4603	207.1677	2.00E-07	1.2714	12.7074	22.8323	
230	78.2181	1.725699	0.808638	196.6919	138.7650	1/3.8/42	1.00E-07	1.7564	35.1092	56.1258	
220	80.1995	1.692891	0.808591	185.7009	217.0891	216.1442	2.00E-06	1.0332	2 2057	3 8668	
220	80.1995	1.692891	0.808591	185,7009	206.8756	211.6879	5.00F-07	1.2035	4.8123	8.3121	
220	80.1995	1.692891	0.808591	185.7009	195.9786	204.9316	3.00E-07	1.3434	8.9530	15.0684	
220	80.1995	1.692891	0.808591	185.7009	180.0713	195.3087	2.00E-07	1.5242	15.2374	24.6913	
220	80.1995	1.692891	0.808591	185.7009	121.9349	162.2022	1.00E-07	2.0150	40.2673	57.7978	
210	82.2344	1.661743	0.808526	175.2299	206.6929	207.9673	2.00E-06	1.2745	1.2744	2.0327	
210	82.2344	1.661743	0.808526	175.2299	203.1326	205.7889	1.00E-06	1.3287	2.6563	4.2111	
210	82.2344	1.661743	0.808526	175.2299	195.2736	201.0331	5.00E-07	1.4403	5.7595	8.9669	
210	82.2344	1.661743	0.808526	175.2299	183.3099	193.9340	3.00E-07	1.5940	10.6241	16.0660	
210	82.2344	1.661743	0.808526	175.2299	166.1873	184.0506	2.00E-07	1.7879	17.8633	25.9494	
210	84.3248	1.681743	0.808443	165.1521	196.3028	197.8190	2.00E-07	1.5163	45.5122	2.1810	
200	84.3248	1.631730	0.808443	165.1521	192.3477	195.4997	1.00E-06	1.5765	3.1520	4.5003	
200	84.3248	1.631730	0.808443	165.1521	183.6960	190.4929	5.00E-07	1.6997	6.7969	9.5071	
200	84.3248	1.631730	0.808443	165.1521	170.6924	183.1327	3.00E-07	1.8664	12.4403	16.8673	
200	84.3248	1.631730	0.808443	165.1521	152.3687	173.0702	2.00E-07	2.0714	20.7015	26.9298	
200	84.3248	1.631730	0.808443	165.1521	132.3002	162.4176	1.50E-07	2.2610	30.1174	37.5824	
190	86.4829	1.602573	0.808329	155.3949	185.9104	187.6936	2.00E-06	1.7833	1.7832	2.3064	
190	86.4829	1.602573	0.808329	155.3949	181.5605	185.2587	1.00E-06	1.8496	3.6982	4.7413	
190	86.4829	1.602573	0.808329	155.3949	172.1184	180.0520	5.00E-07	1.9838	7.9336	9.9480	
190	86.4829	1.602573	0.808329	155.3949	138.1183	162 3618	2.00E-07	2.1819	23 7445	27 6382	
190	86.4829	1.602573	0.808329	155.3949	117.6508	151.8246	1.50E-07	2.5646	34.1738	38.1754	
180	88.7186	1.574133	0.808194	145.9161	175.5123	177.5903	2.00E-06	2.0780	2.0780	2.4097	
180	88.7186	1.574133	0.808194	145.9161	170.7630	175.0625	1.00E-06	2.1503	4.2995	4.9375	
180	88.7186	1.574133	0.808194	145.9161	160.5274	169.7046	5.00E-07	2.2947	9.1772	10.2954	
180	88.7186	1.574133	0.808194	145.9161	145.0514	162.0514	3.00E-07	2.4826	17.0000	17.9486	
180	88.7186	1.574133	0.808194	145.9161	124.9149	151.9127	2.00E-07	2.7005	26.9978	28.0873	
180	88.7186	1.574133	0.808194	145.9161	103.1282	141.5775	1.50E-07	2.8846	38.4493	38.4225	
170	91.0423	1.546247	0.808031	136.674	165.1100	167.5108	2.00E-06	2.4030	2.4008	2.4892	
170	91.0423	1.546247	0.808031	136.674	148 9136	159 4489	1.00E-06	2.4808	4.9606	10 5511	
170	91.0423	1.546247	0.808031	136.674	132,8911	151.7445	3.00E-07	2.8293	18.8534	18,2555	
170	91.0423	1.546247	0.808031	136.674	111.2936	141.7326	2.00E-07	3.0467	30.4390	28.2674	
160	93.465	1.518816	0.807851	127.6379	154.6906	157.4492	2.00E-06	2.7610	2.7586	2.5508	
160	93.465	1.518816	0.807851	127.6379	149.1142	154.8003	1.00E-06	2.8435	5.6861	5.1997	
160	93.465	1.518816	0.807851	127.6379	137.2484	149.2914	5.00E-07	3.0037	12.0430	10.7086	
160	93.465	1.518816	0.807851	127.6379	120.2484	141.5952	3.00E-07	3.2030	21.3468	18.4048	
160	93.465	1.518816	0.807851	127.6379	111.3331	137.6708	2.50E-07	3.2936	26.3377	22.3292	
150	95.9995	1.491714	0.807648	118.7771	144.2568	147.4089	2.00E-06	3.1544	3.1521	2.5911	
150	95.9995	1.491714	0.807648	118.7771	138.2534	144.7341	1.00E-06	3.2407	6.4807	5.2659	
150	95.9995	1.491714	0.807648	118.///1	107 5745	139.2141	3.00E-07	3.4057	24.0276	10.7859	
140	98,6601	1.464851	0.807431	110.0658	133.8070	137.3909	2.00F-06	3.5839	3.5839	2.6091	
140	98.6601	1.464851	0.807431	110.0658	127.3642	134.7132	1.00E-06	7.3490	7.3490	5.2868	
140	98.6601	1.464851	0.807431	110.0658	113.8712	129.2300	5.00E-07		15.3588	10.7700	
130	105.796	1.413132	0.824402	97.09541	123.3389	127.3956	2.00E-06	4.0587	4.0567	2.6044	
130	105.796	1.413132	0.824402	97.09541	116.4421	124.7382	1.00E-06	4.1483	8.2961	5.2618	
130	105.796	1.413132	0.824402	97.09541	102.0935	119.3398	5.00E-07	4.3130	17.2463	10.6602	

Table 5.6 - Bulk and confined fluid properties of Sample 3.

5.3 Results

Different combinations of parameters were tested to quantify the excess suppression as a function of bulk PVT properties. This section summarizes this effort and discusses different relationships that were examined. The final correlation that was developed, and later used in the simulation model to calculate the excess suppression, is also given in this section.

5.3.1 Pressure versus Bulk Saturation Pressure

The first relationship that was investigated was the bubble radius versus the excess suppression value as a function of the saturation pressure. It was seen that a straight-line relationship on a logarithmic scale existed between the radius and the excess suppression for each bulk saturation pressure (in other words, composition). Figures 5.1 through 5.3 show this relationship for the three fluid samples for different bulk saturation pressures.





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Figure 5.2 - Excess suppression as a function of bubble radius for Sample 2.



Figure 5.3 - Excess suppression as a function of bubble radius for Sample 3.

Figures 5.1 through 5.3 show a logarithmic proportionality between the bubble radius and the excess suppression for a given bulk saturation pressure (same fluid

composition). However the trends are different as a function of bulk saturation pressure for the different samples. In Sample 1, the change in excess suppression as a function of composition is minimal. In Samples 2 and 3, the change is significant; however, the trends are in the reverse directions. In Sample 3, the amount of excess suppression decreases with increasing bulk saturation pressure while in Sample 2 it increases with increasing bulk saturation pressure.

One important point to consider while evaluating these trends is that the original fluid compositions and bulk saturation pressures are very different for the three samples. They all represent different compositional characteristics and temperatures. Having different fluid compositions and temperatures impact the capillary pressure levels due to the change in the interfacial tension. Therefore, total suppression is also different for the three samples.

5.3.2 Excess Suppression Pressure versus Molecular Weight

Molecular weight is a decent measure of the compositional variation. For the fluids that contain higher mole fractions of heavier hydrocarbons, the molecular weight is higher. During this study the molecular weight of each fluid composition corresponding to a bulk saturation pressure was calculated by taking weighted sum of the component molecular weights. When the excess suppression was plotted against the molecular weight, the relationship was different for each sample. Figures 5.4 through 5.6 show these cross plots for a confinement of 3 nm.



Figure 5.4 - Excess suppression as a function of average molecular weight for Sample 1.



Figure 5.5 - Excess suppression as a function of average molecular weight for Sample 2.



Figure 5.6 - Excess suppression as a function of average molecular weight for Sample 3.

If the data from the three samples are plotted together, the increase and the decrease of the excess suppression as a function of molecular weight can be seen. An example plot is provided for 3-nm confinement in Figure 5.7. It should be noted that the magnitude of the excess suppression changes as a function of the bubble radius. Figure 5.8 shows the excess suppression values for all the radii evaluated as a function of the molecular weight. As Figure 5.8 depicts, as the radius gets larger, the excess suppression decreases. The trend is the same for all radii.



Figure 5.7 - Excess suppression as a function of molecular weight for all samples

combined.



Figure 5.8 - Excess suppression as a function of molecular weight for all samples combined for all radii.

As shown in Figures 5.7 and 5.8, the excess suppression amount increases with the increasing molecular weight, peaks at around molecular weight of 90, stabilizes and starts to decrease for higher molecular weights. This is because the excess suppression is a function of the capillary pressure, which is a function of the interfacial tension and consequently the fluid composition. Since we have a wide variety of compositions that are being evaluated, the absolute value of the excess suppression and the trend of it change as a function of composition.

5.3.3 Normalization of Excess Suppression

After the examination of the excess suppression behavior with different parameters, it was found that some kind of normalization was necessary to properly compare the different samples at different compositions. Excess suppression ratio, which is the ratio of the excess suppression to the total suppression (P_c +Pexcess), was calculated for each bulk saturation pressure and gas bubble radius (confinement). Normalization was also necessary to account for the change in capillary pressure as a function of composition.

When normalized excess suppression (from now on identified as "excess suppression ratio") was correlated with molecular weight, a decreasing linear relationship was obtained for all the samples with slightly different slopes. Figures 5.9 through 5.11 show the relationships between the molecular weight and excess suppression ratio for Samples 1, 2, and 3 for 3-nm confinement.



Figure 5.9 - Excess suppression ratio as a function of molecular weight for Sample 1.



Figure 5.10 - Excess suppression ratio as a function of molecular weight for Sample 2.



Figure 5.11 - Excess suppression ratio as a function of molecular weight for Sample 3.

This relationship observed in Figures 5.9 through 5.11 implies that the excess suppression trend is consistent when the total suppression amount is taken into account. The contribution of excess suppression to the total suppression decreases as the molecular weight increases. This indicates higher capillary pressure contribution due to higher gasoil interfacial tension for heavier fluids.

As shown in the previous section, the magnitude of the excess suppression changes as a function of bubble radius. However, the same behavior is not observed anymore when the excess suppression ratio is considered. Figure 5.12 shows the excess suppression ratios for all the radii evaluated as a function of the molecular weight for all samples. The excess suppression ratio is very similar for all the radii evaluated. This is an expected result. By normalizing the excess suppression using the total suppression, the capillary pressure impact, which is a function of both the radius and the composition, is taken into account. It should be noted that despite the fact that the samples used in this study are very different in composition and are at different temperatures, the trends are very similar.



Figure 5.12 - Excess suppression ratio as a function of molecular weight for all samples and radii.

5.3.4 Black-oil Representation of Excess Suppression and Excess Suppression Ratio

Even though the molecular weight is a good measure of the excess suppression, it is not possible to use it as a parameter in the black-oil formulation. In black-oil formulation, the reservoir oil is represented by formation volume factor (B_o), solution gas oil ratio (R_s), the oil compressibility (c_o), surface density (ρ_o), and viscosity (μ_o). The correlation that can be input into the black-oil simulator has to be a function of these properties. Among these properties, B_o and R_s are the most viable as they are a strong function of the fluid composition. Yet, R_s is a better measure of the partitioning of oil and gas phases and composition. Both B_o and R_s were plotted against the excess suppression. The results showed that R_s correlates better with the excess suppression ratio.

Similar to molecular weight trends, when R_s was plotted against the excess suppression, the relationship is different for each sample. Figures 5.13 through 5.15 show these cross plots for a confinement of 3 nm.



Figure 5.13 - Excess suppression as a function of R_s for Sample 1.



Figure 5.14 - Excess suppression as a function of R_s for Sample 2.



Figure 5.15 - Excess suppression as a function of R_s for Sample 3.

If Figures 5.13 through 5.15 are compared to Figures 5.4 through 5.6, similar but reversed trends are observed. Reversal of the trends is expected as heavier fluids will have heavier components and consequently lower R_s . While higher molecular weight implies more of heavier components, higher R_s implies more of lighter components in the fluid composition.

If all the data from the three samples are depicted on the same plot, the increase and the decrease of the excess suppression as a function R_s can be seen. An example plot is provided for 3-nm confinement in Figure 5.16. It should be noted that the magnitude of the excess suppression changes as a function of the bubble radius. Figure 5.17 shows the excess suppression values for all the radii as a function of R_s . It is seen from Figure 5.17 that as the radius gets larger, the excess suppression decreases; however the trend is the same for all the radii.



Figure 5.16 - Excess suppression as a function of R_s for Sample 3.



Figure 5.17 - Excess suppression as a function of R_s for all Samples.

When excess suppression ratio is correlated with R_s , a decreasing linear relationship can be obtained for all the samples with different slopes. Figures 5.18 through 5.20 show the relationships between the R_s and excess suppression ratio for Samples 1, 2 and 3 for 3-nm confinement.



Figure 5.18 - Excess suppression ratio as a function of R_s for Sample 1.



Figure 5.19 - Excess suppression ratio as a function of R_s for Sample 2.



Figure 5.20 - Excess suppression ratio as a function of R_s for Sample 3.

As shown in Figure 5.17, the magnitude of the excess suppression changes as a function of the bubble radius. However, the same behavior is not observed when the excess suppression ratio is used. Figure 5.21 shows the excess suppression ratios as a function of the R_s for all the samples, which is very similar for all the radii evaluated. This result is similar to what was observed for the molecular weight and excess suppression ratio relationships for the reasons discussed in the previous section.



Figure 5.21 - Excess suppression ratio as a function of R_s for all samples and radii evaluated.

As Figure 5.22 depicts for 3-nm confinement, R_s and excess suppression ratio has a very good polynomial relationship. Even though the samples evaluated in this study have very different characteristics and sample temperatures, for the similar R_s values, two of the samples produced very similar results in terms of excess suppression ratio. This is encouraging as far as the reliability of the correlation is concerned.



Figure 5.22 - Excess suppression ratio as a function of R_s for all samples.

5.3.5 Final Correlation for Use in Black-Oil Simulation

A single correlation was generated to calculate the excess suppression ratio as a function of R_s . Same correlation was used for all the radii. Calculating excess suppression ratio independent of the radii makes it easier to integrate the correlation into any simulator, because bubble radius would not be a readily available parameter. As all the radii show very similar correlation between excess suppression ratio and the R_s (Figure 5.21), it was possible to generate a single correlation.

$$\frac{Excess \ Suppr.}{Total \ Suppr.} = -2.1x10^{-7}R_s + 0.0009R_s - 0.1022$$
(5.1)

where

Total Suppr. = Excess Suppr. + Capillary Pressure

R_s: solution gas oil ratio, scf/STB

Figure 5.23 shows the best fit used to generate the correlation. A very good correlation was obtained for the data range that was utilized in this study. The validity of the correlation for other samples should be checked in the future.



Figure 5.23 - Best fit for excess suppression ratio as a function of R_s for all samples.

Data from r = 3nm.

CHAPTER 6

IMPACT OF CONFINED FLUID BEHAVIOR ON FLOW

This chapter describes the integration of the confined phase behavior to a blackoil simulator. The modified black-oil formulation to handle PVT properties at different oil and gas pressures are discussed. The impact of confined phase behavior on flow is demonstrated using example simulation models.

As discussed in the previous chapters, the confinement manifests itself as suppression in the bubble-point pressure and as an extension of the undersaturated portion of the formation volume factor curve. The commonly used simulators evaluate the PVT properties of oil and gas at a common pressure disregarding the pressure difference due to capillary pressure. To evaluate the impact of confinement on flow, a simulator with the capability of evaluating oil and gas properties at their corresponding phase pressures had to be used. A reservoir simulator (COZSim), which was developed for DOE/NETL, has this capability. The excess suppression correlation introduced in Chapter 4 has been included in COZSim by third party developers to incorporate the confinement impact more accurately.

6.1 Simulation Model

COZSim is an extended black-oil simulator that was developed by NITEC through DOE/NETL funding. Even though the data required for the simulator is in black-oil format, all the information is converted to compositional form internally using K values. K values are pressure dependent but composition independent. They are
calculated from R_s tables. Table 6.1 shows the components and the phase descriptions used in the simulator.

Table 6.1 - Components and phase descriptions used in the simulator.

Components	Phases		
	Oleic	Gaseous	Aqueous
Water	-	-	w ₁
Oil	x ₂	-	-
HC Gas	X ₃	y ₃	W ₃
CO2	\mathbf{x}_4	y 4	W_4

The K value for oil and water are calculated using (Shank and Vestal, 1989).

$$K = \frac{1 + R_s^m}{R_s^m} \tag{6.1}$$

and for water the equation becomes

$$K = \frac{1 + R_{sw}^{m}}{R_{sw}^{m}} , \qquad (6.2)$$

where

$$R_s^m = R_s \frac{\rho_o^{sc}}{\rho_g^{sc}} \tag{6.3}$$

and

$$R_{sw}^m = R_s \frac{\rho_w^{sc}}{\rho_g^{sc}} \quad . \tag{6.4}$$

Here R_s^m and R_{sw}^m are the molar solution gas oil ratio and the molar solution water gas ratio respectively. ρ_w^{sc} , ρ_g^{sc} , ρ_o^{sc} are water, gas, and oil surface densities, respectively. At undersaturated conditions $y_3 = 1.0$, $y_4 = 0.0$, and $x_4 = 0.0$. From the K value

$$x_2 = 1 / \left[1 + R_s^m \right] \tag{6.5}$$

$$x_3 = \frac{R_s^m}{1 + R_s^m}$$
(6.6)

$$w_1 = 1 / \left[1 + R_{sw}^m \right] \tag{6.7}$$

$$w_{3} = \frac{R_{sw}^{m}}{1 + R_{sw}^{m}}$$
(6.8)

Commonly used reservoir simulators perform flash (VLE) and phase property calculations at a single pressure value, such as the pressure of the gas phase. In COZSim, the flash calculations are performed at the bulk pressure, which is the pressure corresponding to non-confined laboratory conditions. The phase properties are then calculated at the pressures of each phase. This requires iterative solution of the phase properties, capillary pressure, and R_s until they converge.

For the flow simulation, the bulk pressure is one of the solution variables obtained from the discretization of the continuum equations. The excess suppression correlation (Eq. 5.1) relates the bulk pressure to gas pressure as a function of gas-oil capillary pressure and the Rs at bulk pressure, and the capillary pressures are used to determine the phase pressures. This solution enables us to model the possible impact of confined phase behavior on flow by incorporating gas-oil capillary pressure to fluid property calculations.

Figure 6.1 shows the initialization of such a system. For hydrodynamic gravitycapillary equilibrium (initialization), phase pressures are determined using the respective phase gradients. The fluid phase equilibrium and the fluid properties at equilibrium are obtained iteratively.



Figure 6.1 - Initialization of the simulation model (Modified from Gilman and Ozgen,

2013).

6.2 Results

This section introduces simulation models that were designed to illustrate the impact of confinement on flow. The impact of confinement on gas phase formation in each grid block and the oil and gas production will be demonstrated.

6.2.1 Case Design

The cases were designed with wells located at the symmetrical locations at the edge of the grid. Even though three-dimensional models were generated and evaluated, two-dimensional models were preferred for reporting purposes to easily isolate the confinement impact. The simulator only has the capability of producing in field units therefore the grid block sizes were in the order of 100 ft. The wells were set to produce on bottomhole pressure limit to provide a constant pressure sink throughout most of the simulation.

As the formation of the first bubble impacts the confined fluid behavior, a single gas oil capillary pressure, which corresponds to the capillary entry pressure, was specified for each grid block. This implies that each grid block is composed of pores of similar radii and the first gas bubble is formed under the same gas-oil capillary pressure. The reservoir properties, including gas-oil capillary pressures for each block were uniform for the whole model for the preliminary cases. For the remaining cases, the properties were varied starting with the gas-oil capillary pressure values. The bulk bubble-point pressure of the fluid sample used in all the cases was 975 psi and the corresponding R_s was 327 scf/stb. The bulk R_s and viscosity as a function of pressure from the simulator are provided in Figures 6.2 and 6.3. The reservoir was set up to be undersaturated at initial conditions with irreducible water saturation. An example data

set is provided in Appendix A. All the data sets used in this study are provided digitally in Appendix B as supplemental text files.



Figure 6.2 - Viscosity in the model.



Figure 6.3 - R_s in the model.

6.2.2 Uniform Gas-Oil Capillary Pressure

The results discussed in this section are from the cases that have uniform gas-oil capillary pressure and reservoir properties. Three cases with 0 psi, 200 psi and 700 psi gas-oil capillary pressures are compared. Figure 6.4 shows the grid and the location of the wells. Figure 6.5 shows Well_5's production performance under different capillary pressure values. It should be noted that the PC=0.0 case represents the conditions of no confinement impact on PVT properties representing the results of the conventional approach and simulators.



Figure 6.4 - Well locations in the model.



Figure 6.5 - Production profile of Well_5.

As shown in Figure 6.5, the GOR of the well increases quickly for the case with zero capillary pressure (conventional case). As the gas-oil capillary pressure increases, the GOR decreases which results in higher oil production. It should be noted that, due to the symmetry and the uniform properties in the model, the performances of Well_3 and Well_5 are identical.

Figure 6.6 shows the cumulative production values for the model. Larger bubblepoint suppression due to higher gas-oil capillary pressure has a positive impact on the EUR due to the later gas breakthrough and maintaining the oil at undersaturated conditions for a larger pressure range.



Figure 6.6 - Cumulative production profile of the model (Well_3 and Well_5 combined).

6.2.3 Impact of Excess Suppression

The excess suppression, which is correlated to the solution gas ratio, R_s , was included in the bubble-point suppression calculations in the simulator. The magnitude and its additional impact are quantified in this section to determine the significance of incorporating excess suppression in the PVT calculations. If the excess suppression is not included in the calculations, the fluid property calculations are performed based on the gas-oil capillary pressure, and hence, the total suppression would equal to the gas-oil capillary pressure (i.e. excess suppression ratio of zero).

Figure 6.7 compares the results with and without including the excess suppression correlation in the PVT calculations. In this case, the gas-oil capillary pressure in all the simulation blocks is uniform and at 700 psi. As expected, due to the excess suppression of the bubble-point pressure, the GOR starts increasing later, providing extra oil recovery.



Figure 6.7 - Production Performance of the model with and without excess suppression.

6.2.4 Simple Distribution of the Gas-Oil Capillary Pressure

To show the impact of having a capillary pressure distribution within a model, a simplistic distribution of capillary pressures was manually generated. This distribution was based on columns of different gas-oil capillary pressure (Pcog) values that range between 0 psi and 700 psi. The distribution was not symmetrical and different around each well. Figure 6.8 shows the gas-oil capillary pressure distribution used in this model.



Figure 6.8 - Gas-oil capillary pressure distribution.

Figures 6.9 and 6.10 show the pressure and gas saturation distributions in the model one year after the simulation starts. Figures clearly show that for the grid blocks with similar pressure values, the gas saturation is different. The grid blocks with zero capillary pressure have the highest gas saturation values, while the gas saturation is still zero for the grid blocks with high gas-oil capillary pressure due to suppression.



Figure 6.9 - Pressure distribution at the end of one year.



Figure 6.10 - Gas saturation distribution at the end of one year.

Similarly Figures 6.11 and 6.12 show the pressure and gas saturation distribution of the model at the end of ten years. The pressure is depleted to very similar levels in all of the grid blocks. However, the grid blocks that were assigned a high gas-oil capillary pressure, in other words higher suppression, have low or 0% gas saturation, while the grid blocks with zero capillary pressure has gas saturations up to 50%.



Figure 6.11 - Pressure distribution at the end of one year.



Figure 6.12 - Gas saturation distribution at the end of one year.

The difference in gas saturation distribution has a big impact on the production profiles of the wells. Figure 6.13 compares the cumulative production from the model (sum of the production from the two wells) for conventional approach (Pcog=0) and the distributed gas-oil capillary pressure cases. The cumulative oil production is higher for the distributed gas-oil capillary pressure case due to the later gas breakthrough, and hence the lower GOR that was sustained. The gas-oil-ratio starts increasing rapidly when there is no suppression. With suppression, the gas-oil-ratio does not increase as fast and never goes as high. Since the gas is contained in the oil longer, in other words until the grid block reaches to a lower pressure, more oil can be produced. Figure 6.14 shows the rate

and pressure profiles for the total system in the model for the two cases discussed in this section.



Figure 6.13 - Comparison of the cumulative production and GOR profiles.



Figure 6.14 - Production, pressure and GOR profiles of the total system.

The gas-oil capillary pressure determines the level of bubble-point suppression and the way that this parameter is distributed has an impact on the well performance. For a uniform and symmetric system, the wells perform exactly the same as seen in Figure 6.15 for the conventional (Pcog=0) case. The well performance comparison for the distributed gas-oil capillary pressure case is provided in Figure 6.16. Despite the fact that all the properties are uniform, except for the gas-oil capillary pressure, the well performances are drastically different. The well performances are controlled by the suppression levels occurring around each well.



Figure 6.15 - Production, pressure and GOR profiles of the wells. PC=0.0 psi case.



Figure 6.16 - Production, pressure and GOR profiles of the wells. PC distributed case.

As shown in Figure 6.8, although both wells are completed in grid blocks with high suppression, the levels of suppression around each well are different. As the bubble-point is reached at different pressure levels, the gas saturation profiles around each well are also different (Figures 6.0 through 6.12). The difference in profiles manifests itself as difference in GOR behavior and oil production in the wells as shown in Figure 6.16. Well_5, which is located away from zero suppression grid blocks, has lower GOR in

general and higher oil production. Well_3, on the other hand, is located right next to a zero suppression grid block, which causes its GOR to increase rapidly once the pressure reaches the bulk bubble-point pressure. As Figure 6.17 shows, this translates into increased cumulative oil production for Well_5.

Predicting the GOR behavior of a well is very important from an operational perspective. Most of the pumps that are used in unconventional oil fields are not capable of lifting fluids with GOR values higher than 5000 scf/stb. So the GOR level in the well determines the lifespan of the well. When a well's GOR is low and steady like in Well_5, the life of the well is longer than a well like Well_3 in which the GOR increases rapidly. Figure 6.18 compares the cumulative production of the two wells in the model. With a GOR limit of 5000 scf/stb, Well_3 would be abandoned due to pump limits after 4 years of production while Well_5 would continue producing for 10 years. This would increase the cumulative production difference between the wells even further.



Figure 6.17 - Cumulative production and GOR profiles of the wells. PC distributed case.

The results presented in this section indicate that the manner in which the small and large pores (low and high capillary pressure pores) are distributed around a well will impact the well production profiles and the life of the wells.

6.2.5 Random Distribution of the Gas-Oil Capillary Pressure

This case was designed to create a more realistic view of the property distribution in a reservoir. The gas-oil capillary pressure was distributed randomly honoring a normal distribution with a mean value of 400 psi and a standard deviation of 100 psi. The rest of the properties were kept uniform to isolate the impact of the bubble-point suppression. To have a statistically meaningful distribution, a 10,000-grid-block model was generated. To investigate the impact of the distribution on the well behavior, nine wells were used in the model. The gas-oil capillary pressure distribution in the model is provided in Figure 6.18. Figure 6.19 shows the areal distribution of the gas-oil capillary pressure in the model and the well locations.



Figure 6.18 - Gas-oil capillary pressure frequency distribution.



Figure 6.19 - Areal distribution of the gas-oil capillary pressure.

The results obtained from this model are similar to the simple distribution case presented earlier. Due to the bubble-point suppression, the GOR values do not increase for the wells as quickly as the case with no suppression, and this behavior results in increase in oil production. Figures 6.20 and 6.21 compare the performances of the cases with randomly distributed gas-oil capillary pressure and the conventional (Pcog=0.0 psi). As the GOR increases rapidly, the oil rate declines in Pcog=0.0 case. The GOR never increases as much for the case where the gas-oil capillary pressure is distributed, and, consequently, the oil rate and the cumulative oil production is higher for this case.



Figure 6.20 - Production performance of the model.



Figure 6.21 - Cumulative production of the model.

6.2.6 Random Distribution of Permeability as a Function of the Gas-Oil Capillary Pressure

This case was designed to mimic a more realistic system with matrix blocs surrounded by fracture streaks. Fracture streaks were represented by high permeability (1000 md) with zero gas-oil capillary pressure. In the matrix cells, the gas-oil capillary pressure was distributed randomly honoring a normal distribution with a mean of 400 psi and a standard deviation of 100 psi. The gas-oil capillary pressure distribution can be seen in Figure 6.22. The planar view of the gas-oil capillary pressure distribution with the well locations is provided in Figure 6.23.



Figure 6.22 - Gas-oil capillary pressure frequency distribution.



Figure 6.23 - Gas-oil capillary pressure distribution.

The permeability is inversely proportional to the gas-oil capillary pressure; therefore, the grid blocks with higher capillary pressure representing smaller pore/pore throat size have smaller permeability values. The permeability distribution in the matrix is given in Figure 6.24 and the relationship between the gas-oil capillary pressure and the permeability is provided in Figure 6.25. Figure 6.26 shows the areal distribution of the permeability.



Figure 6.24 - Matrix permeability distribution.



Figure 6.25 - The relationship between the permeability and the gas-oil capillary

pressure.



Figure 6.26 - Matrix permeability distribution.

Figure 6.27 shows the performance of the randomly distributed gas-oil capillary pressure case and the zero gas-oil capillary pressure case. In zero gas-oil capillary pressure case, there is no suppression and the GOR increases rapidly. In the case with distributed gas-oil capillary pressure, the GOR stays constant for a long time. When the GOR increases above 2500 scf/stb, the gas production starts to suppress the oil production (Figure 6.28). Since the GOR never reaches those levels in non-zero gas-oil

capillary pressure case, the oil rate is not suppressed and therefore this case produces more oil.



Figure 6.27 - Cumulative production performance.



Figure 6.28 - Production performance.

In the distributed gas-oil capillary pressure case, despite the lower permeability values that high gas-oil capillary pressure grid blocks have, these grid blocks continue feeding oil to the fractures in small amounts, keeping GOR very low at all times. Even though the gas saturation can increase up to 40% in some of the grid blocks, the produced GOR never increases (Figure 6.29). In some grid blocks, the gas comes out of the solution sooner than the surrounding grid blocks due to different suppression levels in this model. Until the gas phase has a continuous path to the well location, it builds up in the grid block, yet cannot be produced. This behavior is similar to the behavior observed

by Kamath and Boyer (1995) in their core experiments. They measured higher critical gas saturation values for the depletion than the displacement and attributed the difference to the dominance of the capillary forces during depletion process.



Figure 6.29 - Gas saturation distribution for the distributed gas-oil capillary pressure case at the end of the simulation.

Figures 6.30 and 6.31 compare the gas saturation and the pressure distribution respectively for the two cases at a given time. Figures 6.30a and 6.31a are from the zero gas-oil capillary pressure case while Figures 6.30b and 6.31b are from the distributed gas-oil capillary pressure case. For the zero gas-oil capillary pressure case, the gas

saturation is a function of pressure and smoothly increases from the center towards the wells following the pressure trend. For the distributed gas-oil capillary pressure case, for similar oil pressure values, the gas saturation is scattered as the gas comes out of the solution at different pressure values. It should be noted that the gas saturation builds up only up to 13% for the zero gas-oil capillary pressure case as most of the gas is being produced by the wells. In the distributed gas-oil capillary pressure case, the gas saturation in certain grid blocks builds up to 41% as the gas is not being produced due to the discontinuity of the gas phase.

Figures 6.32a and 6.32b compare the solution gas oil ratio distribution of the models at the same simulation time for the zero and distributed gas-oil capillary pressure cases, respectively. The upper value of 327.4 represents the original solution gas oil ratio; therefore, the grid blocks at this value are still above the bubble-point pressure and thus undersaturated. These figures clearly depict that, in the zero gas-oil capillary pressure case, the R_s is a function of the pressure and the grid blocks that are in the center of the model are undersaturated. In the distributed gas-oil capillary pressure case, the undersaturated grid blocks are scattered throughout the model, regardless of the current pressure of the reservoir. Due to the bubble-point pressure suppression, the undersaturated region of the oil is extended and the gas comes out of the solution at different pressures



Figure 6.30 - Gas saturation distribution.



Figure 6.31 - Pressure distribution.



Figure 6.32 - Solution gas oil ratio distribution.

Figure 6.33 compares the distributions of the different pressures (oil, gas, and bulk) calculated by the simulator at the end of the simulation period



Figure 6.33 - Distribution of the different phase pressures.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes the conclusions of the study and recommendations for future work.

7.1 Conclusions

The following conclusions are warranted from the research presented in this dissertation:

- 1. Capillary discontinuities and surface forces in confinement of the nano-pores of liquids-rich reservoirs cause significant deviation from the conventional phase behavior. The bubble-point pressure is suppressed in nano-scale pores and the suppression amount is a function of the bubble radius and the interfacial tension. Higher capillary pressure values (that is, the smaller the bubble radius) result in higher bubble-point-pressure suppression. For the samples and the radii considered in this study the bubble point suppression ranges between 5 bars to 100 bars.
- 2. The contribution of the surface forces to phase behavior depends on the configuration of the fluids within the confinement, pore geometry, and the mineralogical content of the pore surface. For the particular examples considered in this research, the contribution of the surface forces was small. However, the results also showed an increasing trend with decreasing pore radius and increasing pore surface-to-volume ratio that indicate the possibility of more significant surface forces. The largest surface force value calculated
for the smallest bubble size was still an order of magnitude smaller than the capillary pressure. Other geometries and mineralogical properties of the solid surface may increase the contribution of the surface forces, yet they were not considered in this study.

- 3. The VLE condition for the first gas bubble to form places significant restrictions on the pore sizes where the gas bubble can form in a closed system. It was calculated for Sample 1 that for a 1-nm radius gas bubble to exist, the required pore size was approximately 38 nm. For larger gas bubble radii, the required pore size quickly exceeds the common range of pore sizes that are observed in liquids-rich unconventional reservoirs.
- 4. The equilibrium gas composition at the bubble-point pressure differs for different bubble-point suppression values. The equilibrium gas becomes lighter as the bubble-point suppression increases. Having differing gas compositions (at the bubble point) in different size pores should impact the gas phase growth and may cause flow due to diffusion. Diffusive flow is a welcome addition to conventional Darcy flow in nano-pore systems.
- 5. For the samples that were studied, it has been shown that for a confined fluid (Pc>0), the undersaturated portion of the formation volume factor versus pressure relationship extends into the lower pressure range, when compared with that for the bulk fluid (Pc=0). For the fluids considered in this study the change in B_0 at bubble point was up to 8 %. This phenomenon alters the fluid expansion and positively impacts the performances of liquids-rich reservoirs.

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- 6. A correlation that can be used in a black-oil simulator to quantify the excess suppression amount was generated as a function of the bulk R_s and the capillary pressure. The quality of the correlation was very good for the samples that the correlation was based on. The results showed that normalization of the excess suppression using the total suppression was necessary to handle the impact of capillary pressure difference for each radius due to different interfacial tension values for different compositions and temperatures.
- 7. The results obtained by using a black-oil simulator showed that the gas saturation profiles in the reservoir and the GOR behavior of the wells differ from that of the conventional approach (no confinement impact on phase behavior) when confinement is included in the phase property calculations. The difference manifests itself as lower GOR values and later gas breakthrough for the wells and different gas saturation values for similar pressures in the reservoir.
- 8. The results showed that the confined fluid behavior has a positive impact on oil production. The improvement in oil production occurs due to later breakthrough of the gas and the extension of the undersaturated property range of the oil; both as a result of the bubble-point suppression.
- 9. The results also showed that the impact on gas saturation is more drastic when a random gas-oil capillary pressure and permeability distribution is used in the simulation model with a fracture streak around the matrix grid blocks to provide a uniform linear pressure sink. This impact manifests itself as gas

saturation build up for some grid blocks with low gas-oil capillary pressure that are surrounded by zero gas saturation grid blocks (high suppression). The gas is trapped in these grid blocks and cannot be produced.

10. The distribution of the gas-oil capillary pressure has an impact on the well production profiles. Different GOR profiles were observed for the wells with different gas-oil capillary distribution (random distribution or manual simple distribution) even though the rest of the properties were uniform in the model.

7.2 Recommendations for Future Work

The following work is suggested for future research:

- Investigate the impact of including other types of surface forces besides van der Waals on bubble-point suppression.
- 2. The excess suppression correlation should be tested for other fluid samples and verified.
- 3. History match of a real field data of an unconventional reservoir should be performed using COZSim to verify and to improve the understanding of the conclusions derived from the conceptual models.
- 4. Sensitivity tests to investigate the impact of average gas-oil capillary pressure value in the normal distribution should be performed. This may provide insight to the magnitude of the gas-oil capillary pressure at which the confinement impact disappears.
- 5. Sensitivity tests with different oil samples should be performed to understand and quantify the impact of confinement for different R_s oils.
- 6. Impact of simulation gridding on the gas trapping should also be investigated.

 Laboratory methods to measure confined phase behavior properties should be investigated.

Nomenclature

A ₁₃₂ :	Hamaker constant for particles 1 and 2 through medium 3.
A _{SGO} :	Hamaker constant for solid and oil through medium gas.
A _{SGS} :	Hamaker constant for solid and solid through medium gas.
A _{SOG} :	Hamaker constant for solid and gas through medium oil.
à :	total surface area, cm ²
A ₀ :	solute-water interaction constant, J-m3
a:	attraction parameter for cubic EOS, $(m^3)^2/bar$
B:	equation parameter, $\sim 2/3$,
B _o :	formation volumes factor, Vres/Vsurf
b:	repulsion parameter for cubic EOS, m ³
C ^E :	equation constant
C∞:	bulk solute concentration, mol/mol
c:	volume correction factor for modified Peng Robinson EOS, m ³
c _o :	oil compressibility, 1/psi
d:	diameter of the sphere particle, m
E:	internal energy, joule
EUR :	Estimated ultimate recover, stb
e:	the electron charge, C
F _{pr} :	the value of the fraction of the confined fluid molecules subjected to the
	attractive field of the pore walls, for random distribution of the fluid molecules
	inside the pores.

f : fugacity, bar

- G: Gibbs free energy, joule
- GOR: Gas oil ratio, scf/stb
- h: Plank's constant $(6.626069 \times 10^{-34} \text{ J.s})$
- J: the rate of nucleation (number of bubbles per unit time and unit volume of liquid),
- k: Boltzman constant (1.380658x10⁻²³)
- kT: thermal energy, ,joule
- K: K-value
- K_c: capillary corrected K value
- m: mass of a molecule, gr
- n: number of moles
- n_r: refractive index
- n_{ion}: ion number density, ions/m3
- N_{mol}: number of molecules per unit volume, moles/m³
- Nav Avagadro number
- P: pressure, bar
- P_b: equilibrium pressure, bar
- P_{bulk}: bulk pressure, bar
- P_c: capillary pressure, bar
- PCH: parachor, dynes $^{1/4}$ cm $^{1/4}$ /moles
- P_{cr}: critical pressure, bar
- P_v^r : vapor pressure over a curved interface under external forces, bar
- P_v^{∞} : vapor pressure for a flat interface in the absence of surface forces, bar

- P_{vo}: vapor saturation pressure, bar
- P_{sat}: oil saturation pressure, bar
- P_{exc}; excess pressure, bar
- r: radius of curvature, m
- r_b : radius of the bubble, m
- r_e: equivalent pore radius, m
- r_p: pore radius, m
- R: universal gas constant (8.3144621 joule/mol°K)
- R₀: initial radius of the stable bubble, m
- R_s: solution gasoil ratio, scf/STB
- S: entropy, joule/°K
- S_{pi}: shift parameter
- T: temperature, °K
- T_{cr}: critical temperature, °K
- TH: film thickness (if water wet), m
- Tr: radius temperature, °K
- u: type selector for common equations of Cubic EOS
- w: type selector for common equations of Cubic EOS
- V: volume, m³
- V_{corr}: corrected volume, m³
- V_{res}: Volume at reservoir conditions, m³
- V_{surf} : Volume at surface conditions, m^3
- v: molar/molecular volume, m³/mol

- x: liquid mole fraction
- x_1^b : the mole fraction at the bulk conditions
- X: relative pressure, the ratio of the vapor pressure to the dew point pressure, bar.
- y: gas/vapor mole fraction
- z: overall composition of the fluid
- Z: z factor
- Zav: average z factor
- z_o: fluid thickness, m
- z_s: solute charge number, valence

Greek Symbols

- σ : interfacial tension, dynes/cm
- ρ_l^m : liquid molar density, gr/cc
- ρ_g^m : gas molar density, gr/cc
- ρa: density of the hot rod fluids, m
- pr : reduced density, gr/cc
- pmax : molecular density of the packed fluid modified by confinement, gr/cc
- ρ : density, gr/cc
- δp: width of the molecule-wall interaction, m
- δ : minimum solute approach distance, m
- δ_s ; range of surface forces
- δ_{con} : a constant distance for a specific fluid (in the order of 10-8 cm).
- σ_{dia} : sphere shaped molecule diameter, m
- Π : surface pressure, bar

Π_{vdW} :	surface pressure, van der Waals interactions, bar or Pa
П _e :	flat-plate electrostatic interaction, bar or Pa
П _s :	flat-plate solute/pore wall adsorption interaction, bar or Pa
Π _{total} :	total surface disjoining forces, bar
8:	dielectric constant
ϵ_p :	the energy parameter of the attractive interaction between two fluid molecules
φ:	fugacity coeffiecient
v _e :	adsorption frequency, s ⁻¹
μ:	chemical potential, joule
$\Delta V_i^\prime:$	residual partial volume, m ³
ω:	accentric factor
ΔH_{vl}^{E} :	Excess enthalpy due to surface forces, joule
θg	the geometric term which is a function of rp, δp and $\sigma dia/2$,
ψ:	electrostatic surface potential, V
к:	Debye-Hückel reciprocal length, m ⁻¹
μ _o :	oil viscosity, cp
θ:	angle, degrees or radian
$\theta R_{\alpha}^2 dR_{c}$	α : work term for phase α , dV α , m ³
θR ² βdR _β	work term for phase β , dV β , m ³
Subscri	pts
i:	component index

g: gas

oil o: liquid 1: solid s: vl: mixture v: vapor water w: phase indicator α: phase indicator β;

Superscripts

- l: liquid
- sc: standard/surface conditions

REFERENCES

- Abu Al-Rub, F. and Datta, R. (1998). Theoretical study of vapor pressure of pure liquids in porous media. Fluid Phase Equilibria 147 (1998) 65-83.
- Ahmadi, G. (2002), ME437 Class Notes, Clarkson University, Potsdam, New York. http://web2.clarkson.edu/projects/crcd/me437/notes/particle_adhesion/particle_adhesi on_page1.html
- Ahmed, T.H. (2007). Equations of State and PVT Analysis, Gulf Publishing Company,
- Bauget, F. and Lenormand, R. (2002). Mechanisms of Bubble Formations by Pressure
 Decline in Porous Media: a Critical Review. SPE 77457, paper presented at the SPE
 Annunal Technical Conference and Exhibition, San Antonio, TX, USA, September
 29-October 2, 2002.
- Bora, R., Maini, B.B., and Chakma, A. (2000).Flow Visualization Studies of Solution Gas Drive Process in Heavy Oil Reservoirs With a Glass Micromodel. SPE 64226, SPEREE 3 (3) June 2000, pp 224-229.
- Bruner,R.K. and Smosna, R. (2011). A Comperative Study of the Mississipian BarnettShale, Fort Wirth Basin, and Devonian Marcellus Shale, Appalachian Basin.DOE/NETL-2011-1478, April 2011.
- Chaudhary, A.S., Ehlig-Economides, C., and Wattenbarger, R. (2011). SPE147596. Paper presented at the SPE ATCE, Denver, Colorado, USA, 30 October-2 November 2011.
- Chen, X., Cao, G., Han, A., Punyamurtula, V.K., Liu, L., Culligan, P.J., Kim, T., and Qiao, Y. (2008). Nanoscale Fluid Transport: Size and Rate Effects, Nano Letter 8 (9): 2988-2992.

- Cipolla, C.L., Lolon, E.P., Erdle, J.C., and Rubin, B. (2010). Reservoir Modeling in Shale-Gas Reservoirs. SPE125530. SPE reservoir Evaluation and Engineering, Volume 13, Number 4, august 2010.
- Corti, D.S. and Debenedetti, P.G. (1998). Statistical mechanics of fluids under internal constraints: Rigorous results for the one-dimensional hard rod fluid. Physical Review E, Volume 57, Number 4, April 1998.

Coussy, O. (2011). Mechanics and Physics of Porous Solids. Wiley 2011.

- Derjaguin, B.V., Chuarev, N.V., and Muller, V.M. (1987). Surface Forces, first edition, Consultants Bureau, New York, 1987.
- El Yousfi, A., Zarcone, C., and Bories, S. (1997). Physical Mechanisms for Bubble Growth during Solution Gas Drive. SPE 38921, paper presented at the SPE Annual Technical Conference and Exhibition, San Antonio, TX, USA, October 2-8, 1997.
- Fan, L., Harris, B.W., Jamaluddin, A.J., Kamath, J., Mott, R., Pope, A.G, shandrygin, A., whitson, C.H., (2005). Understanding Gas-Condensate Reservoirs. Schlumberger Oil Field Review, 2005/2006, p 14.
- Fenwick, D. (1997). PhD Thesis, Petroleum Enginnering Department, Stanford University, Satnford, California, 1997.
- Firoozabadi, A. and Kashchiev, D. (1996). Pressure and Volume Evolution During Gas Phase Formation in Solution Gas Drive Process. SPE26286. SPE Journal, September 1996.
- Hsieh, C.H., Ramey Jr., H.J. (1983), Vapor Pressure Lowering in Geothermal Systems.Society of Petroleum Engineers Journal, February, 1983, pp157-167.

- Huber, P., Gruner, S., Schafer, C., Knorr, K., and Kityk, A. V. (2007). Rheology of Liquids in Nanopores: A Study on the Capillary Rise of Water, n-Hexadecane and n-Tetracosane in Mesoporous Silica. The European Physical Journal - Special Topics, Volume 141, Number 1 (2007), 101-105, DOI: 10.1140/epjst/e2007-00024-0
- Gilman, J.R. and Ozgen, C. (2013). Reservoir Simulation: History Matching and Forecasting. SPE Primer. Manuscript will be distributed in 2013.
- Jiskoot, M.A. (2002). Crude oil and Condensate Oil sampling, Water in Oil and Density Measuremet. Custody Transfer Measurement Symposium (2002), Saudi Aramco, Dharan, Saudi Arabia.
- Jones, S.F., Evans, G.M., and Galvin, K.P. (1999). Bubble nucleation from gas cavities a review. Advances in Colloids and Interface Science 80 (1999) 27-50
- Kamath, J. and Boyer, B.E. (1995). Critical gas Saturation and Supersaturation in Low Permeability Rocks. SPE Formation Evaluation, December 1995, pp247-253.
- Kanda, H., Miyahara, M., and Higashitani, K. (2004). Triple Point of Lennard-Jones
 Fluid in Slit Nanopore: Solidification of Critical Condensate, J. Chem Phys 120 (13):
 6173-6179.
- Khodier, S.H. (2002). Refractive index of standard oils as a function of wavelength and temperature. Optics & Laser Technology 34 (2002) 125-128.
- Kovscek, A.R. (1996). Thermodynamics of Fluid Phase Equilibria, Class Notes, Stanford University, Stanford, California, 1996.
- Lake, L.W. (1989). Enhanced Oil Recovery. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 07632, USA.

- Lee, S.T. and Chien, M.C.H. (1984). A New Multicomponent Surface Tension
 Correlation Based on Scaling Theory. SPE/DOE 12643, paper presented SPE/DOE
 Fourth Symposium on Enhanced Oil Recovery, Tulsa, OK, april 15-18, 1984.
- Lewis, G. N. (1901). The Law of Physico-Chemical Change. Proceedings of the American Academy of Arts and Sciences **37** (4): 49–69.
- Martin J.J. (1973). Cubic Equations of State. I and EC Fundamentals, Vol. 18. Page 81, May 1973.
- Material Characteristic Guide, published by omega.com, Stamford, CT. http://www.omega.com/Green/pdf/REF_LVD-800.pdf
- Meyer, W., Creux, P., Graciaa, A., Franco, F., and Luck, F. (2009). Non-classical Nucleation Model for Cold Production of Heavy Oil. JCPT April 2009, Volume 48, No. 4., pp 49-56.
- Moore, E.B., Ezequiel de la Llave, Welke, K., Scherlisb, D.A. and Molinero, V. (2010).Freezing, Melting and Structure of Ice in a Hydrophilic Nanopore, PhysicalChemistry, Chemical Physics 12 (16): 4124–4134.
- Ozgen, C. (2012). Investigating ROZ Exploitation with COZSim (Developed for DOE/NETL), presentation at the CO2 Conference Week, Midland, TX. December 3-7, 2012, http://www.co2conference.net/wp-content/uploads/2012/12/04-Ozgen-NITEC-COZsimCOZview-the-ROZ-12-7-12.pdf
- Prieve, D.C. and Russel, W.B. (1988). Simplified Predictions of Hamaker Constants from Lifshitz Theory. Journal of Colloid and Interface Science, Vol. 125, No 1, September 1988.

- Saphiro, A.A. and Stenby, E.H. (1997). Kelvin Equation for a Non-ideal Multicomponent Mixture. Fluid Phase Equilibria 134 (1997) 87-101.
- Saphiro, A.A. and Stenby, E.H. (2001). Thermodynamics of the multicomponent vaporliquid equilibrium under capillary pressure difference. Fluid Phase Equilibria 178 (2001) 17-32.
- Sapmanee, K. (2011). Effects of Pore proximity on Behavior and Production Prediction of Gas/Condensate. Master Thesis, Mewbourne School of Petroleum and Geological Engineering, University of Oklahoma, 2011.
- Scherpenisse, W., Wit, K., Zweers, A.E., Shoei, G., and van Wolfswinkel, A. (1994).
 Predicting Gas Saturation Build up During Depressurisation of a North Sea Oil
 Reservoir. SPE 28842, paper presented at the Europen Petroleum Conference,
 London, UK, October 25-27, 1994.
- Scovazzo, P. and Todd, P. (2001). Modeling Disjoining Pressures in Submicrometer Liquid-Filled Cylindrical Geometries. Journal of Colloid and Interface Science. 238 (2001) 230-237.
- Shank,G.D. and Vestal, C.R. (1989). Practical Techniques in Two-Pseudo Component Black-Oil Simulation. SPE reservoir engineering, May 1989
- Singh, S.K., Sinha, A., Deo, G. and Singh, J.K. 2009. Vapor-Liquid Phase Coexistence, Critical Properties, and Surface Tension of Confined Alkanes, J. Phys. Chem 113 (17):7170-7180.
- Travalloni, L., Castier, M., Tavares, F.W. and Sandler, S.I. (2010a). Critical behavior of pure confined fluids from an extension of the van der Waals equation of state. J. of Supercritical Fluids 55 (2010) 455-461.

- Travalloni, L., Castier, M., Tavares, F.W., and Sandler, S.I. (2010b). Thermodynamic modeling of confined fluids using an extension of the generalized Van der Waals theory. Chemical Engineering Science 65 (2010) 3088-3099.
- Tsimpanogiannis, I.N. and Yortsos, Y.C. (2001). An effective Continuum Model for the Liquid-To-Gas Phase Change in a Porous Medium Driven by Solute Diffusion: I.
 Constant Pressure Decline Rates. SPE 71502, paper presented at the SPE Annunal Technical Conference and Exhibition, New Orleans, LA, USA, September 30-October 3, 2001.
- Udell, K. (1982). The Thermodynamics of Evaporation and Condensation in PorousMedia. SPE 10779, paper presented at the 1982 California Regional Meeting of SPE,San Francisco, CA, USA, March 24-26, 1982.
- Wanderlick, T.K. and Davis, H.T. (1989). The statistical mechanics of inhomogeneous hard rod mixtures. Journal of Chem. Phys. 91 (11), 1 December 1989.
- Wang, J. and Liu, Y. (2011). SPE144427. Paper presented at the SPE North American Unconventional Gas Conference and Exhibition held in Woodlands, Texas, 14-16 June 2011.
- Whitson, C.H. and Søreide, I. (1989). Equilibrium Calculations for a Gas-Oil System in a Porous Media Including Capillary Forces. Personal communication with Curtis Whitson.
- Whitson, C.H. and Sunjerga, S. (2012). PVT in Liquid-Rich Shale Reservoirs. SPE 155499, paper presented at the 2012 SPE ATCE, San Antonio, TX, October 8-10, 2012.

- Wilson, G. (1968). A modified Redlich-Kwong EOS, Application to General Physical Data Calculations. Paper 15C, presented at the Annual AIChE National Meeting, Cleveland, May 4-7, 1968.
- Wilt, P.M. (1989). Nucleation Rates and Bubble Stability in Water Carbon Dioxide Solutions. J. Coll. Int. Sci., (1989), vol. 112, pp530-538.
- Yortsos, Y.C. and Parlar, M. (1989). Phase Change in Binary Systems in Porous Media: Application to Solution-Gas Drive. SPE 19697, paper presented at the SPE Annunal Technical Conference and Exhibition, San Antonio, TX, USA, October 8-11, 1989.
- Yortsos, Y.C. (1997). Pressure and Volume During Gas Phase Formation in Solution Gas Drive Processes. SPE 38340, SPEJ, Volume2, June 1997.
- Zarragoicoechea, G.J. and Kuz, V.A. (2004). Critical shift of a confined fluid in a nanopore. Fluid Phase Equilibria 220 (2004) 7-9.
- Zhang, X. and Wang, W. (2006). Square-well fluids in confined space with discretely attractive wall-fluid potentials: Critical point shift. Physical Review E 74, 062601 (2006).

APPENDICES

APPENDIX A

COZSIM DATA SETS

Appendix A-1

Case: Simple distribution of Pcog. Grid: 9x9x1						
!						
STP 60 1	4.65					
!						
UNITS EN	GLISH					
! Table Nam	e-Pock1					
! Table ID =	1					
KRTABLE-W	/OD 1					
!						
! SW	KRW	KROW				
! 0.130	0E000	9.88E-001				
0.186	1.085E-006	8.651E-001				
0.192	1.838E-006	8.519E-001				
0.198	2.96E-006	8.388E-001				
0.204	4.574E-006	8.257E-001				
0.211	9.886E-006	0.120E-001 7 999E-001				
0.223	1.396E-005	7.871E-001				
0.229	1.927E-005	7.744E-001				
0.235	2.61E-005	7.617E-001				
0.242	3.473E-005	7.492E-001				
0.248	4.551E-005	7.367E-001				
0.254	7 507E-005	7 12F-001				
0.266	9.473E-005	6.998E-001				
0.273	1.183E-004	6.876E-001				
0.279	1.464E-004	6.755E-001				
0.285	1.795E-004	6.635E-001				
0.291	2.184E-004	6.516E-001				
0.297	3.163E-004	6.28E-001				
0.310	3.77E-004	6.163E-001				
0.316	4.467E-004	6.047E-001				
0.322	5.262E-004	5.932E-001				
0.328	6.168E-004	5.818E-001				
0.335	1.193E-004	5.704E-001				
0.347	9.654E-004	5.48E-001				
0.353	1.111E-003	5.369E-001				
0.359	1.275E-003	5.258E-001				
0.366	1.456E-003	5.149E-001				
0.372	1.658E-003	5.041E-001				

0.378	1.882E-003 4.933E-001
0.384	2.13E-003 4.826E-001
0.390	2.402E-003 4.721E-001
0.397	2.702E-003 4.616E-001
0.403	3.031E-003 4.512E-001
0.409	3.392E-003 4.409E-001
0.415	3.786E-003 4.307E-001
0.421	4.216E-003 4.206E-001
0.428	4.683E-003 4.106E-001
0.434	5.192E-003 4.006E-001
0.440	5.744E-003 3.908E-001
0 446	6 342E-003 3 811E-001
0 452	6 988E-003 3 715E-001
0.459	7 687E-003 3 62E-001
0.400	8 44E-003 3 526E-001
0.403	0.44E-003 3.320E-001
0.471	1 012E 002 2 241E 001
0.477	1 106E 002 3.341E-001
0.403	1.106E-002 3.25E-001
0.490	1.206E-002 3.16E-001
0.496	1.314E-002 3.072E-001
0.502	1.429E-002 2.984E-001
0.508	1.552E-002 2.898E-001
0.514	1.684E-002 2.813E-001
0.521	1.824E-002 2.728E-001
0.527	1.974E-002 2.646E-001
0.533	2.133E-002 2.564E-001
0.539	2.302E-002 2.483E-001
0.545	2.482E-002 2.404E-001
0.552	2.672E-002 2.326E-001
0.558	2.875E-002 2.249E-001
0.564	3.089E-002 2.173E-001
0.570	3.316E-002 2.099E-001
0.576	3.557E-002 2.026E-001
0.583	3.81E-002 1.954E-001
0.589	4.079E-002 1.883E-001
0.595	4.362E-002 1.814E-001
0.601	4 66E-002 1 746E-001
0.607	4 975E-002 1 68E-001
0.614	5 307E-002 1 614E-001
0.620	5 656E-002 1 55E-001
0.020	6.023E-002 1.487E-001
0.020	6 409E-002 1 426E-001
0.002	6 814E 002 1 266E 001
0.030	7.24E.002 1.300E-001
0.045	7.24E-002 1.308E-001
0.051	7.007E-002 1.25E-001
0.057	8.156E-002 1.194E-001
0.663	8.647E-002 1.14E-001
0.669	9.161E-002 1.087E-001
0.676	9.7E-002 1.035E-001
0.682	1.026E-001 9.844E-002
0.688	1.085E-001 9.354E-002
0.694	1.147E-001 8.877E-002
0.700	1.211E-001 8.414E-002
0.707	1.279E-001 7.965E-002
0.713	1.349E-001 7.53E-002
0.719	1.422E-001 7.109E-002

	0.725	1.499E-001 6.701E-002
	0.731	1.578E-001 6.307E-002
	0.738	1.661E-001 5.926E-002
	0.744	1.748E-001 5.559E-002
	0.750	1.838E-001 5.206E-002
	1.000	1E000 0E000
KRT	ABLE-W	OI 1
	SW	KRW KROW
! _		
	0.130	0E000 9.88E-001
	0.186	1.085E-006 8.176E-001
	0.192	1.838E-006 7.995E-001
	0.198	2.96E-006 7.815E-001
	0.204	4.574E-006 7.638E-001
	0.211	6.825E-006 7.462E-001
	0.217	9.886E-006 7.287E-001
	0.223	1.396E-005 7.114E-001
	0.229	1.927E-005 6.943E-001
	0.235	2.61E-005 6.773E-001
	0.242	3.473E-005 6.605E-001
	0.248	4.551E-005 6.438E-001
	0.254	5.882E-005 6.273E-001
	0.260	7.507E-005 6.109E-001
	0.200	9.473E-005 5.947E-001
	0.273	1.1032-004 5.7072-001
	0.279	1.404E-004 5.028E-001
	0.200	$2.184E_{-004} 5.315E_{-001}$
	0.291	2.164E-004 $5.315E-0012.637E-004$ $5.161E-001$
	0.297	3 163E-004 5 009E-001
	0.304	3 77E-004 4 859E-001
	0.316	4 467E-004 4 71E-001
	0.322	5 262E-004 4 564E-001
	0.328	6 168E-004 4 419E-001
	0.335	7 193E-004 4 276E-001
	0.341	8 351E-004 4 135E-001
	0.347	9.654E-004 3.995E-001
	0.353	1.111E-003 3.858E-001
	0.359	1.275E-003 3.723E-001
	0.366	1.456E-003 3.589E-001
	0.372	1.658E-003 3.458E-001
	0.378	1.882E-003 3.329E-001
	0.384	2.13E-003 3.202E-001
	0.390	2.402E-003 3.077E-001
	0.397	2.702E-003 2.955E-001
	0.403	3.031E-003 2.834E-001
	0.409	3.392E-003 2.716E-001
	0.415	3.786E-003 2.601E-001
	0.421	4.216E-003 2.487E-001
	0.428	4.683E-003 2.376E-001
	0.434	5.192E-003 2.267E-001
	0.440	5.744E-003 2.161E-001
	0.446	6.342E-003 2.057E-001
	0.452	6.988E-003 1.956E-001

	0.545 2.482E-002 7.523E-002 0.552 2.672E-002 6.936E-002 0.558 2.875E-002 6.376E-002 0.558 2.875E-002 6.376E-002	
	0.570 3.316E-002 5.335E-002 0.576 3.557E-002 4.855E-002 0.583 3.81E-002 4.401E-002	
	J.589 4.079E-002 3.972E-002 J.595 4.362E-002 3.57E-002 J.601 4.66E-002 3.193E-002 J.607 4.975E-002 2.84E-002	
	D.6145.307E-0022.513E-002D.6205.656E-0022.209E-002D.6266.023E-0021.929E-002D.6326.409E-0021.671E-002	
	D.638 6.814E-002 1.436E-002 D.645 7.24E-002 1.223E-002 D.651 7.687E-002 1.03E-002 D.657 8.156E-002 8.578E-003	
	0.663 8.647E-002 7.048E-003 0.669 9.161E-002 5.702E-003 0.676 9.7E-002 4.532E-003	
	D.682 1.026E-001 3.527E-003 D.688 1.085E-001 2.677E-003 D.694 1.147E-001 1.972E-003 D.700 1.211E-001 1.399E-003	
	0.707 1.279E-001 9.471E-004 0.713 1.349E-001 6.026E-004 0.719 1.422E-001 3.523E-004 0.725 1.499E-001 1.822E-004	
	0.7231.433E-0011.022E-0040.7311.578E-0017.765E-0050.7381.661E-0012.324E-0050.7441.748E-0012.934E-006	
! KRTA	0.750 1.838E-001 0E000 1.000 1E000	
! !	SL KRO KRG	
•	0.430 0E000 6.23E-001	

0.47	5 2.9	63E	-006	5.	.27E	E-001
0.480) 5.3	34E-	006	5.1	55E	E-001
0.486	5 9.0	43E∙	-006	5.0	041	E-001
0.492	2 1.4	56E	-005	4.9	928	E-001
0.49	7 2.2	25E-	005	4.8	16E	E-001
0.503	3 3.3	58E-	-005	4.	705	E-001
0.508	3 4.8	64E-	-005	4.	595	E-001
0.514	4 6.8	67E-	-005	4.4	486	E-001
0.520	94	82F	-005	4	378	E-001
0.52	5 1 2	81E.	.004	1	271	E-001
0.52	1 1 7		004	1.4	165	
0.00	1 1.7 2 0 0	20E	004	4.	100	
0.000		29E.	-004	4.	009	
0.54	2 2.8	94E	-004	3.	955	E-001
0.548	3 3.6	93E	-004	3.8	852	E-001
0.553	3 4.6	6E-	004	3.	75E	-001
0.559	9 5.8	32E-	004	3.6	649E	E-001
0.564	4 7.2	01E	-004	3.	549	E-001
0.570) 8.8	31E-	-004	3.	45E	E-001
0.576	5 1.0	74E-	-003	3.3	352	E-001
0.58	1 1.2	98E-	-003	3.3	255	E-001
0.58	7 1 5	56E.	.003	3	150	E-001
0.50	1.0 7 1 0		000	21	100	
0.594	2 1.0 2 2 4		003	ა. ი	075	
0.590		97 E.	-003	2.	.970	
0.604	4 2.5	89E	-003	2.8	878	E-001
0.609	9 3.0	34E	-003	2.	786	E-001
0.61	5 3.5	39E	-003	2.0	696	E-001
0.620) 4.1	09E	-003	2.0	607	E-001
0.626	6 4.7	75E-	003	2.5	19E	E-001
0.632	2 5.4	68E-	-003	2.4	433	E-001
0.63	7 6.2	71E-	-003	2.3	347	E-001
0.64	371	65E	-003	2	263	E-001
0.040	2 8 1	50E	-003	2.4	181	E-001
0.040	1 0.1		0000	2.		
0.004	+ 9.2		003	2.0	040	
0.000	J 1.0	48E	-002	2.0	019	E-001
0.66	5 1.1	82E	-002	1.	941	E-001
0.67	1 1.3	29E	-002	1.8	863	E-001
0.676	5 1.4	91E	-002	1.	787	E-001
0.682	2 1.6	69E	-002	1.	713	E-001
0.688	3 1.8	63E·	-002	1.	.64E	E-001
0.693	3 2.0	74E-	-002	1.	568	E-001
0.699	9 2.3	04E-	-002	1.4	498	E-001
0 704	1 2 5	54F	-002	1	43F	-001
0.70	<u>2.0</u> 2 2 ג	26E.	.002	1	262	E-001
0.710	2.0	20L	002	1.2	075	
0.710	1 0 1		002	1.2	.976	
0.72	1 3.4	38E.	-002	1.4	234	E-001
0.72	(3./	82E	-002	1.	1/1	E-001
0.732	2 4.1	52E	-002	1.	111	E-001
0.738	3 4.5	51E-	-002	1.0	052	E-001
0.744	4.9	98E-	002	9.9	43E	E-002
0.749	9 5.4	41E-	-002	9.3	386	E-002
0.75	5 5.9	36E-	-002	8.8	845	E-002
0.76) 64	65F	-002	8	322	E-002
0 76	570	32F.	-002	7 9	815	F-002
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0.788 9.71E-002 5.958E-002
     0.794 1.049E-001 5.536E-002
     0.800 1.132E-001 5.131E-002
     0.805 1.221E-001 4.744E-002
     0.811 1.315E-001 4.374E-002
     0.816 1.414E-001 4.02E-002
     0.822 1.52E-001 3.684E-002
     0.828 1.632E-001 3.364E-002
     0.833 1.75E-001 3.061E-002
     0.839 1.875E-001 2.775E-002
     0.844 2.007E-001 2.505E-002
     0.850 2.146E-001 2.251E-002
     0.856 2.293E-001 2.013E-002
     0.861 2.448E-001 1.791E-002
      0.867 2.611E-001 1.584E-002
     0.872 2.783E-001 1.393E-002
     0.878 2.963E-001 1.216E-002
     0.884 3.153E-001 1.054E-002
     0.889 3.353E-001 9.056E-003
     0.895 3.562E-001 7.71E-003
     0.900 3.782E-001 6.496E-003
     0.906 4.012E-001 5.409E-003
     0.912 4.254E-001 4.444E-003
     0.917 4.507E-001 3.596E-003
      0.923 4.772E-001 2.858E-003
     0.928 5.05E-001 2.224E-003
     0.934 5.34E-001 1.688E-003
     0.940 5.643E-001 1.244E-003
     0.945 5.96E-001 8.824E-004
     0.951 6.291E-001 5.972E-004
     0.956 6.637E-001 3.8E-004
     0.962 6.997E-001 2.221E-004
     0.968 7.374E-001 1.149E-004
     0.973 7.766E-001 4.896E-005
     0.979 8.174E-001 1.465E-005
     0.984 8.6E-001 1.85E-006
     0.990 9.043E-001
                         0E000
     1.000 9.88E-001
                         0E000
KRTABLE-GOI
              1
       SL
              KRO
                        KRG
     0.430
              0E000 6.23E-001
     0.469 1.52E-006 5.005E-001
     0.475 2.963E-006 4.84E-001
     0.480 5.34E-006 4.676E-001
      0.486 9.043E-006 4.515E-001
     0.492 1.456E-005 4.355E-001
      0.497 2.25E-005 4.198E-001
     0.503 3.358E-005 4.043E-001
     0.508 4.864E-005 3.89E-001
      0.514 6.867E-005 3.739E-001
     0.520 9.482E-005 3.591E-001
     0.525 1.284E-004 3.444E-001
     0.531 1.709E-004 3.3E-001
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0.536	2.239E-004	3.159E-001
0.542	2.894E-004	3.019E-001
0.548	3.693E-004	2.883E-001
0.553	4.66E-004	2.748E-001
0.559	5.82E-004	2.616E-001
0.564	7.201E-004	2.487E-001
0.570	8.831E-004	2.361E-001
0.576	1.074E-003	2.237E-001
0.581	1.298E-003	2.116E-001
0.587	1.556E-003	1.998E-001
0.592	1.855E-003	1.883E-001
0.598	2.197E-003	1.772E-001
0.604	2 589E-003	1 663E-001
0.609	3 034E-003	1 557E-001
0.615	3 539E-003	1 455E-001
0.670	4 109E-003	1.400E 001
0.020	4 75E-003	1.000E 001
0.020	5 169E 003	1.200-001
0.032	5.400E-003	1.100E-001
0.037	0.27 IE-003	1.079E-001
0.043	7.105E-003	9.943E-002
0.648	8.159E-003	9.128E-002
0.654	9.26E-003	8.349E-002
0.660	1.048E-002	7.607E-002
0.665	1.182E-002	6.901E-002
0.671	1.329E-002	6.233E-002
0.676	1.491E-002	5.601E-002
0.682	1.669E-002	5.007E-002
0.688	1.863E-002	4.45E-002
0.693	2.074E-002	3.93E-002
0.699	2.304E-002	3.447E-002
0.704	2.554E-002	3E-002
0.710	2.826E-002	2.588E-002
0.716	3.12E-002	2.212E-002
0.721	3.438E-002	1.871E-002
0.727	3.782E-002	1.564E-002
0.732	4.152E-002	1.289E-002
0.738	4.551E-002	1.046E-002
0.744	4.98E-002	8.331E-003
0.749	5.441E-002	6.496E-003
0.755	5.936E-002	4.937E-003
0.760	6.465E-002	3.637E-003
0.766	7.032E-002	2.578E-003
0 772	7 638E-002	1 74F-003
0 777	8 285E-002	1 101E-003
0.783	8 975E-002	6 375E-004
0.788	971E-002	3 241E-004
0.700	1 049F-001	1 337E-004
0.7.54	1.043E 001	3 728E-005
0.000	1.1321-001	2 72E 006
0.000	1 3155 001	J.12E-000
0.011	1 414E 004	
0.010	1.414E-001	
0.022	1.525-001	
0.828	1.032E-001	
0.833	1.75E-001	
0.839	1.875E-001	
0.844	2.007E-001	

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0.850 2.146E-001
      0.856 2.293E-001
      0.861 2.448E-001
      0.867 2.611E-001
      0.872 2.783E-001
      0.878 2.963E-001
      0.884 3.153E-001
      0.889 3.353E-001
      0.895 3.562E-001
      0.900 3.782E-001
      0.906 4.012E-001
      0.912 4.254E-001
      0.917 4.507E-001
      0.923 4.772E-001
      0.928 5.05E-001
      0.934 5.34E-001
      0.940 5.643E-001
      0.945 5.96E-001
      0.951 6.291E-001
      0.956 6.637E-001
      0.962 6.997E-001
      0.968 7.374E-001
      0.973 7.766E-001
      0.979 8.174E-001
      0.984 8.6E-001
      0.990 9.043E-001
      1.000 9.88E-001
!
PCTABLE-WO
               1
!
!
      SW
                        Pcowi
              Pcow
!
    0.130
              1E000
                       1
     1.000
              1E000
                       -1
I
PCTABLE-GO
               1
I
!
      SL
             Pcgo
                      Pcgoi
!
           1E000
                     1
    0.430
    0.811
            1E000
                      1
     1.000
            1E000
                      1
ļ
FLUIDS 1
! water oil
              hcGas co2(not needed)
 1E000 8.708E-001 1.4E000
                                          !31 API
1
                                   ! Temperature
PVT-HCGAS
             1
                     105.0
ļ
             BG
                    VISG
ļ
   Pres
           (bbl/MSCF) (cp)
!
   (psia)
ļ
      ____
          -----
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                  ____
     14.70 191.55294 0.00868
    54.55
            50.63812 0.00876
    94.41
            28.68333 0.00887
    134.26
            19.75276 0.00899
```

174.11	14.90233	0.00912
213.97	11.85159	0.00927
253.82	9.75227	0.00944
293.67	8.21648	0.00963
333.52	7.04169	0.00985
373.38	6.11174	0.01008
413.23	5.35522	0.01035
453.08	4.72577	0.01066
492.94	4.19193	0.01100
532.79	3.73162	0.01141
572.64	3.32885	0.01188
612.50	2.97184	0.01244
652.35	2.65189	0.01312
692.20	2.36279	0.01396
732.05	2 10077	0.01501
771 91	1 86472	0.01633
811 76	1.65625	0.01800
851 61	1 47842	0.02003
801.01	1 33202	0.02000
031.47	1 21820	0.02200
071 17	1 13036	0.02495
1011 02	1.15050	0.02737
1011.03	1.00371	0.03009
1000.00	0.07269	0.03243
1120 59	0.97308	0.03400
1170.00	0.94255	0.03030
1210.44	0.91724	0.03033
1210.23	0.09023	0.04000
1200.14	0.87344	0.04152
1220.00	0.84072	0.04233
1260 70	0.04972	0.04420
1400 56	0.03707	0.04550
1409.00	0.81771	0.04000
1/180 26	0.80903	0.04700
1520 11	0.80107	0.04007
1568.07	0.00107	0.04909
1609.97	0.79575	0.05080
16/9 67	0.78066	0.05101
1040.07	0.76000	0.05271
1728.38	0.76025	0.05339
1768 23	0.76405	0.05444
1808.00	0.76915	0.05520
1000.09	0.75915	0.05694
1047.94	0.75451	0.05064
1007.79	0.73012	0.05700
1927.04	0.74393	0.05054
2007.30	0.74195	0.05907
2007.33	0.73015	0.05977
2047.20	0.73451	0.00040
2007.00	0.73102	0.00114
2120.91	0.72700	0.00100
2206.62	0.72447	0.00240
2200.02	0.72137	0.00309
2270.41	0.71552	0.00312
2200.32	0.71002	0.00434
2366 02	0.71275	0.00434
2000.00	0.71000	0.00004

	2405.88	0.70747	0.06613			
	2445.73	0.70495	0.06671			
	2485.59	0.70252	0.06728			
	2525.44	0.70015	0.06784			
	2565.29	0.69785	0.06839			
	2605.15	0.69562	0.06894			
	2645.00	0.69345	0.06948			
	2684.85	0.69134	0.07001			
	2724.70	0.68928	0.07054			
	2764.56	0.68728	0.07106			
	2804.41	0.68532	0.07158			
	2844.26	0.68341	0.07208			
	2884.12	0.68155	0.07259			
	2923.97	0.67973	0.07309			
	2963.82	0.67796	0.07358			
	3003.68	0.67622	0.07406			
	3043.53	0.67452	0.07455			
	3083.38	0.67286	0.07502			
	3123.23	0.67124	0.07550			
	3163.09	0.66964	0.07597			
	3202.94	0.66808	0.07643			
	3242.79	0.66655	0.07689			
	3282.65	0.66506	0.07735			
	3322.50	0.66359	0.07780			
	3362.35	0.66214	0.07825			
	3402.21	0.66073	0.07869			
	3442.06	0.65934	0.07913			
	3481.91	0.65797	0.07957			
	3521.76	0.65663	0.08000			
	3561.62	0.65532	0.08043			
	3601.47	0.65402	0.08086			
	3641.32	0.65275	0.08129			
	3681.18	0.65150	0.081/1			
	3721.03	0.65027	0.08213			
	3760.88	0.64906	0.08254			
	3800.74	0.64786	0.08295			
	3840.59	0.64669	0.08336			
	3880.44	0.64554	0.08377			
	3920.29	0.64440	0.08417			
	4000.00	0.64217	0.08497			
י P	VT-OILHCO	GAS 1	105.0	! T	emperature	
!	-	50	oo : "			
!	Pressure	BO	CO VI	scosity (Cvisco RS	5
!	(psia) (bbl/STB)	(1/psi) (cp) (1/	osi) (scf/stb)	
!	4470	4 04 000	4 5 000	40.0004		0.05
	14.70	1.01202	1E-006	12.3221	1.295E-005	2.25
	54.55	1.01596	1E-006	11.3028	3.1E-005	10.68
	94.41	1.02055	1E-006	10.3012	4.106E-005	20.49
	134.26	1.02553	1E-006	9.3893	4.788E-005	31.12
	1/4.11	1.03080		0.5/83	5.294E-005	42.36
	213.97	1.03630		7.0032	5.091E-005	54.11
	203.02 202.67	1.04200		1.2342	0.0100-000	70.27
	293.07 222 50	1.04/80		0.0804	0.201E-005	18.19
	333.52 272.20	1.05388		0.1918	0.019E-005	91.64
	313.30	1.00003	1 =-000	5.7592	0.720-005	104.78

413.23	1.06631 1E-006	5.3748 6.897E-005	118.18
453.08	1.07270 1E-006	5.0320 7.054E-005	131.83
492.94	1.07920 1E-006	4.7250 7.194E-005	145.70
532.79	1.08579 1E-006	4.4491 7.321E-005	159.79
572.64	1.09248 1E-006	4.2002 7.435E-005	174.07
612.50	1.09926 1E-006	3.9748 7.54E-005	188.54
652.35	1.10612 1.96E-006	3.7701 7.635E-005	203.19
692.20	1.11306 2.918E-006	3.5835 7.722E-005	218.01
732.05	1.12008 3.782E-006	3.4129 7.803E-005	232.99
771.91	1.12716 4.567E-006	3.2564 7.877E-005	248.12
811.76	1.13432 5.284E-006	3.1126 7.946E-005	263.40
851.61	1.14154 5.942E-006	2.9800 8.01E-005	278.82
891 47	1 14883 6 548E-006	2 8574 8 069E-005	294 37
931.32	1.15617 7.11E-006	2.7438 8.123E-005	310.06
971 17	1 16358 7 633E-006	2 6383 8 174F-005	325.87
1011 03	1 17104 8 12E-006	2 5402 8 222E-005	341.80
1050.88	1 17856 8 575E-006	2 4486 8 266E-005	357 85
1090 73	1 18613 9 003E-006	2 3631 8 307E-005	374.02
1130 58	1 19375 9 406E-006	2 2830 8 346E-005	390.29
1170 44	1 20142 9 785E-006	2 2079 8 382E-005	406.68
1210 29	1 20914 1 014E-005	2 1374 8 415E-005	423 17
1250 14	1 21691 1 048E-005	2 0710 8 446E-005	439 76
1290.00	1 22473 1 081E-005	2 0084 8 475E-005	456 45
1329.85	1 23259 1 111E-005	1 9494 8 502E-005	473.23
1369 70	1 24050 1 141E-005	1 8936 8 528E-005	490 11
1409.56	1 24845 1 169E-005	1 8408 8 551E-005	507.09
1449 41	1 25644 1 195E-005	1 7908 8 573E-005	524 15
1489 26	1 26447 1 221E-005	1 7433 8 593E-005	541.30
1529 11	1 27254 1 246E-005	1 6982 8 612E-005	558 54
1568 97	1 28066 1 269E-005	1 6554 8 629E-005	575.86
1608 82	1 28881 1 292E-005	1 6146 8 645E-005	593.26
1648 67	1 29699 1 314E-005	1 5757 8 66E-005	610 75
1688.53	1.30522 1.335E-005	1.5386 8.673E-005	628.31
1728.38	1.31348 1.355E-005	1.5031 8.686E-005	645.95
1768.23	1.32178 1.374E-005	1.4693 8.697E-005	663.67
1808.09	1.33011 1.393E-005	1.4369 8.707E-005	681.46
1847.94	1.33848 1.412E-005	1.4059 8.717E-005	699.33
1887 79	1 34688 1 429E-005	1 3762 8 725E-005	717 26
1927.64	1.35532 1.446E-005	1.3477 8.732E-005	735.27
1967.50	1.36378 1.463E-005	1.3203 8.739E-005	753.35
2007.35	1.37228 1.479E-005	1.2940 8.745E-005	771.50
2047.20	1.38081 1.495E-005	1.2688 8.75E-005	789.71
2087.06	1.38937 1.51E-005	1.2445 8.754E-005	808.00
2126.91	1.39797 1.525E-005	1.2211 8.757E-005	826.34
2166.76	1.40659 1.539E-005	1.1986 8.76E-005	844.75
2206.62	1.41524 1.554E-005	1.1769 8.762E-005	863.23
2246.47	1.42392 1.567E-005	1.1560 8.763E-005	881.77
2286.32	1.43263 1.581E-005	1.1358 8.764E-005	900.36
2326.17	1.44137 1.594E-005	1.1163 8.764E-005	919.02
2366.03	1.45014 1.606E-005	1.0975 8.764E-005	937.74
2405.88	1.45893 1.619E-005	1.0793 8.762E-005	956.52
2445.73	1.46775 1.631E-005	1.0617 8.761E-005	975.36
2485.59	1.47660 1.643E-005	1.0447 8.759E-005	994.25
2525.44	1.48548 1.654E-005	1.0282 8.756E-005	1013.20
2565.29	1.49438 1.666E-005	1.0122 8.753E-005	1032.21
2605.15	1.50331 1.677E-005	0.9967 8.75E-005	1051.27

2645.00	1.51226	1.688E-005	0.9817	8.746E-005	1070.39
2684.85	1.52124	1.698E-005	0.9672	8.741E-005	1089.56
2724.70	1.53024	1.709E-005	0.9531	8.736E-005	1108.78
2764.56	1.53927	1.719E-005	0.9394	8.731E-005	1128.06
2804.41	1.54832	1.729E-005	0.9261	8.725E-005	1147.39
2844.26	1.55740	1.739E-005	0.9131	8.719E-005	1166.77
2884.12	1.56650	1.749E-005	0.9006	8.713E-005	1186.20
2923.97	1.57562	1.758E-005	0.8884	8.706E-005	1205.68
2963.82	1.58477	1.767E-005	0.8765	8.699E-005	1225.21
3003.68	1.59394	1.776E-005	0.8650	8.691E-005	1244.79
3043.53	1.60313	1.785E-005	0.8537	8.684E-005	1264.42
3083.38	1.61235	1.794E-005	0.8428	8.676E-005	1284.10
3123.23	1.62159	1.803E-005	0.8321	8.667E-005	1303.82
3163.09	1.63085	1.811E-005	0.8217	8.658E-005	1323.59
3202.94	1.64013	1.82E-005	0.8116	8.649E-005	1343.41
3242.79	1.64943	1.828E-005	0.8017	8.64E-005	1363.27
3282.65	1.65875	1.836E-005	0.7921	8.631E-005	1383.18
3322.50	1.66810	1.844E-005	0.7827	8.621E-005	1403.14
3362.35	1.67747	1.852E-005	0.7735	8.611E-005	1423.14
3402.21	1.68685	1.86E-005	0.7646	8.6E-005	1443.18
3442.06	1.69626	1.868E-005	0.7559	8.59E-005	1463.27
3481.91	1.70569	1.875E-005	0.7473	8.579E-005	1483.41
3521.76	1.71514	1.883E-005	0.7390	8.568E-005	1503.58
3561.62	1.72461	1.89E-005	0.7309	8.557E-005	1523.80
3601.47	1.73410	1.897E-005	0.7229	8.545E-005	1544.06
3641.32	1.74361	1.904E-005	0.7152	8.534E-005	1564.36
3681.18	1.75313	1.911E-005	0.7076	8.522E-005	1584.70
3721.03	1.76268	1.918E-005	0.7001	8.51E-005	1605.09
3760.88	1.77225	1.925E-005	0.6928	8.497E-005	1625.52
3800.74	1.78183	1.932E-005	0.6857	8.485E-005	1645.98
3840.59	1.79144	1.938E-005	0.6788	8.472E-005	1666.49
3880.44	1.80106	1.945E-005	0.6719	8.46E-005	1687.04
3920.29	1.81070	1.951E-005	0.6653	8.447E-005	1707.62
4000.00	1.83004	1.964E-005	0.6523	8.42E-005	1748.91
!					
PVT-WATE	RHCGAS	1 105.0	!	Temperature	
!					
! Pressure	BW	CW	Viscosity	Cviscw	RS
! (psia)	(bbl/STB)	(1/psi) (cp)) (1/ps	i) (scf/stb)	
!					
14.70	1.01007	2.585E-006	0.7047	0E000	0.00
!					
INCLUDE					
2DFlat.COZ	GRD				
!					
POROSITY					
81*0.2					
!					
PERMEABI	LITY-X				
81*100					
!					
PERMEABI	LITY-Y				
81*100					
!					
PERMEABI	LITY-Z				
81*10					

L COMPRESS-PV 81*4E-06 1 USE-PCPROD 0 ! to turn off Pc in well potential calculation USE-EXCESSPC 1 ! to turn on excess pressure calculation I PCMULTGO 81*1 ! **! BOX-SETUP** 111911 **! PCMULTGO EQUALS TIMES 0.0 ! PERMEABILITY-X EQUALS TIMES 2.0 ! PERMEABILITY-Y EQUALS TIMES 2.0 ! BOX-CLEAR** L **! BOX-SETUP** 1991911 **! PCMULTGO EQUALS TIMES 0.0 ! PERMEABILITY-X EQUALS TIMES 2.0 ! PERMEABILITY-Y EQUALS TIMES 2.0 ! BOX-CLEAR** I BOX-SETUP 191111 PCMULTGO EQUALS TIMES 700 **! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01 BOX-CLEAR** I BOX-SETUP 192211 PCMULTGO EQUALS TIMES 300 **! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01** BOX-CLEAR ! BOX-SETUP 193311 PCMULTGO EQUALS TIMES 100 **! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01 BOX-CLEAR** 1 BOX-SETUP 194411 PCMULTGO EQUALS TIMES 0.0 **! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01 BOX-CLEAR** I BOX-SETUP 195511 PCMULTGO EQUALS TIMES 100

! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01 BOX-CLEAR L BOX-SETUP 196611 PCMULTGO EQUALS TIMES 300 **! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01 BOX-CLEAR** ! BOX-SETUP 197711 PCMULTGO EQUALS TIMES 700 **! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01 BOX-CLEAR** I BOX-SETUP 198811 PCMULTGO EQUALS TIMES 0.0 **! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01 BOX-CLEAR** I BOX-SETUP 199911 PCMULTGO EQUALS TIMES 700 **! PERMEABILITY-X EQUALS TIMES 0.01 ! PERMEABILITY-Y EQUALS TIMES 0.01 BOX-CLEAR** L SORM 81*0.12 T **REGION-SATFUNC** 81*1 **! BOX-SETUP** 119911 **! REGION-SATFUNC EQUALS PLUS 1 ! BOX-CLEAR ! BOX-SETUP** 1991111 **! REGION-SATFUNC EQUALS PLUS 1 ! BOX-CLEAR** L **REGION-REPORT** 81*13 **REGION-EQUIL** 81*1 L **! PCWO** ! 81*100.0 ! PCGO ! 81*500

L BUILDMODEL ! EQUILIBRIUM 1 FLUID2USE 1 PRESSURE@REF 975 **TEMPERATURE@REF 105** ELEVATION@WOC -5400 ELEVATION@GOC -100 ! ELEVATION@REF -5000 PSATHCG@REF 975 I INITIALIZE 01 OCT 2012 I RUN ! ! list of arrays to write ARRAYLIST PRESSURE PRESSURE-BULK PRESSURE-GAS PRESSURE-OIL PRESSURE-WAT PRESSURE-EXCESS SAT-GAS SAT-OIL SAT-WAT **INPLACE-GAS INPLACE-OIL INPLACE-WAT** SGCRIT SORW SORG SOCRIT SGRES PRES-PCO PRES-PCW MOBILITY-GAS MOBILITY-OIL MOLARDENSITY-OIL MOLARDENSITY-GAS **GRADIENT-GAS GRADIENT-OIL VISCOSITY-GAS VISCOSITY-OIL RS-HCGAS-OIL ENDARRAYLIST** ! WELLPERF Well_3 DIR DOWNSTREAM ! J Κ WIMULT/KH EQRADIUS -1.000000 1 1 9 1 **! WELLPERF** Well_4 ! | J Κ WIMULT/KH DIR DOWNSTREAM EQRADIUS 9 !1 9 1 -1.000000 WELLPERF Well_5 ! J Κ WIMULT/KH DIR DOWNSTREAM EQRADIUS

	1 9 1 1 -1.00 !WELLPERF Well_6 ! I J K WIML !1 5 5 1 -1.0		-1.000000 Well_6 WIMULT/KH -1.000000	DIR	DOW	NSTRE	AM	EQRA	DIUS	
! ! ! ! ! ! ! ! ! ! ! ! ! ! ! ! ! ! !	WELLPERF I J I 1 1	к 1	Vell_7 WIMULT/KH -1.000000	DIR	DOW	NSTRE	AM	EQRA	DIUS	
	WELLPERF I J 1 5 1	Well_12 K WIMULT/KH 1 -1.000000		DIR	DOW	NSTRE	AM	EQRA	DIUS	
	WELLPERF I J 1 9 5	V K 1	Vell_13 WIMULT/KH -1.000000	DIR	DOW	NSTRE	AM	EQRA	DIUS	
	!WELLPERF !IJ !159	Well_14 K WIMULT/KH 1 -1.000000		DIR	DOW	NSTRE	AM	EQRA	DIUS	
	WELLPERF I J 1 1 5	۷ ۲ ۱	Vell_15 WIMULT/KH -1.000000	DIR	DOW	NSTRE	AM	EQRA	DIUS	
	! ! WELLSTATUS ! WELLSTATUS	We	ll_6 Well_14	INJECT	OR	QGA F	S 'ROD	UCER	DEPE	NDENT QLIQUID
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	PENDENT ! WELLSTATUS		Well_15			F	ROD	UCER		QLIQUID
	PENDENT ! WELLSTATUS		Well_12			F	ROD	UCER		QLIQUID
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	! WELLPRESSURI	E	Well_5	300.00	1*	1*		0		
	! ! WELLPRESSUF	RE	Well_7	1000.0	0 1*		1*	0		
	! ! WELLPRESSUF	RE	Well_12	1000.	00 1*		1*	0		
	! ! WELLPRESSUF	RE	Well_13	1000.	00 1*		1*	0		
	WELLPRESSUF	RE	Well_14	1000.	00 1*		1*	0		
	WELLPRESSUF	RE	Well_15	1000.	00 1*		1*	0		
	! WELLPRESSUF	RE	Well_6	2400.0	0 1*		1*	0		
	! ! name WELLCONSTRA ! WELLCONSTR/) INT AINT	qoilp Well_3 Well_4	qgasp q 0.00 0.00	watp 0.00 1000	qliqp 0.00 0.00 0	qga 20 .00	si qwa 00000.0 2000.0	ati 0 0.00 00 0.00	0.00) 0.00

WELLCONSTRAINT Well_5 0.00 0.00 0.00 200000.00 0.00 0.00 ! WELLCONSTRAINT Well 7 0.00 1000.00 0.00 2000.00 0.00 0.00 ! WELLCONSTRAINT Well 12 0.00 1000.00 0.00 2000.00 0.00 0.00 ! WELLCONSTRAINT Well_13 0.00 1000.00 0.00 2000.00 0.00 0.00 Well 14 0.00 1000.00 0.00 2000.00 0.00 ! WELLCONSTRAINT 0.00 ! WELLCONSTRAINT Well 15 0.00 1000.00 0.00 2000.00 0.00 0.00 ! WELLCONSTRAINT 0.00 0.00 Well_6 0.00 0.00 3000.00 0.00 ! ! Max Max Max Limit name WtrCut GOR ! WGR Well 3 WELLLIMIT 1* 20000.0 1* 1 1* 1* ! WELLLIMIT Well 4 4000.0 1 WELLLIMIT Well 5 1* 20000.0 1* 1 ! WELLLIMIT Well 7 1* 4000.0 1* 1 ! WELLLIMIT Well 12 1* 4000.0 1* 1 ! WELLLIMIT Well 13 1* 4000.0 1* 1 1* 4000.0 1* ! WELLLIMIT Well 14 1 1* ! WELLLIMIT Well 15 4000.0 1* 1 T L **WRITEARRAYS** L DATETIME 01 NOV 2012 ! I **WRITEARRAYS** 1 DATETIME 01 DEC 2012 L ! DATETIME 01 APR 2019 **!WRITEARRAYS** DATETIME 01 MAY 2019 **!WRITEARRAYS** DATETIME 01 JUN 2019 **!WRITEARRAYS** DATETIME 01 JUL 2019 **! WRITEARRAYS** L DATETIME 01 AUG 2019 **!WRITEARRAYS** ! DATETIME 01 SEP 2019 **!WRITEARRAYS** L DATETIME 01 OCT 2019 **!WRITEARRAYS** L DATETIME 01 NOV 2019

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APPENDIX B

SUPLEMENTARY ELECTRONIC FILES

This Appendix includes the list of the simulation datasets that were used while analyzing the impact of confined PVT behavior on flow. All the files are text files with the extension COZdat that can directly be run using COZSim. Table B-1 summarizes the names, types and the contents of each file.

File Name	File Type	Description
		Uniform property distribution.
UCOZ033-PE0-2D-10yr.COZdat	Text File	Pcgo=0.0. Grid Size 9X9X1
		Uniform property distribution.
UCOZ034-PE200-2D-10yr.COZdat	Text File	Pcgo=200 psi. Grid Size 9X9X1
		Uniform property distribution.
UCOZ037-PE200-2D-10yr.COZdat	Text File	Pcgo=700 psi. Grid Size 9X9X1
		Unform property distribution. Simple
		Pcgo distribution manually distributed
UCOZ046-PEDISTR-2D-10yr.COZdat	Text File	between 0 and 700 psi. Grid Size 9x9x1
		Unform property distribution. Pcgo =0.0
UCOZ047-PEDISTR-2D-10yr.COZdat	Text File	psi. Grid size 9x9x1
		Unform property distribution. Simple
		Pcgo distribution manually distributed
		between 0 and 700 psi. No excess
UCOZ053-PEDISTR-2D-10yr.COZdat	Text File	suppression. Grid Size 9x9x1

Table B-1 – The names, types and contents of each supplemental electronic file

		Unform property distribution. Random
		Pcgo distribution honoring a normal
		distribution with a mean of 400 psi and
		standard deviation of 100 psi. Grid Size
UCOZ068-PEDISTR-2D-10yr.COZdat	Text File	100x100x1
		Unform property distribution. Pcgo=0.0.
UCOZ069-PEDISTR-2D-10yr.COZdat	Text File	Grid Size 100x100x1
		Random Pcgo distribution honoring a
		normal distribution with a mean of 400
		psi and standard deviation of 100 psi,
		model is surrounded by high
		permeability Pcgo=0.0 strak representing
		fractures. Matrix permeability is
		distributed as a function of Pcgo. Grid
UCOZ081-PEDISTR-2D-10yr.COZdat	Text File	Size 100x100x1
		Pcgo=0.0, model is surrounded by high
		permeability Pcgo=0.0 strak representing
		fractures. Matrix permeability is
		distributed same as UCOZ081-
		PEDISTR-2D-10yr.COZdat . Grid Size
UCOZ082-PEDISTR-2D-10yr.COZdat	Text File	100x100x1