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# Theoretical Treatment of Asphaltene Gradients in the Presence of GOR Gradients

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The modeling of hydrocarbon fluids in oil-field reservoirs is essential for optimizing production. In particular, the often large compositional variations of reservoir crude oils must be understood and modeled. The two most important chemical constituents that govern many chemical and physical properties of subsurface reservoir crude oils are the dissolved gas content, described by the gas−oil ratio (GOR), and the asphaltene content. The modeling of GOR variations of crude oils in reservoirs has been practiced routinely for many decades. However, proper modeling of the asphaltenes and/or heavy ends of reservoir crude oils has been precluded because of the lack of understanding of the chemical and physical properties of asphaltenes in crude oils. Recently, the modified Yen model has codified advances in asphaltene science by providing a framework for understanding the molecular and colloidal structure of asphaltenes in crude oils. Here, a thermodynamic model of asphaltenes in reservoir crude oils is developed that can incorporate the modified Yen model and thus can be used to treat reservoir crude oils. Our objective is to analyze the distribution of reservoir fluids, in particular the asphaltenes. This deviates from most previous studies of asphaltene thermodynamics, which were focused on the phase behavior of asphaltenes. Here, compositional gradients of asphaltenes, as well as the GOR of reservoir crude oils, are analyzed. Asphaltene gradients are shown to be strongly affected by both gravity and solubility. The latter effect is heavily dependent on the dissolved gas content of the reservoir crude oil. Case studies are provided that exhibit the power of this modeling.

## Introduction

The two most important chemical constituents that govern many chemical and physical properties of subsurface reservoir crude oils are the dissolved gas content, described as the gas−oil ratio (GOR), and the asphaltene content. For example, surface or sea floor facilities are built according to gas and liquid volumetric handling. Flow rates are critically dependent on the fluid viscosity, which is a function of both the light-end (e.g., gases) and heavy-end (e.g., asphaltenes) contents of the crude oil. Moreover, reservoir fluids can exhibit variation of important chemical properties, especially the light- and heavy-end contents, from a variety of mechanisms.[1] These variations must be understood for the building of optimal production strategies.

In addition to reservoir fluid complexities, reservoirs generally possess complex architecture. In particular, reservoirs can have (infrequent) large compartments or can consist of numerous small compartments. (A compartment must be penetrated by a well to be drained.) That is, in extreme descriptions, reservoirs can be similar to a kitchen sponge that has a connected porosity or similar to a spool of bubble wrap that has many small individual compartments. Compartmentalization or its inverse, reservoir connectivity, is the biggest problem in almost all deepwater projects around the world.[1] There are many mechanisms that can produce reservoir fluid variability. Often this variation in the fluid can address compartmentalization because different compartments are likely to

be filled with different fluids. If a stair-step discontinuous fluid property is found (in a single phase) in the reservoir, then compartmentalization is often indicated.[1] In contrast, continuous and monotonic trends of reservoir fluid properties often imply connectivity because they suggest that there is massive fluid flow across the reservoir. If the reservoir fluids are equilibrated, especially in the heavy ends, then reservoir connectivity is more strongly implied.[1] This follows because the mobilities of the heavy ends are very low, so equilibrated heavy ends are not compatible with substantially restricted flow in the reservoir. Consequently, it becomes more important than ever to model all components of reservoir fluids.

Modeling GOR in reservoir fluids has been performed for decades using variants of the van der Waals equation of state [or cubic equations of state (EOS)]. These equations have been very useful for describing a variety of fluid parameters. For example, heuristics have been developed to indicate when GOR gradients are expected.[2] In large measure, in compressible fluids, the greater expansion of the lightest components as they go higher in the column will create the thermodynamic drive to give GOR gradients. In contrast, incompressible fluids do not yield density variations and thus do not yield GOR gradients.[1,2] The success of cubic EOS to predict GOR gradients in reservoir crude oils has been confirmed in live crude oil centrifugation experiments.[3] (Live crude oils are those oils that, under reservoir pressure and temperature conditions, contain dissolved gases.) However, treating solids, such as asphaltenes, as a pseudocomponent in a gas−liquid

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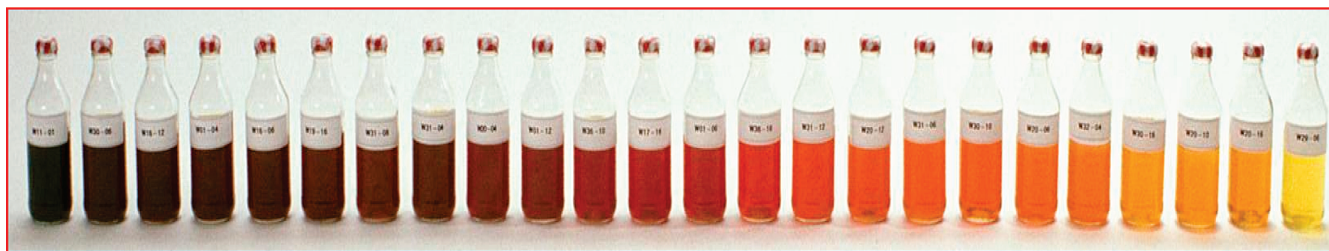
**Figure 1.** Samples of dead (degassed) crude oils from a single oil column.[7] The color variation of these samples is caused primarily by differing asphaltene contents. In the past, this variation could not be modeled.

equilibrium is not proper but has been used. Inappropriate modeling of this nature might fit data, but it is far from predictive for asphaltene gradients when compared to methods below.

A new technology, "downhole fluid analysis" (DFA), has enabled the determination of complex reservoir fluid gradients in a cost-effective manner.[1] DFA consists of sending optical spectrometers and other fluid sensors into oil wells, extracting reservoir fluids at known depths under controlled conditions, and performing chemical analysis of these live crude oils.[1] DFA has had immediate application for measurement of the GOR gradients in the reservoir.[4] The use of EOS to analyze corresponding gradients has also been successful.[5]

There has been a fundamental deficiency in analyzing reservoir fluids that has gone unsolved for decades and that has been rooted in uncertainties in asphaltene science.[6] The asphaltenes could not be treated in any first principles modeling effort because the aggregation state of asphaltenes in live crude oils had been unknown. In addition, the asphaltene molecular architecture had been unknown, and even the asphaltene molecular weight had previously been the subject of an orders-of-magnitude debate.[6] Without knowing the molecular and colloidal properties of asphaltenes, there is no way to properly handle the gravity effects in an EOS for heavy ends; consequently, they cannot be properly modeled. The magnitude of this inability to model asphaltenes is depicted in Figure 1, where 24 sample bottles of dead (degassed) crude oils from a single reservoir oil column are shown.[7] This figure shows that enormous variations in the concentration of asphaltenes can occur in a single oil column, from 0% to 5%.[8] However, there was no ability to model this variation with an EOS. As a result, virtually all advanced reservoir models incorporate cubic EOS to treat (dissolved) gas and liquid hydrocarbons, but almost none of these reservoir models incorporate any treatment for gradients of asphaltenes. Moreover,

because the magnitude of the asphaltene gradients can vary by a factor of 50, as determined in field studies,[9] it is essential to understand and model these gradients.

Fortunately, there have been recent advances in asphaltene science that have resolved molecular and colloidal structures of asphaltenes, at least in crude oils that flow. These advances, described in detail elsewhere,[6] are enabling a first-principles approach to modeling asphaltenes. They are codified in a new paradigm of asphaltenes, the "modified Yen model".[10] This model provides a framework for understanding the dispersion of asphaltenes in crude oil. In addition, it has found application in oil-field case studies and, using the theoretical approach in this paper, has successfully addressed some of the largest risk factors for the reservoir.[9-13]

The modified Yen model clarifies what the relevant structures of asphaltenes in reservoir crude oils are, as shown in Figure 2. Because the effects of gravity on the asphaltenes depend on the size of the asphaltene particles, this model enables the treatment of asphaltenes and asphaltene gradients in the reservoir. At very low concentrations, colored heavy ends should be molecularly dispersed (either asphaltene or colored resins). At higher asphaltene concentrations, the larger species are present. For example, in stable "black" crude oils (black crude oils have a relatively low GOR), the asphaltene nanoaggregates dominate.[10] With increasing concentrations and with weaker liquid-phase solvation, asphaltene nano-aggregate clusters can appear.[10] Presumably, at much higher asphaltene concentrations, large asphaltene species will form. However, this is of lesser interest here because many of these very asphaltic crude oils will not flow and thus cannot be produced conventionally. It must be emphasized that, frequently, only one particular form of asphaltenes is found in reservoir crude oil, such as asphaltene nanoaggregates in black oil.[9] This is in contrast to many ad hoc asphaltene analyses that assume changing asphaltene structures with depth.

Previous theoretical treatment of the asphaltene properties has focused on the phase behavior,[14] particularly within a "flow assurance" context, and relates to colloidal destabilization

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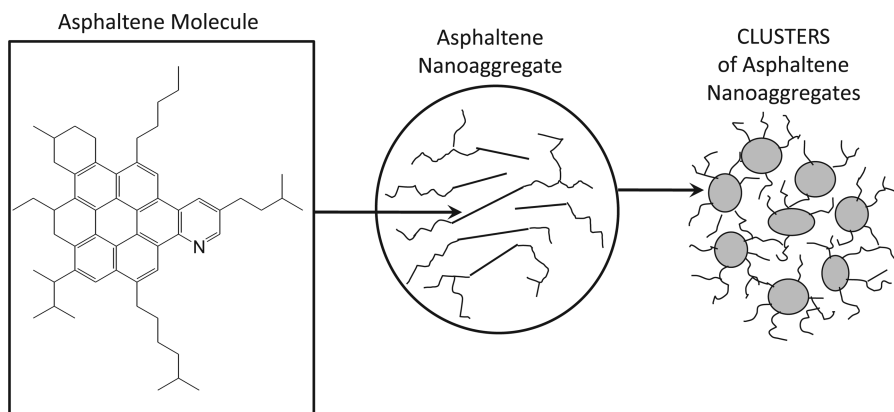
**Figure 2.** Asphaltene structures per the modified Yen model:[10] (left) the predominant asphaltene molecular architecture; (center) asphaltene nanoaggregates consisting of about six molecules; (right) asphaltene clusters consisting of about seven nanoaggregates. The specific asphaltene species that is present in a reservoir crude oil is dependent on the concentration, liquid-phase solubility parameter, and other conditions.

of asphaltenes, leading to solids deposition in pipelines, production tubing, and even the reservoir.[15] This successful treatment contains elements that are quite useful for developing a more generalized treatment of asphaltenes that properly incorporates the effects of gravity. The approach we will describe herein has been used to successfully treat the results from centrifugation of a live black crude oil.[16]

In this paper, a thermodynamic model is developed to describe asphaltene distributions in reservoir crude oils. Three terms are explicitly developed: gravity, solubility, and entropy. The solubility term is shown to depend heavily on the GOR of the crude oil and its variation with depth; thus, the light- and heavy-end treatments are intimately related. The relationship of this formalism with the previous phase behavior work is discussed. An oil-field case study is shown where the gravity term dominates, and a second field case study is shown where the solubility term dominates. The methods described here, coupled with the foundations of the modified Yen model, provide new powerful methods for addressing the complexities of reservoir crude oils.

### Thermodynamic Model

We will use a simple, two-component, Flory−Huggins type of model to describe the asphaltene and maltene system. Basic modeling of asphaltenes in reservoir crude oils has been described previously.[17] However, this early work suffered from two fundamental limitations: (1) at the time, there was no understanding of the molecular and colloidal structure of crude oil, which precluded the proper understanding of the gravity effects, and (2) possible GOR variations were not included, which precluded any consideration of the effects of the changing solubility. Here, we overcome both limitations. In our case, the amount of methane, and possibly other components of the maltene, varies as a function of the height.

We extend the two-component Flory−Huggins model that has been used to desribe the phase behavior of asphaltenes.[15,18] In this model, the asphaltenes are the first component, and the

rest of the oil, or the maltene, is lumped together for the second component. In the case considered here, the properties of the maltene, such as its molar volume and molar mass, can vary as a function of the height, but we assume that the properties of the asphaltene are independent of the height. We will also assume that the concentration of the asphaltene is small enough that it does not affect the equilibrium distribution of the rest of the oil. We will take this equilibrium distribution as a given property of the oil and see how it affects the equilibrium distribution of the asphaltene.

The size of the relevant asphaltene particle can be chosen depending on the nature of the crude oil. This has been shown to be applicable to reservoir crude oils.[10] Here, we do not modify the asphaltene solubility parameter as a function of its colloidal or molecular dispersion. If there were sufficient data to motivate this, our approach could incorporate this complication.

More specifically, at each height $h$, there are $n_m(h)$ maltene molecules and $n_a(h)$ asphaltene molecules. These numbers are allowed to vary in order to find the minimum of the free energy. The average volume of a maltene molecule is $v_m(h)$. This can vary somewhat as a function of $h$ as the composition and density of the maltene change. The asphaltenes can be in single molecules, nanoaggregates, or nanoaggregate clusters. In this paper, we will assign all of the asphaltenes to be in only one of these three forms. This assumption can be relaxed in future treatments, especially if motivated by more oil-field data. We will take $v_a$ to be the average size of the asphaltene particles in the fluid, and we will assume that it is constant as a function of height. The total volume of the fluid at each height is $V_T(h) = v_m n_m + v_a n_a$. Unlike in the calculations of the onset of asphaltene instability, we will be assuming that the fluid remains a single phase or stable colloidal dispersion at all heights. Thus, there is only one volume of the single phase, and we will take $V_T(h)$ to be constant as a function of the moles of asphaltenes and solvent. (We note that in many of the calculations of the effect of gravity, including those in ref 17, the energy is calculated as a function of the pressure and temperature. Here, instead we are calculating it as a function of the volume and temperature, and we hold the volume fixed at each height. Thus, strictly speaking, the energy $\Delta G$ defined below is really the Helmoltz free energy, $\Delta A$. In this case, given the way we define the chemical potential below, we do not need to explicitly include a term of the form $\rho v_a g h$, where $\rho$ is the average density at height $h$. This term arises in our case because of the constraint of constant volume.)

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The volume fractions of the maltene and asphaltene at each height are given by $\phi_m(h) = v_m n_m / V_T$ and $\phi_a(h) = v_a n_a / V_T$, respectively, and they sum to 1:

$$\phi_m(h) + \phi_a(h) = 1 \tag{1}$$

The solubility parameter of the asphaltene is $\delta_a$, and the solubility parameter of the maltenes, $\delta_m(h)$, depends on the composition and density of the maltene at each height.

The free energy at height $h$ for the asphaltene and solvent oil is given by

$$\Delta G(h) = \Delta G_{entropy}(h) + \Delta G_{sol}(h) + \Delta G_{grav}(h) \tag{2}$$

where $\Delta G_{entropy}(h)$ is the free energy due to the entropy of mixing, $\Delta G_{sol}(h)$ is the free energy due to the solubility of the asphaltene in the maltene, and $\Delta G_{grav}$ is the free energy due to gravity. When the difference in sizes between the solute and solvent is not taken into account, the entropy of mixing is given by

$$\Delta G_{entropy}(h) = kT[n_m(h) \ln x_m(h) + n_a(h) \ln x_a(h)] \tag{3}$$

where $x_m(h)$ and $x_a(h)$ are the mole fractions of the maltene and asphaltene, respectively. Once there is a difference in size between the solute and solvent, several different values for the entropy of mixing have been used, including the one given above for molecules of equal size. Alternatively, for asphaltene phase behavior, the Flory−Huggins entropy expression for polymer solutions has been used successfully;[15] we use this here. It is given by

$$\Delta G_{entropy} = kT(n_m \ln \phi_m + n_a \ln \phi_a) \tag{4}$$

Because this form of the entropy depends largely on the volume fraction of the asphaltenes, the exact molecular or colloidal dispersion of the asphaltenes in the crude oil has a much smaller effect on the asphaltene gradient than if entropy term depended solely on the mole fractions of the different asphaltene species.

The part of the free energy due to the solubility of the asphaltenes is given by

$$\Delta G_{sol} = n_m(h) \, \phi_a(h) \, v_m(h) \, [\delta_a - \delta_m(h)]^2 \tag{5}$$

The solubility term is independent of the type of colloidal dispersion of the asphaltenes provided that the asphaltene solubility parameter also does not depend on this. The free energy due to gravity is given by

$$\Delta G_{grav}(h) = g[n_m(h) \, v_m(h) \int_0^h \rho_m(h') \, dh' + n_a(h) v_a \rho_a h] \tag{6}$$

where $\rho_a$ and $\rho_m$ are the densities of the asphaltene and maltene, respectively. The density of asphaltene solutions is impacted very little by the aggregation state of the asphaltene at a given mass fraction.[19] Because the density and average volume per molecule is changing in this simplified model for the maltene, there is some ambiguity in defining the gravitational free energy of the maltene. Because the density does not vary much in the examples considered below, there are several choices that we could make for this term, which all give similar answers, as long as we require this term to depend only on the relative height and not on the absolute height. Here, we are using the work to move a volume element of size $v(h)$ from the reference height $h = 0$ to the height $h$ to calculate this free energy. We assume that the density of this volume element

changes as a function of height, so that it equals the density of the maltene at each height.

Because the sum of the asphaltene and maltene volume fractions at each height is equal to 1, we can eliminate $\phi_m$ and $n_m$ from the expression for the free energy to obtain

$$\Delta G(h) = kT \left[ n_a \ln \phi_a + \left( \frac{V_T}{v_m} - \frac{n_a v_a}{v_m} \right) \ln(1 - \phi_a) \right]$$
$$+ n_a v_a (1 - \phi_a)(\delta_a - \delta_m)^2 + g n_a v_a [\rho_a h - \int_0^h \rho_m(h') \, dh']$$
$$+ g V_T \int_0^h \rho_m(h') \, dh' \tag{7}$$

The chemical potential of the asphaltene at height $h$ is then the derivative of $\Delta G(h)$ with respect to $n_a$ with $V_T$ ($h$) held fixed at each height:

$$\mu_a(h) = kT \left[ \ln \phi_a - \frac{v_a}{v_m} \ln(1 - \phi_a) + 1 - \frac{v_a}{v_m} \right]$$
$$+ (1 - 2\phi_a) v_a (\delta_a - \delta_m)^2 + g v_a [\rho_a h - \int_0^h \rho_m(h') \, dh'] \tag{8}$$

In equilibrium, the derivative of $\Delta G$ with respect to $n_a(h)$ equals zero, with the constraint that $\sum_h n_a(h)$ equals the total number of asphaltene molecules. Using a Lagrange multiplier $\lambda$ to enforce this constraint, we have

$$\frac{\partial \Delta G(h)}{\partial n_a(h)} = \frac{\partial}{\partial n_a(h)} \left[ \lambda \sum_h n_a(h) \right] \tag{9}$$

which gives

$$\mu_a(h) = \lambda \tag{10}$$

for all heights $h$. Thus, the condition for equilibrium is that the chemical potentials for the asphaltene are the same at all heights, so that

$$\mu_a(h_1) = \mu_a(h_2) \tag{11}$$

Setting the chemical potentials at heights $h_1$ and $h_2$ equal, we find

$$\frac{\phi_a(h_1)}{\phi_a(h_2)} \left( \frac{\phi_m(h_2)}{\phi_m(h_1)} \right)^{v_a / v_m} = \exp\{ - [\text{Grav}(h_1, h_2) + \text{Ent}(h_1, h_2)$$
$$+ \text{Sol}(h_1, h_2)] / kT \} \tag{12}$$

In this equation, $\text{Grav}(h_1, h_2)$, $\text{Ent}(h_1, h_2)$, and $\text{Sol}(h_1, h_2)$ are the contributions to the chemical potential due to gravity, entropy, and solubility, respectively. The gravity term is given by

$$\text{Grav}(h_1, h_2) = v_a g \left[ \int_0^{h_1} \Delta\rho(h) \, dh - \int_0^{h_2} \Delta\rho(h) \, dh \right] \tag{13}$$

where $\Delta\rho(h) = \rho_a - \rho_m(h)$. The entropy term is given by

$$\text{Ent}(h_1, h_2) = kT v_a \left[ \frac{1}{v_m(h_2)} - \frac{1}{v_m(h_1)} \right] \tag{14}$$

and the solubility term is

$$\text{Sol}(h_1, h_2) = v_a \{ [1 - 2\phi_a(h_1)][\delta_a - \delta_m(h_1)]^2$$
$$- [1 - 2\phi_a(h_2)][\delta_a - \delta_m(h_2)]^2 \} \tag{15}$$

If the expression for the entropy in eq 3 is used instead of the Flory−Huggins version, then the left-hand side of eq 12, which comes from the entropy, gets modified. The volume fractions are replaced by mole fractions, and the ratio $v_a / v_m$ in

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the exponent is replaced by 1. In addition, there is no entropy term in the exponent on the right-hand side of eq 12. This entropy term is, in effect, an excess entropy due to use of the Flory−Huggins entropy instead of the ideal gas entropy of eq 3.

When the asphaltene volume fraction is much less than 1, eq 12 becomes

$$\frac{\phi_a(h_1)}{\phi_a(h_2)} = \exp\{-[\mathrm{Grav}(h_1,h_2) + \mathrm{Ent}(h_1,h_2) + \mathrm{Sol}(h_1,h_2)]/kT\} \tag{16}$$

where now the solubility term is given by

$$\mathrm{Sol}(h_1,h_2) = v_a\{[\delta_a - \delta_m(h_1)]^2 - [\delta_a - \delta_m(h_2)]^2\} \tag{17}$$

If, in addition, the composition of the solvent oil does not change as a function of the height, then this reduces to the familiar expression

$$\frac{n_a(h_1)}{n_a(h_2)} = e^{-v_a g(h_1 - h_2)\Delta\rho/kT} \tag{18}$$

## Comparison with Data and the Relative Sizes of the Different Energies

In this section, we examine two extreme cases in terms of the relative magnitude of the gravity, solubility, and entropy effects. A total of six case studies have been published elsewhere using the modified Yen model.[9,11,12] In addition, this theoretical model, coupled with the modified Yen model, successfully accounted for centrifugation data of a black oil of moderate GOR where the asphaltene concentration varied by a factor of 10 and the colored resins varied by a factor of 2.[16] Our objective here is to provide support for our theoretical approach but not to do an exhaustive analysis of case studies. Moreover, because these case studies cost roughly $0.5 billion each and take many years, it takes a while to accumulate large numbers of case studies.

In the first case considered here, the Tahiti reservoir is examined. In this reservoir, the GOR is quite low. Consequently, the GOR gradient is very small and the asphaltene gradient is dominated by the gravity term. This oil has an API gravity of 28 and contains several percent of asphaltene. In the second case, the fluid is a near-critical fluid that exhibits a large GOR gradient. This oil has an API gravity of 35. The colored heavy ends in this case are dominated by colored resin molecules instead of asphaltenes, so they are largely molecularly dispersed. The large GOR gradient produces a large solubility contrast, whereas the small (molecular) size reduces the magnitude of the gravity term. Consequently, with the near-critical fluid, the heavy-end gradient is dominated by the solubility term.

There has been a general misunderstanding as to the origin of GOR gradients with respect to gravity, so we address this issue here. Crude oils with low GOR are rather incompressible, in contrast to high-GOR crude oils. If a crude oil has no compressibility, then the hydrostatic head pressure of the crude oil column does not give rise to a density gradient. (The hydrostatic head pressure at any point is the pressure exerted by the height of the oil column above that point; this pressure is, in addition to the ambient pressure, at the top of the reservoir.) Equation 18 can then be used to give the GOR gradient that is directly due to the gravity term. By substituting reasonable parametric values into eq 18, one finds that a
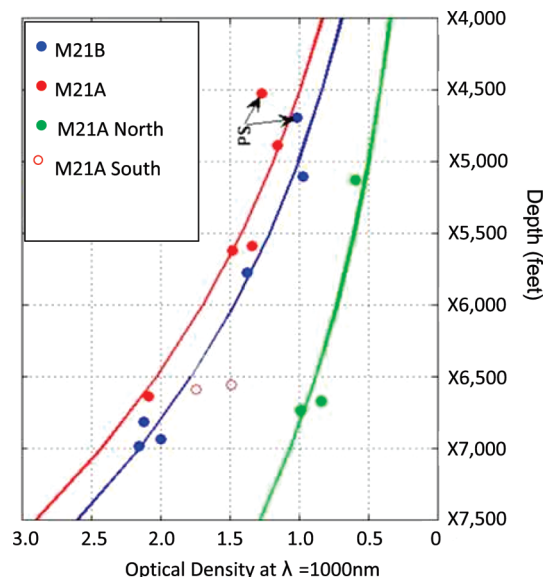


**Figure 3.** Asphaltene gradient (linear in optical density at 1000 nm) versus depth in the Tahiti reservoir. The gradient is predominantly due to gravity acting on the asphaltene nanoaggregates.[1,13] There is a small GOR gradient and low GOR so the solubility term is relatively small. The solid lines show the fits using gravity effects (eq 18).

factor of 2 decrease in the methane content in the crude oil occurs in a height of roughly 100 km. In other words, the gravity term in eq 18 alone does not yield any significant GOR gradient. Instead, the GOR gradient induced by gravity is via compressibility. If the fluid is compressible, then it will be energetically favorable for the lightest components (which are also the most compressible) to be on top. This is because higher in the reservoir the hydrostatic head pressure will be less, causing the fluid to expand. The light components will expand more, so the gravitational energy will be reduced the most if they collect toward the top. Thus, the fluid will have lower density and more methane at the top of the column and higher density and less methane at the base of the column. In addition, once there is separation due to this combination of compressibility and gravity, the solubility effects will enhance the compositional variation.

In the Tahiti reservoir, the crude oil GORs are relatively low, ~100 m³/m³. Consequently, there is a small GOR gradient, and variation of the solubility term in the 1000 m oil column is relatively small. The gravity term (eq 18) acting directly on the colloidal asphaltene nanoaggregates is largely responsible for producing the asphaltene concentration gradient. Figure 3 shows the DFA-measured asphaltene gradient in the Tahiti reservoir.[1,13] The coloration as measured by DFA at a specific, convenient wavelength has been shown to be linear in the asphaltene content, with a small offset at the origin due to some coloration of the resin fraction.[1,13] In addition, it has been established that aggregation of asphaltenes does not affect the asphaltene optical density associated with electronic transitions.[20] Thus, no nonlinearties are introduced relating the asphaltene concentration and optical absorption.[20] The asphaltene gradient in Figure 3 is consistent with a nanoaggregate distribution of asphaltenes in the crude oil.[1,13] That is, there is only one (centroid) size of the asphaltene particles throughout the entire oil column. There is

(20) Ruiz-Morales, Y.; Wu, X.; Mullins, O. C. *Energy Fuels* **2007**, *21*, 944.

not a changing distribution of sizes with the height in the column. Similarly, a heavy oil column has recently been shown to consist of clusters.[9] Again, only a single size of the asphaltene particle is found in that case.

In the original Tahiti study, the effects of solubility and entropy were not included because it was assumed that the predominant effect was from gravity. By fitting just the gravity term (eq 18) to the data, the asphaltene nanoaggregate diameter was found to be about 1.6 nm. If we include the solubility term (assuming a solubility parameter of 21.85 $MPa^{1/2}$), this is decreased slightly to about 1.5 nm, and if both the solubility and entropy terms are included (as in eq 16), it is increased to about 1.8 nm. Thus, the solubility term does have a very small effect on the compositional gradient and tends to increase it. The entropy term has a somewhat larger effect. Although the change is small, the larger value for the asphaltene diameter found by including the solubility and entropy effects is more physical and more consistent with laboratory data for asphaltene nano-aggregates[10] than the value found using only the gravity term. We also note that, although the oil column is quite long, the temperature gradient was fairly small (about 0.01 K/m), and an analysis taking into account the gravity effects along with the temperature gradient gave very similar results. Finally, we emphasize that we have used very few parameters to characterize the asphaltenes and that these parameters have been measured in the laboratory, allowing our theoretical approach to be validated against specific known parameters.

Next, we contrast the Tahiti case study, where gravity dominates, with the Norway case study, where the solubility term dominates. Figure 4 shows the GOR gradient obtained by DFA in a well for both the Tahiti and Norway case studies. As can be seen in the figure, the Norway reservoir has a large GOR variation over a range of only 30 m, while the Tahiti reservoir has a much smaller variation of the GOR over a much larger oil column spanning 1000 m. Thus, not only does the Norway oil have a higher GOR than the Tahiti oil, it also has much larger gradients in the GOR. As we shall see below, this will cause the solubility effects to dominate the asphaltene gradient.

In the Norway well, the oil is very close to its critical point, so variations in the oil properties, including the GOR and optical density, are significant, as described elsewhere.[1,4,5] For this light oil, we expect the colored component to be more resinlike and thus molecularly dispersed. In particular, the resins and this oil absorb light only at shorter wavelengths.[16] For condensates, where asphaltenes have very poor solubility, such as this Norway example, optical obsorption occurs at short wavelengths. Thus, the bulk of the absorption is expected from molecularly dispersed species. Here, we employ our thermodynamic model on the *colored* resin molecules. It is known that the colored resin molecular size is similar to that of asphaltene molecules with similar spectral characteristics.[21] For this condensate, we use the DFA visible color measurement at $\lambda = 647$ nm for determination of the colored (asphaltene-like) resin content.

To simulate the pressure−volume−temperature (*PVT*) properties and compositions of the oil as a function of the
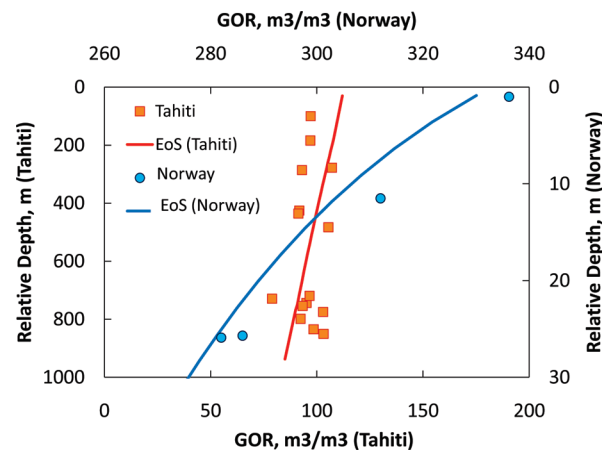


**Figure 4.** GOR variations of the reservoir crude oils for the Tahiti reservoir (squares) and the Norway reservoir (circles). For the Tahiti reservoir, this GOR variation occurs over an oil column height of 1000 m (left ordinate), while for the Norway reservoir, the GOR variation is for an oil column height of 30 m (right ordinate). The GOR gradient of the Norway oil field is much larger; consequently, the impact of the solubility term on the asphaltene gradient is huge. For the Tahiti oil field, the GOR gradient is very small; consequently, the gravity term dominates the asphaltene gradient.
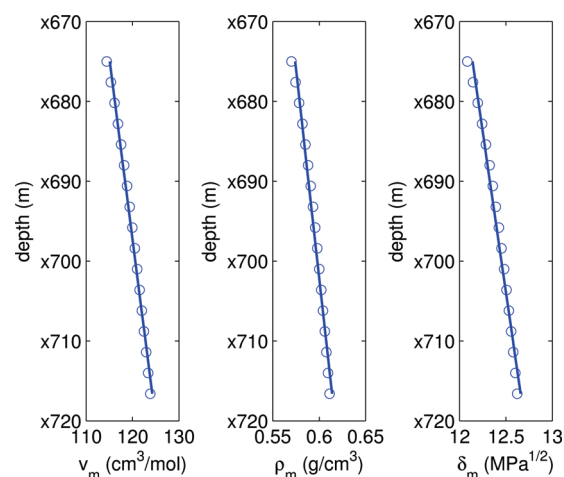


**Figure 5.** Maltene properties for the Norway crude oil versus depth: (left) maltene molar volume vs depth; (middle) maltene density vs depth; (right) maltene solubility parameter vs depth.

depth, the Peng−Robinson EOS and characterization procedure of Zuo et al.[22] was used. The measured composition of the fluid from a region close to the gas−oil contact was used as a reference point. The EOS was applied to estimate the molar volume, density, and solubility of the maltene. The values of these parameters are shown in Figure 5. The linear fits, shown with solid lines in the figures, are used in the calculations below.

For purposes of fitting the data, we assume that the asphaltene has a solubility parameter of 21.85 $MPa^{1/2}$ for an asphaltene sample at 20 °C.[23] For the condensate, the colored component is probably more resin-like, in which case the solubility parameter could be somewhat lower. The solubility parameter could also be affected by the temperature and pressure, as will be discussed in the next section.

(21) Groenzin, H.; Mullins, O. C. *Energy Fuels* **2000**, *14*, 677.
(22) Zuo, J. Y.; Freed, D. E.; Mullins, O. C.; Zhang, D.; Gisolf, A. Interpretation of DFA Color Gradients in Oil Columns Using the Flory−Huggins Solubility Model. Paper SPE 130305 presented at the CPS/SPE International Oil and Gas Conference and Exhibition in China, Beijing, China, June 8−10, 2010.

(23) Ting, P. D.; Hirasaki, G. J.; Chapman, W. G. *Pet. Sci. Technol.* **2003**, *21*, 647−661.
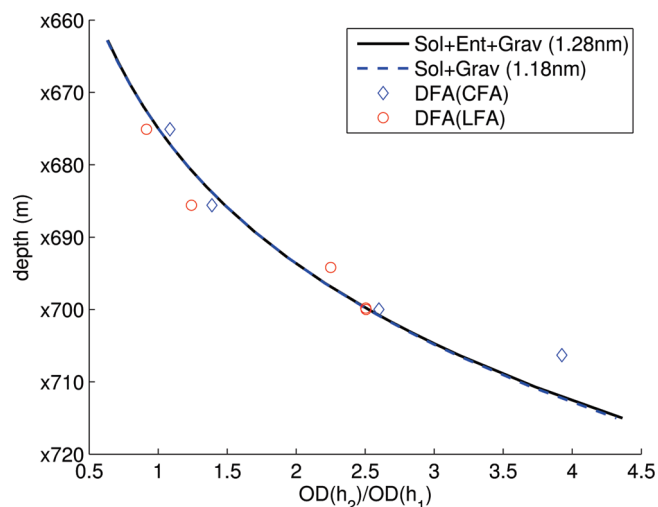
**Figure 6.** Coloration variation (due to colored resins) in a condensate oil column as measured by DFA.

**Table 1. Values of the Gravity, Solubility, and Entropy Terms (Norway)**

| depth (m) | Grav/$v_a kT$ (nm$^{-3}$) | Sol/$v_a kT$ (nm$^{-3}$) | Ent/$v_a kT$ (nm$^{-3}$) |
|---|---|---|---|
| ×675 | −0.000 | −0.001 | 0.003 |
| ×680 | −0.006 | −0.215 | 0.050 |
| ×685 | −0.011 | −0.427 | 0.098 |
| ×690 | −0.016 | −0.638 | 0.146 |
| ×695 | −0.022 | −0.847 | 0.193 |
| ×700 | −0.027 | −1.055 | 0.239 |
| ×705 | −0.032 | −1.262 | 0.284 |

**Table 2. Values of the Gravity, Solubility, and Entropy Terms (Tahiti)**

| depth (m) | Grav/$v_a kT$ (nm$^{-3}$) | Sol/$v_a kT$ (nm$^{-3}$) | Ent/$v_a kT$ (nm$^{-3}$) |
|---|---|---|---|
| ×405 | −0.000 | −0.000 | 0.000 |
| ×505 | −0.0778 | −0.0208 | 0.0414 |
| ×605 | −0.156 | −0.0409 | 0.0834 |
| ×705 | −0.234 | −0.0598 | 0.125 |
| ×805 | −0.312 | −0.0778 | 0.167 |
| ×905 | −0.389 | −0.0946 | 0.209 |
| ×005 | −0.465 | −0.110 | 0.250 |
| ×105 | −0.541 | −0.125 | 0.292 |
| ×205 | −0.616 | −0.139 | 0.333 |

Next, we use all three terms, gravity, solubility, and entropy, to analyze the observed heavy-end gradients in the oil column. Figure 6 shows the measured coloration profile in the condensate oil column, as measured by DFA. In addition, fits to the theory are also shown. The solid line shows the fit using the gravity, solubility, and entropy terms, while the dashed line shows the fits with just the gravity and solubility terms.

For the fits in Figure 6, the size of the colored resin molecule is the only fitting parameter. With the value of 21.85 MPa$^{1/2}$ for the solubility parameter, we find that the (hard-sphere) diameter of the asphaltene particles is 1.28 nm, which is comparable to known measured diameters of colored resin molecules.[21] The large GOR gradient (cf. Figure 4) creates a large gradient in the solubility parameter of the condensate. In turn, this creates and dominates the large gradient of the colored resins. If the entropy term is neglected, then the diameter of colored resin size is reduced slightly ($d = 1.18$ nm). Essentially, entropy acts to create a more homogeneous column. Thus, a somewhat larger gravity term is needed to produce the same gradient. For this condensate, ignoring the large solubility term would give an unphysical size of 4 nm for the resin molecule. This is in contrast to the Tahiti case, where including the entropy and solubility terms changed the diameter by only a small amount.

As noted above, the compositional grading due to gravitational effects is much smaller than that due to the solubility changes for the Norway case study. To compare the relative sizes of the gravity, entropy, and solubility terms in eqs 13−16, we first note that the volume of the asphaltene particle, $v_a$, only occurs in these terms as an overall multiplicative factor. Thus, in Table 1, we show the sizes of Grav/$v_a kT$, Ent/$v_a kT$, and Sol/$v_a kT$ as a function of the height, where we have again taken $\delta_a$ to be 21.85 MPa$^{1/2}$ and the temperature is $T = 135$ °C. The values given in Table 1 depend on the solubility parameters of both the asphaltene and maltene, the density of both the asphaltene and maltene, and the volume of only the maltene. As can be seen in the table, the gravity term is considerably smaller than the solubility term, by a factor of about 40. Both terms are negative, so they are both responsible for a greater concentration of asphaltenes deeper in the well. The entropy term is only about a factor of 4 less than the solubility term, and it has the opposite sign. Thus, the entropy term has considerably more effect on the calculated size of the

asphaltene particle than the gravity term does, and it tends to lessen the effect on compositional grading due to the solubility and gravity terms. This latter effect is not surprising because the entropy is larger when the large and small molecules are well mixed.

This can be contrasted with a similar table for the Tahiti case. The values for Grav/$v_a kT$, Ent/$v_a kT$, and Sol/$v_a kT$ for the Tahiti well, shown in Table 2, were found in a manner similar to those for the Norway well. In this case, Sol/Grav is about 0.25, which is significantly less than the factor of 40 found for the condensate. Thus, the solubility term is small, but it is still a quarter of the gravity term, which is why including it did have a small effect on the diameter. Similarly, Ent/Grav is about −0.54, so the entropy term is just over half the gravity term. Because the entropy and solubility terms have opposite signs, they partially cancel each other out. However, as was seen above, including both of them still has some effect on the diameter. In comparing Table 1 with Table 2, we note that, for the Norway case, Grav/$v_a kT$ changes by about $1.0 \times 10^{-3}$ nm$^{-3}$ per meter, while for the Tahiti case, Grav/$v_a kT$ changes by about $0.8 \times 10^{-3}$ nm$^{-3}$. Thus, over the same depth, the gravity terms divided by the asphaltene volume for the Norway case and the Tahiti case are very similar. However, the full effect of the gravity term is obtained by multiplying this value by the volume of the asphaltene particle, which is noticeably larger for the Tahiti case than for the Norway case. In addition, because the Tahiti column is much longer, the gravity term produces significant asphaltene gradients over its entire length. On the other hand, for the solubility term, Sol/$v_a kT$ changes by about 0.04 and $0.2 \times 10^{-3}$ nm$^{-3}$ per meter for the Norway and Tahiti cases, respectively. The difference between these two terms is so great that, even when they are multiplied by their respective $v_a$ and looked at over the entire column, the solubility effect in the Norway case is much greater than the solubility effect in the Tahiti case.

### Dependence of the Asphaltene Volume on the Asphaltene Solubility Parameter

Finally, in this last section, we consider how the calculated size of the asphaltene particle depends on the size of the solubility parameter. The solubility parameter of asphaltenes can vary somewhat, depending on the type of asphaltene. In
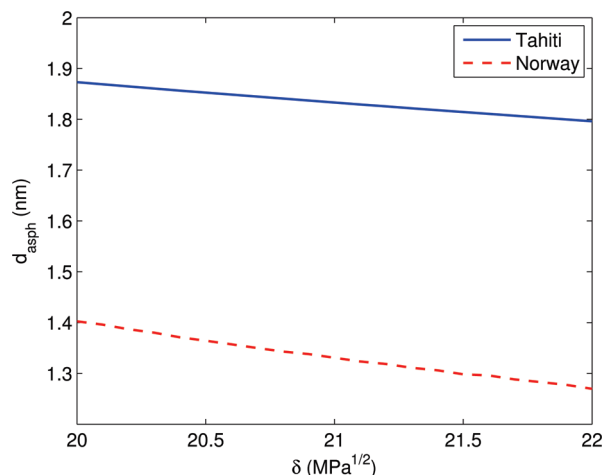
**Figure 7.** Asphaltene diameter versus asphaltene solubility parameter.

addition, it also varies with temperature. For example, in ref 18, the slight decrease in the solubility parameter as the temperature is increased was found to be described by

$$\delta_a(T) = \delta_a(T_0)\,[1 - 1.07 \times 10^{-3}(T - T_0)] \qquad (19)$$

where $T_0$ is the reference temperature for the asphaltene solubility parameter. On the other hand, the effect of the pressure on the asphaltene solubility parameter is usually ignored because the asphaltenes are incompressible.

As the asphaltene solubility parameter is varied, either due to different reservoir temperatures or due to different types of asphaltene, the fitted diameters found in the previous section will be affected. To see how the asphaltene diameters depend on the solubility parameter, we have looked at a range of asphaltene solubility parameters. For each solubility parameter, we found the volume that gives a good fit to the data. We have done this for the case where there are entropy, solubility, and gravity effects, for both the Norway and Tahiti cases. The results are shown in Figure 7. In this figure, we show the asphaltene diameters $d_a$ that we obtained as a function of solubility parameter $\delta_a$. As can be seen in the plot, as the solubility parameter is increased, the calculated value of

$d_a$ decreases. The effect is greater for the Norway data, which is to be expected because this is the case where the solubility effect plays a much greater role. (In this case, the solubility parameter of the colored resins could be as low as about 18 MPa$^{1/2}$. This would give a value for the diameter closer to 1.6 nm, which is somewhat higher than expected. However, a more sophisticated anaylsis, which uses a distribution of sizes that is allowed to vary as a function of the height, again gives an average diameter of about 1.3 nm for the colored component of the oil, with a solubility parameter of about 18 MPa$^{1/2}$. This approach will be described in ref 22.)

### Conclusions

New asphaltene science, coupled with new technology, is providing new methods for treating some of the largest technical uncertainties in the oil business today, such as reservoir connectivity. To proceed with these methods, new theoretical treatments are mandated. Here, we show that the governing factors that control equilibrium distributions of asphaltenes in reservoir oil columns are gravity, solubility, and entropy. The gravity term is heavily dependent on the form of the dispersion of the asphaltene (or heavy resin): molecules, nanoaggregates, or nanoaggregate clusters. The solubility term is heavily dependent on the GOR gradient. Both gravity and the solubility term tend to increase asphaltene gradients, while entropy tends to decrease these gradients. For large GOR gradients, the solubility term dominates and determines the asphaltene distribution. For small GOR gradients, the gravity term can dominate. Oil-field case studies are shown, exhibiting each circumstance. Moreover, for these two case studies, the asphaltene distributions are consistent with an equilibrium distribution, implying reservoir connectivity. In both cases, subsequent production data proved connectivity, thus establishing the validity of the methods herein. The combination of new science and new technology within the proper theoretical formalism presents a powerful approach for addressing major concerns in the oil industry. Indeed, the rapid uptake by the industry of these novel approaches is a strong motivation to continue the scientific understanding of the asphaltenes.