Analytical Solution for Compositional Profile Driven by Gravitational Segregation and Diffusion

O. Obidi, A. H. Muggeridge, V. Vesovic*

Department of Earth Science and Engineering, Imperial College London,
London SW7 2AZ, United Kingdom

* Author to whom correspondence should be addressed (v.vesovic@imperial.ac.uk)

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Abstract

An improved analytical solution is presented, based on irreversible thermodynamics, that describes the equilibrium distribution of the components of a non-ideal fluid mixture in an 1D, hydrostatic and isothermal system. In such a system, the vertical compositional profile of the fluid at equilibrium will be determined by the interaction of gravitational and chemical potentials. The new analytical solution estimates this profile from the overall composition of the fluid. It is thus more general than the existing solution which requires a knowledge of the fluid composition at a given depth and assumes that the vertical compositional profile of this fluid is already at equilibrium. The solution is demonstrated by comparison against results obtained from previously published molecular dynamics simulations of segregation in a binary mixture and against numerical simulations of a real hydrocarbon reservoir system.
I. INTRODUCTION

A multicomponent fluid system is in a state of thermodynamic equilibrium when its Gibbs free energy is at a minimum. In the absence of an external field, such a system displays a uniform composition, temperature and pressure throughout. In the presence of an external pressure field (either imposed or resulting from gravity) a gradient in chemical potential will be established which in turn will cause a diffusive flux that can result in a non-uniform equilibrium compositional profile. Baro- or pressure diffusion can have a significant influence on the distribution of components in multi-component fluid mixtures especially for the thermodynamic systems that extend over a large domain or are near the critical point. Such non-uniform equilibrium profiles have been seen in natural systems such as oil reservoirs [1-5] and have been postulated to occur at the core-mantle boundary [6]. Baro-diffusion can be an important consideration when separating components from a mixture in a centrifuge [7], considering the impact of nitrogen diffusing into austentic stainless steel [8] and predicting the yield from thermonuclear devices [9]. Kocherginsky [10], amongst others, investigated the impact of pressure diffusion in membrane separation, whilst Runstedtler [11] has shown that baro-diffusion can have an important impact when predicting mass transfer in a solid oxide fuel cell.

Oil and gas reservoirs are important examples of naturally occurring systems where the pressure gradient driving the diffusion is a result of gravity and where the segregation is of practical significance [1-5]. For oil reservoirs it is important to predict the influence that baro-diffusion has on the initial hydrocarbon component distribution in order to be able to: (i) estimate the value of the hydrocarbon resource in the reservoir [5,12]; (ii) obtain an indication of the reservoir connectivity [13,14] and (iii) design suitable recovery schemes, especially if the compositional gradient results in changing phase behaviour with depth [15]. Identifying poor connectivity early on in a field development ensures that wells can be optimally placed, thus maximizing the recovery. Oil recovery schemes that involve the injection of another fluid require that the injected fluid is miscible with the oil. As the injected fluid changes the pressure distribution in the reservoir a careful consideration of the vertical compositional gradient has to be carried out [14,16] to ensure that the requirement for miscibility is achieved at all depths. Temperature, which also increases with depth in most reservoirs, can also drive segregation of components through temperature diffusion (the Soret effect), [17-20] sometimes counteracting the gravity driven segregation. Typically, temperature has the greatest effect when there is also a horizontal temperature gradient which may alter the compositional distribution via natural convection or when the system is near its critical point [5,17,20-21].

Over the years a number of models [5,16,19-27 and references therein] have been developed to predict the distribution of components within the oil reservoirs. Most models have focussed on predicting the vertical distribution of components, although some have also examined the 3D distribution [17,18,27]. The level of sophistication varies from models assuming an isothermal reservoir to those considering thermal diffusion, convection, external fluxes and biochemical degradation [5,16,19-27]. The general aim is to predict how compositional profiles change over geological time-
scales, the steady-state profile and to estimate time scales to reach steady-state. Although large advances have been made [17-30], the lack of experimental thermophysical data, the incomplete characterization of geological heterogeneities, unknown boundary and initial conditions and incomplete understanding of some of the processes have led to only moderate success in predicting the observed distributions in composition, even when fully general numerical simulators are used. It is therefore useful to have range of simple analytical solutions that can be used to predict end member cases and thus bound the compositional profiles that may be expected in different circumstances, as well as to validate numerical simulations.

In this work we present a new, more general, analytical solution, based on irreversible thermodynamics, to describe the equilibrium distribution of the components of a non-ideal fluid mixture in a 1D, hydrostatic and isothermal system. In isothermal models, which are a precursor and a basic component of all the advanced models, the compositional segregation is governed by an interaction of gravity and chemical potential and it is possible to estimate the steady-state compositional profile by knowing the profile at a given reference depth [31]. The partial success of the technique has been compromised by the requirement that the reservoir needs to be at a steady state at the time of measurement. This is not always the case especially if late filling has taken place or if there are barriers to flow within the reservoir. The present solution is more general in that it only assumes that the mixture composition is known and does not require the reservoir to be at steady state nor does it invoke the ideal mixture assumption. The resulting increase in versatility indicates that it can replace the existing model, and thereby serve as a vital tool for the validation of numerical models, as well as providing a fast method for the petroleum industry to predict the steady-state compositional profile of the reservoir fluid without the requirement that the reservoir itself has reached the steady state.
II. ANALYTICAL SOLUTION

We consider a one-dimensional column of static, isothermal, multicomponent fluid subject to a gravitational field in the negative $z$ direction. In such a column, molecular diffusion will induce a compositional variation, leading to the segregation of heavier species to the bottom of the column. We are interested in predicting the equilibrium composition profiles for each species.

At equilibrium, the variation of the chemical potential of each species $i$, $\mu_i$, is governed by [32,33],

$$
\frac{d\mu_i}{dz} = -M_i g,
$$

(1)

while the pressure variation with depth is given by hydrostatic equilibrium,

$$
\frac{dp}{dz} = -\rho g,
$$

(2)

where $M_i$ is the molecular weight, $g$ is the acceleration due to gravity and $\rho$ is the molar density of the fluid. The variation of chemical potential as a function of temperature, pressure and composition can be expressed thermodynamically as,

$$
d\mu_i = v_i dp + \sum_{j=1}^{n-1} \frac{\partial \mu_i}{\partial x_j} dx_j,
$$

(3)

where $v_i$ is the molar volume and the $x_i$ is the mole fraction of component $i$. If we assume that the multi-component mixture is ideal then the chemical potential of species $i$ in the mixture, $\mu_i$, can be related to the chemical potential of the same species in its pure form, $\mu_i^o$ using

$$
\mu_i = \mu_i^o + RT \ln x_i
$$

(4)

where $R$ is the universal gas constant and $T$ is the temperature. By making use of Eq. (4) to evaluate the derivatives, $\frac{\partial \mu_i}{\partial x_j}$, in Eq. (3) and combining the resulting expression with Eqs. (1-2) we obtain,

$$
\frac{RT \ dx_i}{x_i \ dz} = (\rho v_i - M_i) g
$$

(5)

Equation (5) governs the compositional variation of each species, expressed in terms of mole fraction $x_i$, in a one-dimensional column [25,29,31].
Provided the density variation over the column height is small (which is usually the case, see for example references [25,29,31]) Eq. (5) can be integrated analytically, as long as the composition at a reference point is known. For a column of height $L$ ($-L/2 \leq z \leq L/2$), using the bottom of the column, $z = -L/2$, as the reference point, one obtains,

$$x_i(z) = x_i(-L/2) \exp[\theta_i(z + L/2)]$$

(6)

where $\theta_i$ is defined as

$$\theta_i \equiv \frac{\rho_{av}v_i - M_i}{RT}g$$

(7)

and $\rho_{av}$ is the average density of the mixture within the domain. Thus, the steady state mole fraction of each component at any point along the vertical height of the column can be calculated.

This solution and its variants including the thermal diffusion component have been used by various authors to validate both their experimental and numerical work. For instance, Galliero and Montel [29] used a simplified version of Eq. (6) to validate their molecular dynamics simulations for simple Lennard-Jones mixtures under the influence of gravity. More recently, Touzet et al. [21] used the solution given by Eq. (6) to validate their isothermal microgravity experiments and molecular dynamic simulations on a synthetic ternary mixture of methane, $n$-butane and $n$-dodecane at typical petroleum reservoir conditions.

Although useful, the applicability of Eq. (6) to practical problems is to a certain extent limited by the need to have a prior knowledge of mole fraction of each component at one depth at the steady state. For systems that are not at steady state such a measurement is not available and a steady state then needs to be deduced first by some other means. A further problem in natural systems, such as hydrocarbon reservoirs, occurs even if the system is at steady state because uncertainty in the compositional measurement due to either sampling issues or in establishing a correct reference depth will tend to propagate and can result in erroneous compositional profiles.

In this work we extend the domain of Eq. (6) by removing the need to have the measurements of the mole fraction of each species at a reference point. Instead we assume that the overall composition is known or can be estimated. The measurement of the overall composition does not require the assumption of steady state as the mass is conserved at all times providing there are no sources or sinks within the reservoir. If we define the overall mole-fraction of component $i$, $\bar{x}_i$, as,

$$\bar{x}_i \equiv \frac{\int_{-L/2}^{L/2} p x_i \, dz}{\sum_{j=1}^{n} \left( \int_{-L/2}^{L/2} p x_j \, dz \right)} = \frac{1}{L} \int_{-L/2}^{L/2} x_i \, dz$$

(8)
where the second part of Eq. (8) was obtained by invoking the assumption of small density changes along the column, we can perform the integration and by eliminating \( x_{i(-L/2)} \) by means of Eq. (6) we obtain,

\[
x_{i(z)} = L \bar{x}_i \theta_i \frac{\exp[\theta_i(\xi + L/2)]}{\exp(\theta_iL) - 1}
\]

(9)

The above expression forms the basis of a new steady state solution for an ideal mixture under the influence of gravity and molecular diffusion in a closed system. We will now make use of it to explore the extent of segregation of each species, a measure that is, for a petroleum engineer, equally informative and useful as the actual compositional profile. Traditionally, the vertical segregation is defined as the difference in the mole fraction between the top and the bottom of the column.

\[
S_i \equiv x_{i(L/2)} - x_{i(-L/2)}
\]

(10)

It is easy to show, by means of Eq. (9), that the vertical segregation is given by a simple expression,

\[
S_i = L \theta_i \bar{x}_i
\]

(11)

The above expression shows that the segregation in an isothermal system under the influence of gravity and molecular diffusion, is directly proportional to the thickness of the system, \( L \), and the parameter \( \theta_i \). It is however not directly proportional to the overall mole fraction, \( \bar{x}_i \), of species \( i \) as the average density \( \rho_{av} \), that enters the parameter \( \theta_i \), is also a function of the overall composition. It is interesting to note that the use of the compositional profile based on knowing the composition at a reference depth (see Eq. (6)) results in a less amenable equation.

Equation (11) was derived under the assumption that the density variation is small. For very large values of \( L \), corresponding to large segregation, the resulting density variation will lead to a breakdown of this assumption. Assuming complete segregation of the component \( i \) puts a limit on the maximum value of \( L \), namely \( L_{\text{max}} = 1/\theta_i \bar{x}_i \). For values of \( L \) larger than \( L_{\text{max}} \), Eqs. (9) and (11) will give unphysical results. Hence, the derived solution is not suitable for the estimation of the compositional profile if two separate phases are present in the column.

It is relatively straightforward to extend the derivation of the segregation, Eq. (11), to a non-ideal mixture by including the thermodynamic factor \([\Gamma]\) in the driving force for the molecular diffusion flux. This results in the compositional variation of each species being governed by a set of coupled differential equations

\[
[\Gamma] \frac{d}{dz} \ln(\bar{x}) = \vec{\theta}
\]

(12)
Providing elements in the thermodynamic factor, \([\Gamma]\), are approximately constant, within the range of composition one is interested in, we can derive the expression for the segregation in a real mixture as follows,

\[
S_i \approx L \bar{x}_i \sum_{j=1}^{n-1} (\Gamma_{ij}^{-1} \theta_j)
\]  

(13)

Eq. (13) reduces to Eq. (11) if we assume that the mixture is ideal, as the inverse of the thermodynamic factor is an identity matrix.

In principle one can use the measurements of the compositional profile at any time to determine the overall composition. If one assumes that the system of interest formed with a uniform distribution of species, one can use this initial composition, \(x_i^0\), instead of the overall composition in Eqs. (9) and (11). In which case Eq. (9) reduces to the one derived first by Besong [34].
III. TEST OF NEW ANALYTICAL SOLUTION

The analytical solution presented in the previous section was derived by assuming that the variation of density as a result of segregation along the column thickness is negligible. In order to test this assumption and also the applicability of the analytical steady state solution, derived for an ideal mixture under the influence of gravity and molecular diffusion, we first compare the predictions of our proposed analytical solution against results obtained by molecular dynamic simulations carried out by Galliero and Montel [29]. They studied the transient and the steady state solutions for gravitational segregation in simple fluids, under greatly enhanced gravitational forces, in order to investigate extreme segregation and non-uniform density distributions. The model fluids used in their MD simulations were mixtures composed of spheres interacting through the Lennard-Jones (LJ) potential. The species differed only in their mass and hence one can make the simplifying assumption that the molar volume of each species is the same. The simulations were carried out in terms of reduced units, where the energy and length scaling parameters correspond to the well-depth of the LJ potential, \(\epsilon\), and the distance at which the LJ potential is equal to zero, \(\sigma\), respectively.

We computed the steady state compositional profile, Eq. (9), for the equimolar, binary mixture consisting of methane and what reference [29] termed super-methane. The super methane species differs from methane only in its molecular weight, which was assumed to be ten times that of methane. The simulations were performed for a column of dimensionless thickness \(\zeta^* = 19.495\), a reduced temperature of \(T^* = 2.0\) and an overall reduced density of \(\rho^* = 0.6\) [29]. In order to convert from the reduced units we used methane LJ parameters of \(\sigma = 0.3704\) nm, \(\epsilon/k_B = 145.85\) K and \(M_w = 16.04\) g.mol\(^{-1}\) [35]. The simulations were performed at four values of \(g^*\) \((g^* = \sum_{i=1}^{n} x_i M_i \sigma / \epsilon)\), where \(g^*\) is the acceleration due to gravity, ranging from \(g^* = 0.02\) to \(g^* = 0.32\). The reduced gravity parameters used in the MD simulation of the methane-super methane mixture correspond to a wide range of column thicknesses varying from 546 m \((g^* = 0.02)\) to 8741 m \((g^* = 0.32)\). The largest column thickness exceeds the \(L_{\text{max}}\) value for this system \((L_{\text{max}} = 6850\) m\) and hence we performed the comparisons only for the three lower values of \(g^*\).

Fig. 1 shows the compositional profiles of methane obtained for \(g^* = 0.08\) and \(g^* = 0.16\), as a way of example. As expected the top of the column exhibits methane enrichment which becomes more pronounced as \(g^*\) increases. The agreement between the profiles obtained using our new analytical expression, Eq. (9), and the MD simulations [29] is very good, as illustrated in Fig. 2 which displays the relative deviation in mole fraction. The deviations between the analytical solution and the MD simulation do increase with an increase in \(g^*\), as does the variation in the mixture density with depth, but only at the highest \(g^*\) \((g^* = 0.16)\) does the maximum relative deviation in mole fraction approach 0.08. For the two lower values of \(g^*\) agreement to within 0.01 is obtained.
FIG. 1. Steady-state molar fraction profiles of the light component ($x_1$) in a binary equimolar isotopic mixture ($M_2/M_1 = 10$) at $T^* = 2$ and $\rho^* = 0.6$ under various gravity fields: (a) $g^* = 0.08$; (b) $g^* = 0.16$; (●) MD simulations [29]; (-- --) the analytical solution given by Eq. (9).

FIG. 2. Relative deviation, $\Delta = x_{\text{analytical}} - x_{\text{MD}}$, of the steady state composition of the light component of our new analytical solution from the MD simulations carried by Galliero and Montel [29]: (▲) $g^* = 0.16$; (●) $g^* = 0.08$ and (x) $g^* = 0.02$.

We have made use of the simulated compositional profiles to calculate the density profiles, noting that the reduced density of $\rho^* = 0.6$, at which the simulations were performed [29], corresponds to an overall mass density of 1730 kg/m³. Table 1 summarizes the segregation, $S$, and the density difference between the top and the bottom of the column for each case.
TABLE 1: Comparison between analytical and Molecular Dynamics results [29]

<table>
<thead>
<tr>
<th>$g^*$</th>
<th>Corresponding &quot;real&quot; height of hydrocarbon column (m)</th>
<th>Density difference between top and bottom of column (kg/m$^3$)</th>
<th>Segregation (Analytic)</th>
<th>Segregation (MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>546</td>
<td>220</td>
<td>0.080</td>
<td>0.078</td>
</tr>
<tr>
<td>0.08</td>
<td>2185</td>
<td>865</td>
<td>0.319</td>
<td>0.306</td>
</tr>
<tr>
<td>0.16</td>
<td>4370</td>
<td>1600</td>
<td>0.638</td>
<td>0.565</td>
</tr>
<tr>
<td>0.32</td>
<td>8741</td>
<td>2400</td>
<td>-</td>
<td>0.849</td>
</tr>
</tbody>
</table>

The generally good agreement indicates that our new solution can predict the steady state compositional profile accurately, even if the density difference is large ($g^*$=0.08). For density differences that approach the overall mixture density ($g^*$=0.16), the predicted segregation is within 0.07 of the simulated one. However, for unrealistically large density differences that imply the presence of two phases ($g^*$=0.32), the solution yields unphysical results and should not be used. The original analytical solution, Eq. (6), will produce similar profiles to the new analytical solution, as it also assumes that the mixture density does not vary with depth. The position of these profiles will be determined by the mole fraction chosen as the reference point. Fig 1b indicates that the simulation data do not lie on a smooth curve, as a result of the relatively high uncertainty [29]. Hence, the composition profiles obtained by Eq (6) would lie within a narrow band centered on the current analytical solution, Eq (9). The width of the band would be determined by the uncertainty of the data. This would also be the case if the real measured data is used to determine the reference point, as such data, at least in the petroleum industry, can have rather large uncertainty. So, in this sense the current analytical solution offers a more reliable and in most cases a more accurate compositional profile.

We also compared the predictions of the analytical solution with those from a full transient solution to examine the impact of initial conditions on segregation timescales in natural systems. The steady state solution was obtained by numerically solving the governing differential equation. For component $A$ in a binary mixture this is,

$$\frac{\partial c_A}{\partial t} = -\frac{\partial}{\partial z} \left( \rho D_{AB} \frac{\partial x_A}{\partial z} \right) - \frac{x_A M_A D_{AB}}{RT} \rho g \tag{14}$$

where $c_A$ is the molar concentration of species A and $D_{AB}$ is the binary diffusion coefficient. In order to numerically solve Eq. (14), we used an explicit operator-splitting, finite-difference scheme in which at each time-step we solve first for the diffusion and then for pressure flux [36]. The time step was determined by stability criteria, while approximately 100 grid points in the x-direction where sufficient
for most simulations. For the purposes of this work it was assumed that the steady state is reached when the mole fractions of all components change by less than $1\times10^{-8}$ between two successive iterations at each grid point. We opted to use a binary, ideal fluid formed of methane and n-decane as this mixture shows significant segregation and is a good proxy for an oil composed of a light and a heavy pseudo component. Furthermore, the thermophysical properties of the mixture have been well studied and are readily available. We solved the diffusional-gravitational equation, Eq. (14), using two initial conditions, (i) a uniform composition within the column and (ii) a segregated column where the pure methane and pure decane occupy the upper and lower part of the reservoir respectively. The idea is to show that both initial conditions would give the same steady state, as long as the model is initialized with the same number of moles of each species.

The thickness of the hypothetical reservoir was set to be 1000 m. This value is rather larger than a rock formation thickness in a real reservoir, but it is reasonable if we consider the difference in depth between the bottom and the top of the reservoir. It was chosen to be sufficiently large that it would produce a significant segregation and thus critically test the analytical solution. The temperature and pressure were chosen as $T = 393$ K and $P = 75$ MPa. The mixture is a single-phase fluid at these conditions and far away from the critical point. The relevant thermodynamic properties were obtained from REFPROP 8.0 [37]. The diffusion coefficient in Eq. (14) was estimated using the correlation presented in Ref [38], its magnitude only governs the approach to steady state, but not the values at the steady state itself. As a measure of the non-ideality of the methane/n-decane mixture we compared the thermodynamic factor, $\Gamma$, obtained from the Peng-Robinson EOS to that of an ideal mixture. $\Gamma$ is a scalar, as this is a binary mixture, and in this case its variation, with composition, from unity never exceeds 3%. This near unity of $\Gamma$ indicates that treating the mixture as ideal is a reasonable approximation.

We performed numerical simulations using several different overall compositions, but for illustrative purposes we present only the results using the overall molar composition of 40% of methane and 60% of n-decane. The numerical solution was obtained by initializing the reservoir using two limiting compositions, as discussed above. The first case was a uniform binary mixture of the above composition with an initial perturbation in the methane compositional gradient of 0.0002/m. This perturbation was added to the system in order to act as a driving force for the diffusion process. Secondly, we simulated a fully segregated system with the methane occupying about 17% of the total volume of the reservoir in order for the reservoir to have an overall mole fraction of methane of 0.4. As expected, both initial compositions converged to identical steady-state profiles. Not surprisingly the uniform initial composition reached steady state an order of magnitude quicker than the fully segregated initial composition. It also required an order of magnitude smaller number of grid blocks to achieve a converged result. Fig. 3 shows the steady state composition profile of methane obtained from both the numerical and analytical solutions, Eq. (9). The agreement between the numerical and analytical solutions was better than $1.5\times10^{-5}$ in mole fraction. The solution confirms that the top of the
reservoir is enriched with methane, while the heavier component (n-decane) segregates at the bottom of the reservoir.

![Graph showing methane composition profile.](image)

**FIG. 3.** Comparison of the steady state methane composition profile produced by numerical simulation (○) and the analytical solution (solid line).

The segregation factor for methane calculated by means of Eq. (11) of 0.02864 compares well with that of 0.02858 obtained from the numerical solution.

Although we chose a rather extreme example in terms of the density difference between the light and heavy components, the density profile is a rather weak function of column height. The difference at steady state between the density at the top and the bottom of reservoir is approximately 8.0 kg.m\(^{-3}\). This represents only a 1.1% variation in density across the reservoir. This further substantiates our assumption that the density variation over the column height is small. It is worth pointing out that the simulation was performed at constant pressure and for real reservoirs the pressure will increase with depth. Although for oil reservoirs this will have a marginal effect on density, for reservoirs containing highly compressible fluids this will induce an additional variation in density.
IV. NATURAL GAS FIELD EXAMPLE: LABARGE

In this section we use the analytical model to analyze the segregation observed in a real natural hydrocarbon reservoir affected by baro-diffusion: the LaBarge gas field in the Greater Green River Basin in Wyoming. The composition of the gas in the field is unusual in that CO₂ and CH₄ are the main constituents. The CO₂ molar composition in the gas varies with depth increasing from 66% at the crest of the structure to 90% at the gas water contact (GWC), while the molar composition of CH₄ decreases from 23% at the crest to 5% at the GWC. This indicates a significant segregation of these two components. Previous work [39-42] has suggested that the reservoir was simultaneously charged with two fluids of different compositions about 50 million years ago. The first fluid was almost pure CO₂ (90%) while the second one was CH₄ rich with a significant amount of CO₂ (40%). Subsequent mixing via gravity and molecular diffusion has led to the current compositional profile which has not yet reached steady-state.

In order to investigate and verify whether the new analytical solution can be used to predict the steady state composition in the LaBarge field, we solved Eq. (14) numerically for a binary mixture formed of the two major species, CH₄ and CO₂, in a one-dimensional vertical system, 1200 m thick. This corresponds to the height difference between the bottom and top of the reservoir. We integrated over the observed compositional profile of CH₄ to find the overall CH₄ mole fraction (\(x_{CH₄} = 0.147\)) in the reservoir. We then assumed that the remainder of the reservoir gas was composed entirely of CO₂. This overall composition was used to initialize the numerical model. The resulting system was simulated using the measured initial pressure and temperature of 44.8 MPa and 410 K, respectively, while the thermophysical properties were obtained from references [37,38].

Fig. 4 shows the measured variation in the methane composition as a function of increasing depth with the profiles predicted by the analytical solution and numerical simulation after 620 million years. We observe that the transient compositional profile, at this time, obtained by the numerical simulation, matches the measured CH₄ profile. This profile equates to a segregation of \(S = 0.184\). The calculated steady state profile, also illustrated in Fig 4, indicates that the final segregation would be only \(S = 0.0177\), thus confirming that the current fluid compositional distribution in the LaBarge field is far from the steady-state. The numerical solution suggests that it would take a further 4300 million years for the fluids to reach steady state by baro-diffusion. We note that the timescales, measured in millions of years, are estimated based on only considering diffusional-gravitational fluxes in 1D and are not expected to be realistic for the real LaBarge field. The difference between the analytical solution and the numerical simulation results at steady state never exceeds 0.0005 in mole fraction, while the segregation at steady state obtained from the analytical solution of \(S = 0.0172\) compares well with \(S = 0.0177\) obtained from the numerical model.

These results indicate that the proposed analytical solution can be used to determine not only the steady state compositional profile, but also to confirm whether or not the observed compositional...
segregation has reached the steady state. In contrast the currently available solution [31], which uses
the composition measured in the field at a particular depth, will give the wrong steady state profile if
the field is not yet at steady state. This is also illustrated in Fig. 4 where we show, for the Labarge
field, the two different (and wrong) steady state profiles that are calculated by the currently available
method using two different measured compositions at different reference depths. Deploying these
predictions to estimate the value of fluids in reservoir could result in significant errors.

FIG. 4. The depth profile of mole fraction of methane in LaBarge compared with the calculations: (●) measured
values [40]; (- - - -) profile obtained by numerical simulation after 620 Myears; (_____) analytical solution, Eq. (9);
(—·—) traditional analytical solution [31] using a reference depth of 1824 m; (—·—) traditional analytical
solution [31] using a reference depth of 2321 m.
V. CONCLUSIONS

A new analytical solution has been presented that describes the equilibrium distribution of the components of a non-ideal fluid mixture in a 1D, hydrostatic and isothermal system. This solution is more general than that presented in references [25,29,31] as: (i) it can be used to calculate the steady state profile of components from the overall composition of the fluid of interest; (ii) it is not limited to ideal fluid mixtures and (iii) it does not require the fluid system to be at steady state, unlike the existing solution [25,29,31] that will predict the wrong steady state profile if the fluid system is not already at steady state at the time of measurement.

The new solution was tested by comparison with numerical solutions obtained from molecular dynamics simulations [29] and real hydrocarbon reservoir fluid systems. It should prove a useful tool, particularly for the petroleum industry, to estimate the expected steady-state compositional profile of fluids. The steady state composition predicted at a particular depth can then be compared with the composition measured at that depth. If the compositions are different then this is an indication that the reservoir is not at steady state, which would imply that either there is poor vertical communication for flow or that the reservoir filled more recently than expected. This in turn can affect the proposed development plan for the reservoir. Of course the proposed analytical solution does require an estimate of the overall composition which would need more measurements of composition at different depths or using the overall produced composition if the reservoir is already under production. In either case if such an estimate is available the current solution will generate a more reliable and in most cases a more accurate compositional profile than the traditional approach. The solution also provides another means for validating numerical tools developed for the investigation of baro-diffusion in complex fluid systems.
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