



## A new approach to thermal segregation in petroleum reservoirs: Algorithm and case studies

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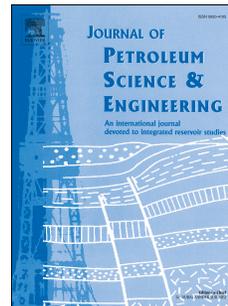
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## Credit Author Statement

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G. Galliero: Software, Resources, Writing – Review and Editing.

W. Yan: Supervision, Methodology, Visualisation, Writing – Review and Editing.

A.A. Shapiro: Supervision, Project Administration, Software, Writing – Review and Editing.

# A new approach to thermal segregation in petroleum reservoirs: Algorithm and case studies

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## Abstract

In many petroleum reservoirs, the fluid properties vary through the reservoir thickness. Variation of the composition, i.e. compositional grading, can affect reserve estimation, production and enhanced oil recovery strategies. Apart from gravity, the geothermal gradient may also contribute to the fluid distribution. Thermodiffusion is the governing phenomenon determining the contribution of the geothermal gradient. The non-equilibrium thermodynamics models are applied for the calculation of the compositional gradients under the varying temperature.

In order to determine the variations in pressure and composition with depth and to be able to indicate if/where a gas-oil contact exists, we have developed a model based on the principles of irreversible thermodynamics, within the approach to thermodiffusion in porous media proposed by Montel et al. (2019). Based on the relationships where pressure, chemical potentials, and thermal gradient are linked, the distribution of hydrocarbons in a petroleum reservoir is described. A computational algorithm accounting for non-ideality of the mixture, characterization, and phase transitions has been developed. The model and the computational procedure have been validated by comparison with the case studies reported in the literature for a North Sea reservoir, and with sample component distributions produced by application of molecular dynamics simulations. It has been shown that the model is capable of predicting the fluid distributions with depth with no or a minimum of adjustable parameters. The thermal gradient modifies the predicted fluid distributions making them closer to the observed data points. Depending on the mixture composition, the thermal diffusion may either enforce the effect of gravity or counteract it.

## 1. Introduction

The properties of oil and gas in petroleum reservoirs vary in horizontal and vertical direction. Variation of the reservoir pressure and temperature is accompanied by variation of the composition of the hydrocarbon mixtures. Proper understanding of this variation is of great importance in field development planning.

Numerous factors can influence the change in the composition of reservoir fluids. Hydrocarbon migration, natural convection, water aquifer, biodegradation, and reservoir compartmentalization are among these factors (Nikpoor et al., 2016). The gravity force, and the corresponding pressure variation

with depth, is the basic force forming the fluid distribution. The heat flux from the Earth interacts with the gravity force, creating the so-called geothermal gradient. While the gravity moves heavier components down into the reservoir, action of the thermal gradient is more controversial (Sage and Lacey, 1939; A. M. Schulte, 1980; Whitson and Belery, 1994): It may both enforce and dump the segregation. The thermal forces can cause the phenomenon of thermal diffusion, or the Soret effect, leading to a compositional gradient, both vertically and horizontally (Dougherty and Drickamer, 1955; Montel et al., 1989; Montel and Gouel, 1995).

The effect of gravity on the compositional variation with depth in hydrocarbon reservoirs was studied by a number of authors (Montel and Gouel, 1995; A M Schulte, 1980; Wheaton, 1991; Høier and Whitson, 2001; Lee, 1989). The thermal effects have also been studied. The non-equilibrium thermodynamic models and different expressions for the thermal diffusion were used for the calculation of the compositional gradients. This procedure avoids non-physical compositional gradients and gives valuable information on the connectivity between the different sampling points (Espósito et al., 2017; Firoozabadi, 2016).

The key parameters for non-equilibrium reservoir modeling are thermodiffusion coefficients. Denbigh (1951) described the effect of thermal diffusion by introducing the concept of heat of transport. Afterwards, several approaches to describe the heats of transport were introduced. Rutherford and Drickamer (1954) presented an approach to evaluate the heats of transport based on a molecular model. Haase (1962) and Kempers (1989) proposed thermal diffusion relations based on the assumption that the coupling coefficients are equal to thermostatic values such as enthalpy. Dougherty and Drickamer (1955) considered thermal diffusion as a dynamic parameter in the expression that they presented for the binary mixtures. Ghorayeb and Firoozabadi (2000) proposed equations for the thermodiffusion coefficients of a multicomponent mixture, involving thermodynamic functions and a single correction multiplier. They analyzed the general flow relations based on the non-equilibrium thermodynamics. Saghir et al. (2005) investigated the mathematical and numerical methods for the simulation of the Soret effect in both free and porous media. Rahman and Saghir (2014) reviewed all the experimental and theoretical approaches for finding the thermodiffusion coefficients where they addressed techniques and models based on non-equilibrium thermodynamics. A thorough evaluation of the different thermodiffusion models against available data, including the advanced statistical model (Shapiro, 2004) was carried out by Bagnoli et al. (2004).

A number of authors applied the non-equilibrium thermodynamics, involving thermal gradients, to describe segregation in petroleum reservoirs. Bedrikovetsky (1993) introduced the approach to solve thermogravitational segregation problems for binary and multicomponent systems. Montel and Gouel (1995) a way to estimate the compositional profile in a fluid column which could be used in numerical simulators. Shapiro and Stenby (1996) considered the state of the mixture in a two-phase capillary transition zone attached to the gas-oil contact. They showed that the mechanical equilibrium in this zone is not always possible, so that the fluxes will arise. Pedersen and Lindeloff (2003) assumed a stationary state with an influence of temperature gradient and expressed the change in component compositions in terms of thermodiffusion coefficients depending on partial molar enthalpies of the components. As the gravitational segregation is well quantified, the current practice in the petroleum industry consists of tuning the thermodiffusion parameters to match the available compositional field data (Montel et al., 2019).

A key problem in non-equilibrium modeling of segregation in petroleum reservoirs is that there is no general approach to the computation of the thermodiffusion coefficients that could be used for all non-

isothermal cases without any fitting parameters. The experimental data are scarce and involve mainly binary mixtures. The models are being tuned to the data (although not always successfully), but their predictive capacity is difficult to evaluate. Another problem is that, although the compositional gradients in reservoirs can be evaluated by reservoir data analysis, the quality of the data is often poor, and the number of representative samples from a given reservoir may be insufficient for modeling. There is a need for an efficient engineering model for segregation accounting for thermal effects with a minimum number of involved coefficients and adjustment parameters.

Montel et al. (2019) proposed a new simplified approach to thermodiffusion modeling, reducing the impact of thermodiffusion in a multicomponent mixture to a single integral parameter of thermodiffusion that may be evaluated on the basis of the equations of state for the mixture. Effect of the thermal gradient on the segregation of the mixture may thus be evaluated. Montel et al. showed that this approach is in agreement with the data of the molecular dynamics simulations of monophasic fluids under specific selection of the component model parameters.

In this paper, we have developed a numerical algorithm and built a predictive model to describe the fluid distribution in the reservoirs validating the proposed approach by Montel et al. (2019) including cases with a gas-oil contact. The mixtures are modelled by traditional cubic equations of state. The data for real reservoirs, as well as the data from molecular dynamics simulations were used for validation of the model. The results indicate that the model of Montel et al. is capable of modeling the real, as well as the simulated reservoir data with a minimum number of adjusted parameters.

## 2. The governing equations

Consider a hydrocarbon mixture in a thick petroleum reservoir under the action of the geothermal gradient. There is no mass flux, but an energy flux through the system. The composition varies with depth. This variation is described by a system of equations for chemical potentials. This system has been derived in the framework of the non-equilibrium thermodynamics (Bedrikovetsky, 1993). A simpler version of the system has been suggested by Montel et al. (2019). The theory behind this approach is explained in Appendix A. Montel et al. represent this system in the form of

$$\nabla_T \mu_i = M_i \mathbf{g} + \left( q_i - \frac{L_D}{L_i} Q \right) \nabla T \quad (i = 1, \dots, N) \quad (1)$$

Here  $\nabla_T \mu_i$  is the chemical potential derivative over depth  $z$  under fixed temperature;  $\nabla T$  is the vertical geothermal gradient, which is supposed to be known in advance. Eq. (1) is, within some changes, the thermal segregation equation, as formulated in the previous, above-cited works. The approach of Montel et al. makes it possible to express the coefficients in this equation in terms of the thermodynamic quantities, which are possible to calculate based on the existing thermodynamic models. The procedure for calculation is described below.

The values  $q_i$  and  $Q$  are defined as:

$$q_i = s_i - s_i^* = s_i^{res} = -R \ln \varphi_i - RT \frac{\partial \ln \varphi_i}{\partial T} - R \ln Z \quad (2)$$

$$Q = S^{res} = -R \ln Z - R \sum_i x_i \left( \ln \varphi_i + T \frac{\partial \ln \varphi_i}{\partial T} \right) \quad (3)$$

Here  $s_i$  is a partial molar entropy of the  $i$ th component in the mixture;  $s_i^*$  is the partial molar entropy in the reference state;  $Z$  is the compressibility factor;  $\varphi_i$  is the fugacity coefficient of the mixture. In practice, for equilibrium properties, the reference state is the ideal gas at the pressure and temperature of

a system under consideration. For transport properties, the reference state is usually the ideal gas at the same volume and temperature as the mixture considered. The reason is that the diffusion in liquids is limited by the free space available for a molecule to move. That is, the free volume is a key parameter determining the intensity of molecular motion. It is determined as a difference between the liquid volume and the covolume occupied by the molecules. That is why the reference state at the same volume and temperature is preferable over the reference state at the same pressure and temperature. For a chemical potential, the difference between the two reference states is  $RT \ln Z$ . The reader is referred to (Michelsen and Mollerup, 2007) for details.

At this point we assume that the reference entropy of the component “ $i$ ” alone diffusing in and out the elementary volume is its ideal entropy at reference temperature and volume of the fluid. We use the classical Peng-Robinson EoS with Peneloux volume translation as the equation of state (EoS) to compute all the thermodynamic quantities.

The phenomenological diffusion coefficient  $L_i$  is expressed in terms of the effective diffusion coefficients  $D_i$ , and is approximated by:

$$L_i = \frac{D_i}{R \left( 1 + x_i \frac{\partial \ln \varphi_i}{\partial x_i} \right)} \quad (4)$$

For detailed derivation, we refer to Montel et al. (2007 and 2019). The average diffusion mobility  $L_D$  is linked to the effective diffusion coefficient  $D_i$  of the components:

$$\frac{L_i}{L_D} = \sum_k \frac{x_k}{L_k} L_i \quad (5)$$

In dense fluids, the effective diffusion coefficient is about inversely proportional to the cross-section of its molecule, i.e. to the molecular volume at an exponent  $\tau$  of about 2/3 (Reid et al., 1959). The correlation of Wilke and Chang (1955) gives good results, in particular for hydrocarbon homologous series. In terms of a cubic equation of state, it may be assumed that  $D_i$  is proportional to  $b_i^{-\tau}$ , where  $b_i$  is the covolume of the component  $i$  proportional to  $b_i \propto T_{c_i}/P_{c_i}$  where  $T_{c_i}$  and  $P_{c_i}$  are the critical temperature and the critical pressure, respectively. It is worth mentioning that for practical application with an equation of state, we chose to use the covolume of the component instead of its volume at boiling point and there is room for improvement. We postulate  $D_i \sim (T_{c_i}/P_{c_i})^{-\tau}$ , and the proportionality constant is eliminated in expression (4). With this formulation, it is deduced that:

$$\frac{L_i}{L_D} = L_i \sum_k \frac{x_k}{L_k} = \frac{\left( \frac{T_{c_i}}{P_{c_i}} \right)^{-\tau}}{\left( 1 + x_i \frac{\partial \ln \varphi_i}{\partial x_i} \right)} \sum_k x_k \frac{\left( 1 + x_k \frac{\partial \ln \varphi_k}{\partial x_k} \right)}{\left( \frac{T_{c_k}}{P_{c_k}} \right)^{-\tau}} \quad (6)$$

Under known (though varying) temperature, Eq. (1) represents a system of  $N$  differential equations for  $N$  unknowns: pressure  $P(z)$  and molar fractions  $x_1(z), \dots, x_{N-1}(z)$ . It is solved by discretization by  $z$ . Assume that the pressure and composition at some reference depth  $z^{ref}$  are known. Select the step  $\Delta z = z - z^{ref}$ . Eq. (1) may then be approximated by

$$\Delta_T \mu_i = M_i \mathbf{g}(z - z^{ref}) + \left( q_i - \frac{L_D}{L_i} Q \right) \nabla T (z - z^{ref}) \quad (i = 1, \dots, N)$$

Transfer to the fugacity coefficients  $\varphi_i$  results in

$$\frac{x_i}{x_i^{ref}} = \frac{P^{ref}}{P} \frac{\varphi_i^{ref}}{\varphi_i} e^{\left( M_i \mathbf{g} + \left( q_i - \frac{L_D}{L_i} Q \right) \nabla T \right) \frac{(z - z^{ref})}{RT}} \quad (7)$$

This is an integral form of equation (1) provided that the step  $z - z^{ref}$  is small. If the segregation over a large thickness is to be calculated, several such steps are made, and each time  $z^{ref}$  is changed to a depth from the previous step (see detailed description of the algorithm below).

An additional equation is the balance

$$\sum_i x_i = 1 \quad (8)$$

The system of equations (7) (8) should be solved at each depth  $z$  in order to determine the pressure and the composition at this depth. The details of the methodology are provided below.

### 3. The algorithm

Equations (7) and (8) apply to single-phase fluids, both liquid and vapor, and can be used to determine pressure and composition throughout a fluid column at a steady state. The gradient calculations require depth, fluid composition, pressure, temperature at a specific reference condition as an input. For non-isothermal systems, the temperature gradient must also be specified. The results of the gradient calculation include composition and pressure at any user-specified depth. The algorithm of the proposed method of predicting fluid compositional grading is shown in Fig. 1.

We start from a point in the oil/gas fluid column where we have the initial composition and pressure; and go up/down with a constant depth interval and the corresponding step by temperature. At each depth, the system of equations (7), (8) is solved in order to compute pressure and composition.

The calculation step is accomplished by using the Newton-Raphson scheme that solves the system for pressure and composition at the same time. For notational convenience, we define the fugacity that has been corrected with the effect of gravity and thermal diffusion,  $\tilde{f}_i$ , as:

$$\tilde{f}_i = x_i^{ref} P^{ref} \varphi_i^{ref} e^{\left( M_i \mathbf{g} + \left( q_i - \frac{L_D}{L_i} Q \right) \nabla T \right) \frac{(z - z^{ref})}{RT}} \quad (9)$$

The fugacity at the new point where the new composition and pressure is calculated is defined as:

$$f_i = x_i P_i \varphi_i \quad (10)$$

We define the vector equation for vector  $F$  being the difference of the fugacities (9) and (10), and the variable set  $u$ , as follows:

$$F = \begin{bmatrix} f_1 - \tilde{f}_1 \\ f_2 - \tilde{f}_2 \\ \vdots \\ f_{NC} - \tilde{f}_{NC} \\ \sum_{i=1}^{NC} x_i - 1 \end{bmatrix} = 0 \quad (11)$$

$$\mathbf{u} = [x_1, x_2, \dots, x_{NC}, P]^T \quad (12)$$

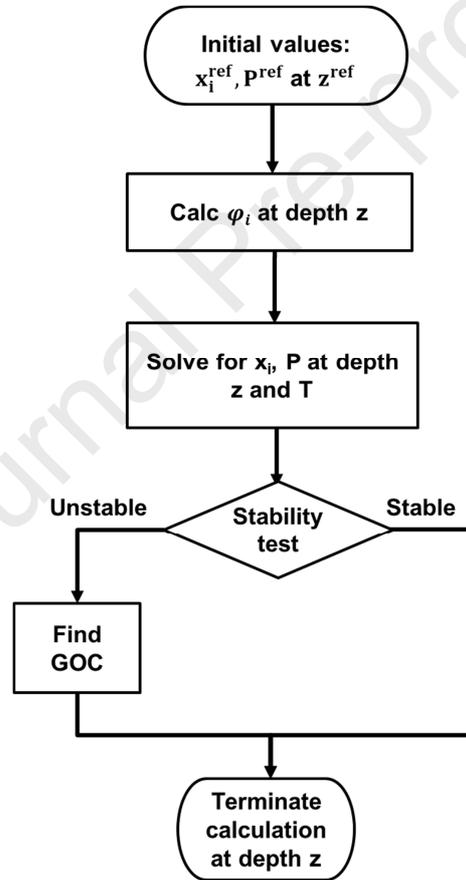
We set up the Newton-Raphson scheme to solve equation (10):

$$F'^{(k-1)}(u^{(k)} - u^{(k-1)}) = -F^{(k-1)} \quad (13)$$

Here superscript  $k$  refers to iteration step  $k$  and  $F'$  is the Jacobian  $\left\{ \frac{\partial F_i}{\partial u_j} \right\}$ .

With a suitable initial estimate, i.e.  $u^0 = [x_i^{ref}, P^{ref}]^T$ , and a suitable selection of the step  $z - z^{ref}$ , as described in the paragraph after equation (7), the Newton-Raphson procedure is convergent.

After the pressure and composition are computed, they must be checked, to see if the proposed solution is thermodynamically stable. We refer to (Michelsen and Mollerup, 2007) for details of the stability check using the tangent distance plane condition. If, at some depth, there exists at least one composition such that the tangent plane distance condition is violated, we have stepped over a gas-oil contact (GOC). After we find the GOC, we have a switch from one phase to another and continue the calculation until the composition profile for the whole column is obtained.



**Fig. 1** The algorithm for solving the equations and predicting the composition and pressure at a single depth.

## 4. Sample cases

### 4.1 Initial data

In this section, the proposed approach is applied to some cases of thermo-gravitational segregation involving reservoir fluids.

The first two cases are reservoir fluid columns, an oil and a gas condensate, in different geographic locations, which do not show compositional variation along the vertical depth.

- Case 1: an oil column of 450 m in height subjected to a geothermal gradient of 0.029 K/m. The temperature and the pressure at the reference depth (200 m) are 87.5°C and 641 bar, respectively. The lumped composition at the reference depth at the top of the column and thermodynamic properties of the pseudo components (critical pressure, temperature, acentric factor) are provided in Table 1 (where  $C_i$  is a fraction of the component co-volume).

**Table 1 Thermodynamic properties of pseudo-components used to describe the oil at the reference depth at the top of the reservoir.**

Pseudo-components	Mole %	$M$ (g/mol)	$T_c$ (K)	$P_c$ (bar)	$\omega$	$C_i$
N2C1	36.273	16.12	190.26	46.33	0.0117	-0.220
CO2	37.262	44.01	304.10	73.70	0.2389	-0.030
C2	4.795	30.07	305.43	48.84	0.0986	-0.070
C3C4	5.373	49.52	388.85	40.40	0.1653	-0.010
C5C10	6.061	99.29	572.15	30.20	0.2924	0.020
C11C19	4.948	196.19	728.15	20.60	0.4746	0.025
CN1	2.849	331.82	883.15	15.20	0.7300	0.030
CN2	2.439	569.31	1173.15	13.50	0.9790	0.035

- Case 2: a gas column of 180 m in height subjected to a geothermal gradient of 0.0334 K/m. The temperature and the pressure at the reference depth (124 m) are 134.9°C and 347.6 bar, respectively. The lumped composition at the reference depth and the critical properties are provided in Table 2.

**Table 2 Thermodynamic properties of pseudo-components used to describe the gas at the reference depth at the top of the reservoir.**

Pseudo-components	Mole %	$M$ (g/mol)	$T_c$ (K)	$P_c$ (bar)	$\omega$	$C_i$
N2C1	29.181	17.24	184.5	45.00	0.0144	-0.230
CO2	69.018	44.01	304.1	73.70	0.2389	-0.070
C2	0.920	30.07	305.4	48.84	0.0986	-0.070
C3C5	0.481	50.03	402.2	40.00	0.1660	0
C6C15	0.280	100.60	633.2	34.40	0.3550	0.012
C16C24	0.080	230.60	883.2	21.80	0.5800	0.017
C25P	0.040	400.00	983.2	15.10	0.8260	0.021

The following three cases have been studied in ref. (Pedersen and Hjermsstad, 2015). The compositional gradient was observed due to gravity segregation. We have investigated whether thermal diffusion may play an important role in the fluid distribution.

- Case 3: A North Sea petroleum reservoir of 327 m in height subjected to a geothermal gradient of 0.025 K/m. The lumped composition at the reference depth and the critical properties are provided in Table 3. The reference temperature and pressures are 366.15 K and 284 bar at 175 m (Pedersen and Hjermsstad, 2015).

**Table 3 Thermodynamic properties of components used to describe the North Sea reservoir fluid (case 3). Data from (Pedersen and Hjermsstad, 2015).**

Components	Mole %	$M$ (g/mol)	$T_c$ (K)	$P_c$ (bar)	$\omega$	$C_i$
N2	0.42	28.00	126.15	33.94	0.0400	-0.12839
CO2	0.69	44.00	304.25	73.76	0.2250	-0.09435
C1	50.04	16.00	190.65	46	0.0080	-0.22
C2	7.85	30.10	305.35	48.84	0.0980	-0.14
C3	6.77	44.10	369.75	42.46	0.1520	-0.05
iC4	1.04	58.10	408.05	36.48	0.1760	0
nC4	3.2	58.10	425.25	38	0.1930	0
iC5	1.16	72.20	460.35	33.84	0.2270	0
nC5	1.55	72.2	469.55	33.74	0.251	0
C6	1.88	86.2	507.35	29.69	0.296	-0.034
C7	3.5	96	543.05	29.6	0.338	-0.008
C8	3.75	107	564.05	27.86	0.374	0.004
C9	2.28	121	588.45	25.83	0.42	0.014
C10C11	3.26	140.1	619.05	23.76	0.483	0.02
C12C13	2.59	167.6	658.15	21.58	0.57	0.157773
C14C16	2.93	204.7	705.85	19.59	0.685	0.166154
C17C18	1.46	243.6	749.95	18.24	0.795	0.175389
C19C21	1.65	275.3	784.25	17.54	0.881	0.182112
C22C24	1.17	317	826.45	16.84	0.984	0.187264
C25C29	1.24	370.4	878.05	16.23	1.098	0.192625
C30C37	0.96	456.8	956.45	15.62	1.229	0.199598
C38C80	0.63	640.9	1120.95	14.72	1.159	0.213483

- Case 4: A North Sea petroleum reservoir of 57.5 m in height subjected to a geothermal gradient of 0.025 K/m. The lumped composition at the reference depth and the critical properties are provided in Table 4. The reference temperature and pressures are 363.15 K and 243.3 bar at 6.5 m from top (Pedersen and Hjermsstad, 2015).

**Table 4 Thermodynamic properties of components used to describe the North Sea reservoir fluid (case 4). Data from (Pedersen and Hjermsstad, 2015).**

Components	Mole %	$M$ (g/mol)	$T_c$ (K)	$P_c$ (bar)	$\omega$	$C_i$
N2	1.05	28.00	126.15	33.94	0.0400	-0.12839
CO2	0.87	44.00	304.25	73.76	0.2250	-0.09435
C1	44.54	16.00	190.65	46	0.0080	-0.22

C2	7.75	30.10	305.35	48.84	0.0980	-0.14
C3	4.61	44.10	369.75	42.46	0.1520	-0.05
iC4	0.89	58.10	408.05	36.48	0.1760	0
nC4	2.26	58.10	425.25	38	0.1930	0
iC5	0.97	72.20	460.35	33.84	0.2270	0
nC5	1.19	72.2	469.55	33.74	0.251	0
C6	1.65	86.2	507.35	29.69	0.296	-0.034
C7	2.67	96	543.05	29.6	0.338	-0.008
C8	3.25	107	564.05	27.86	0.374	0.004
C9	2.34	121	588.45	25.83	0.42	0.014
C10C11	5.07	140.1	619.05	23.76	0.483	0.02
C12C13	4.03	167.6	658.15	21.58	0.57	0.157773
C14C16	4.56	204.7	705.85	19.59	0.685	0.166154
C17C18	2.27	243.6	749.95	18.24	0.795	0.175389
C19C21	2.56	275.3	784.25	17.54	0.881	0.182112
C22C24	1.81	317	826.45	16.84	0.984	0.187264
C25C29	1.93	370.4	878.05	16.23	1.098	0.192625
C30C37	1.49	456.8	956.45	15.62	1.229	0.199598
C38C80	0.97	640.9	1120.95	14.72	1.159	0.213483

- Case 5: A North Sea petroleum reservoir of 39 m height subjected to a geothermal gradient of 0.025 K/m. The lumped composition at the reference depth and the critical properties are provided in Table 5. The reference temperature and pressures are 347.15 K and 195.6 bar at 11 m from top (Pedersen and Hjermstad, 2015).

**Table 5 Thermodynamic properties of components used to describe the North Sea reservoir fluid (case 5). Data from (Pedersen and Hjermstad, 2015).**

Components	Mole %	$M$ (g/mol)	$T_c$ (K)	$P_c$ (bar)	$\omega$	$C_i$
N2	1.57	28.00	126.15	33.94	0.0400	-0.12839
CO2	0.32	44.00	304.25	73.76	0.2250	-0.09435
C1	39.37	16.00	190.65	46	0.0080	-0.22
C2	5.69	30.10	305.35	48.84	0.0980	-0.14
C3	4.82	44.10	369.75	42.46	0.1520	-0.05
iC4	1.11	58.10	408.05	36.48	0.1760	0
nC4	3.09	58.10	425.25	38	0.1930	0
iC5	1.4	72.20	460.35	33.84	0.2270	0
nC5	1.81	72.2	469.55	33.74	0.251	0
C6	2.48	86.2	507.35	29.69	0.296	-0.034
C7	3.95	96	543.05	29.6	0.338	-0.008
C8	4.66	107	564.05	27.86	0.374	0.004
C9	3.4	121	588.45	25.83	0.42	0.014
C10C11	5.41	140.1	619.05	23.76	0.483	0.02

C12C13	4.3	167.6	658.15	21.58	0.57	0.157773
C14C16	4.86	204.7	705.85	19.59	0.685	0.166154
C17C18	2.42	243.6	749.95	18.24	0.795	0.175389
C19C21	2.73	275.3	784.25	17.54	0.881	0.182112
C22C24	1.93	317	826.45	16.84	0.984	0.187264
C25C29	2.06	370.4	878.05	16.23	1.098	0.192625
C30C37	1.59	456.8	956.45	15.62	1.229	0.199598
C38C80	1.03	640.9	1120.95	14.72	1.159	0.213483

We assume that the reservoir fluids in the column are in the stationary state achieved during a long time of reservoir formation; at least, the times during which the state is changed are much larger than the observation times. Then, the model developed above is applicable. The computations have been carried out using the gradient model described above combined with the Peng-Robinson EoS, for which the binary interaction parameters are provided in Tables 6 to 8. The properties of the pseudo-components ( $T_c$ ,  $P_c$ ,  $\omega$ ) were deduced from the constraint of iso-chemical potential at initial reservoir conditions (Montel and Gouel, 1984): the EoS parameters of the pseudo-components must be the same as the values obtained by the EoS mixing rules applied to initial reservoir fluid compositions (Montel et al., 2019).

**Table 6 Values of non-zero binary interaction parameters ( $k_{ij}$ ) in case 1**

N2C1	N2C1	CO2	C2
CO2	0.1		0.13
C2		0.13	
C3C4		0.13	
C5C10	0.03	0.12	0.01
C11C19	0.05	0.07	0.02
CN1	0.06	0.06	0.02
CN2	0.07	0.06	0.02

**Table 7 Values of non-zero binary interaction parameters ( $k_{ij}$ ) in case 2**

N2C1	N2C1	CO2	C2
CO2	0.1		
C2		0.096	
C3C5		0.11	
C6C15	0.04	0.07	0.01
C16C24	0.07	0.07	0.02
C25P	0.08	0.06	0.02

**Table 8 Values of non-zero binary interaction parameters ( $k_{ij}$ ) in the North Sea reservoir fluid case. Data from (Pedersen and Hjermstad, 2015).**

N2	N2	CO2
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CO2	-0.017	
C1	0.0311	0.12
C2	0.0515	0.12
C3	0.0852	0.12
iC4	0.1033	0.12
nC4	0.08	0.12
iC5	0.0922	0.12
nC5	0.1	0.12
C6	0.08	0.12
C7	0.08	
C8	0.08	
C9	0.08	
C10-C11	0.08	
C12-C13	0.08	
C14-C16	0.08	
C17-C18	0.08	
C19-C21	0.08	
C22-C24	0.08	
C25-C29	0.08	
C30-C37	0.08	
C38-C80	0.08	

The model computations for the first two cases were validated by comparison with the data generated by the non-equilibrium molecular dynamics (NEMD) simulations, with the approach described in Appendix B. These simulations were performed in the following way: An initial coarse-grained representation compatible with the properties of a mixture under study was defined. The Lennard-Jones chain fluid was used as an initial choice for the molecular parameters (sphere diameter, potential depth and number of segments). The corresponding-states law was used for the parametrization of pseudo components properties (critical properties,  $T_c$  and  $P_c$ , and acentric factors  $\omega$ ) and viscosity. More details on NEMD simulations to produce quasi-experimental thermophysical data are provided in refs. (Privat et al., 2019; Galliero et al., 2017; Galliero and Montel, 2009). To make the problem manageable by the NEMD simulations, we used a thermodynamic lumping technique, reducing the number of components of the studied fluids (8 pseudo-components in the oil case 1, as shown in Table 1 and 7 pseudo-components in case 2 as shown in Table 2). Lumping was carried out with a standard approach based on volatility under engineering constraints (the groups correspond to boiling points cuts) (Montel and Gouel, 1984). In both cases, a small amount of nitrogen was lumped with methane (N2C1).

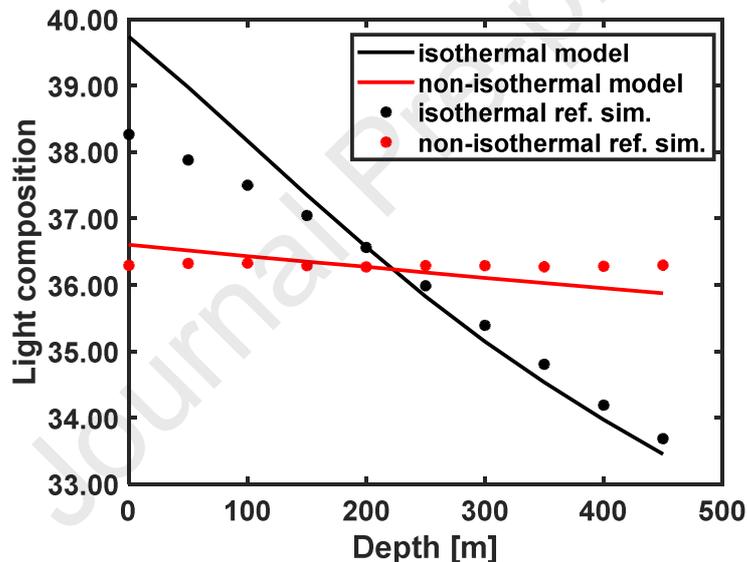
The last parameter to define for the gradient computations is the exponent  $\tau$  appearing in the mobility ratio in equation 6. As an initial value, we take  $\tau = 0.6$ , as in the correlation of Wilke and Chang (1955). This value is known to apply well to the hydrocarbon homologous series. The sensitivity to this value is checked in the following section.

## 4.2. Results of the computations

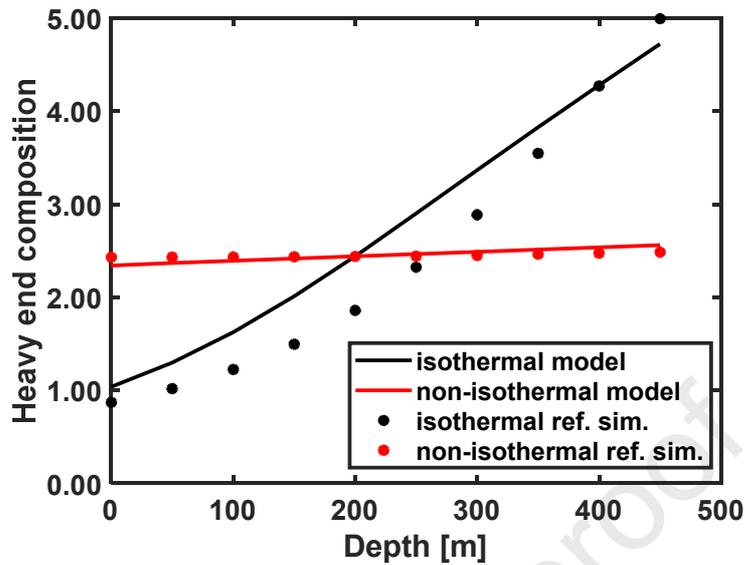
As mentioned previously, the two first fluid columns were simulated by NEMD subject to gravity, with and without the thermal gradient to build the reference solutions used to validate the thermodynamic model.

The NEMD compositional profiles for some of the heavy and light pseudo components of the oil are shown in Figures 2 and 3. The algorithm described above makes use of a reference depth composition whereas the NEMD simulations compute segregation based on the average composition over depth. Thus, for the sake of comparison, we select the composition obtained from the non-isothermal NEMD simulation at the reference depths as a reference composition for our calculations.

Figures 2 and 3 demonstrate a qualitative agreement between results from NEMD simulations and those obtained from the thermodynamic model described in section 2, with or without the thermal gradient. The results indicate that the thermodynamic model captures well the influence of thermodiffusion on the compositional profiles without any fitting parameters.

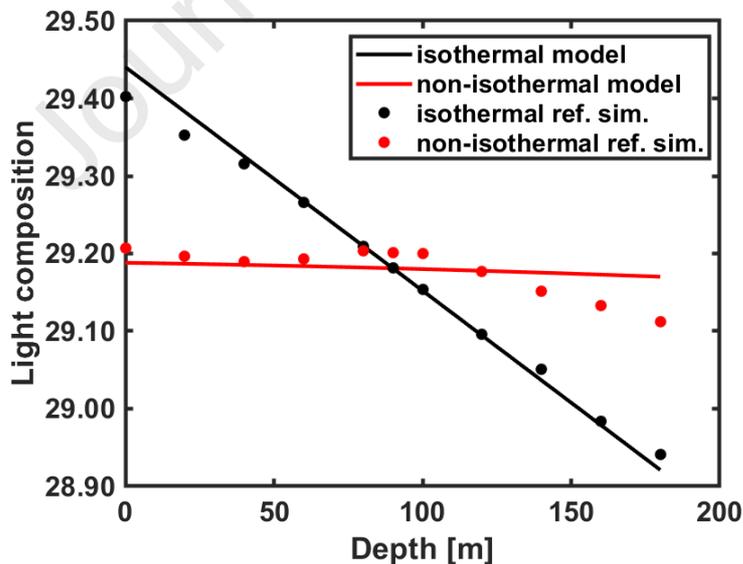


**Fig. 2** Compositional profile (mole %) of the light components (N2C1) of the oil for isothermal and non-isothermal cases

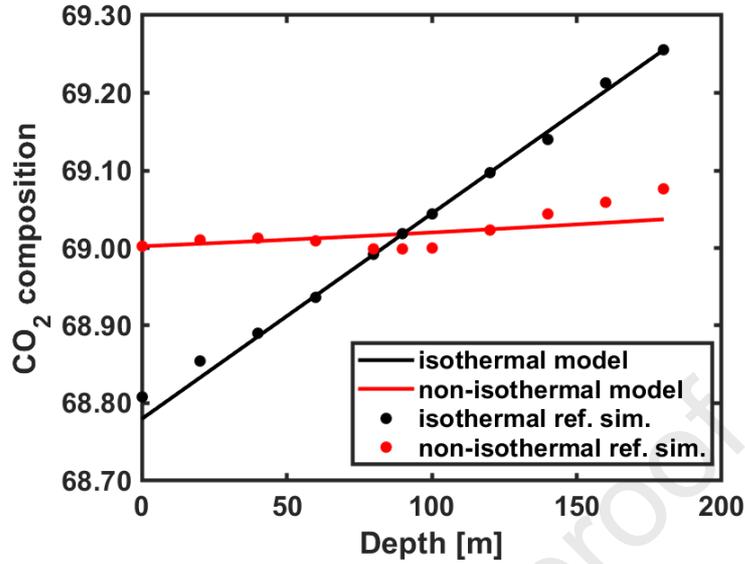


**Fig. 3** Compositional profile (mole %) of the heavy components (CN2 cut) of the oil for isothermal and non-isothermal cases

The NEMD compositional profiles of the N<sub>2</sub>C<sub>1</sub> and CO<sub>2</sub> components for case 2 i.e. the gas reservoir are shown in Figures 4 and 5. Here again, the figures show a good qualitative and a reasonable quantitative agreement between results from NEMD simulations and those obtained from the proposed thermodynamic models without using any fitting parameter. Addition of the thermal gradient modifies the dependencies in the right direction, and the data is approximated with a reasonable accuracy.

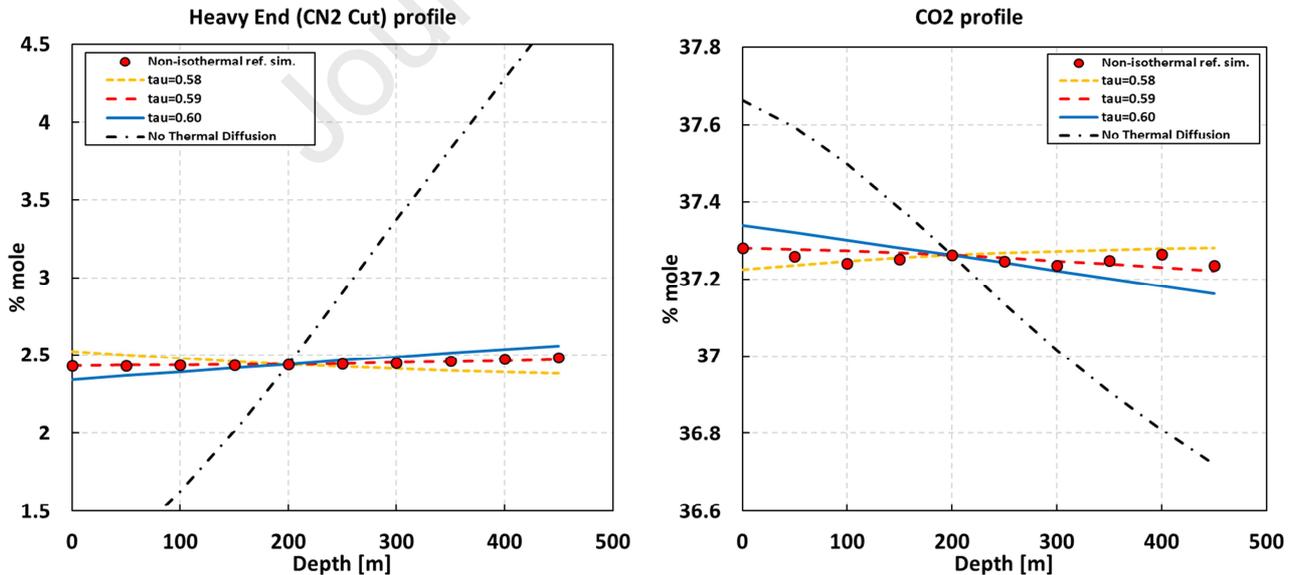


**Fig. 4** Compositional profile (mole %) of the light components (N<sub>2</sub>C<sub>1</sub>) in the gas for isothermal and non-isothermal cases



**Fig. 5 Compositional profile (mole %) of CO<sub>2</sub> in the gas for isothermal and non-isothermal cases**

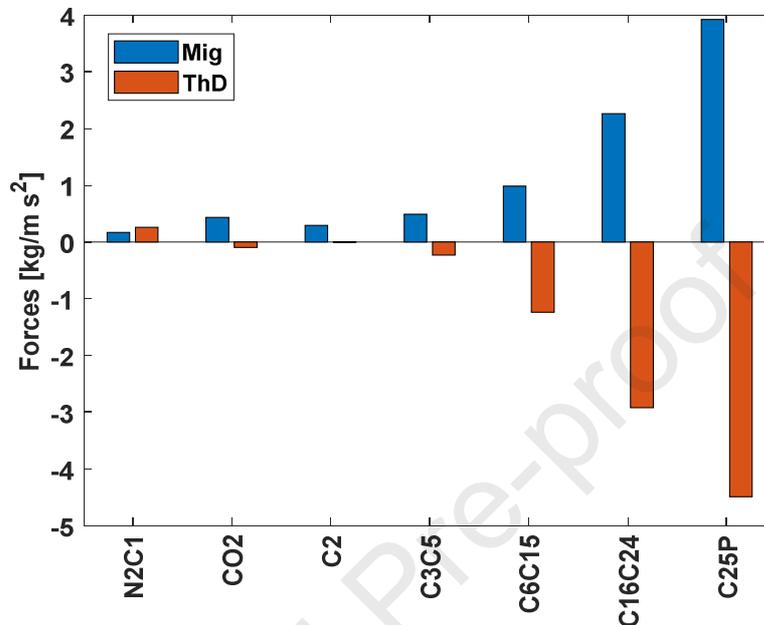
Although there is no fitting in these cases, it should be pointed out that the sensitivity to exponent  $\tau$  is high. An illustration of the sensitivity to exponent  $\tau$  is shown in Fig. 6 for the two key components in the first case. A reason for high sensitivity to  $\tau$  is that this parameter determines the effective molecular sizes and, hence, free volumes. The diffusion coefficients in liquids and dense gases are very sensitive to the free volume, since not much space is left for the molecules to move. It looks like  $\tau = 0.59$  is a better value to approximate the composition profiles for this case, although this cannot be generalized onto other cases without additional computations.



**Fig. 6 Sensitivity of heavy end (CN<sub>2</sub> cut) and CO<sub>2</sub> profiles to exponent  $\tau$**

Fig. 7 presents the balance of the gravity and thermal contributions in the component segregation. As can be seen in the figure, the thermal gradient forces  $\text{ThD} = \left( q_i - \frac{L_D}{L_i} Q \right) \nabla T$ , compensates the gravity force,  $\text{Mig} = M_i \mathbf{g}$ . This results in a much smaller variation of the fluid composition with depth than

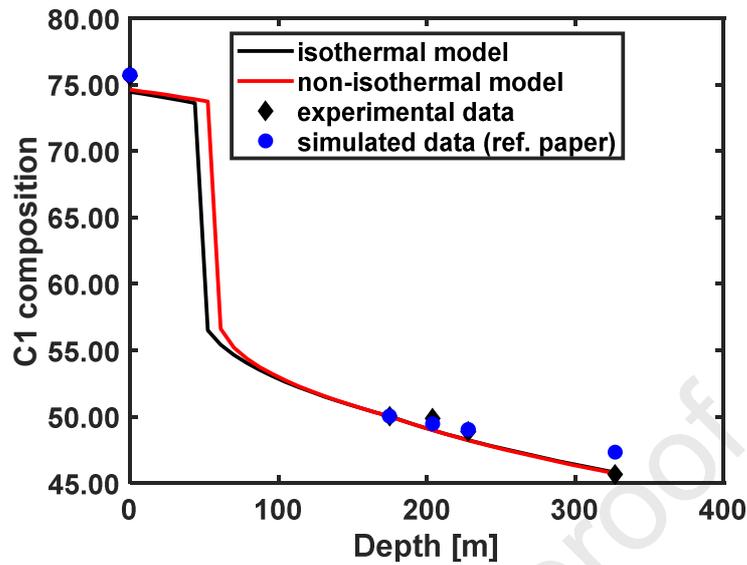
predicted by the gravity only. If the only gravity, without including the thermal diffusion effect, would be considered, the compositional profile could not be captured. The negative sign of thermal forces for CO<sub>2</sub> molecule, despite its small size, indicates that the compositional gradient is affected by thermodiffusion phenomena in CO<sub>2</sub> rich reservoirs.



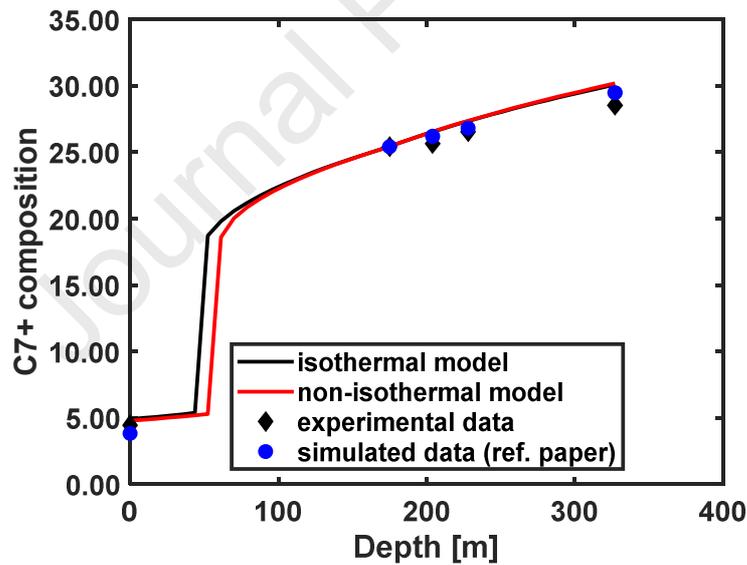
**Fig. 7 Comparison of thermal diffusion forces (orange color) and gravity forces (blue color) for different components**

Compositional data for methane and C<sub>7+</sub> for the North Sea reservoir cases are presented in Figures 8 to 13. The results show that including the thermal diffusion in this case improves the compositional profile prediction, although not to such an extent as in the previous examples. The role of thermal diffusion coefficients in the segregation is not as significant as of the gravity forces. However, with account of the thermal effect, the fluid compositions become closer to the reservoir data. Changing the exponent  $\tau$  by  $\pm 0.01$  does not change the results, unlike in the previous synthetic reservoir cases. It is worth mentioning that the gas-oil contact (GOC) predicted in the third case with our model is different from the GOC reported in the reference paper while the simulated reservoir pressure profiles are similar for both models. Furthermore, no GOC could be captured with our model in the fifth case. The thickness in this case is only 39 m, which could be insufficient to capture the change.

These data were also simulated by Pedersen and Hjermstad (2015) using the Haase model for the thermodiffusion coefficients. These coefficients were represented as the enthalpy differences relative to some reference state. This reference state was treated as an adjustable parameter. The simulation in the present work does not require the adjustable parameters and still predicts the compositional variation and its trend with a reasonable accuracy. In all cases, introduction of the thermal gradient slightly improves the prediction of compositional grading. This asserts the qualitative validity of the assumptions behind the model.



**Fig. 8** Compositional profile (mole %) of methane for the case 3 (North Sea) for isothermal and non-isothermal cases and the simulated results from the reference paper (Pedersen and Hjørnstad, 2015)



**Fig. 9** Compositional profile (mole %) of C7+ in for the case 3 (North Sea) for isothermal and non-isothermal cases and the simulated results from the reference paper (Pedersen and Hjørnstad, 2015)

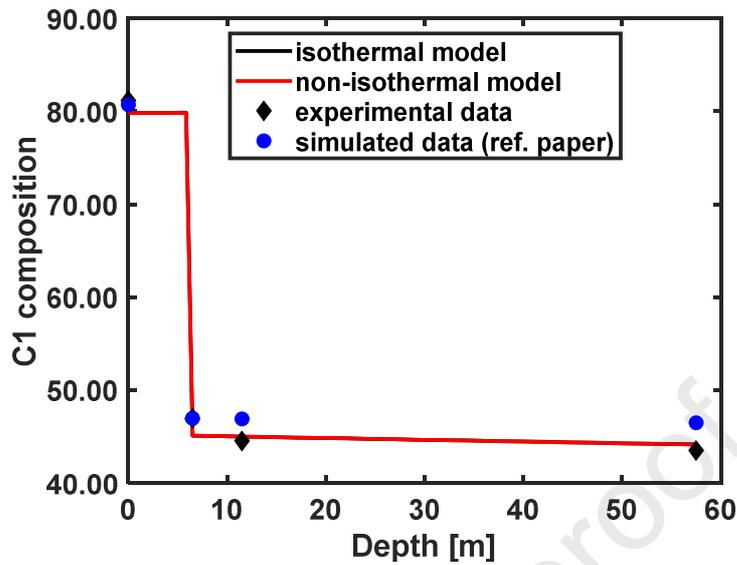


Fig. 10 Compositional profile (mole %) of methane in for the case 4 (North Sea) for isothermal and non-isothermal cases and the simulated results from the reference paper (Pedersen and Hjermsstad, 2015)

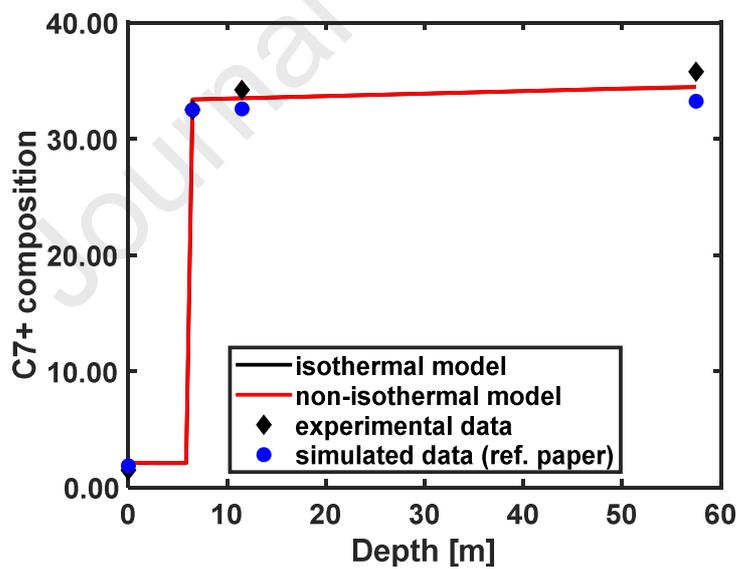
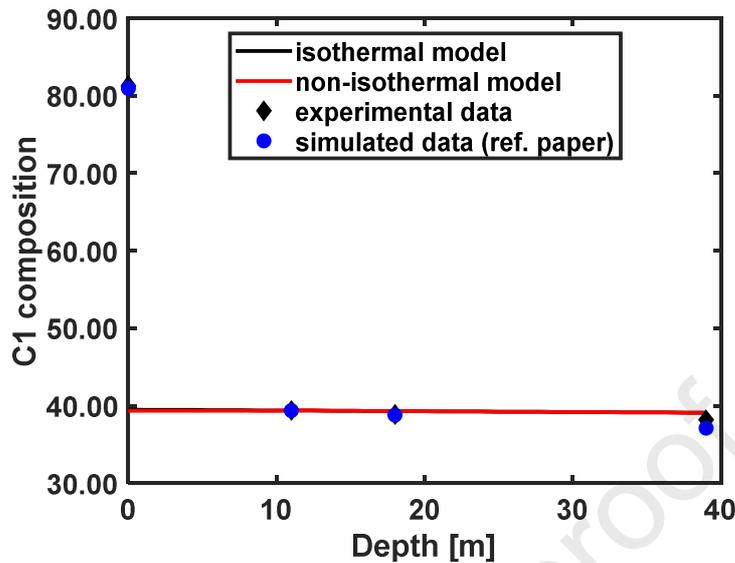
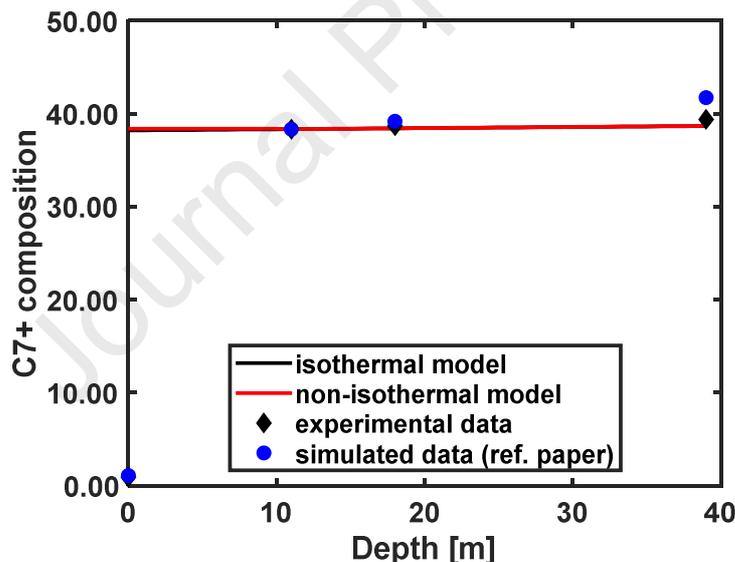


Fig. 11 Compositional profile (mole %) of C7+ in for the case 4 (North Sea) for isothermal and non-isothermal cases and the simulated results from the reference paper (Pedersen and Hjermsstad, 2015)



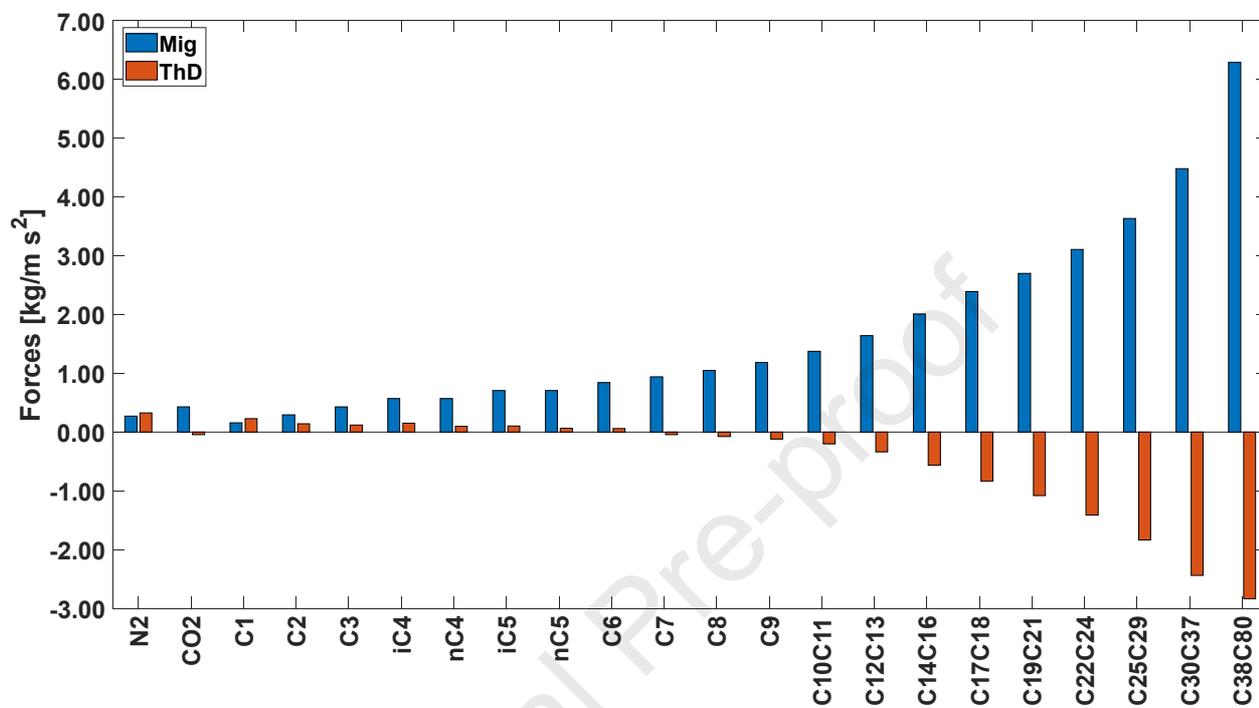
**Fig. 12** Compositional profile (mole %) of C1 for the case 5 (North Sea) for isothermal and non-isothermal cases and the simulated results from the reference paper (Pedersen and Hjørnstad, 2015)



**Fig. 13** Compositional profile (mole %) of C7+ for the case 5 (North Sea) for isothermal and non-isothermal cases and the simulated results from the reference paper (Pedersen and Hjørnstad, 2015)

Fig. 14 shows the magnitude of the gravity and thermal forces contributions in the component segregation in the North Sea reservoir case (case 3). As can be seen, thermal and gravity forces influence the segregation in the opposite direction like in the first two cases. However, in the North Sea reservoir cases, the effect of thermal forces on the fluid compositions is not as significant as the effect of the gravity forces. Unlike for the first two cases, the trend of the reservoir fluid compositions can be described with a reasonable accuracy using gravity segregation alone. The reason may be that compositional grading in the reservoir is much dependent on the composition of the fluid. In the first two cases, the compositions of the fluids are much less diverse, and fractions of light components are

much higher than for the North Sea reservoir cases. A higher fraction of the heavy ends may significantly enhance the gravity contribution to the segregation.



**Fig. 14 Comparison of thermal diffusion forces (orange color) and gravity forces (blue color) for different components in the North Sea reservoir case 3**

## 5. Conclusion

Petroleum mixture distributions with depth under the action of the gravity and thermal forces have been studied based on a new thermodynamic model. The model, based on traditional equations of state for petroleum mixtures, involved also a novel way to account for the action of the thermal gradients. This way makes it possible to predict the fluid distributions “from scratch”, without involvement of adjustable parameters. The approach has been validated on two examples of reservoir fluids studied by application of steady-state non equilibrium molecular dynamics simulations, and on three cases of compositional grading in North Sea petroleum reservoirs. In the first two cases, the contribution of the thermal forces are significant and opposite to the gravity. Involvement of the thermal effects is so necessary for qualitatively correct predictions of the compositional variation with depth. In the examples of the North Sea reservoir, the involvement of the effect of thermodiffusion improves the prediction of the compositional profile, but its role is not as significant as in the previous two cases. The model predictions are also slightly superior to the previously performed simulations based on the Haase model for the thermodiffusion. Unlike the previous model, where the reference constant has been treated as an adjustable parameter, the new model does not require any adjustment.

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## Nomenclature

$b_i$	<i>covolume of component “i”</i>
$C_i$	<i>volume translation of component “i” (as related to the component co-volume)</i>
$D_i$	<i>diffusion coefficient of component “i”</i>
EoS	<i>Equation of State</i>
$f_i$	<i>fugacity of component i</i>
$F$	<i>vector of differences between corrected fugacity and the fugacity</i>
$F'$	<i>Jacobian</i>
$g$	<i>gravitational acceleration</i>
$k$	<i>permeability</i>
$L_i, L_D$	<i>Onsager phenomenological coefficients</i>
$M_i$	<i>molecular weight of component “i”</i>
$M$	<i>average molecular weight</i>
$n_i$	<i>number of moles of component “i”</i>
$N$	<i>number of components in the mixture</i>
$P$	<i>pressure</i>
$P_{c_i}$	<i>critical pressure of component “i”</i>
$q_i$	<i>partial molar heat of transport of component i.</i>
$Q$	<i>Total molar heat of transport</i>
$R$	<i>gas constant</i>
$T$	<i>temperature</i>
$T_{c_i}$	<i>critical pressure of component “i”</i>
$u$	<i>variable set</i>
$x_i$	<i>molar fraction of component i.</i>
$z, z^{ref}$	<i>depth</i>

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$Z$	<i>compressibility factor</i>
$\varphi_i$	<i>Fugacity coefficient of component <math>i</math></i>
$\mu_i$	<i>chemical potential of component “<math>i</math>”</i>
$\mu_i^{res}$	<i>the residual chemical potential of component “<math>i</math>”</i>
$\omega_i$	<i>acentric factor of component “<math>i</math>”</i>

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## Appendix A. Theory of the thermal effect on segregation.

This appendix discusses in brief the main statements from the approach of Montel et al. (2019) applied to derivation of Eq. (1).

Following the standard derivations in the framework of the continuous nonequilibrium thermodynamics (de Groot and Mazur, 1962; Kuiken, 1994) Montel et al. represent the mass fluxes  $J_i$  of the components of the mixture in a porous medium in the form

$$J_i = -n_i L_P \frac{VVP - Mg}{T} + n_i \sum_j L_{ij} (q_i \nabla T - \nabla_T \mu_i + M_i g)$$

Here  $L_P$  is the convective resistance coefficient (permeability-viscosity ratio, in standard formulations);  $L_{ij}$  are phenomenological diffusion coefficients; and  $q_i$  are thermodiffusion heats of transport (Denbigh, 1951). Unlike many standard approaches, Montel et al. assume that the diffusion fluxes of the components may be treated independently, regardless the convective flux. This is motivated by the

peculiarities of the mass transfer in the porous medium. Then, the matrix  $L_{ij}$  becomes the  $N \times N$  matrix, which off-diagonal coefficients may for simplicity be assumed to be zero:

$$L_{ij} = \delta_{ij}L_i$$

Equating of the mass fluxes  $J_i$ , with account of the last equation, to zero, and application of the Gibbs-Duhem relation for exclusion of the pressure gradient results in Eq. (1).

Any theory of thermodiffusion should rely upon an expression for the heats of transport  $q_i$ . Many authors (Haase, 1962; Kempers, 1989; Pedersen and Lindeloff, 2003) relate these values to partial molar enthalpies, or their differences with the values at a reference state:

$$q_i = \frac{h_i - h_i^*}{T} = \frac{\mu_i - \mu_i^*}{T} + s_i - s_i^*$$

Montel et al. argue that the chemical potential of a diffusion component should be equal to the potential in the reference state, so that the heats of transport may only be expressed in terms of the partial molar entropies:

$$q_i = s_i - s_i^*$$

These expressions for the heats of transport are supported by the nonequilibrium molecular dynamic simulations (NEMD), as described below in Appendix B.

## Appendix B. Non-Equilibrium Molecular Dynamics Simulations.

This appendix provides a brief presentation on how Non-Equilibrium Molecular Dynamics simulations of cases 1 and 2 have been performed. Further technical details could be found in Galliero and Montel (2009).

Molecular dynamics is a numerical technique based on the explicit simulations of the physical movements of molecules over time at the nanoscale (Allen and Tildesley, 2017). The trajectories of the molecules are simply deduced by numerically solving Newton's equation of motion for a system of interacting particles. The force between the particles are based on molecular force fields which are so the only input of the system. The physical properties, such as thermodiffusion, emerge from the collective behaviours of the interacting molecules and are so a result of the simulations.

To mimic what is occurring over hundreds of meters while using simulations on nanometres system, the idea is to magnify the external fields (thermal gradient and gravity), while ensuring that the linear response is maintained. Even if the magnification can reach values of about  $10^{10}$ , i.e. the ratio between the two scales (reservoir and simulation box), it has been shown that such a NEMD approach gives consistent results on both gravitational segregation (Galliero and Montel, 2008) and thermal diffusion (Galliero et al., 2017) of hydrocarbon fluids.

Among other, such a numerical method has been used to verify some of the thermodynamic algorithm employed to deal with segregation and thermodiffusion (Galliero and Montel, 2008, 2009). In addition, it has provided some evidence of a close connection between thermodiffusion and partial molar entropy (Montel et al. 2019), following the seminal idea of Rosenfeld (1977).

### **Highlights**

A new theory for segregation under gravity and thermal forces has been developed

A numerical algorithm containing no adjustment parameters has been produced

Sample calculations show a capability of the new method to model fluid distribution in petroleum reservoirs

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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