



Thermodiffusion and coupled phenomena / Thermodiffusion et phénomènes couplés

## Thermodiffusion: From microgravity experiments to the initial state of petroleum reservoirs

Mathieu Touzet<sup>a</sup>, Guillaume Galliero<sup>a,\*</sup>, Veronique Lazzeri<sup>a</sup>, M. Ziad Saghir<sup>b</sup>, François Montel<sup>c</sup>, Jean-Claude Legros<sup>d</sup>

<sup>a</sup> LFC (UMR-5150 with CNRS and Total), Université de Pau et des Pays de l'Adour, BP 1155, 64013 Pau cedex, France

<sup>b</sup> Department of Mechanical and Industrial Engineering, Ryerson University, 350 Victoria St, Toronto M5B 2K3, Ontario, Canada

<sup>c</sup> Total S.A., avenue Larribau, 64018 Pau cedex, France

<sup>d</sup> MRC, Université Libre de Bruxelles, Avenue F.D. Roosevelt 50, CP 165/62, B-1050 Bruxelles, Belgium

### ARTICLE INFO

#### Article history:

Available online 21 April 2011

#### Keywords:

Thermodiffusion  
Soret effect  
Species separation  
Molecular dynamics  
Simulations

### ABSTRACT

Microgravity experiments and molecular dynamics simulations have been performed to study thermodiffusion of ternary mixtures composed of methane, *n*-butane and *n*-dodecane in petroleum reservoir conditions. The simulations showed in both cases that methane and *n*-butane tend to migrate towards the hot side while *n*-dodecane tends to migrate towards the cold side. Some of the experimental results showed the same trend but with much larger amplitudes. Finally, a simulation of an idealized fluid column composed of one of the ternary mixture emphasizes that thermodiffusion can have a large impact on the vertical distribution of the components in a petroleum reservoir.

© 2011 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

## 1. Introduction

It is generally believed that the gravity field, through gravitational segregation, and the reverse geothermal gradient, through thermodiffusion, are two phenomena that model the vertical composition of the fluid in a petroleum reservoir [1–4]. It is believed that the thermodiffusion effect may even promote unstable situations from a convective point of view in some particular cases [5]. Nevertheless, the main difficulties in better evaluating such an influence is the lack of experimental data on the thermodiffusion of multicomponent mixtures in petroleum reservoir conditions.

So, in this work, both microgravity experiments (FOTON M3 Flight) and molecular dynamics (MD) simulations on six *n*-alkane ternary mixtures composed of methane, *n*-butane and *n*-dodecane in various proportions have been performed. These mixtures have been studied at typical petroleum reservoir conditions, i.e. high pressure (35 MPa) and rather high temperature (333.15 K) [6]. The initial idea was to obtain thermal diffusion ratios using experimental and numerical approaches in a more than two compounds mixture that can be taken as a highly idealized model for a reservoir fluid. Unfortunately, because of probable problems during the post-flight gas chromatography analysis of the sample, some experimental results should be taken with care as described in the results section.

Apart from the measurement themselves, a very interesting point was to quantify the relative effect of the gravity field (through segregation) and of the geothermal gradient (through thermodiffusion) on such synthetic mixtures in 1D highly idealized petroleum reservoir. So, as thermogravitation (i.e. a gravity field combined with a thermal gradient) experiments on a system mimicking a reservoir fluid column are hardly feasible, we have performed molecular dynamics simulations using a recently developed scheme [5,7] that allows studying both pure segregation and thermogravitation. Additionally,

\* Corresponding author.

E-mail address: guillaume.galliero@univ-pau.fr (G. Galliero).

**Table 1**

Composition in molar fraction of the six mixtures.

Mixture	Molar fraction of C1	Molar fraction of C4	Molar fraction of C12
1	0.2	0.1	0.7
2	0.2	0.2	0.6
3	0.2	0.3	0.5
4	0.2	0.4	0.4
5	0.2	0.5	0.3
6	0.2	0.6	0.2

classical thermodynamic modelling using an equation of state has been carried out. It will be shown on the model systems simulated why thermodiffusion must not be neglected when estimating the initial state distribution of the components in a petroleum reservoir and how this effect can sometimes lead to an unstable fluid column and so promote convection.

## 2. Experimental procedure

### 2.1. Studied systems

The thermodiffusion experimental study has been conducted for six different ternary mixtures composed of methane, *n*-butane and *n*-dodecane. The molar fraction of methane was fixed at 0.2 for all of the mixtures while the molar fractions of the two others components varied, from 0.7 to 0.2 for *n*-dodecane as can be seen in Table 1.

The particular cells used to carry the mixtures have been designed specifically for the experiment [6]. The six cells were gathered in two triads controlled individually and allow to work at 373 K and 35 MPa. The system also enables to control the temperature of both sides of each cell in order to create a thermal gradient. Moreover, each cell contains in its middle an automated valve that separates and isolates the 3.22 cm<sup>3</sup> of the cell in two equal compartments. In the laboratory, the cells with their valve in the open position were filled by the six mixtures at 35 MPa. This pressure was needed to ensure that the fluid was maintained in the liquid state during the experiment.

Once in space, the thermal gradient was applied, where one side was maintained at 328 K and the other cell's side was heated at 338 K. This thermal gradient was maintained for 200 hours for one triad of cells (mixtures 4 to 6) and only 120 hours for the other ones because of technical problems. After these periods of time, the thermal gradient was stopped while the valves were closed automatically in order to isolate the two parts of the mixture.

### 2.2. Analysis of the samples

After the flight, the cells were recovered to analyze the mixtures contained in the twelve half-cells in the PVT laboratory of Total. The system of analysis planned to determine the concentration of every species in the cells was a gas chromatography. Unfortunately, this injection system included different defects that caused several problems (mainly a saturation of the chromatograph's detector and a loss of pressure) during the first analyses. So, to get rid of the problems of saturation and loss of pressure, it was decided to proceed to a dilution of the samples before analyzing. Phase diagrams of the six mixtures 30 times diluted with the *n*-pentane were realized to target the conditions of pressure and temperature where the samples remain in a one-phase state.

Special equipment called PVT Unit was used to dilute, mix and homogenize the samples, then to transfer in an isobaric way to the injection system. To improve the repeatability of the analyses, an automatic injection system (VESPAC) was used. Once an analysis has been done, each peak detected have been integrated in order to determine its area and then to deduce the mass fraction of the respective component. Indeed, the area under a chromatograph peak is proportional to the mass concentration of the species. To avoid errors that might be introduced by possible inhomogeneity in mixtures, several analyses were done for each half-cell and the results were averaged.

## 3. Numerical procedure

### 3.1. Fluid models

In complement to the experimental measurements, molecular dynamics simulations have been performed on simple fluids in order to study both thermodiffusion and gravitational segregation. To do so, two simple fluid models have been used in order to describe the normal alkanes: the Lennard-Jones (LJ) model, composed of simple spheres and the Lennard-Jones chain (LJC), composed of *N* freely jointed spheres (segments) [8]. In both models, non-bonded interactions between atoms *i* and *j* have been described by the usual truncated Lennard-Jones 12–6 potential given by Eq. (1):

$$U_{LJ}^{ij} = \begin{cases} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] & \text{if } r_{ij} < r_c \\ 0 & \text{elsewhere} \end{cases} \quad (1)$$

**Table 2**  
Molecular parameters used in this work for both LJ and LJC models.

Lennard-Jones			Lennard-Jones chain		
Species	$\varepsilon$ (J mol <sup>-1</sup> )	$\sigma$ (Ang)	$N$	$\varepsilon$ (J mol <sup>-1</sup> )	$\sigma$ (Ang)
C1	1213	3.704	1	1213	3.704
C4	2855	5.104	2	2075	3.979
C12	4579	7.12	5	2490	4.042

where  $\varepsilon_{ij}$  is the potential strength,  $\sigma_{ij}$ , the “atomic diameter”, which is the distance at which the potential is null,  $r_{ij}$  the distance between the two atoms considered and  $r_c (= 2.5\sigma_{ij})$  the cut off radius. Concerning the LJC model, the bonded intramolecular interactions are modelled by a simple strong spring-type potential with an equilibrium distance equal to the atomic diameter of the species involved. Cross interactions between unlike atoms/molecules have been described by Lorentz–Berthelot combining rules for both LJ and LJC models.

Molecular parameters of methane have been taken from Galliero et al. [9]. With respect to the molecular parameters of C4 and C12, they have been adjusted so that the fluid models (LJ and LJC) provide an accurate estimation of the density (during NPT simulations) and the viscosity of the pure species simulated in the range of thermodynamic conditions studied in this work. The experimental database used for the adjustment is the one provided by REFPROP8 software (NIST database). In addition, for the LJC model, the number of segments  $N$  has been imposed to be  $N = 2$  for C4 and  $N = 5$  for C12, values which are consistent with those usually employed in SAFT like equation of state. All molecular parameters are provided in Table 2.

### 3.2. Simulation details

In order to study the thermodiffusion by MD simulations, we have used a boundary driven non-equilibrium molecular dynamics (NEMD) in-house code already validated on various systems and based on the algorithm proposed by Hafskjold et al. [10]. Concerning gravitational segregation, we have employed an algorithm recently developed [5,7] which allows to study both pure segregation (i.e. a gravity field without a thermal gradient) and stable thermogravitation (i.e. a gravity field plus a reverse thermal gradient without convection).

The Verlet velocity algorithm has been used to integrate the motion's equation with a reduced time step of 0.002. Classical periodic boundary conditions combined with a Verlet neighbours list have been applied [11]. Simulations have been performed on systems composed of 1500–3000 molecules/centre of forces. Non-equilibrium runs of more than  $2.10^7$  time steps have been employed. The first  $0.5 \times 10^6$  non-equilibrium time steps have discarded (to ensure that the stationary state is reached) to compute thermal diffusion ratios. In order to estimate errors on the computed variables, the sub-blocks average method has been applied [11].

## 4. Results

### 4.1. Thermal diffusion ratios

Knowing the initial and final composition of the mixtures within each half-cell along with their associated temperatures, the thermodiffusion ratios of the three components have been calculated by using Eq. (2):

$$k_{T_i} = -T \frac{\nabla x_i}{\nabla T} \quad (2)$$

where  $k_{T_i}$  is the thermodiffusion ratio of the component  $i$ ,  $T$  is the average temperature of the cell,  $\nabla x_i$  is the molar fraction gradient of the component  $i$  between the hot half-cell and the cold half-cell and  $\nabla T$  is the temperature gradient between the two half-cells.

The temperature at the edge of the cold side was 328 K while the one at the edge of the hot side was 338 K so it was considered that the average temperature of the cell was 333 K. Moreover, the temperature gradient was determined as the gradient between the average temperature of the cold side and the average temperature of the hot side. The percentages of mass concentration and molar concentration of each component along with the thermodiffusion ratios are summarized in Table 3. In addition, Table 3 contains the results that were obtained by MD simulations on the two fluid models.

Concerning MD results it appears that both fluid models provide very similar results whatever the concentration, which is consistent with previous results on binary mixtures [12]. In all systems both methane and *n*-butane (in a less pronounced manner at least when using the LJC model) tend to migrate towards the hot areas relatively to the normal-dodecane which tends to migrate towards the cold areas. Such behaviour is the classical one for non-polar binary mixtures, i.e. the heavier components tend to migrate towards the cold area whereas the lighter move towards the hot zone.

Concerning experimental results, it appears that some of them should be taken with care. First, it seems that the cells for which  $x_{C12} = 0.2$  and  $0.7$  have a very strange behaviour, because the heavier compound tends to accumulate in the hot part relatively to the other compounds which is unexpected for simple non-polar fluids as normal alkane. In addition, the

**Table 3**

Thermal diffusion ratios obtained by microgravity experiments and by MD simulations on LJ and LJC fluid models. Statistical errors on MD value are of the order of 10–20%, those on experiments are higher.

		$k_T$ exp	$k_T$ LJ	$k_T$ LJC
$x_{C12} = 0.2$	C1	28.2	−0.16	−0.15
	nC4	−20.4	−0.1	−0.02
	nC12	−7.8	0.26	0.17
$x_{C12} = 0.3$	C1	−1.3	−0.14	−0.14
	nC4	0.68	−0.14	−0.08
	nC12	0.67	0.28	0.22
$x_{C12} = 0.4$	C1	−2.6	−0.14	−0.15
	nC4	−1.6	−0.14	−0.09
	nC12	4.2	0.28	0.24
$x_{C12} = 0.5$	C1	0.14	−0.13	−0.17
	nC4	−0.53	−0.16	−0.06
	nC12	0.39	0.29	0.24
$x_{C12} = 0.6$	C1	−11.3	−0.15	−0.16
	nC4	−1.9	−0.1	−0.07
	nC12	13.3	0.25	0.23
$x_{C12} = 0.7$	C1	12	−0.14	−0.17
	nC4	0.95	−0.08	−0.03
	nC12	−12.9	0.22	0.2

amplitudes of the experimentally measured values are by far larger (roughly one order of magnitude) than those deduced from the molecular simulations. Such discrepancies are unexpected as long as results obtained by MD simulations for binary mixtures of *n*-alkane are usually in good agreement with experimental ones (measured on earth).

It should be pointed out that the curious behaviour of some experimental results is probably linked to difficulties encountered during the analysis of the sample as mentioned previously.

#### 4.2. Thermogravitation

In complement to the measurements of the thermodiffusion effect in ternary C1–C4–C12 mixtures, an interesting point is to estimate what is the impact of gravity (through gravitational segregation) relatively to that induced by a geothermal gradient (through thermodiffusion). For such simple mixture, we can expect that these two external fields that occur in a petroleum reservoir have an opposite effect on the vertical distribution on the components along the fluid column. As it seems hardly feasible to perform experiments, we have performed MD simulations to quantify the relative contribution of gravity and geothermal gradient on a highly idealized 1D petroleum reservoir composed of C1–C4–C12.

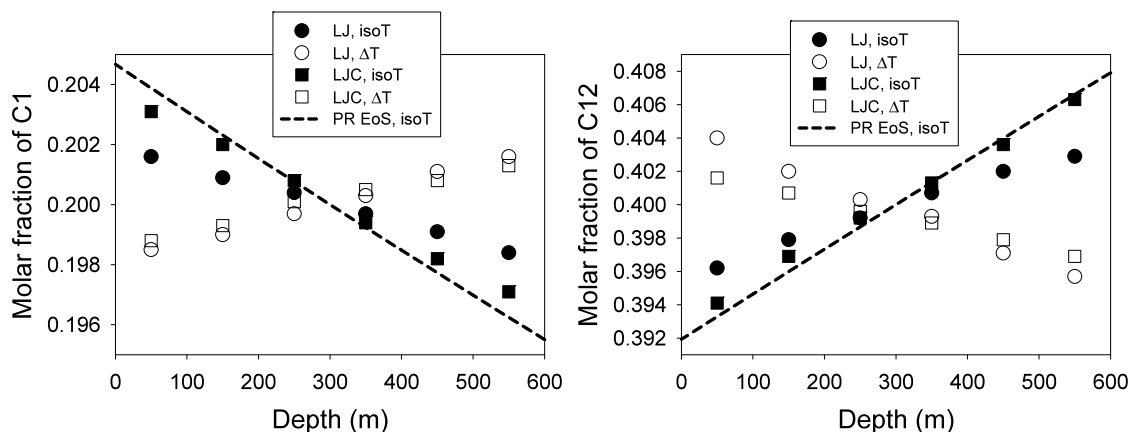
So, we have simulated a fluid column of a height of 600 m composed of a C1–C4–C12 mixture with 0.2:0.4:0.4 in molar fraction (mixture 4 in Table 1) at an average temperature of 333.15 K and an initial pressure of 35 MPa. Two cases have been studied, a pure segregation case in which the system is isothermal and subject to gravity only and a thermogravitation case in which the systems is subject both to the gravity field and usual reverse geothermal gradient of 3 K/100 m (systems heated from below). The technique employed is described in Refs. [5] and [7]. Both LJ and LJC fluid models have been employed.

In addition to the MD simulations, we have performed a conventional thermodynamic modelling of this mixture [4,5] for the pure segregation case (i.e. without thermal modelling). We use Peng–Robinson (PR) Equation of State (EoS) with volume shifts.

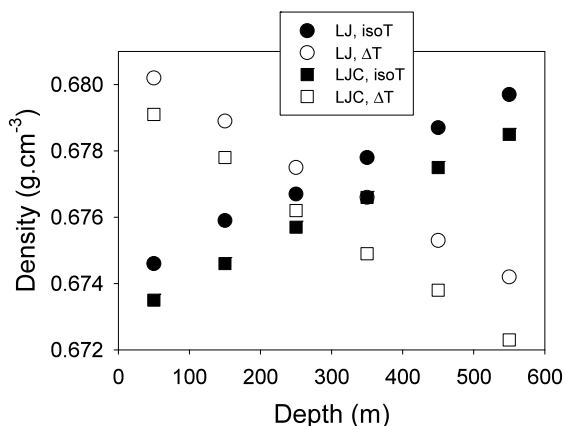
Results provided in Fig. 1 are very interesting. As expected, when only a gravity field is present (pure segregation, i.e. isoT), it appears that methane tends to be enriched at the top of the fluid column and *n*-dodecane accumulated at the bottom of the idealized petroleum reservoir whatever the approach. It should be noticed that the concentration gradients are larger when employing the thermodynamic modelling than when using MD simulations for both molecular models. In addition, the LJC fluid model induces a more pronounced segregation than the LJ model. These results indicate that the fluid modelling (and the combining/mixing rules) is very important when accurate results on mixtures are required [5]. Concerning butane, it tends to be slightly enriched at the top compared to the bottom of the fluid column for both fluid models.

However, when a reverse geothermal gradient is present together with the gravity field, the results are largely modified for such ternary mixtures. In fact, molar fraction gradients of C1 and C12 are reversed because of the thermodiffusion effect, see Fig. 1. More precisely, with a reverse thermal gradient, *n*-dodecane is enriched at the top of the reservoir whereas this is the contrary for methane because of thermodiffusion whatever the fluid model.

This behaviour of the component distribution is a consequence of the fact that, for the C1–C4–C12 mixture simulated, thermodiffusion has a larger impact than gravitational segregation on the vertical distribution of the components. Such result on this particular mixture emphasizes the importance of thermodiffusion, in addition to gravitational segregation,



**Fig. 1.** Molar fractions (methane: left figure, *n*-dodecane: right figure) versus depth in a ternary C1–C4–C12 mixture for pure segregation (isoT) and thermogravitation ( $\Delta T$ ) cases using MD simulations (LJ and LJC) and thermodynamic modelling (PR EoS).



**Fig. 2.** Densities versus depth in a ternary C1–C4–C12 mixture for pure segregation (isoT) and thermogravitation ( $\Delta T$ ) cases using two different molecular models (LJ and LJC).

when trying to estimate the initial vertical distribution of the components in a petroleum reservoir of a large vertical extension.

Another very interesting point is that the density gradient is inverted when the reverse thermal gradient is present (i.e. the density is higher at the top of the fluid column than at the bottom) because of the thermal compression effect and of the thermodiffusion, as seen on Fig. 2. At the MD scale the system is stable as long as the Rayleigh number remains small and below the threshold in the simulations [7]. However, this reverse density gradient indicates that such a situation is unstable from a dynamic point of view at a real scale and so convection can occur for such system [5].

## 5. Conclusion

Ternary hydrocarbon mixtures composed of methane, normal butane and normal dodecane for six different concentrations were investigated by microgravity experiments as well as using MD simulations at  $T = 333.15$  K and  $p = 35$  MPa. The mole fraction of methane was fixed at 0.2 while that of *n*-dodecane was varied from 0.2 to 0.7 in the mixtures.

From MD results, it appears that both methane and *n*-butane tend to migrate towards the hot areas relatively to the *n*-dodecane which tends to migrate towards the cold areas. Concerning experimental results, it has been found that the amplitudes of the measured values are by far larger (roughly one order of magnitude) than those deduced from the molecular simulations. However, some of the experimental results should be taken with care as long as difficulties have been encountered during the gas chromatography analysis of the sample.

Finally, using MD simulations and thermodynamic modelling an idealized 1D fluid column of 600 m composed of one of the ternary mixture has been studied under a gravity field with or without a geothermal gradient. The most important result is that when a reverse thermal gradient is present, *n*-dodecane is enriched at the top of the reservoir and methane is enriched at the bottom of the reservoir contrary to what occurs when there pure segregation occurs (i.e. without thermal gradient). In addition, because of thermal expansion and thermodiffusion, it has been found that the density gradient can

even be inverted in the situation where the thermal gradient is present (i.e. the density is higher at the top of the fluid column than at the bottom). Such a result emphasizes the fact thermodiffusion can have a large impact on the vertical distribution of the components in a petroleum reservoir and should be included to determine accurately the initial state of a reservoir.

### Acknowledgements

This work has been fully supported under ESA contract 14228/00/NL/SH (DSC-SCCO3 project), by the Canadian Space Agency and by Total Oil Company. The authors want to thank all the colleagues that have participated in this team work.

### References

- [1] C. Lira-Galeana, A. Firoozabadi, J.M. Prausnitz, Computation of compositional grading in hydrocarbon reservoirs. Application of continuous thermodynamics, *Fluid Phase Equilib.* 102 (1994) 143–158.
- [2] L. Høier, C.H. Whitson, Compositional grading—theory and practice, *SPE Reserv. Evaluation Eng.* 4 (2001) 525–535.
- [3] K. Ghorayeb, A. Firoozabadi, T. Anraku, Interpretation on the unusual fluid distribution in the Yufutsu gas-condensate field, *SPE J.* 8 (2003) 114–123.
- [4] F. Montel, J. Bickert, A. Lagisquet, G. Galliero, Initial state of petroleum reservoir: A comprehensive approach, *J. Petrol. Sci. Eng.* 58 (2007) 391–402.
- [5] G. Galliero, F. Montel, Understanding compositional grading in petroleum reservoirs thanks to molecular simulations, Society of Petroleum Engineers Paper 121902, Amsterdam, 2009.
- [6] S. Srinivasan, M.Z. Saghir, Measurements on thermodiffusion in ternary hydrocarbon mixtures at high pressure, *J. Chem. Phys.* 131 (2009) 124508.
- [7] G. Galliero, F. Montel, Nonisothermal gravitational segregation by molecular dynamics simulations, *Phys. Rev. E* 79 (2008) 041203.
- [8] K.J. Johnson, E.A. Müller, K.E. Gubbins, Equation of state for Lennard-Jones chains, *J. Phys. Chem.* 98 (1994) 6413–6419.
- [9] G. Galliero, C. Boned, A. Baylaucq, F. Montel, Molecular dynamics comparative study of Lennard-Jones a-6 and exponential a-6 potentials: Application to real simple fluids (viscosity and pressure), *Phys. Rev. E* 73 (2006) 061201.
- [10] B. Hafskjold, T. Ikeshoji, S.K. Ratjke, On the molecular mechanism of thermal diffusion in liquids, *Mol. Phys.* 80 (1993) 1389–1412.
- [11] M.P. Allen, D.J. Tildesley, *Computer Simulations of Liquids*, Oxford Science, Oxford, 1987.
- [12] J.M. Simon, B. Rousseau, D.K. Dysthe, B. Hafskjold, Thermal diffusion in methane–*n*-decane mixtures by molecular dynamics using spherical and flexible multicenter models, *Entropie* 35 (1999) 29–32.