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Theoretical models for the thermo-gravitational separation process in porous media filled by N-component mixtures*

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Abstract. The aim of this work is to present a theoretical analysis of the separation of an N-component mixture. In this study, two analytical models explaining the thermo-gravitational separation of components in N-component mixtures for vertical cavity filled by a porous medium are presented and assessed. The basic state and the separation are expressed in terms of the separation ratio, and the Lewis, cross-diffusion and Rayleigh numbers. Our computational analysis confirms that, for the given values of the mass fractions, thermodiffusion can be measured with a thermo-gravitational column, strongly supporting the experimentally determined transport coefficients.

1 Introduction

Transport properties of fluid mixtures have attracted much interest because of their numerous applications. For instance, the double-diffusion process plays an important role in the transport of contaminants in soil, in crystal growth and in the separation of components in a mixture [1–3]. More details about the fundamental and industrial applications are presented by Legros *et al.* [4], Vafai [5], Nield and Bejan [6], Baytaş and Pop [7]. Many works have been devoted to improving the thermo-gravitational separation in a mixture. In 1939, Furry, Jones and Onsager [8] developed a theory that allowed the separation of binary gases in a thermo-gravitational column to be predicted. A thermo-gravitational column is a rectangular vertical cavity that is differentially heated and filled with a mixture. The difference in temperature produces a unicellular flow which separates the components between the bottom and the top of the column. The theory developed in [8] is called the FJO theory. In their model the influence of the mass fraction in the buoyancy term is neglected (the "forgotten effect"). In order to improve the separation in thermo-gravitational columns, Lorenz and Emery [9] introduced a porous medium in the cavity and Bennacer *et al.* [10] suggested splitting the thermo-gravitational column into three sub-domains filled with a porous medium. Nowadays, thermo-gravitational columns are used to determine the transport properties of binary and ternary mixtures. Several approaches have been developed for the experimental determination of the diffusion, thermal diffusion, and Soret coefficients for binary and ternary mixtures. Blanco *et al.* [11] measured the thermodiffusion coefficients of binary and ternary mixtures using a thermo-gravitational column, while Kolodner *et al.* [12] and Gebhardt and Kölher [13] used optical techniques to determine the transport coefficients of ternary mixtures. If the heaviest component of the mixture has a negative Soret coefficient, it will be transported to the warmer part of the column by the thermodiffusion effect and to the bottom of the cavity by the gravitational field. These phenomena prevent a negative thermodiffusion coefficient from being measured in ground conditions and for this reason Bou-Ali *et al.* [14] have made measurement of the thermodiffusion coefficients in the International space station. The mixture of 1,2,3,4-tetrahydronaphthalene (THN), isobutylbenzene (IBB) and n-dodecane (nC12) at mass fraction 0.8-0.1-0.1 were chosen as a benchmark to validate space measurements since, at this composition it allows for ground measurements [14]. Nowadays, binary mixtures are widely studied and their transport coefficients measured accurately. This is however not the case for ternary mixtures, as the cross-diffusion effect is still poorly understood and the measured cross-diffusion coefficients are highly dispersed [14, 15]. In order to improve our understanding of multi-component mixtures numerical and theoretical studies have been performed. Larre *et al.* [16] have studied the onset of convection in infinite horizontal layers filled with a ternary mixture without taking the cross-diffusion effect into account. Haugen and Firoozabadi [17, 18] have developed a model for measuring the thermodiffusion and

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diffusive coefficients in N-components mixture. Theirs model is based on the transient duration to the steady state. The authors obtained good agreement when comparing the transports coefficients determined with their theoretical model with the literature for seven binary mixtures [19]. Ryzhkov *et al.* [20] obtained an analytical expression of the basic flow for an N-component mixture in a thermo-gravitational column. Their dimensionless formulation introduced the matrix of Schmidt numbers $\mathbf{Sc}$ with $(N-1)^2$ elements. Their theoretical models are based on the parallel flow approximation and the FJO theory. The stability of the unicellular flow in an infinite or finite thermo-gravitational column is studied in [21,22]. Larabi *et al.* [23] proposed a method to indirectly validate the measured transport coefficients of ternary mixtures in space conditions. Shevtsova *et al.* [24] and Lyubimova and Zubova [25] performed three- and two-dimensional numerical simulations of the Soret-driven convection of a cell filled by binary or ternary mixtures. Ghorayeb and Firoozabadi [26] numerically predicted the mass fraction of ternary hydrocarbon mixtures in a two-dimensional reservoir. The aim of the present study is to extend Larabi *et al.*'s work [23] and the FJO theory [8] to an N-component mixture. A two-dimensional vertical cavity filled with a porous medium saturated by an N-component mixture is considered. The governing equations are obtained and solved using the parallel flow approximation and the "forgotten effect" for a multi-component mixture. The mass fraction, temperature, velocity and separation are analytically expressed as functions of the filtration Rayleigh number, Lewis number, separation ratio and cross-diffusion numbers. All the theoretical results are assessed by numerical simulations and the difference between the two theoretical studies and the numerical results is quantified.

2 Problem statement

2.1 Mathematical formulation

This study focuses on the thermo-gravitational separation process in a vertical cavity filled with a porous medium saturated by an N-component mixture. L is the height of the cavity along the y-axis and h the thickness along the x-axis. The porous medium is considered homogeneous and isotropic. Figure 1 illustrates the system under consideration along with the thermal boundary conditions. The vertical walls are maintained at uniform temperature while the horizontal walls are thermally insulated. All boundaries are assumed stiff and impermeable. The problem is described by Darcy's law, the mass conservation of each component in the mixture and the energy conservation equation. The Oberbeck-Boussinesq approximation is considered and all the thermophysical coefficients of the fluid are assumed to be constant except for the density in the buoyancy term

$$\rho^d = \rho_0^d \left[1 - \beta_T (T^d - T_0^d) - \sum_{i=1}^{n-1} \beta_{ci} (C_i^d - C_{i0}^d) \right], \quad (1)$$

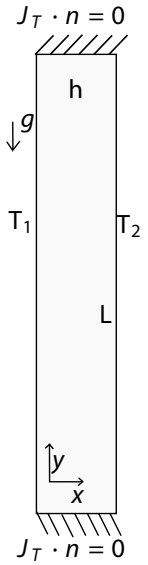

Fig. 1. Vertical thermo-gravitational column and thermal boundary conditions. $\boldsymbol{g}$ is the gravity vector.

where the superscript d stands for the dimensional formulation, N is the number of components in the mixture, ρ^d is the density of the mixture and ρ_0^d is the density at the reference temperature and mass fraction. β_T and β_{Ci} are the thermal expansion coefficient and the mass fraction expansion coefficient, respectively, of component i at the reference temperature and mass fraction. T, C_i and C_{i0} are the temperature, the mass fraction of component i and the initial or reference mass fraction of component i, respectively. The fluid is assumed to be incompressible. The convective flow and the heat and mass transfer are governed by the following dimensionless equations [23]:

$$\boldsymbol{\nabla} \cdot \boldsymbol{V} = 0, \quad (2)$$

$$\boldsymbol{V} = -\boldsymbol{\nabla} P + Ra \left(T + \boldsymbol{\psi}^T \cdot \boldsymbol{C} \right) \boldsymbol{e}_y, \quad (3)$$

$$\varepsilon \partial_t \boldsymbol{C} + (\boldsymbol{V} \cdot \boldsymbol{\nabla}) \boldsymbol{C} = \mathbf{Le}^{-1} \cdot \nabla^2 \left(\mathbf{Cr} \cdot \boldsymbol{C} - \mathbf{1} \cdot T \right), \quad (4)$$

$$\partial_t T + \boldsymbol{V} \cdot \boldsymbol{\nabla} T = \nabla^2 T, \quad (5)$$

where the reference scales are h for the geometric parameter and $h^2\kappa/a$ for the time ($\kappa = (\rho c_p)_p/(\rho c_p)_f$), with $(\rho c_p)_p$ the volumetric heat capacity of the saturated porous medium and $(\rho c_p)_f$ the mixture heat capacity. Furthermore $T = (T^d - T_2)/\Delta T$, where T^d is the dimensional temperature, $\Delta T = T_1 - T_2$. The mass fraction is scaled by $C_i = (C_i^d - C_0)/\Delta C_i$. $\Delta C_i = -\Delta T D'_{Ti}/D_{ii}$, where D_{ii} is the mass diffusion coefficient of the component i. $\boldsymbol{C}$ is a vector of length $(N-1)$ and $\mathbf{D}$ is the diffusion matrix of size $(N-1) \times (N-1)$. D'_{Ti} is the thermal diffusion coefficient of the component i. $\mathbf{1}$ is a vector of length $(N-1)$ equal to $\mathbf{1} = [1 \ldots 1]$. P is the pressure and $\boldsymbol{V}$ the filtration velocity vector. All vectors are column and the superscript T is the transposed vector. The filtration velocity represents the mean fluid velocity taken over a representative elementary volume and is equal to $\boldsymbol{V} = \varepsilon \boldsymbol{V}_f$, where ε is the normalized porosity $\varepsilon = \varepsilon^* (\rho c)_f/(\rho c_p)^*$ and ε^* is the

cell porosity. The thermal filtration Rayleigh number

$$Ra = \frac{Khg\beta_T \Delta T}{\nu a}\,, \tag{6}$$

where $a = \lambda/(\rho c_p)_f$ is the equivalent thermal diffusivity, λ is the thermal conductivity of the mixture, K is the permeability of the porous medium and $(\rho c_p)_f$ is the specific heat capacity of the mixture. The separation ratio vector (length: $N-1$) is given by

$$\psi_i = -\frac{\beta_{ci} \cdot D'_{Ti}}{\beta_T \cdot D_{ii}}\,. \tag{7}$$

Note that the definition of the separation ratio is different than in Ryzhkov *et al.* [21, 22]. The matrix of Lewis numbers $Le_{ii} = a/D_{ii}$ and the cross-diffusion numbers $Cr_{ij} = (D_{ij}/D_{ii})(\Delta C_j/\Delta C_i)$ are of size $(N-1)\times(N-1)$. Note that the matrix $\mathbf{Le}$ is diagonal and the matrix $\mathbf{Cr}$ has the main diagonal elements equal to unity, hence, they both comprise only $(N-1)\times(N-1)$ independent coefficients. In conclusion, the problem under consideration, accounting for separation ratios, Rayleigh number and porosity, depends on $(N-1)^2+N+1$ dimensionless parameters. The dimensionless boundary conditions for $x=0$ and $x=1$ are

$$\boldsymbol{V}\cdot\boldsymbol{n} = 0, \qquad \boldsymbol{J}_i\cdot\boldsymbol{n} = 0, \tag{8}$$

$$T(x=0,y) = 1, \qquad T(x=1,y) = 0, \tag{9}$$

where $\boldsymbol{n}$ is the unit vector and $\boldsymbol{J}_i$ is the dimensionless mass flow of the component i,

$$\boldsymbol{J}_i = -\mathbf{Le}^{-1}\cdot\nabla(\mathbf{Cr}\cdot\boldsymbol{C}_i - \mathbf{1}\cdot T). \tag{10}$$

The dimensionless boundary conditions for $y=0, A$ are

$$\boldsymbol{V}\cdot\boldsymbol{n} = 0, \qquad \boldsymbol{J}_i\cdot\boldsymbol{n} = 0, \tag{11}$$

$$\partial_y T(x,y=0) = 0, \qquad \partial_y T(x,y=A) = 0, \tag{12}$$

where $A = L/h$ is the aspect ratio of the column. Ryzhkov *et al.* [21, 22] or Lyubimova and Zubova [25] reduced the number of dimensionless parameters of this problem by working in the standard basis of the matrix of Schmidt numbers. This method, based on the matrix diagonalization technique, uncouples the equation of conservation of each mass fraction. This transformation would be useful when studying the stability of flows in multi-component mixtures. We intend to implement it in our forthcoming work on such stability.

2.2 Ternary mixture THN(0.8)-IBB(0.1)-nC12(0.1)

We used the data of the benchmark DCMIX1 [14] to provide the values of the diffusion coefficients so that our results would apply to a real-world ternary mixture. This benchmark was composed of 1,2,3,4-tetrahydronaphthalene (THN), isobutylbenzene (IBB) and *n*-dodecane (nC12) with mass fractions 0.8-0.1-0.1. All the transport coefficients were taken from [14]. Note that in this work we are adopting a component order different from the one in ref. [14], component 1 being THN and 2 nC12. Consequently the numerical values of diffusion and thermodiffusion coefficients need to be changed: the thermodiffusion coefficients were equal to $D'_{T1} = 0.65\cdot 10^{-12}\,\mathrm{m^2/(s\,K)}$ and $D'_{T2} = -0.49\cdot 10^{-12}\,\mathrm{m^2/(s\,K)}$. The mean values were used for the pure diffusive coefficients $D_{11} = 5.96\cdot 10^{-10}\,\mathrm{m^2/s}$, $D_{22} = 6.79\cdot 10^{-10}\,\mathrm{m^2/s}$. The measured values for the cross-diffusion coefficients were dispersed, while the Soret coefficients S_{T1} and S_{T2} were in good agreement. The value of the cross-diffusion coefficients were determined by using the equations from [13]

$$D'_{T1} = D_{11}\,S_{T1} + D_{12}\,S_{T2}, \tag{13}$$

$$D'_{T2} = D_{22}\,S_{T2} + D_{21}\,S_{T1}. \tag{14}$$

The results obtained were $D_{12} = 0.15\cdot 10^{-10}\,\mathrm{m^2/s}$ and $D_{21} = 1.1\cdot 10^{-10}\,\mathrm{m^2/s}$. In porous media, tortuosity affects all the transport coefficients, a tortuosity equal to $\tau = 1.35$ has been determined by Costesèque *et al.* [27]. The thermodynamic coefficients $\beta_T = 8.48\cdot 10^{-4}/\mathrm{K}$, $\beta_{c1} = -0.136$, $\beta_{c2} = 0.120$, $\mu = 1.719\cdot 10^{-3}\,\mathrm{kg/(m\cdot s)}$ and the density $\rho = 925.3\,\mathrm{kg/m^3}$ were taken from [28]. For the thermal conductivity of the mixture inside the pores, an average value was considered based on the thermal diffusivity of each pure component found in [29], $\lambda = 0.128\,\mathrm{W/(m\cdot K)}$. The dimensionless numbers obtained using these thermodynamic coefficients are listed in table 1.

Table 1. Dimensionless numbers for the ternary mixture THN-IBB-nC12 with mass fractions 0.8-0.1-0.1 in a porous medium of permeability $K = 10^{-10}\,\mathrm{m^2}$, normalized porosity $\varepsilon = 0.25$ and thermal diffusivity $a = 2.0\cdot 10^{-7}\,\mathrm{m^2/s}$.

Dimensionless number	THN	nC12
Lewis number (Le)	613	538
Separation factor (ψ)	0.17	0.10
Cross-diffusion number (Cr)	$Cr_{12} = -0.016$	$Cr_{21} = -0.24$

3 Parallel Flow Approximation

3.1 Basic flow

For binary mixtures, a previous study [30] showed that the Parallel Flow Approximation (PFA) was valid in shallow cavities. With the PFA, the streamlines are assumed to be parallel to the vertical walls of the thermo-gravitational column, thus the horizontal velocity is taken equal to zero. The PFA is valid far from the horizontal walls. The basic state is approximated by

$$\boldsymbol{V} = v(x)\,\boldsymbol{e}_y, \tag{15}$$

$$\boldsymbol{C}(x,y) = \boldsymbol{m}\,y + \boldsymbol{f}(x), \tag{16}$$

$$T(x,y) = m_T\,y + g(x). \tag{17}$$

Equations (15)–(17) describe a unicellular flow for which there is only one convective roll in the thermo-gravitational column. By inserting eqs. (15)–(17) into the

system of eqs. (2)–(5), the following system for $v(x)$, $T(x)$ and $\boldsymbol{f}(x)$ is obtained:

$$\partial_x^2 v(x) - \omega^2\, v(x) = 0, \qquad \partial_x^2 T(x) = 0, \tag{18}$$

$$\mathsf{Le}^{-1} \cdot \mathsf{Cr} \cdot \partial_x^2 \boldsymbol{C}(x,y) = \boldsymbol{m}\, v(x), \tag{19}$$

where

$$\omega^2 = Ra\, \boldsymbol{\psi}^T \cdot \mathsf{Le} \cdot \mathsf{Cr}^{-1} \cdot \boldsymbol{m}.$$

The PFA is not valid close to the horizontal walls, thus, the boundary condition on the latter must be modified. In order to provide for the lack of boundary condition, the following hypotheses are considered:

- the mass flow rate is assumed to be equal to zero through any horizontal cross-section

$$\int_0^1 v(x)\, \mathrm{d}x = 0, \tag{20}$$

- the conservation of each component in the cavity is assumed

$$\int_0^1 \int_0^A \boldsymbol{C}(x,y)\, \mathrm{d}x\, \mathrm{d}y = 0, \tag{21}$$

- the thermal flow rate through any horizontal cross-section is equal to zero

$$\int_0^1 (\boldsymbol{V} \cdot T + \boldsymbol{J}_T) \cdot \boldsymbol{n}\, \mathrm{d}x = 0. \tag{22}$$

$\boldsymbol{J}_T$ is the thermal flow equal to $\boldsymbol{J}_T = -\nabla T$. A last boundary condition is required to solve the system of eqs. (18)-(19). In order to obtain another boundary condition, the curl operator was applied to eq. (3) and evaluated for $x = 0, 1$:

$$\partial_x v = Ra\, \partial_x (T + \boldsymbol{\psi}^T \cdot \boldsymbol{C}). \tag{23}$$

The temperature was

$$T = 1 - x. \tag{24}$$

The solution for the velocity and the mass fraction depend on the sign of ω, if $\omega^2 > 0$ then

$$v(x) = -\psi_0 \left[\frac{1 - \cosh(\omega)}{\sinh(\omega)} \cosh(\omega\, x) + \sinh(\omega\, x) \right], \tag{25}$$

$$\boldsymbol{C}(x,y) = \frac{\mathsf{Le} \cdot \mathsf{Cr}^{-1} \cdot \boldsymbol{m}}{\omega^2} \left[v(x) + Ra\, x - \frac{Ra}{2} \right] + \boldsymbol{m} \left(y - \frac{A}{2} \right). \tag{26}$$

If $\omega^2 = 0$, then

$$v(x) = Ra \left[\boldsymbol{\psi}^T \cdot (\mathsf{Cr} \cdot \mathbf{1}) + 1 \right] \left(\frac{1}{2} - x \right), \tag{27}$$

$$\boldsymbol{C}(x,y) = Ra \mathsf{Le} \cdot \mathsf{Cr}^{-1} \cdot \boldsymbol{m} \left(\frac{x^2}{4} - \frac{x^3}{6} - \frac{1}{24} \right) + \mathsf{Cr} \cdot \mathbf{1} \left(\frac{1}{2} - x \right) + \boldsymbol{m} \left(y - \frac{A}{2} \right). \tag{28}$$

On the other hand, if $\omega^2 < 0$ then

$$v(x) = -\psi_0 \left[\frac{\cos(\omega) - 1}{\sin(\omega)} \cos(\omega\, x) + \sin(\omega\, x) \right], \tag{29}$$

$$\boldsymbol{C}(x,y) = -\frac{\mathsf{Le} \cdot \mathsf{Cr}^{-1} \cdot \boldsymbol{m}}{\omega^2} \left[v(x) + Ra\, x - \frac{Ra}{2} \right] - 2\, x\, \mathsf{Cr}^{-1} \cdot \mathbf{1} + \boldsymbol{m} \left(y - \frac{A}{2} \right), \tag{30}$$

where $\psi_0 = \frac{Ra}{\omega} (1 + \boldsymbol{\psi}^T \cdot \mathsf{Cr}^{-1} \cdot \mathbf{1})$.

3.2 Vertical Mass fraction Gradient and separation

For vertical cavities, a unicellular flow separates each component i between the top and bottom of the cavity. Thus the separation of the component i is equal to $\boldsymbol{S} = A \cdot \boldsymbol{m}$, $\boldsymbol{m}$ is a vector of length $N - 1$ and is called the Vertical Mass fraction Gradient (VMG). In order to determine the VMG of each component, the mass flow rate of each component through a horizontal cross-section is assumed equal to zero:

$$\int_0^1 (\boldsymbol{V} C_i + \boldsymbol{J}_i) \cdot \boldsymbol{n}\, \mathrm{d}x = 0. \tag{31}$$

Solving this coupled system of equations gives the separation of each component of an N-component mixture. If $\omega = 0$, an analytical expression can be obtained:

$$\boldsymbol{m} = 10 Ra \left(\boldsymbol{\psi}^T \cdot (\mathsf{Cr} \cdot \mathbf{1}) + 1 \right) \left[(Ra \mathsf{Le})^2 + 120 \mathsf{Cr}^2 \right]^{-1} \mathsf{Le} \cdot \mathbf{1}. \tag{32}$$

For a mixture, the two experimental control parameters of a thermo-gravitational column are the column thickness and the difference in temperature. Figure 2 shows the influence of the control parameters of a thermo-gravitational column on the separation component for a ternary mixture. The separation is strongly influenced by the thickness of the cavity.

4 Furry, Jones and Onsager model

4.1 Basic flow

In 1939 [8] the thermo-gravitational separation process was analytically studied for vertical cavities filled with a binary mixture of gases. In [8], the mass fraction influence on the density was neglected as opposed to the temperature influence on the term of the gravitational force. This model is called the FJO model. Applying the curl operator and the FJO model to eq. (2), the system of eqs. (2)–(5) leads to

$$\boldsymbol{\nabla} \cdot \boldsymbol{V} = 0, \tag{33}$$

$$\partial_x v(x) = Ra \partial_x T(x), \tag{34}$$

$$\varepsilon \partial_t \boldsymbol{C} + (\boldsymbol{V} \cdot \boldsymbol{\nabla})\, \boldsymbol{C} = \mathsf{Le}^{-1} \cdot \nabla^2 (\mathsf{Cr} \cdot \boldsymbol{C} - \mathbf{1} \cdot T), \tag{35}$$

$$\partial_t T + \boldsymbol{V} \cdot \boldsymbol{\nabla} T = \nabla^2 T. \tag{36}$$

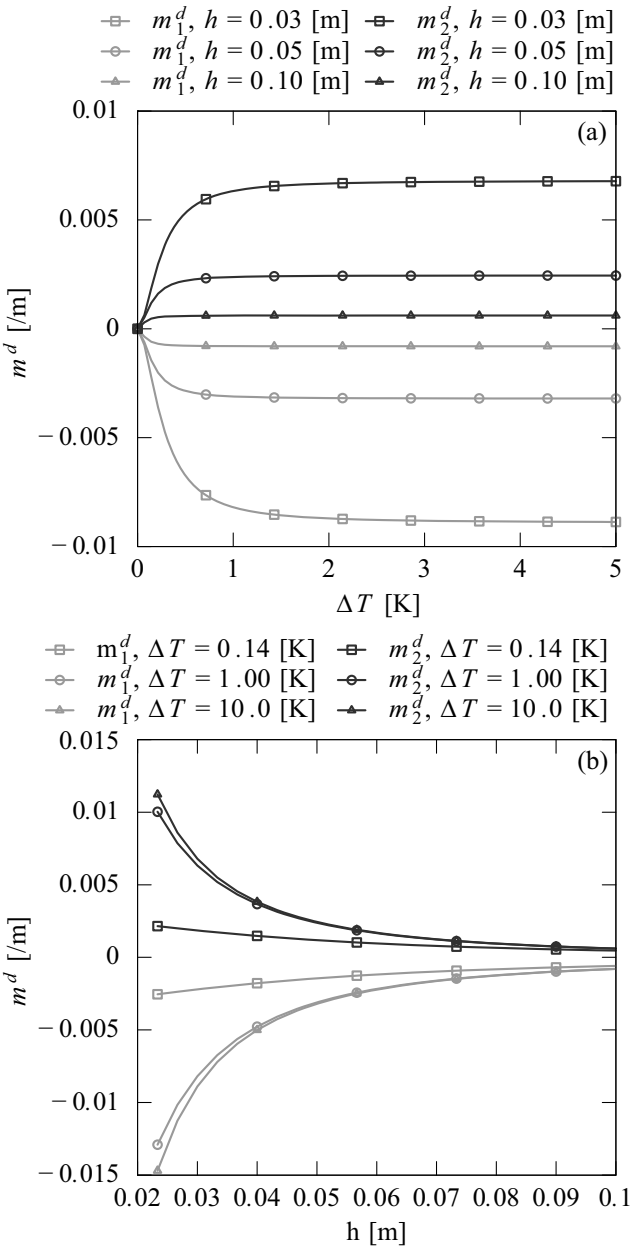

Fig. 2. Influence of the control parameters (the temperature difference (a) and the cavity thickness (b)) on the vertical mass fraction gradient of components 1 and 2 for a ternary mixture ($Le_1 = 613$, $Le_2 = 538$, $\psi_1 = 0.17$, $\psi_2 = 0.10$, $Cr_{12} = -0.016$, $Cr_{21} = -0.24$).

The basic state under the parallel flow approximation and the FJO model is obtained from the system of eqs. (33)–(36) using the boundary conditions (8), (9) and the three hypotheses:

- the conservation of each component in the cavity,
- the thermal flow rate through any horizontal cross-sections is equal to zero,
- the mass flow rate of each component through a horizontal cross-section is equal to zero,

$$v(x) = \frac{1}{2}\, Ra\,(1 - 2\,x), \tag{37}$$

$$\boldsymbol{C}(x,y) = \frac{Ra}{2}\mathbf{Le}\cdot\mathbf{Cr}^{-1}\cdot\boldsymbol{m}\left(\frac{x^2}{2} - \frac{x^3}{3} - \frac{1}{12}\right) + \mathbf{Cr}^{-1}\cdot\mathbf{1}\left(\frac{1}{2} - x\right) + \boldsymbol{m}\left(y - \frac{A}{2}\right), \tag{38}$$

$$T(x) = 1 - x. \tag{39}$$

4.2 Vertical Mass fraction Gradient and separation

In order to determine an analytical expression for the VMG, the mass flow rate of each component through a horizontal cross-section is assumed to be equal to zero. This assumption allows an analytical expression for the separation to be obtained:

$$\boldsymbol{m} = 10Ra\left[\mathbf{Cr}^{-1}\cdot\mathbf{Le}Ra^2 + 120\mathbf{Le}^{-1}\cdot\mathbf{Cr}\right]^{-1}\cdot\mathbf{Cr}^{-1}\cdot\mathbf{1} \tag{40}$$

$$= 10Ra\left[(Ra\,\mathbf{Le})^2 + 120\mathbf{Cr}^2\right]^{-1}\cdot\mathbf{Le}\cdot\mathbf{1}. \tag{41}$$

The VMGs for the $N-1$ components are expressed in terms of the Lewis number, the cross-diffusion numbers and the thermal Rayleigh number in eq. (40). For the component N, the VMG can be obtained using the relation

$$\sum_{i=1}^{N} C_i = 0. \tag{42}$$

The same results were obtained for a binary mixture ($N = 2$) by Furry, Jones and Onsager [8] and for a ternary mixture ($N = 3$) by Larabi *et al.* [23]. For the FJO model, the separation ratio ($\boldsymbol{\psi}$) was neglected. Figure 3 shows the VMG of component 1 (obtained by the PFA model)

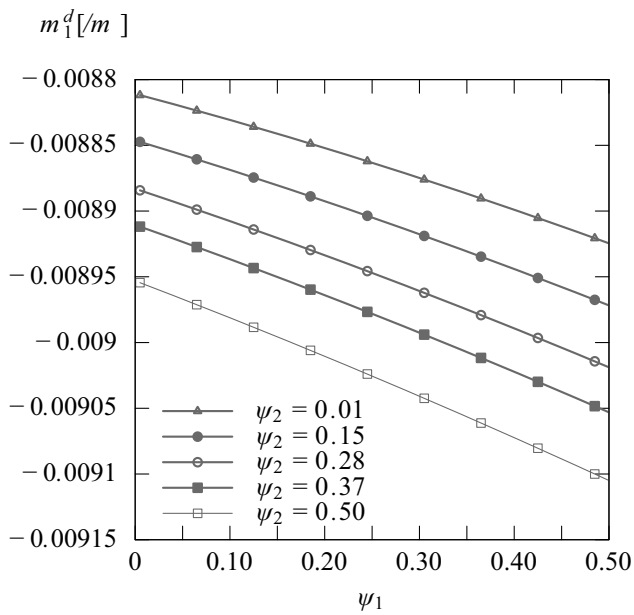

Fig. 3. Influence of the separation ratio on the VMG obtained from the PFA for a ternary mixture ($Le_1 = 613$, $Le_2 = 538$, $Cr_{12} = -0.016$, $Cr_{21} = -0.24$) for a temperature difference equal to $\Delta T = 5\,\mathrm{K}$ and a thickness $h = 3\cdot 10^{-2}\,\mathrm{m}$.

according to the separation ratio. For the same dimensionless parameters the VMG obtained by the FJO model is $m^d_{1fjo} = -8.80 \cdot 10^{-3}$/m. However, the PFA predicts a VMG between $-8.80 \cdot 10^{-3}$/m and $-9.15 \cdot 10^{-3}$/m for $(\psi_1, \psi_2) \in [0, 0.5]^2$ (fig. 3). If the influence of the cross-diffusion can be neglected, then the analytical expression for the VMG leads to

$$m_i = \frac{10\, Le_i\, Ra}{(Le_i\, Ra)^2 + 120}\,. \tag{43}$$

Larabi *et al.* [23] studied the influence of the cross-diffusion on the VMG for the case of ternary mixture. Equation (40) in the dimensional form leads to a relation between D'_{Ti}, D_{ij}:

$$10\, Kg\Delta T^2 \frac{D'_{Ti}\beta_T}{D^2_{ii}\,\nu} \sum_{j=1}^{N-1} \left[\left(\frac{K\, hg\beta_T \Delta T}{\nu\, D_{ii}} \right)^2 + 120 \sum_{k=1}^{N-1} \frac{D_{ik} D_{kj} D'_{Tj}}{D_{kk} D_{jj} D'_{Ti}} \right]^{-1} + m^d_i = 0. \tag{44}$$

If the cross-diffusion effect can be neglected then eq. (44) leads to

$$D'_{Ti} = -\frac{m^d_i}{10 Kg\Delta T^2} \frac{\nu\, D^2_{ii}}{\beta_T} \left[\left(Khg\Delta T \frac{\beta_T}{D_{ii}\nu} \right)^2 + 120 \right]. \tag{45}$$

5 Direct simulation

5.1 Flow in the cavity

In order to assess the hypothesis considered for the theoretical models (PFA and FJO), a direct numerical simulation was performed using the Comsol Multiphysics software. The system of eqs. (2)–(5) and the boundary conditions (8) were solved numerically for a ternary mixture using a finite elements method. The aspect ratio of the thermo-gravitational column was $A = 20$. A rectangular mesh was used and the spatial resolution was 50×200:

$$y_i = \frac{A}{2} \left[\cos\left(\frac{\pi\, i}{N_y - 1} \right) + 1 \right] \quad \text{for } i = 0, \ldots, N_y - 1. \tag{46}$$

The grid was uniform in the x-direction and distributed as y_i in eq. (46) (with $N_y = 200$) for the y-direction. The order of convergence with this distribution was equal to 2.5. The streamlines and the temperature are presented for the stationary state in fig. 4. As expected, there was a unicellular flow in the cavity, the streamlines were parallel to the vertical walls and the temperature depended linearly on the thickness of the column.

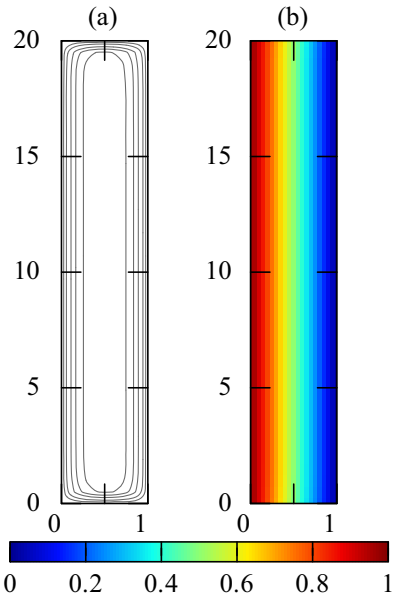

Fig. 4. (a) Streamlines and (b) temperature in a thermo-gravitational column filled with a ternary mixture ($Le_1 = 613$, $Le_2 = 538$, $\psi_1 = 0.17$, $\psi_2 = 0.10$, $Cr_{12} = -0.016$, $Cr_{21} = -0.24$) at the stationary state for a temperature difference equal to $\Delta T = 6\,$K and a thickness $h = 3 \cdot 10^{-2}\,$m ($Ra = 0.4013$).

5.2 Assessment of the theoretical models

In order to quantify the error, two norms were used:

$$E_2 = 100 \cdot \frac{\|x_{the} - x_{num}\|_2}{\|x_{num}\|_2}\,, \tag{47}$$

$$E_\infty = 100 \cdot \frac{\|x_{the} - x_{num}\|_\infty}{\|x_{num}\|_\infty}\,, \tag{48}$$

where x_{the} and x_{num} are the theoretical and numerical values, respectively, $\|\ldots\|_2$ is the 2-norm and $\|\ldots\|_\infty$ is the infinity norm. E_2 and E_∞ are the mean error and the worst case error. These norms were calculated for all the numerical values on figs. 5, 6, 7 and 8 and are reported in table 2. The horizontal velocity was neglected for the two theoretical models, while for the PFA, the vertical velocity was as given by eq. (25) if $\omega^2 > 0$ and by eq. (29) if $\omega^2 < 0$. For the FJO model the vertical velocity was a linear function depending only on the Rayleigh number. The velocity profiles obtained in the two cases ($\omega^2 > 0$ and $\omega^2 < 0$) are illustrated in fig. 5. The results using the two theoretical models are compared to the direct simulation for a difference in temperature of $\Delta T = 10\,$K. For the PFA, the two errors are lower than 1%, so the PFA is in very good agreement with the numerical results. The FJO model based on physical considerations leads to an error of 5% for the velocity. In fig. 6 the VMG of components 1 and 2 are presented according to the temperature using the three methods. As table 2 shows, the two theoretical models are in good agreement with the numerical results. Figures 7 and 8 present the mass fraction of THN and nC12 in the cavity at the stationary state for a difference

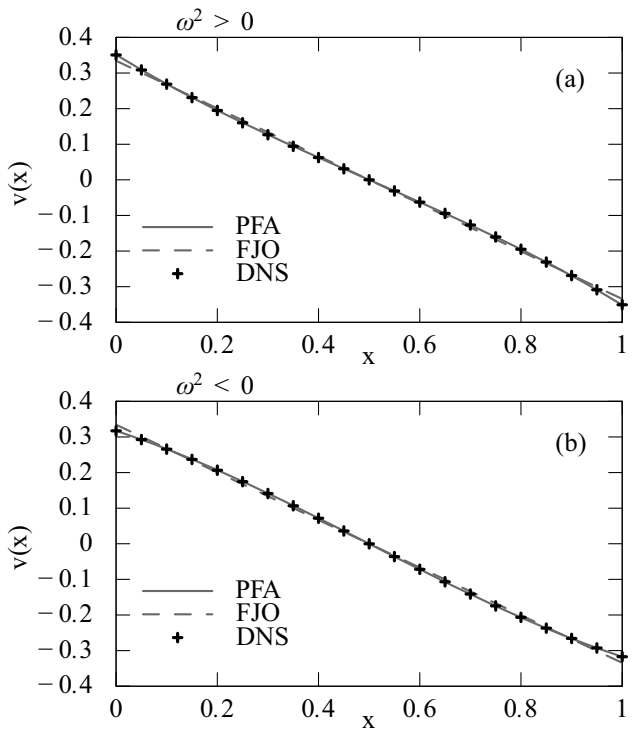

Fig. 5. Numerical (DNS) and theoretical (PFA and FJO) horizontal profiles of the vertical velocity in the thermo-gravitational column at the stationary state for ternary mixtures (a) $\psi_1 = 0.17$, $\psi_2 = 0.10$, (b) $\psi_1 = -0.17$, $\psi_2 = -0.10$ and $Le_1 = 613$, $Le_2 = 538$, $Cr_{12} = -0.016$, $Cr_{21} = -0.24$ for $\Delta T = 10\,\mathrm{K}$ and $h = 3 \cdot 10^{-2}\,\mathrm{m}$ ($Ra = 0.6688$).

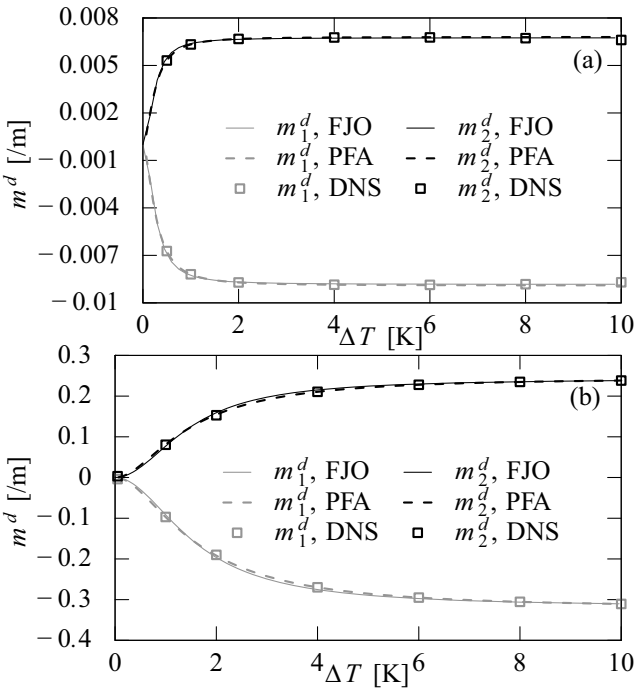

Fig. 6. Theoretical (PFA and FJO) and numerical (DNS) Vertical Mass fraction Gradient according to the temperature difference for a ternary mixture ($Le_1 = 613$, $Le_2 = 538$, $\psi_1 = 0.17$, $\psi_2 = 0.10$, $Cr_{12} = -0.016$, $Cr_{21} = -0.24$) for a thickness equal to (a) $h = 3 \cdot 10^{-2}\,\mathrm{m}$ and (b) $5 \cdot 10^{-3}\,\mathrm{m}$.

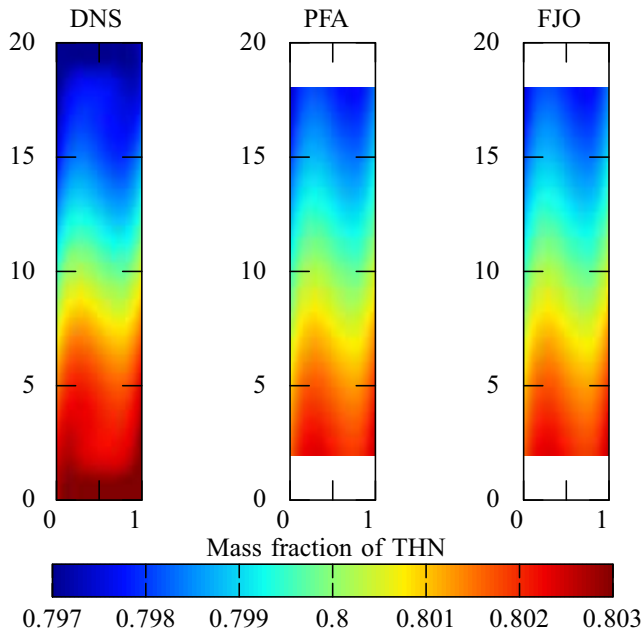

Fig. 7. Theoretical (PFA and FJO) and numerical (DNS) mass fraction of component 1 ($Le_1 = 613$, $Le_2 = 538$, $\psi_1 = 0.17$, $\psi_2 = 0.10$, $Cr_{12} = -0.016$, $Cr_{21} = -0.24$) in the cavity at the stationary state for a temperature difference of 6 K and a thickness of $3 \cdot 10^{-2}\,\mathrm{m}$ ($Ra = 0.4013$).

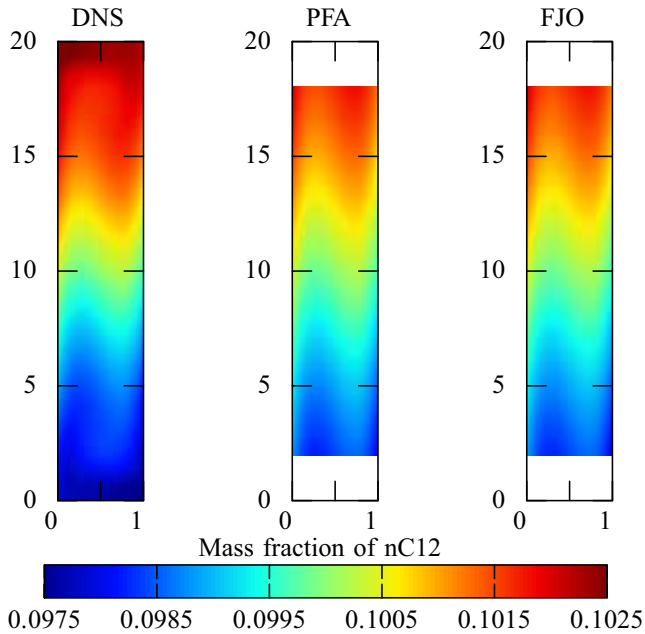

Fig. 8. Theoretical (PFA and FJO) and numerical (DNS) mass fraction of component 2 ($Le_1 = 613$, $Le_2 = 538$, $\psi_1 = 0.17$, $\psi_2 = 0.10$, $Cr_{12} = -0.016$, $Cr_{21} = -0.24$) in the cavity at the stationary state for a temperature difference of 6 K and a thickness of $3 \cdot 10^{-2}\,\mathrm{m}$ ($Ra = 0.4013$).

in temperature of 6 K and a thickness of $3 \cdot 10^{-2}\,\mathrm{m}$ using the two theoretical models and the numerical simulations. The THN is the heaviest component of the ternary mixture THN(0.8)-IBB(0.1)-nC12(0.1) and nC12 is the lightest component. In fig. 7 the THN is more concentrated at

Table 2. Mean and worst case error between the numerical and theoretical results (PFA and FJO).

Figure	PFA		FJO	
	E_2	E_∞	E_2	E_∞
5(a)	0.16%	0.21%	3.47%	4.64%
5(b)	0.17%	0.15%	3.72%	5.41%
6(a)	0.92%	2.16%	1.15%	2.24%
6(b)	0.62%	1.10%	1.73%	2.06%
7	10^{-3}%	10^{-3}%	10^{-3}%	10^{-3}%
8	0.01%	0.05%	0.04%	0.06%

the bottom of the cavity and in fig. 8 nC12 is at the top of the thermo-gravitational column, which is consistent with physics and the sign of the VMG observed in fig. 6. The white zones observed in figs. 7 and 8 are the zones in the thermo-gravitational column where the streamlines are not parallel to the vertical walls so neither the PFA nor FJO results are valid. The white zones represent 20% of the area of the column and the coloured zone 80%. The norms reported in table 2 are calculated for 80% of the cavity. As can be observed in the table the error for the mass fraction in 80% of the column is less than 0.1%, the two theoretical models are a perfect match for the simulations.

6 Conclusion

In this paper a theoretical analysis for the separation of an N-component mixture in a vertical porous thermo-gravitational column is proposed. Two theoretical models for the separation of N-component mixtures are presented. These models, based on the parallel flow approximation allow the separation to be determined for each component of an N-component mixture. The mass fraction, velocity and temperature at the stationary state were obtained analytically. These models indirectly validate the measured transport coefficients. The Furry-Jones-Onsager theory was extended to the N-component mixture and the separation was expressed as a function of the Rayleigh number, the matrix of Lewis numbers and the cross-diffusion numbers. In order to assess the theoretical work, direct numerical simulations were performed for a cavity with an aspect ratio of 20. A good match was obtained for the mass fraction in 80% of the cavity. The theoretical and numerical results for the separation in the cavity were in good agreement, thus validating the assumptions made in the theoretical models. A quantitative analysis of the errors for these models was performed.

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Author contribution statement

DM and AM conceived the original idea and developed the theory. MAL and DM planned and carried out the simulations. DM wrote the manuscript in consultation with MAL and AM.

References

1. W.R. Wilcox, Prog. Cryst. Growth Charact. Mater. **26**, 153 (1993).
2. J.S. Turner, Annu. Rev. Fluid Mech. **17**, 11 (1985).
3. H.E. Huppert, R.S.J. Sparks, Annu. Rev. Earth Planet. Sci. **12**, 11 (1984).
4. J.C. Legros, Y. Gaponenko, A. Mialdun, T. Triller, A. Hammon, C. Bauer, W. Khler, V. Shevtsova, Phys. Chem. Chem. Phys. **17**, 27713 (2015).
5. K. Vafai, *Handbook of Porous Media* (CRC Press, 2015).
6. D.A. Nield, A. Bejan, *Convection in Porous Media* (Springer, 1998).
7. A.C. Baytaş, I. Pop, Int. J. Therm. Sci. **41**, 861 (2002).
8. W.H. Furry, R.C. Jones, L. Onsager, Phys. Rev. **55**, 1083 (1939).
9. M. Lorenz, A.H. Emery, Chem. Eng. Sci. **11**, 16 (1959).
10. R. Bennacer, A. Mohamad, M. El-Ganaoui, Int. J. Therm. Sci. **48**, 1870 (2009).
11. P. Blanco, M. Bou-Ali, J.K. Platten, D.A. de Mezquia, J.A. Madariaga, C. Santamara, J. Chem. Phys. **132**, 114506 (2010).
12. P. Kolodner, H. Williams, C. Moe, J. Chem. Phys. **88**, 6512 (1988).
13. M. Gebhardt, W. Köhler, Eur. Phys. J. E **38**, 24 (2015).
14. M.M. Bou-Ali, A. Ahadi, D. Alonso de Mezquia, Q. Galand, M. Gebhardt, O. Khlybov, W. Köhler, M. Larrañaga, J. Legros, T. Lyubimova, A. Mialdun, I. Ryzhkov, M. Saghir, V. Shevtsova, S. Van Vaerenbergh, Phys. J. E **38**, 30 (2015).
15. V. Sechenyh, J. Legros, A. Mialdun, J. Ortiz de Zrate, V. Shevtsova, J. Chem. Phys. **120**, 535 (2016).
16. J.K. Larre, J.K. Platten, G. Chavepeyer, Int. J. Heat Mass Transf. **40**, 545 (1997).
17. K. Haugen, A. Firoozabadi, J. Chem. Phys. **122**, 014516 (2005).
18. K. Haugen, A. Firoozabadi, J. Chem. Phys. **127**, 154507 (2007).
19. K. Haugen, A. Firoozabadi, J. Chem. Phys. **124**, 054502 (2006).
20. I.I. Ryzhkov, V.M. Shevtsova, Phys. Fluids **19**, 027101 (2007).
21. I.I. Ryzhkov, V.M. Shevtsova, Phys. Fluids **21**, 014102 (2009).
22. I.I. Ryzhkov I.I., V.M. Shevtsova, Phys. Rev. E **79**, 026308 (2009).
23. M.A. Larabi, D. Mutschler, A. Mojtabi, J. Chem. Phys. **144**, 244902 (2016).
24. V.M. Shevtsova, D.E. Melnikov, J.C. Legros, Phys. Rev. E **73**, 047302 (2006).
25. T. Lyubimova, N. Zubova, Eur. Phys. J. E **38**, 19 (2015).
26. K. Ghorayeb, A. Firoozabadi, SPE J. **5**, 158 (2000).
27. P. Costeseque, S. Gaillard, P. Jamet, Y. Thbault, Entropie **239**, 149 (2002).
28. M. Larraaga, M., Bou-Ali, D. Alonso de Mezquia, D.A.S. Rees, J.A. Madariaga, C. Santamaria, J.K. Platten, Eur. Phys. J. E **38**, 28 (2015).
29. J.F. Dutrieux, J.K. Platten, G. Chavepeyer, M.M. Bou-Ali, J. Chem. Phys. B **106**, 6104 (2002).
30. M. Ouriemi, P. Vasseur, A. Bahloul, L. Robillard, Int. J. Therm. Sci. **45**, 752 (2006).