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1 **A Cahn-Hilliard Approach to**
2 **Thermodiffusion in Porous Media**

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5 **Abstract**

6 We consider a fluid-saturated porous medium exposed to a non-uniform temper-
7 ature field, and describe it as a non-isothermal biphasic mixture comprising a solid
8 and a two-constituent fluid. We model such a system by assuming that the fluid
9 free energy density depends on the gradient of the solute mass fraction. This consti-
10 tutive choice induces a coupling between the temperature gradient and the solute
11 diffusive mass flux, which adds itself to the standard Soret effect. We present numer-
12 ical simulations of a thermogravitational cell to show how the modified constitutive
13 framework, which is mandatory in diffuse-interface problems (e.g. the Cahn-Hilliard
14 model), could lead to some novel interpretations of thermodiffusion, and enrich the
15 phenomenological description of the considered benchmarks.

16 **Keywords:** Soret Effect, Thermodiffusion, Mixture Theory, Cahn-Hilliard Model.

17 **AMS Subject Classification:** 05A16, 65N38, 78M50.

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1 Introduction

The onset of a mass flux by means of a thermal gradient is a phenomenon known as *thermodiffusion*, and its manifestation is said to be the Soret effect. Dually, the *Dufour effect* consists of the generation of a heat flux by means of the concentration gradient of a solute in a fluid solution. Such phenomena are referred to as *coupled phenomena* or *cross-effects*, as they represent the experimental evidence of the coupling between the flux of a given extensive quantity and the gradient of a state variable that is not directly power-conjugate to it (Bear and Bachmat, 1990). In the following, we shall be merely concerned with thermodiffusion and Soret effect.

In this work, we study a system comprising a porous medium and a two-constituent fluid that rearranges its composition under the action of a thermal gradient. In particular, we analyse two experiments in which an initially uniform fluid undergoes a separation of its constituents due to a mass flux initiated by a temperature gradient. Such experiments, performed by using a device known as thermogravitational cell, have been investigated, for example, by Jamet et al. (1992), Fargue et al. (1998), and Benano-Melly et al. (2001). In the experimental setting pertaining to the so-called *pure* Soret effect (Tyrrell, 1956), an initially uniform solution is put between two horizontal plates, kept at different temperatures. To reduce convection, the upper plate is held at a temperature higher than that of the lower one. Under these conditions, a stationary state can be attained, in which the thermal gradient balances the gradient of concentration. In the case of the thermogravitational cell, the fluid mixture is initially uniform, but the surfaces kept at different temperatures are vertical, which implies that the fluid velocity influences the mass transport of the mixture constituents by means of convection currents as well as solutal and thermal dispersion (Benano-Melly et al., 2001). We remark, however, that both in the description given by Tyrrell (1956) and in that provided by Benano-Melly et al. (2001), the common feature of thermodiffusion is the capability of developing a concentration gradient from an initially uniform mixture.

As second-order contributions, the Soret and Dufour effects are often disregarded. There are cases, however, in which they play an appreciable role. Ingle and Horne (1973)

47 and Rowley and Horne (1980) addressed thermal diffusion and the Dufour effect in mix-
48 tures of organic fluids of different composition. The Soret effect was observed in vari-
49 ous physical frameworks, such as solar ponds (Celestino et al., 2006) and compact clays
50 (Rosanne et al., 2001). Moreover, the thermally induced solutal separation has been inves-
51 tigated by several authors (Fargue et al., 1998; Zhang et al., 1999; Benano-Melly et al.,
52 2001; Rauch and Köhler, 2002, 2003; Fargue et al., 2004; Grillo et al., 2011; Srinivasan
53 and Saghir, 2013) both for organic and inorganic compounds. A review on experimental
54 results about the Soret effect is provided by Platten (2006).

55 Thermodiffusion has attracted several scientists also in more recent times and, in fact,
56 studies on Soret and Dufour effects in non-Darcy porous media have been conducted, for
57 example, by RamReddy et al. (2016), Yadav and Kim (2015), Mallikarjuna et al. (2014),
58 and Srinivasacharya et al. (2014). Soret and Dufour effects have also been investigated by
59 Harinath Reddy et al. (2016) for the case of “*radiation absorption fluid*”, and by Chandra
60 Shekar et al. (2016) for the case of magnetohydrodynamic “*natural convective heat and*
61 *solute transfer*”. Moreover, Veeresh et al. (2016) analysed “*thermal diffusion effects in*
62 *unsteady magnetohydrodynamic*” problems.

63 The theory of thermodiffusion constitutes an important chapter of Non-Equilibrium
64 Thermodynamics. The mathematical apparatus on which it is developed relies on the
65 Curie Principle and the Onsager-Casimir reciprocity relations (De Groot and Mazur,
66 1984; Bear and Bachmat, 1990). These are invoked to express the mass and heat fluxes
67 as functions of both the gradient of temperature and the gradient of the solutal relative
68 chemical potential.

69 In fact, thermodiffusion is the manifestation of a symmetry-breaking that occurs in
70 a mixture exposed to a thermal gradient, with the system passing from a uniform to a
71 non-uniform distribution of mass, and the separation of the mixture’s components being
72 the most relevant effect of the non-uniformity of the chemical potential.

73 The main idea of our work is to capture the symmetry-breaking associated with the
74 phenomenon of thermodiffusion in the constitutive formulation of the Helmholtz free
75 energy density, \hat{A}_f , of a two-constituent fluid. To this end, we choose the mass fraction of

76 one of the constituents of the mixture as the order parameter of the system, and prescribe
77 \hat{A}_f to be a function of all the state variables of the standard framework of thermodiffusion
78 and of the gradient of the selected order parameter. In particular, we assume that \hat{A}_f is
79 of the Cahn-Hilliard type.

80 The Cahn-Hilliard model was originally conceived for two-phase flows of non-miscible
81 (or weakly miscible) fluids (Anderson and McFadden, 1998; Lowengrub and Truskinovsky,
82 1998). It is a mean-field approach that is able to describe also separation processes, which
83 are driven by the presence of a superficial tension between the phases, culminating with
84 the formation of a *diffuse interface* between two species. Such separation process can be
85 affected also by the presence of a thermal field (Jasnow and Vinals, 1996). Choosing a
86 Helmholtz free energy density of the Cahn-Hilliard type allows to account for end-wall
87 effects and for the spatial resolution of the solutal mass fraction at the constitutive level,
88 and induces a spontaneous coupling between mass diffusion and thermal gradients. We
89 remark that this coupling stems from the constitutive framework, rather than being a
90 consequence of the Curie Principle and Onsager's relations. From the theoretical view-
91 point, its major consequence is the production of a non-standard Soret effect, which adds
92 itself to the one of standard thermodiffusion. To quantify the relevance of our theoretical
93 predictions, we reproduce numerically the experiments in a thermogravitational cell by
94 enforcing both the standard and the non-standard (i.e., Cahn-Hilliard based) model of
95 thermodiffusion. We show how the latter may be used as an additional tool for fitting
96 experimental curves, thereby supplying a correction to the results obtained within the
97 classical framework.

98 Although the Cahn-Hilliard model has been employed especially in the numerical
99 treatment of two-fluid systems, there is an analogy between this higher order theory
100 and the one developed in the framework of Mixture Theory. Indeed, the Cahn-Hilliard
101 model describes the two-fluid system by means of the usual mass and momentum balance
102 law of a single-fluid system, plus an evolution law for an *order parameter*, which in fact
103 can be retrieved from the mass balance law of one of the two fluids, if it is regarded as
104 a component of a binary mixture. This leads to the definition of two distinct regions,

105 each of which is occupied by one of the two fluids only, and a third region, the *diffuse*
106 *interface*, whose characteristic dimensions should be smaller than the other two bulk
107 domains. In the latter, the mixture model can be employed *tout court*, while in the other
108 two, the order parameter acts as a weight, switching off those terms in the equations
109 that pertain to the mixture description. From our understanding, in a two-fluid system,
110 the explicit modelling of a diffuse interface could be done for two main reasons: (a) to
111 avoid the numerical treatment of the discontinuities at the interface between the fluids,
112 which pertains to the *sharp interface* models (Yue et al., 2004); (b) when the dynamical
113 phenomena occurring in that layer influence the entire system, as in the case of an evident
114 surface tension, or non negligible diffusion in the transition zone. Still, the mathematical
115 introduction of a diffuse interface, arising in the Cahn-Hilliard model, has been used
116 for miscible fluids in which dynamical effects that mimic the presence of an interfacial
117 tension are, at least instantaneously, relevant (Joseph et al., 1996). This could be the case
118 of a mixing problem, in which the Korteweg stress, i.e., an additional stress appearing
119 in the momentum balance law of the whole system due to the presence of a gradient of
120 composition, should be taken into account as a surface tension that vanishes as far as the
121 mixing layer spreads (Davis, 1988). Moreover, a dedicated literature (Swernsath et al.,
122 2010; Chen et al., 2017, 2015; Dias et al., 2010) introduces the effects of the Korteweg
123 stress tensor also for treating the injection of miscible fluids in porous media, or in the
124 case of unsaturated flow Cueto-Felgueroso et al. (2009).

125 Our study has been inspired by some discrepancies between the experimental and
126 the numerical studies of the curves “separation ratio vs permeability” associated with
127 a thermogravitational cell (Benano-Melly et al., 2001; Jamet et al., 1992; Fargue et al.,
128 1998). Numerical results obtained within the classical framework of thermodiffusion were
129 compared with the experimental ones by Jamet et al. (1992), and quite a relevant dis-
130 agreement was noticed. It was observed that the evolution of the fluid in the thermo-
131 gravitational cell is strongly influenced by the permeability and porosity of the porous
132 medium (Jamet et al., 1992; Davarzani and Marcoux, 2011), by the characteristic dimen-
133 sion of the cell, the initial mass fraction of the solute, and the physico-chemical properties

134 of the mixture. Jamet et al. (1992) firstly attributed the discrepancy between the numer-
135 ical and the experimental results to an anisotropic permeability. Subsequently, Benano-
136 Melly et al. (2001) considered also the effect of dispersion. Latest results are due to
137 Nasrabadi et al. (2007), who showed that, by adding a compositional dependence of the
138 Soret coefficient on the density (by means of a pressure dependent density), it is possi-
139 ble to obtain, at least for a binary mixture in a porous thermogravitational column, a
140 good agreement between the experimental and numerical results, even though no further
141 contribution of dispersion in the model is observed. The strong effect of the buoyancy
142 term on the goodness of the results of the proposed classical models on thermodiffusion
143 was also observed by Madariaga et al. (2011). For a non porous column (Thomaes cell),
144 thermodiffusion is strongly affected by non trivial natural convection, which, in some
145 cases (i.e., when the mean velocity of the mixture in the column is high), requires a full
146 3D treatment (Chavepeyer et al., 2002). A review has been given by Costeséque et al.
147 (2002). Another fact concerns the *closure problem*, which could lead to a more or less re-
148 alistic coarse scale approximation of the problem (effective thermodiffusion coefficients)
149 (Quintard et al., 1997; Davarzani et al., 2010).

150 In the following, we show that adopting a Helmholtz free energy density of the Cahn-
151 Hilliard type supplies a correction to the mass flux determined within the standard theory
152 of thermodiffusion. Such a correction produces an additional coupling between the ther-
153 mal gradient and the mass flux, and introduces a dispersive-like effect, which is related
154 to the gradient of the solute mass fraction rather than to the fluid velocity. Although
155 we are aware of the fact that the experimental set-up of the thermogravitational cell
156 gives rise to convection currents, we focus here only on the effects associated with the
157 use of a Helmholtz free energy density of the Cahn-Hilliard type. This may contribute
158 to enrich the phenomenological picture of thermodiffusion and to stimulate alternative
159 interpretations of the effects related to it.

160 The paper is structured as follows: In section 2, the mathematical model is developed
161 in detail, and the Second Principle of Thermodynamics is exploited to determine con-
162 sistent generalisations of the Fick and Darcy's laws in the context of Porous Media. In

163 section 3, we review the standard theory of thermodiffusion, and reformulate it within
 164 the Cahn-Hilliard framework. In section 4, we present the benchmark problems used for
 165 our numerical simulations, and introduce the employed numerical methods and model
 166 parameters. In section 5, we discuss in detail the obtained results, and validate our model
 167 by comparing its outputs with the experimental and numerical findings of other Authors.
 168 Particular care will be given to weighting the influence of the Cahn-Hilliard correction.
 169 Finally, in section 6, we summarise our results, and suggest some possible research topics.

170 2 Mathematical Model

171 We consider a physical system consisting of a two-constituent fluid, \mathcal{F} , and a porous
 172 medium, \mathcal{P} . The fluid is free to move throughout the void space of \mathcal{P} , and is assumed to
 173 saturate it completely. Due to the hypothesis of saturation, the porosity of \mathcal{P} coincides
 174 with the volumetric fraction of \mathcal{F} , denoted by ϕ , and the volumetric fraction of \mathcal{P} is given
 175 by $1 - \phi$. At a sufficiently coarse scale of observation, the system under investigation
 176 can be studied by means of Hybrid Mixture Theory (Hassanizadeh, 1986; Bennethum
 177 et al., 2000). In this context, \mathcal{F} and \mathcal{P} can also be referred to as the fluid and solid phase,
 178 respectively.

179 We focus only on the case in which \mathcal{P} is rigid, at rest, and incompressible. In particular,
 180 its mass density, ϱ_s , is regarded as a given constant. Thus, the velocity of the solid porous
 181 medium, \mathbf{u}_s , is null at all times and all points. These assumptions, the mass balance law
 182 of the solid phase, and the saturation constraint imply that ϕ is independent of time. In
 183 the sequel, we shall also assume that ϕ is constant in space.

184 2.1 Balance laws

185 The mass balance law of the fluid phase, \mathcal{F} , is given by

$$\partial_t(\phi\varrho_f) + \operatorname{div}(\phi\varrho_f\mathbf{u}_f) = 0, \quad (1)$$

186 where ρ_f is mass density and \mathbf{u}_f is the velocity of \mathcal{F} . Sometimes it is convenient to
 187 rewrite (1) in terms of the solid phase velocity, \mathbf{u}_s , and the relative velocity $\mathbf{u}_{fs} \equiv \mathbf{u}_f - \mathbf{u}_s$,
 188 which describes the motion of \mathcal{F} relative to \mathcal{P} . However, since the velocity of the solid
 189 phase is null in the present context, it holds that $\mathbf{u}_{fs} = \mathbf{u}_f$. We denote by \mathcal{C}_1 and \mathcal{C}_2 the
 190 constituents of the fluid phase, and select \mathcal{C}_1 as the reference constituent. The composition
 191 of \mathcal{F} is determined by the mass fractions of \mathcal{C}_1 and \mathcal{C}_2 , which are indicated by c_1 and c_2 ,
 192 respectively. Since it holds that $c_1 + c_2 = 1$, it suffices to determine the mass fraction
 193 of the reference constituent, $c_1 \equiv c$, to obtain also $c_2 = 1 - c$, and thus define the local
 194 amounts of \mathcal{C}_1 and \mathcal{C}_2 in \mathcal{F} . By introducing the velocity of \mathcal{C}_1 , \mathbf{u}_{1f} , and the relative velocity
 195 $\mathbf{v} \equiv \mathbf{u}_{1f} - \mathbf{u}_f$, the mass balance law of \mathcal{C}_1 can be written as

$$\phi_{\rho_f} \dot{c} + \operatorname{div} \mathbf{J}_M = 0, \quad (2)$$

196 where $\mathbf{J}_M \equiv \phi_{\rho_f} c \mathbf{v}$ is the mass flux vector associated with \mathcal{C}_1 , while $\dot{c} \equiv \partial_t c + \mathbf{u}_f \cdot \nabla c$
 197 is the substantial derivative of c with respect to the velocity of \mathcal{F} . In addition to (1)
 198 and (2), also the balance laws of momentum, energy, and entropy have to be introduced.
 199 Following Hassanizadeh (1986), it can be shown that, if gravity is the only external force
 200 acting on the system, if inertial forces are negligible, and the relative velocities \mathbf{u}_{fs} and
 201 \mathbf{v} are sufficiently small (i.e., $\|\mathbf{u}_{fs}\|^2 \ll 1$ and $\|\mathbf{v}\|^2 \ll 1$), the momentum balance laws of \mathcal{F}
 202 and \mathcal{C}_1 reduce, respectively, to (Hassanizadeh, 1986)

$$\operatorname{div} \boldsymbol{\sigma} + \mathbf{m} + \phi_{\rho_f} \mathbf{g} = \mathbf{0}, \quad (3a)$$

$$\phi_{\rho_f} c \nabla \vartheta = \mathbf{f}. \quad (3b)$$

203 In (3a), $\boldsymbol{\sigma}$ is the Cauchy stress tensor of the fluid phase, \mathbf{g} is the gravity acceleration
 204 vector, and \mathbf{m} represents the interaction forces exchanged between \mathcal{P} and \mathcal{F} . In (3b), \mathbf{f} is
 205 the dissipative part of the interaction forces exchanged between the two fluid constituents,
 206 and $\vartheta \equiv \vartheta_1 - \vartheta_2$ is the relative chemical potential of \mathcal{C}_1 with respect to \mathcal{C}_2 , whereas ϑ_1 and
 207 ϑ_2 are the chemical potentials of the constituents \mathcal{C}_1 and \mathcal{C}_2 , respectively. Furthermore,

208 the energy balance law for the system as a whole can be written as

$$\phi \varrho_f T \dot{\eta}_f + (1 - \phi) \varrho_s T \partial_t \eta_s = -\operatorname{div} \mathbf{J}_Q - \phi \varrho_f \vartheta \dot{c} - \mathbf{m}_d \cdot \mathbf{u}_{fs}, \quad (4)$$

209 where T is absolute temperature, η_f and η_s are the entropy densities per unit mass of the
 210 fluid and the solid phase, respectively, \mathbf{J}_Q is referred to as the *effective* heat flux vector of
 211 the system, and \mathbf{m}_d is the dissipative part of \mathbf{m} . The balance laws (1)–(4) are completed
 212 with the Second Law of Thermodynamics, which, in the local form of the Clausius-Duhem
 213 inequality, requires the system’s overall entropy production, Λ , to be non-negative at all
 214 times and all points of the system, i.e., $\Lambda \geq 0$ (De Groot and Mazur, 1984).

215 2.2 Constitutive laws

216 The quantities $\boldsymbol{\sigma}$, \mathbf{m} , \mathbf{m}_d , ϑ , \mathbf{f} , η_f , η_s , and \mathbf{J}_Q will be determined constitutively, and
 217 should thus comply with the condition $\Lambda \geq 0$. Our constitutive model is based on the
 218 theory developed by Hassanizadeh (1986) and Bennethum et al. (2000), and is then spe-
 219 cialised to the problem at hand by enforcing the following further hypotheses (Grillo
 220 et al., 2011): (1). Radiative sources of energy and mass-exchange processes are excluded
 221 from the present study; (2). The fluid phase is macroscopically inviscid; (3). The mass
 222 density of \mathcal{F} , ϱ_f , is an assigned constitutive function of the mass fraction, c , and absolute
 223 temperature, T , i.e., we set $\varrho_f = \hat{\varrho}_f(c, T)$; (4). The physical processes relevant to the
 224 investigated problem necessitate the following list of independent constitutive variables
 225 $\text{ICV} = \{T, c, \nabla T, \nabla c, \mathbf{u}_{fs}, \mathbf{v}\}$. To provide an explicit mathematical expression of the quan-
 226 tities introduced so far, and of other constitutive variables necessary for the description
 227 of the system, we introduce the Helmholtz free energy densities of the solid and the fluid
 228 phase, A_s and A_f , and express them constitutively as $A_s = \hat{A}_s(T)$ and $A_f = \hat{A}_f(c, \nabla c, T)$.
 229 Within this constitutive framework, the entropy densities of \mathcal{P} and \mathcal{F} , i.e., η_s and η_f , the
 230 Cauchy stress tensor borne by \mathcal{F} , $\boldsymbol{\sigma}$, and the Gibbs free energy density of the fluid phase,

231 G_f , are given by:

$$\eta_s = -\frac{\partial \hat{A}_s}{\partial T}, \quad (5a)$$

$$\eta_f = -\frac{\partial \hat{A}_f}{\partial T} + \frac{p}{\varrho_f^2} \frac{\partial \hat{\varrho}_f}{\partial T} = -\frac{\partial \hat{G}_f}{\partial T}, \quad (5b)$$

$$\boldsymbol{\sigma} = -\phi p \mathbf{I} - \nabla c \otimes \left(\phi \varrho_f \frac{\partial \hat{G}_f}{\partial \nabla c} \right), \quad (5c)$$

$$G_f = \hat{G}_f(c, \nabla c, T, p) = \hat{A}_f(c, \nabla c, T) + \frac{p}{\hat{\varrho}_f(c, T)}, \quad (5d)$$

232 where p is the fluid pressure, \mathbf{I} is the second-order identity tensor, and the non-hydrostatic
233 contribution

$$\boldsymbol{\sigma}_K \equiv -\nabla c \otimes \left(\phi \varrho_f \frac{\partial \hat{G}_f}{\partial \nabla c} \right) \quad (6)$$

234 is the Korteweg stress tensor. Furthermore, the relative chemical potential, ϑ , reads

$$\begin{aligned} \vartheta &= \left(\frac{\partial \hat{A}_f}{\partial c} - \frac{p}{\varrho_f^2} \frac{\partial \hat{\varrho}_f}{\partial c} \right) - \frac{1}{\phi \varrho_f} \operatorname{div} \left(\phi \varrho_f \frac{\partial \hat{A}_f}{\partial \nabla c} \right) \\ &= \frac{\partial \hat{G}_f}{\partial c} - \frac{1}{\phi \varrho_f} \operatorname{div} \left(\phi \varrho_f \frac{\partial \hat{G}_f}{\partial \nabla c} \right). \end{aligned} \quad (7)$$

235 Finally, by introducing the system's heat flux vector, \mathbf{q} , and the entropy flux vector

$$\mathbf{q}_\eta \equiv \frac{\mathbf{q}}{T} + \frac{1}{T} \left(\phi \varrho_f \frac{\partial \hat{A}_f}{\partial \nabla c} \right) \dot{c} = \frac{\mathbf{q}}{T} + \frac{1}{T} \left(\phi \varrho_f \frac{\partial \hat{G}_f}{\partial \nabla c} \right) \dot{c}, \quad (8)$$

236 the effective heat flux vector \mathbf{J}_Q is written as $\mathbf{J}_Q \equiv T \mathbf{q}_\eta$. The presence of ∇c among the
237 arguments of \hat{G}_f , cf. (5d), implies that \mathbf{q}_η cannot be written as the ratio between the \mathbf{q}
238 and T , as is the case in standard Continuum Thermodynamics (Mićunović, 2009; Gurtin
239 et al., 2010). Nevertheless, by construction it does hold that $\mathbf{q}_\eta = \mathbf{J}_Q/T$.

240 A well-known model, constructed upon a free energy density depending on a scalar
241 field and its gradient, is the Cahn-Hilliard model (cf., for example, (Gurtin, 1996) for a
242 review). It describes the evolution of a two-phase system, in which the distribution of
243 the phases is represented by a scalar order parameter, and the free energy is written as
244 the sum of a contribution depending on the order parameter only, and a contribution

245 depending on the gradient of the order parameter. The order parameter solves a mass
 246 diffusion equation, in which the mass diffusive flux depends linearly on the gradient of
 247 the chemical potential of the diffusing substance. In this context, the chemical potential
 248 is the functional derivative of the system's free energy.

249 Since in our work mass diffusion plays a central role, our thermodynamic model is
 250 grounded on the Cahn-Hilliard theory. For this purpose, we consider a Helmholtz free
 251 energy density of the Cahn-Hilliard type, given by

$$\hat{A}_f(c, \nabla c, T) = \hat{A}_{\text{st}}(c, T) + \frac{1}{2}\lambda\|\nabla c\|^2, \quad (9)$$

252 where $\hat{A}_{\text{st}}(c, T)$ may be referred to as the *standard* Helmholtz free energy density, and λ
 253 is a coefficient having the meaning of a mixing free energy. By plugging (9) into (5d), the
 254 Gibbs free energy density becomes

$$\hat{G}_f(c, \nabla c, T, p) = \hat{G}_{\text{st}}(c, T, p) + \frac{1}{2}\lambda\|\nabla c\|^2, \quad (10)$$

255 where the standard part, $\hat{G}_{\text{st}}(c, T, p)$, is given by

$$\hat{G}_{\text{st}}(c, T, p) = \hat{A}_{\text{st}}(c, T) + \frac{p}{\hat{\varrho}_f(c, T)}. \quad (11)$$

256 Also the chemical potential, ϑ , can be written as $\vartheta = \vartheta_{\text{st}} + \vartheta_{\text{CH}}$, where

$$\vartheta_{\text{st}} = \frac{\partial \hat{G}_f}{\partial c} = \frac{\partial \hat{G}_{\text{st}}}{\partial c}, \quad (12a)$$

$$\vartheta_{\text{CH}} = -\frac{1}{\phi_{\varrho_f}} \operatorname{div} \left(\phi_{\varrho_f} \frac{\partial \hat{G}_f}{\partial \nabla c} \right) = -\frac{1}{\phi_{\varrho_f}} \operatorname{div} (\phi_{\varrho_f} \lambda \nabla c). \quad (12b)$$

257 We refer to ϑ_{st} and ϑ_{CH} as to the *standard* and the *Cahn-Hilliard* chemical potential,
 258 respectively. The standard part of the Gibbs free energy of the fluid phase, \mathcal{F} , can be
 259 written as

$$\hat{G}_{\text{st}}(c, T, p) = c \hat{\vartheta}_{\text{st}1}(c, T, p) + (1 - c) \hat{\vartheta}_{\text{st}2}(c, T, p), \quad (13)$$

260 where

$$\hat{\vartheta}_{\text{st1}}(c, T, p) = \frac{RT}{M_1} \log \left[\frac{cM_2}{(1-c)M_1 + cM_2} \right] + \alpha_1(T)p + \beta(T), \quad (14a)$$

$$\hat{\vartheta}_{\text{st2}}(c, T, p) = \frac{RT}{M_2} \log \left[\frac{(1-c)M_1}{(1-c)M_1 + cM_2} \right] + \alpha_2(T)p + \beta(T), \quad (14b)$$

261 are the standard chemical potentials associated with the constituents \mathcal{C}_1 and \mathcal{C}_2 of \mathcal{F} ,
 262 respectively, R is the gas constant, M_1 and M_2 are the molar masses of \mathcal{C}_1 and \mathcal{C}_2 , and
 263 $\alpha_1(T)$, $\alpha_2(T)$, and $\beta(T)$ are given functions of the temperature. We remark that $\hat{\vartheta}_{\text{st1}}$ and
 264 $\hat{\vartheta}_{\text{st2}}$ are consistent with the equality

$$c \frac{\partial \hat{\vartheta}_{\text{st1}}}{\partial c} + (1-c) \frac{\partial \hat{\vartheta}_{\text{st2}}}{\partial c} = 0. \quad (15)$$

265 When the Cahn-Hilliard model is used to describe binary systems comprising two non-
 266 miscible fluids, the term $\frac{1}{2}\lambda\|\nabla c\|^2$ introduces a partial miscibility regularisation (Lowen-
 267 grub and Truskinovsky, 1998), and λ is referred to as the capillarity coefficient (Jamet,
 268 2001). In this case, λ should be supplied constitutively. However, it is possible to de-
 269 termine λ by having recourse to the definition of *Cahn number* (Choi and Anderson,
 270 2012; Lowengrub and Truskinovsky, 1998). Hence, we may set $\lambda = CL^2\vartheta_{\text{ref}}$, where L is
 271 the characteristic length of the computational domain, ϑ_{ref} is a referential, characteristic
 272 chemical potential, and $C \equiv \xi/L$ is the Cahn number, i.e., the ratio between the char-
 273 acteristic meso-scale length ξ , which represents the interface width, and L . Despite these
 274 considerations, in all the forthcoming numerical simulations, λ will be taken equal to a
 275 constant known from the outset.

276 2.3 Entropy production

277 The constitutive relations (5)–(7) allow to obtain an explicit expression for the rate of
 278 overall entropy production, Λ , which is equal to the ratio between the overall power

279 dissipated by system and the absolute temperature (Grillo et al., 2011), i.e.,

$$\Lambda = -\frac{\mathbf{m}_d \cdot \mathbf{u}_{fs}}{T} - \frac{\nabla \vartheta \cdot \mathbf{J}_M}{T} - \frac{\nabla T \cdot (\mathbf{J}_Q - \vartheta \mathbf{J}_M)}{T^2} \geq 0. \quad (16)$$

280 In this work, we admit that the dynamic regime of the fluid phase is compatible with
 281 Darcy's law. Thus, we express the dissipative force \mathbf{m}_d , which is defined by $\mathbf{m}_d \equiv \mathbf{m} - p \nabla \phi$
 282 (Hassanizadeh, 1986), as a linear constitutive function of the filtration velocity $\mathbf{w} \equiv$
 283 $\phi \mathbf{u}_{fs}$, i.e., we set $\mathbf{m}_d = -\mathbf{r} \mathbf{w}$, where \mathbf{r} is a second-order tensor referred to as resistivity
 284 tensor. Here, we assume that \mathbf{r} is symmetric and positive-definite. By accounting for the
 285 definitions (5c) and (6), we solve (3a) with respect to \mathbf{w} , thereby obtaining

$$\mathbf{w} = -\frac{\mathbf{k}}{\mu} \left[(\nabla p - \varrho_f \mathbf{g}) - \frac{1}{\phi} \operatorname{div} \boldsymbol{\sigma}_K \right], \quad (17)$$

286 where \mathbf{k} is the permeability tensor, μ is the dynamic viscosity of the fluid, and the identity
 287 $\phi \mathbf{r}^{-1} = \mathbf{k} / \mu$ has been used. Equation (17) is a generalisation to Darcy's law in which the
 288 divergence of the Korteweg stress tensor contributes to the fluid filtration velocity. By
 289 computing $\boldsymbol{\sigma}_K$ explicitly, and recalling that ϕ is assumed to be constant throughout this
 290 work, we obtain $-\phi^{-1} \operatorname{div} \boldsymbol{\sigma}_K = \operatorname{div}(\varrho_f \lambda \nabla c \otimes \nabla c)$. If the variability of ϱ_f is neglected, this
 291 expression takes on the form (Collins et al., 2013; Diegel et al., 2015)

$$-\phi^{-1} \operatorname{div} \boldsymbol{\sigma}_K = \operatorname{div}(\varrho_f \lambda \nabla c \otimes \nabla c) = \varrho_f \lambda (\nabla \nabla c) \nabla c - \varrho_f \vartheta_{CH} \nabla c, \quad (18)$$

292 where $\vartheta_{CH} = -\lambda \Delta c$ is the Cahn-Hilliard chemical potential (12b), obtained under the
 293 hypotheses that ϕ , ϱ_f , and λ are constants. Since \mathbf{r} is positive-definite, the first term on
 294 the right-hand-side of (16) is always non-negative, i.e.,

$$\Lambda_F \equiv -\frac{\mathbf{m}_d \cdot \mathbf{u}_{fs}}{T} = \frac{\mathbf{r} : (\mathbf{w} \otimes \mathbf{w})}{\phi T} \geq 0, \quad \forall \mathbf{w}, \quad (19)$$

295 where Λ_F is the part of the overall rate of entropy production associated with the fluid
 296 flow. Equation (19) implies that, to satisfy the inequality (16), it is sufficient to require
 297 that the part of Λ due to mass diffusion and heat conduction, denoted by Λ_{MQ} hereafter,

298 has to be non-negative. This requirement can be put in one of the two equivalent forms

$$\Lambda_{\text{MQ}} = -\frac{\nabla\vartheta \cdot \mathbf{J}_M}{T} - \frac{\nabla T \cdot (\mathbf{J}_Q - \vartheta \mathbf{J}_M)}{T^2} \geq 0, \quad (20a)$$

$$\Lambda_{\text{MQ}} = -\mathbf{J}_M \cdot \nabla \left(\frac{\vartheta}{T} \right) - \mathbf{J}_Q \cdot \frac{\nabla T}{T^2} \geq 0, \quad (20b)$$

299 and is enforced in order to extract constitutive information on the heat flux vector \mathbf{J}_Q
300 and on the mass diffusive flux vector \mathbf{J}_M .

301 **3 Thermodiffusion**

302 In spite of the fact that (20a) and (20b) are interchangeable representations of Λ_{MQ} ,
303 selecting one of these two possible forms has repercussions on the constitutive expressions
304 of the fluxes \mathbf{J}_M and \mathbf{J}_Q and on the interpretation of the phenomenological coefficients
305 featuring in these expressions. A thorough review on this issue was written by De Groot
306 and Mazur (1984). In this work, we adhere to the formulation given in (20b) (cf. De Groot
307 and Mazur (1984), Ch. 5, Sec. 3, p. 49).

308 **3.1 Standard thermodiffusion**

309 In this section, we make a brief review on standard thermodiffusion. For this purpose, we
310 take a step backwards and consider the thermodynamic framework in which the Helmholtz
311 free energy density of the fluid phase is a function of c and T only, i.e., $A_f = \hat{A}_f(c, T) \equiv$
312 $\hat{A}_{\text{st}}(c, T)$. When this is the case, the relative chemical potential reduces to the standard
313 one, i.e., $\vartheta = \vartheta_{\text{st}}$, and Λ_{MQ} becomes

$$\Lambda_{\text{MQ}} = -\mathbf{J}_M \cdot \nabla \left(\frac{\vartheta_{\text{st}}}{T} \right) - \mathbf{J}_Q \cdot \frac{\nabla T}{T^2} \geq 0. \quad (21)$$

314 Hence, within the linear theory of the phenomenological laws for isotropic media, the
315 fluxes \mathbf{J}_M and \mathbf{J}_Q are connected with the gradients $-\nabla(\vartheta_{\text{st}}/T)$ and $-(\nabla T)/T^2 = \nabla(1/T)$

316 through the formulae (De Groot and Mazur, 1984; Rauch, 2006)

$$\mathbf{J}_M = -L_{MM} \nabla \left(\frac{\vartheta_{st}}{T} \right) - L_{MQ} \frac{\nabla T}{T^2}, \quad (22a)$$

$$\mathbf{J}_Q = -L_{QM} \nabla \left(\frac{\vartheta_{st}}{T} \right) - L_{QQ} \frac{\nabla T}{T^2}, \quad (22b)$$

317 where L_{MM} , L_{MQ} , L_{QM} , and L_{QQ} are scalar phenomenological coefficients, constrained to
 318 satisfy Onsager's reciprocal relations $L_{MQ} = L_{QM}$. By working out the gradient of ϑ_{st}/T ,
 319 splitting the gradient of ϑ_{st} , and introducing the specific relative enthalpy h_{st} , i.e.,

$$\nabla \vartheta_{st} = \nabla_T \vartheta_{st} + \frac{\partial \vartheta_{st}}{\partial T} \nabla T, \quad (23a)$$

$$h_{st} \equiv \vartheta_{st} - T \frac{\partial \vartheta_{st}}{\partial T}, \quad (23b)$$

320 the expressions of \mathbf{J}_M and \mathbf{J}_Q become

$$\mathbf{J}_M = -\frac{L_{MM}}{T} \nabla_T \vartheta_{st} - (L_{MQ} - h_{st} L_{MM}) \frac{\nabla T}{T^2}, \quad (24a)$$

$$\mathbf{J}_Q = -\frac{L_{QM}}{T} \nabla_T \vartheta_{st} - (L_{QQ} - h_{st} L_{QM}) \frac{\nabla T}{T^2}. \quad (24b)$$

321 The partial gradient $\nabla_T \vartheta_{st}$ is obtained by holding temperature fixed and differentiating
 322 with respect to all other state variables. Since it follows from (12a) that ϑ_{st} depends on
 323 the mass fraction, c , temperature, T , and pressure, p , i.e., $\vartheta_{st} = \hat{\vartheta}_{st}(c, T, p)$, it holds that

$$\nabla_T \vartheta_{st} = \frac{\partial \hat{\vartheta}_{st}}{\partial c} \nabla c + \frac{\partial \hat{\vartheta}_{st}}{\partial p} \nabla p. \quad (25)$$

324 Substituting the second term on the right-hand-side of (25) into (24a) and (24b) leads
 325 to the baro-diffusion factor (Landau and Lifschitz, 1984) $k_p \equiv p \frac{\partial \hat{\vartheta}_{st}/\partial p}{\partial \hat{\vartheta}_{st}/\partial c}$, which vanishes
 326 identically for $c = 0$ and $c = 1$. Since the baro-diffusion factor usually has a negligible
 327 influence on the fluxes \mathbf{J}_M and \mathbf{J}_Q , we approximate $\nabla_T \vartheta_{st}$ with the first summand on the

328 right-hand-side of (25). Furthermore, by introducing the quantities

$$D \equiv \frac{1}{\varrho_f} \frac{L_{MM}}{T} \frac{\partial \hat{\vartheta}_{st}}{\partial c}, \quad (26a)$$

$$S_{st} \equiv \frac{1}{(1-c)c} \frac{L_{MQ}/L_{MM} - h_{st}}{T(\partial \hat{\vartheta}_{st}/\partial c)}, \quad (26b)$$

$$Q \equiv \frac{L_{QM}}{L_{MM}}, \quad (26c)$$

$$\kappa \equiv \frac{L_{QQ}}{T^2}, \quad (26d)$$

329 we recast (24a) and (24b) in the form

$$\mathbf{J}_M = -\varrho_f D [\nabla c + S_{st} c (1-c) \nabla T], \quad (27a)$$

$$\mathbf{J}_Q = -\varrho_f D Q \nabla c - \left(\kappa - h_{st} \frac{\varrho_f D Q}{T(\partial \hat{\vartheta}_{st}/\partial c)} \right) \nabla T. \quad (27b)$$

330 In (26a)–(26d), D and S_{st} are the diffusion coefficient and the standard Soret coefficient,
 331 respectively, Q is the *heat of transport*, and κ is the thermal conductivity (De Groot and
 332 Mazur, 1984; Rowley and Horne, 1980). Due to the symmetry requirement $L_{MQ} = L_{QM}$,
 333 S_{st} and Q must satisfy the relation (Rauch, 2006; Grillo et al., 2011)

$$(1-c)c \frac{\partial \hat{\vartheta}_{st}}{\partial c} T S_{st} = Q - h_{st}. \quad (28)$$

334 Within the considered constitutive framework, the specific relative enthalpy, h_{st} , is usually
 335 neglected. This is particularly the case when the fluid phase is regarded as incompressible,
 336 or when the Boussinesq-Oberbeck approximation is invoked. Finally, although appreciable
 337 for some physical processes (Ingle and Horne, 1973), in the present work we claim that
 338 the contribution of the Dufour effect to the overall heat flux vector is negligible. Thus,
 339 we approximate \mathbf{J}_Q with standard Fourier's law, i.e., from here on we set

$$\mathbf{J}_Q = -\kappa \nabla T. \quad (29)$$

3.2 Thermodiffusion within the Cahn-Hilliard framework

In this section, we highlight the implications brought about by the use of a Gibbs free energy density of the Cahn-Hilliard type. For our purposes, we consider the expression of the residual rate of entropy production given in (20b) and, by adopting the same argument as in section 3.1, we express the fluxes \mathbf{J}_M and \mathbf{J}_Q as

$$\mathbf{J}_M = -L_{MM} \nabla \left(\frac{\vartheta}{T} \right) - L_{MQ} \frac{\nabla T}{T^2}, \quad (30a)$$

$$\mathbf{J}_Q = -L_{QM} \nabla \left(\frac{\vartheta}{T} \right) - L_{QQ} \frac{\nabla T}{T^2}. \quad (30b)$$

We do not speculate on \mathbf{J}_Q any further, since it will be approximated as in (29) in the sequel. Rather, we work out (30a), which can be rewritten as

$$\begin{aligned} \mathbf{J}_M &= -L_{MM} \nabla \left(\frac{\vartheta_{st} + \vartheta_{CH}}{T} \right) - L_{MQ} \frac{\nabla T}{T^2} \\ &= -L_{MM} \nabla \left(\frac{\vartheta_{st}}{T} \right) - L_{MM} \nabla \left(\frac{\vartheta_{CH}}{T} \right) - L_{MQ} \frac{\nabla T}{T^2}. \end{aligned} \quad (31)$$

According to the procedure shown in section 3.1, and recalling (26a) and (26b), we obtain

$$\begin{aligned} \mathbf{J}_M &= -\varrho_f D [\nabla c + S_{st} c(1-c) \nabla T] \\ &\quad + \varrho_f D \frac{\vartheta_{CH}}{T(\partial \hat{\vartheta}_{st} / \partial c)} \nabla T - \frac{\varrho_f D}{\partial \hat{\vartheta}_{st} / \partial c} \nabla \vartheta_{CH}. \end{aligned} \quad (32)$$

From here on, we call *Cahn-Hilliard "Soret coefficient"* the quantity

$$S_{CH} := \frac{-\vartheta_{CH}}{(1-c)cT(\partial \hat{\vartheta}_{st} / \partial c)}. \quad (33)$$

This definition allows to rephrase the expression of the mass flux vector \mathbf{J}_M as

$$\mathbf{J}_M = -\varrho_f D [\nabla c + (S_{st} + S_{CH})c(1-c) \nabla T] - \frac{\varrho_f D}{\partial \hat{\vartheta}_{st} / \partial c} \nabla \vartheta_{CH}. \quad (34)$$

We define *effective Soret coefficient* the sum $S_{\text{eff}} \equiv S_{st} + S_{CH}$. According to (34), the inclusion of the Cahn-Hilliard theory into the standard framework of thermodiffusion

352 yields two corrections of the mass flux vector, \mathbf{J}_M . These manifest themselves through
353 the additional ‘‘Soret coefficient’’, S_{CH} , which is generated by the Cahn-Hilliard relative
354 chemical potential, ϑ_{CH} , and a term proportional to the gradient of ϑ_{CH} . We remark that,
355 while the standard Soret coefficient, S_{st} (which is typically expressed constitutively as a
356 function of temperature and mass fraction), can be either positive or negative, and its
357 sign may change in response to changes of mass fraction and temperature (Kita et al.,
358 2004), the sign of S_{CH} depends essentially on the sign of ϑ_{CH} . Since ϕ is assumed to be
359 constant in this work, and the Boussinesq-Oberbeck approximation will be enforced (i.e.,
360 ρ_f will be regarded as constant everywhere, except in the buoyancy term, $\rho_f \mathbf{g}$, of Darcy’s
361 law (17)), ϑ_{CH} reduces to $\vartheta_{CH} = -\text{div}(\lambda \nabla c) = -\lambda \Delta c$ (see (12b)). Thus, the sign of ϑ_{CH}
362 changes in space and time according to the sign of the Laplacian of the mass fraction.

363 4 Benchmark problems

364 As stated in the Introduction, a typical framework in which thermodiffusive effects are
365 accounted for is the thermally induced separation of the components of a two-constituent
366 mixture in response to the combined action of a thermal gradient and density-driven fluid
367 flow. Hereafter, we employ a Finite Element model to reproduce numerically two experi-
368 ments of thermally induced separation in a thermogravitational cell (Benano-Melly et al.,
369 2001; Costeséque et al., 2002; Jamet et al., 1992). In both experiments, a thermogravita-
370 tional cell of length L and width $H = hL$ (h is a positive real number smaller than unity)
371 is used, in which a porous medium with uniform and constant porosity ϕ is saturated by
372 a two-constituent fluid. The fluid is prepared in such a way that, at the initial time of
373 observation, the mass fractions of its constituents are uniformly distributed. In the course
374 of time, however, a separation process occurs, thereby leading to a slightly nonuniform
375 distribution of the mass fractions within the cell. In the first experiment, the employed
376 fluid is a mixture of pure water and heavy water (hereafter referred to as HDO) in a
377 porous matrix of aluminium oxide, Al_2O_3 (Benano-Melly et al., 2001; Costeséque et al.,
378 2002). The second experiment adopts a mixture of tetracosane, $\text{C}_{24}\text{H}_{50}$, and dodecane,

379 $\text{C}_{12}\text{H}_{26}$, (Jamet et al., 1992; Fargue et al., 1998). In the following, the constituent \mathcal{C}_1 ,
 380 whose mass fraction, c , features in the model equations, will be assumed to be HDO in
 381 the first experiment, and $\text{C}_{24}\text{H}_{50}$ in the second one.

382 4.1 Summary of the model equations

383 The mathematical model considered in this work is based on the mass balance laws (1)
 384 and (2), and on the energy balance law (4). These are three scalar equations in the three
 385 unknowns represented by pressure, p , mass fraction, c , and temperature, T . The model
 386 is closed since \mathbf{w} , \mathbf{J}_Q , and \mathbf{J}_M are specified in (17), (29), and (34), respectively, while η_s ,
 387 η_f , and ϑ are prescribed in (5a), (5b), and (7), respectively.

388 To reduce the computational complexity of the model equations, which are highly
 389 coupled and non-linear, we enforce the Boussinesq-Oberbeck approximation. Accordingly,
 390 the mass density of the fluid phase is expressed as a function of c and T only in the
 391 buoyancy term of Darcy's law, i.e., in $\varrho_f \mathbf{g} = \hat{\varrho}_f(c, T) \mathbf{g}$, and is set equal to a reference
 392 constant, ϱ_0 , everywhere else. Moreover, we neglect the Korteweg stress tensor, $\boldsymbol{\sigma}_K$, in
 393 the generalised Darcy's law (17), and the term $\mathbf{m}_d \cdot \mathbf{u}_{fs} = -\phi^{-1} \mathbf{r} \mathbf{w} \cdot \mathbf{w}$ in (4). The latter
 394 simplification is done under the assumption that the terms of order higher than the first
 395 in \mathbf{w} are not significant in the present study.

396 Substituting the expression of \mathbf{J}_M , given in (34), into (2) leads to an equation that
 397 involves the derivatives of the mass fraction up to the fourth order. This is due to the fact
 398 that \mathbf{J}_M features the gradient of the Cahn-Hilliard chemical potential, ϑ_{CH} , which, in turn,
 399 contains the derivatives of c up to the second order. Rather than following this approach,
 400 we treat ϑ_{CH} as an additional unknown of the model, and determine c consistently with
 401 the constitutive relation (12b), which becomes $\vartheta_{\text{CH}} = -\text{div}(\lambda \nabla c)$ due to the considered
 402 approximations, and is solved together with the balance laws. Thus, the model equations

403 take on the form

$$\operatorname{div}(\varrho_0 \mathbf{w}) = 0, \quad (35a)$$

$$\phi \varrho_0 \dot{c} + \operatorname{div} \mathbf{J}_M = 0, \quad (35b)$$

$$\vartheta_{\text{CH}} = -\operatorname{div}(\lambda \nabla c), \quad (35c)$$

$$C_{\text{eff}} \partial_t T + \operatorname{div}(\varrho_0 C_{\text{pf}} T \mathbf{w}) = \operatorname{div}(\kappa \nabla T) - \phi \varrho_0 \vartheta_{\text{CH}} \dot{c}, \quad (35d)$$

404 where \mathbf{w} is now given by standard Darcy's law, i.e.,

$$\mathbf{w} = -\frac{\mathbf{k}}{\mu} (\nabla p - \hat{\varrho}_f(c, T) \mathbf{g}), \quad (36)$$

405 C_{eff} is referred to as the effective thermal capacity of the fluid-solid mixture, i.e.,

$$C_{\text{eff}} = \phi \varrho_0 C_{\text{pf}} + (1 - \phi) \varrho_s C_{\text{ps}}, \quad (37)$$

406 while C_{pf} and C_{ps} are the specific heats at constant pressure of the fluid and solid phase,
407 respectively. Both are assumed to be constant in the present framework.

408 It is worth to remark that, with respect to a standard problem of thermodiffusion,
409 there are two relevant differences. The first difference is related to the introduction of
410 the Cahn-Hilliard ‘‘Soret coefficient’’, S_{CH} [cf. (33)], and the second one is due to the
411 contribution $\nabla \vartheta_{\text{CH}}$ to the overall mass flux vector \mathbf{J}_M . The presence of these two non-
412 standard terms requires a special numerical treatment.

413 Notice that the additional term in the energy balance law (35d) could be split into
414 two terms: the divergence of an additional flux $\operatorname{div}(\vartheta_{\text{CH}} \mathbf{J}_M)$, directed in the sense of the
415 mass flux, which in our case is negligible ($\simeq 1 \cdot 10^{-6}$ W/m²) compared to the conductive
416 ($\simeq 1 \cdot 10^5$ W/m²) and the convective ($\simeq 1 \cdot 10^2$ W/m²) fluxes; a term $-\mathbf{J}_M \cdot \nabla \vartheta_{\text{CH}}$ that
417 reminds of an energy loss due to the mass exchange, whose order of magnitude is even
418 smaller ($\simeq 1 \cdot 10^{-9}$ W/m³).

419 Equations (35a)–(35d) apply in an open set $\Omega \subset \mathbb{R}^d$, with $d = 2$ or $d = 3$, which
420 constitutes the computational domain. The boundary of the cell, $\partial\Omega$, is assumed to be

421 impervious, i.e., no-flux conditions are imposed to the filtration velocity, \mathbf{w} , and the mass
 422 flux vector, \mathbf{J}_M , on all parts of $\partial\Omega$. The lower and the upper boundaries, Γ_l and Γ_u , are
 423 assumed to be thermally insulated, while the lateral boundaries, Γ_c and Γ_h , are kept at
 424 constant temperatures. In formulae, the set of boundary conditions read:

$$T|_{\Gamma_c} = T_c, \quad T|_{\Gamma_h} = T_h, \quad (38a)$$

$$\mathbf{J}_Q \cdot \mathbf{n} = 0, \quad \text{on } \Gamma_l \cup \Gamma_u, \quad (38b)$$

$$\mathbf{J}_M \cdot \mathbf{n} = 0, \quad \text{on } \partial\Omega, \quad (38c)$$

$$\mathbf{w} \cdot \mathbf{n} = 0, \quad \text{on } \partial\Omega, \quad (38d)$$

425 where \mathbf{n} is the unit vector normal to $\partial\Omega$, and $T_c < T_h$. In addition to (38a)–(38d), we
 426 also impose

$$-\lambda \nabla \vartheta_{\text{CH}} \cdot \mathbf{n} = 0, \quad \text{on } \partial\Omega, \quad (39)$$

427 thereby requiring that ϑ_{CH} satisfies homogeneous Neumann conditions on the whole
 428 boundary of the thermogravitational cell.

429 In the standard numerical treatment of the Cahn-Hilliard model, it is rather customary
 430 to set the normal derivative of the total chemical potential equal to zero at the boundary
 431 of the computational domain, i.e., $\partial_n \vartheta = \nabla \vartheta \cdot \mathbf{n} = 0$, on $\partial\Omega$, and to impose some “wetting
 432 angle condition” on $\partial\Omega$ (Diegel et al., 2015; Jamet, 2001; Zhang et al., 1999). Within our
 433 framework, the latter condition is a consequence of (38c), and is expressed through a
 434 restriction on the normal derivative of the solutal concentration, $\partial_n c = \nabla c \cdot \mathbf{n}$, which
 435 has to hold on $\partial\Omega$. We emphasise, however, that $\partial_n c$ need not be zero in our approach.
 436 Rather, in order to guarantee the solvability of the formulated mathematical problem, it
 437 is only required to satisfy some auxiliary constraint on $\partial\Omega$. In this sense, we speak in our
 438 work of a “generalised wetting condition”.

439 In the present study, the combination of (38b), (38c), and (39) implies the boundary
 440 condition $\partial_n \vartheta = 0$ as well as the “wetting condition”, $\partial_n c = 0$, on $\Gamma_l \cup \Gamma_u$. This is due to
 441 the fact that Fourier’s law (29) prescribes the equality $\mathbf{J}_Q = -\kappa \nabla T$, and (38b) becomes
 442 $\mathbf{J}_Q \cdot \mathbf{n} = -\kappa \nabla T \cdot \mathbf{n} = 0$ on $\Gamma_l \cup \Gamma_u$, thereby yielding $\nabla T \cdot \mathbf{n} = 0$ on $\Gamma_l \cup \Gamma_u$. Hence, the

443 boundary condition (38c) reads

$$\mathbf{J}_M \cdot \mathbf{n} = -\frac{L_{MM}}{T} \nabla \vartheta \cdot \mathbf{n} = -\frac{L_{MM}}{T} (\nabla \vartheta_{st} \cdot \mathbf{n} + \nabla \vartheta_{CH} \cdot \mathbf{n}) = 0, \quad \text{on } \Gamma_1 \cup \Gamma_u, \quad (40)$$

444 with $\vartheta = \vartheta_{st} + \vartheta_{CH}$. In fact, (40) is equivalent to $\partial_n \vartheta = 0$ on $\Gamma_1 \cup \Gamma_u$. Moreover, since
 445 (39) implies that the normal derivative of ϑ_{CH} vanishes on $\partial\Omega$, it must also hold $\partial_n \vartheta_{CH} =$
 446 $\nabla \vartheta_{CH} \cdot \mathbf{n} = 0$ on $\Gamma_1 \cup \Gamma_u$, and Equation (40) thus leads to

$$\begin{aligned} \mathbf{J}_M \cdot \mathbf{n} &= -\frac{L_{MM}}{T} \nabla \vartheta_{st} \cdot \mathbf{n} = -\frac{L_{MM}}{T} \frac{\partial \vartheta_{st}}{\partial c} \nabla c \cdot \mathbf{n} = 0 \\ \Rightarrow \nabla c \cdot \mathbf{n} &= 0, \quad \text{on } \Gamma_1 \cup \Gamma_u. \end{aligned} \quad (41)$$

447 We conclude that the boundary conditions (38c) and (39) are equivalent to requiring the
 448 vanishing of the normal derivatives of the chemical potential and of the mass fraction
 449 (i.e., the so-called “wetting angle condition”) on $\Gamma_1 \cup \Gamma_u$, as is usually the case in the
 450 numerical treatment of the Cahn-Hilliard model.

451 Looking at the boundary $\Gamma_c \cup \Gamma_h$, we notice that, by expressing \mathbf{J}_M as in (34) and
 452 invoking (39), the boundary condition (38c) becomes a homogeneous Robin-like condition
 453 on c . In fact, enforcing (39) allows to retrieve the zero-flux boundary condition of standard
 454 thermodiffusion (Benano-Melly et al., 2001), i.e.,

$$\mathbf{J}_M \cdot \mathbf{n} = -(\varrho_f D[\nabla c + (S_{st} + S_{CH})c(1-c)\nabla T]) \cdot \mathbf{n} = 0, \quad \text{on } \Gamma_c \cup \Gamma_h, \quad (42)$$

455 which could be considered as a “generalised wetting angle condition”. It is important
 456 to emphasise that, in the case of (42), the “wetting angle condition” is understood in a
 457 generalised way, i.e., it does *not* reduce to $\partial_n c = \nabla c \cdot \mathbf{n} = 0$, as in (41). Rather, (42)
 458 places the restriction that $\partial_n c$ and $\partial_n T$ balance each other according to the equation

$$\partial_n c + (S_{st} + S_{CH})c(1-c)\partial_n T = 0, \quad \text{on } \Gamma_c \cup \Gamma_h. \quad (43)$$

459 We remark that the condition $\partial_n c = 0$ would be unphysical on $\Gamma_c \cup \Gamma_h$, since it would

460 necessarily imply the wrong result $\partial_n T = 0$ on $\Gamma_c \cup \Gamma_h$ (there is, indeed, no reason why
 461 the normal derivative of the temperature —and, thus, the normal heat flux, within our
 462 approximation— should vanish on this portion of the boundary). Note, also, that we
 463 speak of “Robin-like” boundary condition because Equation (42), or (43), is non-linear in
 464 c due to the term $c(1 - c)$. A Robin condition, instead, consists of a linear combination of
 465 a function and its derivative, restricted over a subset of the boundary of a computational
 466 domain.

467 4.2 Numerics

468 Equations (35a)–(35d) are implemented in a Finite Element software and have thus to be
 469 written in weak form. The procedure followed to obtain the weak form of (35a) and (35d)
 470 is standard, and will not be repeated here. Rather, we shall briefly sketch the main
 471 steps towards the weak formulation of (35b) and (35c). Since the mass fraction c is
 472 subjected to the Robin condition (38c), and its derivatives up to the fourth order are
 473 involved in the strong form of the problem, we choose the test function associated with
 474 the mass fraction as $\tilde{c} \in H^2(\Omega)$. Moreover, since ϑ_{CH} has to comply with the Neumann
 475 condition (39), and its derivatives up to the second order feature in (35a)–(35d), we
 476 take $\tilde{\vartheta} \in H^1(\Omega)$ as test function associated with ϑ_{CH} (Salsa, 2008). Here, $H^k(\Omega)$, with
 477 $k = 1, 2$, denotes the Sobolev space $H^k(\Omega) = \{u \in L^2(\Omega) : D^\alpha u \in L^2(\Omega)\}$, where
 478 $D^\alpha u = \frac{\partial^{|\alpha|} u}{\partial x_1^{\alpha_1} \dots \partial x_d^{\alpha_d}}$ is the distributional derivative of u of order α , and $\alpha = (\alpha_1, \dots, \alpha_d) \in \mathbb{N}^d$
 479 is an arbitrary d -dimensional multi-index of length equal to, or smaller than, k , i.e.,
 480 $|\alpha| = \alpha_1 + \dots + \alpha_d \leq k$ (Brezis, 1986).

481 By multiplying (35b) by $\tilde{\vartheta}$, and (35c) by \tilde{c} , integrating over Ω , invoking Gauss’ The-

482 orem, and enforcing the boundary conditions (38d) and (39), we obtain

$$\int_{\Omega} \tilde{\vartheta} [\phi \varrho_0 \dot{c}] dV = - \int_{\Omega} \nabla \tilde{\vartheta} \cdot [\varrho_0 D \nabla c] dV \quad (44a)$$

$$\begin{aligned} & - \int_{\Omega} \nabla \tilde{\vartheta} \cdot [\varrho_0 D (S_{\text{st}} + S_{\text{CH}}) c (1 - c) \nabla T] dV \\ & - \int_{\Omega} \nabla \tilde{\vartheta} \cdot \left[\frac{\varrho_0 D}{\partial \hat{\vartheta}_{\text{st}} / \partial c} \nabla \vartheta_{\text{CH}} \right] dV, \\ \int_{\Omega} [\tilde{c} \vartheta_{\text{CH}} - \nabla \tilde{c} \cdot (\lambda \nabla c)] dV & = \int_{\Gamma_c \cup \Gamma_h} \tilde{c} [\lambda (S_{\text{st}} + S_{\text{CH}}) c (1 - c) \partial_n T] dA. \end{aligned} \quad (44b)$$

483 To determine the finite element formulation of (44a) and (44b), we cover the computa-
484 tional domain Ω with a conforming, regular mesh \mathcal{T}_h consisting of N_h non-overlapping
485 triangular elements $\{K_i\}_{i=1}^{N_h}$, and we introduce the finite dimensional spaces

$$\mathcal{V}_h^{(m)} = \{ \tilde{c}_h \in H^2(\Omega) : \tilde{c}_h|_{K_i} \in \mathbb{P}_m, \text{ for } i = 1, \dots, N_h \}, \quad (45a)$$

$$\mathcal{V}_h^{(n)} = \{ \tilde{\vartheta}_h \in H^1(\Omega) : \tilde{\vartheta}_h|_{K_i} \in \mathbb{P}_n, \text{ for } i = 1, \dots, N_h \}, \quad (45b)$$

486 where \mathbb{P}_m and \mathbb{P}_n are the set of polynomials of order m and n , respectively. The simulations
487 reported in this paper were conducted with $m = 2$ and $n = 1$. For completeness, we
488 mention that polynomials of order 3 and 1 have been employed for discretising the test
489 functions associated with pressure and temperature, respectively. In our simulations, the
490 maximum element size is taken to be $\max_{i=1}^{N_h} \ell_i \approx 2.5 \cdot 10^{-4}$ m, where ℓ_i is the characteristic
491 length of the i th finite element K_i .

492 To avoid the possibility of obtaining numerical variations in the results of the same
493 order of magnitude as the truncation error, the mass fraction, c , has been rescaled as
494 $c = c_0 \bar{c}$, with c_0 and \bar{c} being the initial and the ‘‘normalised’’ mass fraction, respectively.
495 This is done, in particular, because of the very low reference mass fraction in the HDO-
496 H₂O mixture (see Table 1). Consequently, the mass balance law of the constituent \mathcal{C}_1 is
497 transformed into

$$\phi \varrho_0 \dot{\bar{c}} = \text{div} \left[\varrho_0 D \left(\nabla \bar{c} + (S_{\text{st}} + S_{\text{CH}}) \bar{c} (1 - c_0 \bar{c}) \nabla T + \frac{1}{\partial \hat{\vartheta}_{\text{st}} / \partial \bar{c}} \nabla \vartheta_{\text{CH}} \right) \right]. \quad (46)$$

Our numerical solutions are normalised in such a way that the rescaled initial mass fraction in the computational domain is unitary for both the considered benchmarks, since $c_0 = c(x, 0)$ is the “true” initial mass fraction of \mathcal{C}_1 . All the quantities introduced in the model are coherently rescaled.

The weak form of the system of equations (35a)–(35d) has been spatially solved by means of Newton’s method, and the time discretisation has been performed adaptively by means of a Backward Differentiation Formula (BDF).

4.3 Model Parameters

The first experiment here studied considers a mixture of water (H_2O) and heavy water (HDO). Benano-Melly et al. (2001) assumed that the mass fraction of heavy water, identified with the constituent \mathcal{C}_1 of the mixture, and playing the role of the solute, is so small that the term $(1 - c)c$ in (34) can be approximated as $(1 - c)c \approx c$. In our simulations, however, we kept the nonlinear term $(1 - c)c$, even when it was quite small, for the sake of generality. In addition to the boundary conditions (38a)–(38d) and (39), we impose that the initial mass fraction is uniformly distributed within the thermogravitational cell, and given by $c_0 = 5.8 \cdot 10^{-6}$. The value attributed to c_0 has been obtained from the work by Jamet et al. (1992), in which the initial distribution of the solute was expressed in molarity and taken equal to $C_0 = 2.9 \cdot 10^{-4}$ mol/l. The mass density of the mixture is expressed constitutively by the formula (Benano-Melly et al., 2001)

$$\varrho_f = \hat{\varrho}_f(c, T) = \varrho_0 [1 - \beta(T - T_{\text{ref}}) + \gamma(c - c_{\text{ref}})], \quad (47)$$

where β and γ are the (constant) thermal and solutal expansion coefficients of the fluid, respectively, and T_{ref} and c_{ref} are reference values of the temperature and solutal mass fraction. In particular, the dependence of $\hat{\varrho}_f$ on c is neglected in (47) (i.e., γ is set equal to zero), because the difference between the mass density of heavy water and the mass density of the mixture as a whole is very small (incidentally, this also implies that no reference value of the mass fraction, c_{ref} , needs to be prescribed). Thus, the mass density

523 actually used in the numerical simulations is $\hat{\varrho}_f(T) = \varrho_0 [1 - \beta(T - T_{\text{ref}})]$. Moreover, the
 524 viscosity of the mixture is assumed to be constant.

525 The second experiment considers a mixture of tetracosane-dodecane, $\text{C}_{24}\text{H}_{50}$ - $\text{C}_{12}\text{H}_{26}$.
 526 The constituent \mathcal{C}_1 , identified with the tetracosane, $\text{C}_{24}\text{H}_{50}$, is assumed to have uniform
 527 initial mass fraction $c_0 = 0.15$, a value much higher than that assigned in the first
 528 experiment. This higher concentration is expected to lead to a stronger contribution of
 529 both the standard and the non-standard thermodiffusion effects. While the viscosity of
 530 the mixture as a whole is regarded as a constant also in this experiment, the mass density
 531 ϱ_f is prescribed by the empirical formula [slightly adapted from Jamet et al. (1992)]

$$\varrho_f = \hat{\varrho}_f(c; x) = \frac{758.30 \cdot (1 - 5.712x)}{1 - 758.30 \cdot (1 - 5.712x) \cdot 8 \cdot 10^{-5}c}, \quad (48)$$

532 where $x \in [0, H]$ is the space coordinate along the direction of the width of the thermo-
 533 gravitational cell.

534 The parameters employed for simulating both these experiments are listed in Table 1.
 535 In particular, $\Delta T \equiv T_h - T_c$ represents the temperature difference between the hot side,
 536 Γ_h , and the cold side, Γ_c , of the computational domain, Ω , while the reference temperature
 537 T_{ref} is defined as the arithmetical mean between T_c and T_h , i.e., $T_{\text{ref}} \equiv (T_c + T_h)/2$. By
 538 reading off T_{ref} and ΔT from Table 1, we obtain $T_c = 309.15$ K, $T_h = 334.15$ K. It
 539 is also worthwhile to remark that the initial value of the tetracosane mass fraction, c_0 ,
 540 has been computed by using the experimental values reported in Table 2: $c_0 = \frac{\chi_1}{\chi_1 + \chi_2} \approx$
 541 0.15 , while the reference mass density of the mixture, ϱ_0 , has been taken equal to $\varrho_0 =$
 542 758.30 kg/m³. Note that this value is close enough to the value of the density that would be
 543 computed according to the assumption of ideal mixture (Oldenburg and Pruess, 1998):
 544 $\varrho_0 = \left(\frac{c_0}{\varrho_1} + \frac{1-c_0}{\varrho_2} \right)^{-1} \approx 757.93$ kg/m³, where the true densities ϱ_1 and ϱ_2 refer to the
 545 densities of the “pure” constituents $\text{C}_{24}\text{H}_{50}$ and $\text{C}_{12}\text{H}_{26}$.

546 The modelling choice (48), done to comply with Jamet et al. (1992), requires some
 547 words of explanation. Indeed, as in (47), the equation of state for the fluid mass density
 548 should express ϱ_f as a function of the state variables that are regarded as independent,
 549 i.e., temperature, T , and solutal concentration, C , in the approach followed in this work.

550 In particular, by slightly adapting Equation (15) of Jamet et al. (1992) to our framework
 551 and notation, we prescribe

$$\varrho_f = \tilde{\varrho}_f(C, T) = \varrho_0 \{1 - \beta[T - T_c]\} \{1 + \alpha_c C\}, \quad \Rightarrow \quad (49a)$$

$$\varrho_f = \hat{\varrho}_f(c, T) = \frac{\varrho_0 \{1 - \beta[T - T_c]\}}{1 - \varrho_0 \{1 - \beta[T - T_c]\} \alpha_c c}, \quad (49b)$$

552 where $c = C/\varrho_f$ is the solutal mass fraction, and T_c is the temperature imposed by means
 553 of the Dirichlet boundary condition $T|_{\Gamma_c} = T_c$ on the cold boundary, $\Gamma_c \subset \partial\Omega$. To obtain
 554 (48) from (49b), we proceed in two steps: First, we set $\alpha_c = 8 \cdot 10^{-5}$ and $\varrho_0 = 758.30 \text{ kg/m}^3$
 555 (note that Jamet et al. (1992) use the value 741.1 kg/m^3 in lieu of 758.30 kg/m^3). Then,
 556 upon using Equation (15) of Jamet et al. (1992), we write

$$1 - \beta[T - T_c] = 1 + \alpha_x x, \quad (50)$$

557 which, evaluated at $x = H$, yields $T_h - T_c = \Delta T = -(\alpha_x H)/\beta$, and $\beta = -(\alpha_x H)/\Delta T$.
 558 This result can be used to estimate the thermal expansion coefficient, β . Indeed, setting
 559 $\alpha_x = -5.712 \text{ m}^{-1}$ (Jamet et al., 1992) leads to $\beta \approx 10^{-3} \text{ K}^{-1}$, a value of the same order
 560 of magnitude as those prescribed by Jamet et al. (1992) for $\text{C}_{24}\text{H}_{50}$ and $\text{C}_{12}\text{H}_{26}$, i.e.,
 561 $\beta_{\text{Jamet}}^{\text{C}_{24}\text{H}_{50}} = 8.1 \cdot 10^{-4} \text{ K}^{-1}$ and $\beta_{\text{Jamet}}^{\text{C}_{12}\text{H}_{26}} = 9.6 \cdot 10^{-4} \text{ K}^{-1}$, respectively.

562 We emphasise that (50) amounts to *impose*, rather than to compute, the temperature
 563 distribution in the thermogravitational cell, and to identify it with

$$T \equiv T(x) = T_c - \frac{\alpha_x H}{\beta} \frac{x}{H} = T_c + \Delta T \frac{x}{H}. \quad (51)$$

564 Although this result complies with the conditions $\nabla T \cdot \mathbf{n} = 0$ on $\Gamma_1 \cup \Gamma_u$ as well as $T|_{\Gamma_c} = T_c$
 565 and $T|_{\Gamma_h} = T_h$, Equation (51) is, in fact, the solution of $\text{div}(\kappa \nabla T) = \kappa \partial^2 T / \partial x^2 = 0$, which
 566 is obtained from (35d) in the stationary limit, and by neglecting the terms $\text{div}(\varrho_0 C_{\text{pf}} T \mathbf{w})$
 567 and $\phi \varrho_0 \vartheta_{\text{CH}} \dot{c}$. In this work, this approximation is employed only for the simulation of the
 568 mixture $\text{C}_{24}\text{H}_{50}$ - $\text{C}_{12}\text{H}_{26}$.

5 Results

In this section, we validate our model by recomputing the numerical experiments discussed by Jamet et al. (1992) and Benano-Melly et al. (2001), and we show how the introduction of the term $\frac{1}{2}\lambda\|\nabla c\|^2$ into the Helmholtz free energy density of the fluid phase (in fact, a mixture of two fluid constituents) produces a small, yet visible, correction to the results obtained within the setting of standard thermodiffusion. This correction manifests itself in (34) through the Cahn-Hilliard Soret coefficient, S_{CH} , and the term proportional to $\nabla\vartheta_{\text{CH}}$, and has repercussions on the evolution of the solute (i.e., the constituent \mathcal{C}_1).

5.1 Validation of the model

It has been shown in some works (cf. e.g. Benano-Melly et al. (2001); Fargue et al. (1998); Jamet et al. (1992); Rowley and Horne (1980)) that, if an initially uniform fluid mixture saturating a porous medium is exposed to a thermal gradient, and is subjected to the buoyancy effect due to gravity, a separation of the mixture's constituents will be initiated. The degree of separation depends on the properties of the constituents and on permeability of the porous medium. A typical behaviour that can be registered in a thermogravitational cell, while the mixture evolves in time, is reported in Figure 1a.

Benano-Melly et al. (2001) pointed out that, depending on the sign of the Soret coefficient, at the steady state the heaviest constituent of the mixture finds itself at the bottom of the cell, close to the cold side. The distortion of the mass fraction isolines shown in Figure 1a is the outcome of the motion induced by the coupling between gravity and the horizontal thermal gradient. The interaction between these two entities characterises the results of the thermogravitational cell experiment. Consistently with expectations, in our simulations the steady state is approached in a characteristic time that depends on the considered mixture. After the formation of an initial horizontal gradient of mass fraction, so that the mass fraction isolines are all parallel to the vertical symmetry axis of the cell, the evolution of the system towards the steady state is characterised by a distortion and rotation of the isolines, whose consequence is the redistribution of the

fluid mixture with the heaviest constituent at the bottom. Figure 1a has been produced for comparison with similar results previously obtained by Benano-Melly et al. (2001) and Fargue et al. (1998).

The quantity introduced to measure the degree of separation achievable in the mixture occupying a thermogravitational cell is the *separation ratio* (Benano-Melly et al., 2001)

$$b_{\infty} \equiv \frac{c_{B\infty}/(1 - c_{B\infty})}{c_{T\infty}/(1 - c_{T\infty})}, \quad (52)$$

where $c_{B\infty}$ and $c_{T\infty}$ denote, respectively, the mass fractions of the solute reached, at the stationary state, at the bottom and at the top of the thermogravitational cell. The separation ratio, b_{∞} , depends on the geometry of the cell, on the applied thermal gradient, and on the material properties of both the fluid mixture and the porous medium filling the cell. For instance, in the case of an isotropic porous medium (so that its permeability tensor is spherical, i.e., $\mathbf{k} = k\mathbf{I}$, and entirely represented by the scalar permeability k), and for a prescribed set of model parameters, the separation ratio can be expressed as a function of the scalar permeability. In particular, it is possible to determine an optimal value of k , denoted by k_{\star} hereafter, such that b is maximum. Benano-Melly et al. (2001) supply an approximated formula relating the maximum separation ratio, b_{∞}^{\max} , with the assigned parameters, i.e.,

$$\log(b_{\infty}^{\max}) = \frac{S_{\text{st}}\Delta TL\sqrt{120}}{24H}. \quad (53)$$

According to (53), for a given thermal gradient, $\Delta T/H$, and cell height, L , the maximum separation ratio achievable in the cell can be determined once S_{st} is known, and vice versa. More details on this topic can be found in the works by Lorenz and Emery (1959), and Emery and Lorenz (1963).

In studying the separation of heavy water, HDO, in the HDO-H₂O mixture, Benano-Melly et al. (2001) observed a discrepancy between the experimental results and the analytical and numerical predictions of the separation ratio and the steady state. A similar discrepancy was also observed by Jamet et al. (1992) also for the C₂₄H₅₀-C₁₂H₂₆ mixture. To the best of our understanding, both Benano-Melly et al. (2001) and Jamet

621 et al. (1992) conducted their investigations within the standard setting of thermodiffusion,
622 and determined suitable transport and flow properties in order to obtain a good fitting
623 of the experimental data. In particular, Benano-Melly et al. (2001) considered dispersion
624 in the solutal mass flux vector, Jamet et al. (1992) assumed that the porous matrix was
625 transversely isotropic with respect to the permeability, and Fargue et al. (1998) studied
626 the influence of a variable dispersive effect on the reduction of the discrepancy between
627 the numerical and the experimental results.

628 To validate the model presented in this paper, we start by showing that our numerical
629 simulations are able to reproduce the same trend as that of the curves obtained by Jamet
630 et al. (1992). To this end, we first consider standard thermodiffusion, which amounts to
631 set $\lambda = 0 \text{ m}^4/\text{s}^2$ in (9) and, consequently, to switch off all the terms of the model featuring
632 the subscript “CH”. The outputs of our numerical simulations are reported in Figure 2,
633 in which the separation ratio for both the HDO-H₂O and the H₂₄C₅₀-H₁₂C₂₆ mixture is
634 plotted as a function of the permeability of the porous medium. The parameters used
635 for these numerical simulations are specified in Tables 1 and 2. The value of the Soret
636 coefficient, S_{st} , has been taken from Benano-Melly et al. (2001) and Fargue et al. (1998)
637 for the HDO-H₂O mixture, and from Jamet et al. (1992) for the H₂₄C₅₀-H₁₂C₂₆ mixture.

638 Although our results are in agreement with both the analytical and the numerical
639 curves obtained by Jamet et al. (1992), and in spite of the fact that all these curves seem
640 to reproduce qualitatively the arrangement of the experimental points, none of them meets
641 quantitatively the experimental data. To do so, the numerical and analytical curves should
642 be shifted to the right. It is also worthwhile to emphasise that the maximum separation
643 ratio, as predicted by both the analytical and the numerical computations, is close to
644 the one determined experimentally, but it corresponds to a value of permeability that
645 is quite smaller than the experimental one. For example, with the choice of parameters
646 supplied in Tables 1 and 2, and for the HDO-H₂O mixture, the maximum separation ratio
647 is $b_{\infty}^{\text{max}} = 1.0563$. Nevertheless, this value is obtained for a permeability different from the
648 experimental one, which is instead approximatively given by $k \approx 1.0 \cdot 10^{-10} \text{ m}^2$. We recall
649 here that the analytical curves in Figure 2 were obtained by Lorenz and Emery (1959)

650 and Emery and Lorenz (1963).

651 5.2 Influence of the Cahn-Hilliard terms

652 According to Fargue et al. (1998), while the growth of the separation ratio is related to
653 the augmentation of S_{st} , the offset to the right of the bell-like curves in Figures 2a and 2b
654 is primarily due to the increase of the coefficient D in the mass flux vector \mathbf{J}_M . Within the
655 standard setting of thermodiffusion, this may occur either for higher solutal and thermal
656 diffusion coefficients or in response to dispersion, which adds itself to diffusion, thereby
657 contributing to increment D . Beside these behaviours, in our work we also observed that,
658 if the factor λ is switched on in (9), the increase of λ produces both an increase of the sep-
659 aration ratio and an offset of the bell-like curves to the right. We remark that switching
660 on λ means to activate the Cahn-Hilliard chemical potential ϑ_{CH} , its gradient, and the ad-
661 ditional Soret coefficient S_{CH} , which all contribute to the mass flux vector in a non-trivial
662 way. In particular, in our simulations we observed that the shift of the curves depicted in
663 Figure 3a can be attributed to the last summand on the right-hand-side of (34), which
664 is proportional to $\nabla\vartheta_{CH}$, and describes a transport of mass that can be interpreted as a
665 “second-order diffusion”. Indeed, the term $\nabla\vartheta_{CH}$ involves the third-order derivatives of
666 the mass fraction. The contribution associated with $\nabla\vartheta_{CH}$ is principally active at the top
667 and at the bottom of the thermogravitational cell, and is otherwise irrelevant unless the
668 mass fraction is distributed in a sufficiently non-uniform way. Looking at Figure 3a, we
669 notice that the strength of the non-standard thermodiffusive effects depends also on the
670 permeability. Indeed, for permeabilities sufficiently smaller than k_* , the separation ratios
671 obtained for different values of λ lie closer to each other than those obtained for $k \approx k_*$.
672 Moreover, also the initial mass fraction of the solute is a key parameter that can affect
673 the weight of the terms triggering the non-standard thermodiffusion.

674 To estimate the influence of the non-standard terms generated by nonzero values of λ ,
675 we compute $\varepsilon = 100 \left[\frac{\max_{\Omega} |c_{st} - c_{\lambda}|}{\max_{\Omega} c_{st}} \right]$, where c_{st} is the mass fraction determined within the
676 standard setting of thermodiffusion, i.e., for $\lambda = 0$, and c_{λ} is the mass fraction calculated
677 for nonzero values of λ . The evolution of ε in time and its relation with the permeability

678 of the porous medium are shown in Figures 3b and 3c for the HDO-H₂O mixture. The
 679 discrepancies shown in Figure 3a are consistent with the curves plotted in Figure 3c,
 680 where ε becomes noticeable only for permeabilities close to $k_* \in [1, 3] \cdot 10^{-11} \text{ m}^2$. From
 681 Figure 3b, one can observe that the effect of λ manifests itself also in the asymptotic
 682 value of ε , which characterises the stationary conditions of the system.

683 It should be mentioned that, in order for the Cahn-Hilliard chemical potential, ϑ_{CH} ,
 684 to give non-negligible contributions to thermodiffusion, it is necessary to build a non-null
 685 gradient of mass fraction inside the thermogravitational cell. When the mass fraction
 686 c is initially uniform in the cell, and S_{st} is set equal to zero *a priori*, the terms S_{CH}
 687 and $\nabla\vartheta_{\text{CH}}$ are unable to generate a mass flux and, consequently, no separation can be
 688 observed, regardless of the magnitude of the imposed thermal gradient. Conversely, if a
 689 nontrivial pattern of mass fraction is present (e.g. in the experiment studied by Rowley
 690 and Horne (1980)), the contributions to the mass flux stemming from S_{CH} and $\nabla\vartheta_{\text{CH}}$
 691 are visible, even without the presence of the standard Soret coefficient. Such evidence
 692 is highlighted in Figure 4a, where the transient evolution in time of the mass fraction
 693 at the top, c_{T} , and at the bottom, c_{B} , is reported. To obtain the results in Figure 4a,
 694 we imposed a non-uniform initial distribution of solute in the domain (see Figure 4b).
 695 The non-uniform mass fraction used as initial condition for this numerical experiment is
 696 “prepared” by taking the stationary distribution of C₂₄H₅₀ obtained by solving (35a)–
 697 (35d) with $S_{\text{st}} = 1.2 \cdot 10^{-4} \text{ 1/K}$ and $\lambda = 3.8 \text{ m}^4/\text{s}^2$. Recalling the expression of the effective
 698 Soret coefficient, $S_{\text{eff}} = S_{\text{st}} + S_{\text{CH}}$, the lines with no markers correspond to $S_{\text{eff}} = 0$, the
 699 lines with circles to $S_{\text{eff}} = S_{\text{CH}}$, and the lines with asterisks to $S_{\text{eff}} = S_{\text{st}}$. This is done
 700 to visualise the effect of S_{CH} and S_{st} on the mass fraction. When $S_{\text{eff}} = 0$, and the mass
 701 flux vector reduces to $\mathbf{J}_{\text{M}} = -\rho_{\text{f}} D \nabla c$, the mass fractions at the top and the bottom
 702 of the cell tend towards a common value, thereby making the mixture uniform at the
 703 steady state. Also in the second case, i.e., when $S_{\text{eff}} = S_{\text{CH}}$, the mass fractions c_{B} and
 704 c_{T} converge to the same common value as in the first case. However, the time required
 705 to approach the steady state is more than six times longer than the one needed when
 706 $S_{\text{eff}} = 0$. Finally, when $S_{\text{eff}} = S_{\text{st}}$, the mass fractions c_{B} and c_{T} approach stationary values

707 over a characteristic time comparable with that of the first case, but these values are
 708 different from one another, i.e., $c_{B\infty} \neq c_{T\infty}$, thereby allowing for a nontrivial separation
 709 ratio. Starting with an initial separation ratio $b_0 = 2.3407$, we obtain $b_\infty = 1.0384$. We
 710 recall that the initial value of the separation ratio is linked to a simulation in which
 711 $S_{\text{eff}} = S_{\text{st}} + S_{\text{CH}}$, i.e., it is the value of b obtained with the same S_{st} , but also with the
 712 Cahn-Hilliard contribution. This value of b , then, is clearly amplified of about 40% by the
 713 presence of the Cahn-Hilliard effect. The corresponding curve is reported in Figure 2d.

714 5.3 Main results

715 This section is dedicated to the main results of our study, i.e., the description of the role
 716 played by S_{CH} on the curves expressing the separation ratio versus the permeability, and
 717 the determination of a relation between the effective Soret coefficient $S_{\text{eff}} = S_{\text{st}} + S_{\text{CH}}$
 718 and the permeability.

719 Looking at Figure 2c, one can see that our separation ratios are in good agreement with
 720 those obtained by Fargue et al. (1998), and fit the experimental data quite satisfactorily
 721 for $\lambda = 2.7 \cdot 10^4$ 1/K and $S_{\text{st}} = 1.0 \cdot 10^{-5}$ 1/K. We emphasise that, while we determined our
 722 results by introducing the Cahn-Hilliard correction to standard thermodiffusion, Fargue
 723 et al. (1998) considered different values of the dispersion coefficient, which correspond to
 724 the dashed blue curve and to the red curve marked with circles. Although λ is quite big
 725 in this example, the value of $S_{\text{st}} = 1.0 \cdot 10^{-5}$ 1/K is the same as that taken by Fargue
 726 et al. (1998) (and a little bit smaller than that in Table 1). It is useful to mention that the
 727 Soret coefficient $S_{\text{st}} = 1.0 \cdot 10^{-5}$ 1/K would not allow to reach the congruence actually
 728 achieved with the separation ratios determined experimentally if neither S_{CH} nor any
 729 other contribution to the mass flux vector (as, for instance, dispersion) were taken into
 730 account. Indeed, the curve corresponding to $S_{\text{st}} = 1.0 \cdot 10^{-5}$ 1/K and $\lambda = 0$, i.e., the solid
 731 line in Figure 2c, is far away from the experimental predictions.

732 The results regarding the $\text{C}_{24}\text{H}_{50}$ - $\text{C}_{12}\text{H}_{26}$ mixture are reported in Figure 2d. Different
 733 ent choices of the pair (S_{st}, λ) are made to fit the experimental data. However, only for
 734 $S_{\text{st}} = 1.2 \cdot 10^{-4}$ 1/K and $\lambda = 3.8$ m^4/s^2 the experimental points corresponding to high

735 permeabilities are fitted satisfactorily. The uncertainty in the selection of the appropriate
 736 pair (S_{st}, λ) could be due to a lack of information about the considered mixture, and a
 737 possible misreading of the numerical points, for which the precise position of the opti-
 738 mum value of k could be less plausible (Fargue et al., 1998). Moreover, in the related
 739 simulations, the fluid viscosity μ , although evaluated with the formula reported in Jamet
 740 et al. (1992), is here taken as a constant, namely $\mu = \hat{\mu}(c_0)$.

741 Finally, in Table 3, we reported the maximum and minimum S_{eff} for each of the
 742 curves shown in Figure 2d. Indeed, as previously noticed, while S_{st} is a constant value,
 743 as prescribed by the literature, S_{CH} can vary within the domain according to the sign of
 744 ∇c .

745 From Table 3 we see that both $S_{\text{eff,max}}$ and $S_{\text{eff,min}}$ diminish with diminishing S_{st} ,
 746 but the discrepancy between S_{st} and S_{CH} increases with increasing λ , even though S_{st} is
 747 lower when a higher value of λ is considered. This happens to balance the value of S_{eff} ,
 748 which is ruled by the sum of S_{st} and S_{CH} . We remark that the value of S_{eff} can also be
 749 smaller than S_{st} , since S_{CH} may be negative. To give an idea of these occurrences, we
 750 refer to Figure 1b and Figure 1c. In these figures, the ends of the computational domain
 751 have been zoomed, since the actual width of the cell is too thin. Figure 1b refers to a
 752 small value of k , whereas Figure 1c refers to a higher value of k . The normalised isolines
 753 of the mass fraction at the steady state are shown in the first column of each of these
 754 two figures. In these columns, the blue isolines represent smaller values of S_{CH} , whereas
 755 the red isolines are for higher values. One can see that S_{CH} diminishes at the hot and at
 756 the bottom boundaries of the cell, where it also attains negative values, and increases at
 757 the cold and top boundaries of the cell. In the case of low permeability (see the second
 758 and third column of Figures 1b), the mass fraction isolines are arranged almost linearly
 759 in the domain, so that the majority of the solute is at the bottom left corner of the
 760 cell. Thus, in this case, the arrangement of the solute is preferentially at the bottom.
 761 The corresponding S_{CH} is then negative at the bottom and at the cold side, and positive
 762 at the top. For higher permeabilities, the mass fraction isolines feature a rather curvy
 763 pattern (Figure 1c). Also in this case, the heaviest constituent in the mixture evolves in

764 such a way that it is more concentrated at the bottom of the cell. However, the Cahn-
765 Hilliard Soret coefficient, S_{CH} , is now distributed variably from the left to the right. The
766 negative values of S_{CH} can be found at the hot side and the positive ones at the cold
767 side, whereas at the bottom and at the top ends both positive and negative values can be
768 observed. We recall that S_{CH} depends on the Laplacian of the mass fraction through ϑ_{CH} ,
769 which, in the case under study, is positive at the cold side. Therefore, at a given instant
770 of time, the maximum and the minimum of S_{eff} are attained in the domain. The mean
771 value of the effective Soret coefficient is approximatively in the middle of the domain at
772 each height. The sign of this coefficient is then ruled by the sign of the second gradient
773 of the mass fraction itself, since S_{CH} depends on the non-standard chemical potential, as
774 defined in (33).

775 A remarkable difference between the two considered experiments analysed in this
776 paper is the choice of λ . Although we determined λ by having recourse to the Cahn
777 number (Lowengrub and Truskinovsky, 1998), the way in which this number is defined
778 may necessitate revisions. In particular, the choice of the characteristic mesoscale, and
779 the characteristic coarse scale could lead to quite big variations of the Cahn number.
780 Moreover, if the solute mass fraction is low in the domain, then a higher λ is required to
781 make the Cahn-Hilliard contribution weighty. This is the case of the mixture HDO-H₂O,
782 for which the optimal λ is $\lambda = 2.7 \cdot 10^4 \text{ m}^4/\text{s}^2$. Vice versa, for the mixture C₂₄H₅₀-C₁₂H₂₆,
783 the solute mass fraction is three orders of magnitude higher, thereby producing a required
784 λ that is in the neighbourhood of unity.

785 6 Conclusions and outlook

786 In this work, we studied the evolution of the composition of a two-constituent fluid
787 mixture flowing through a porous medium exposed to a non-uniform thermal field. The
788 mixture's composition was described by the mass fraction of one constituent, denoted by
789 \mathcal{C}_1 . In accordance with the standard theory of Thermodiffusion, the thermal gradient de-
790 veloped in the mixture, ∇T , contributes to transport the mass of \mathcal{C}_1 by inducing the term

791 $\mathbf{J}_{\text{MQ}}^{\text{st}} \equiv -\varrho_{\text{f}} D S_{\text{st}} c(1 - c) \nabla T$, which augments the purely diffusive(-dispersive) Fick's mass
792 flux vector associated with \mathcal{C}_1 . The magnitude of the Soret coefficient, S_{st} , determines
793 the thermodiffusive strength.

794 We proposed a generalisation of the standard framework of thermodiffusion based on
795 the assumption that the Helmholtz free energy density of the fluid is of the Cahn-Hilliard
796 type [cf. Equation (9)]. The main consequence of this hypothesis is that the mass flux
797 vector acquires two additional quantities: The first quantity is proportional to $\nabla \vartheta_{\text{CH}}$,
798 with ϑ_{CH} being referred to as the Cahn-Hilliard chemical potential [cf. Equation (12b)],
799 while the second one is given by $-\varrho_{\text{f}} D S_{\text{CH}} c(1 - c) \nabla T$, and is formally identical to $\mathbf{J}_{\text{MQ}}^{\text{st}}$
800 except for the fact that S_{st} is replaced by the Cahn-Hilliard Soret coefficient S_{CH} [cf.
801 Equation (33)].

802 We tested our model by solving two benchmark problems taken from the literature,
803 and compared our results with those of other authors [cf. Figures 2a, 2b, 2c, and 2d]. In
804 particular, we focused on the determination of the separation ratio attainable in a thermo-
805 gravitational cell. Following Jamet et al. (1992), Fargue et al. (1998), and Benano-Melly
806 et al. (2001), we simulated these experiments by considering the fluid mixtures HDO-
807 H_2O and $\text{C}_{24}\text{H}_{50}$ - $\text{C}_{12}\text{H}_{26}$. Firstly, we observed that, since the Cahn-Hilliard contributions
808 arise when the mass fraction varies in space, their strength increases with the separation
809 ratio. Moreover, it is necessary to adapt the effective Soret coefficient $S_{\text{eff}} = S_{\text{st}} + S_{\text{CH}}$ to
810 obtain the required separation. Secondly, we noticed that the discrepancies between the
811 analytical and the experimental values of the optimal permeability and the corresponding
812 separation ratio could be imputed to dispersion, which affects the coefficient D , and to a
813 lack of knowledge of all the parameters of the model. Still, for the mixture HDO- H_2O , the
814 introduction of S_{CH} , and the definition of the effective Soret coefficient S_{eff} , led to a good
815 agreement with the experimental curves that express the separation ratio as a function
816 of the permeability [cf. Figures 2c and 2d]. For the mixture $\text{C}_{24}\text{H}_{50}$ - $\text{C}_{12}\text{H}_{26}$, instead, our
817 best fit of the experimental data could only approximate the expected curve. This was
818 due to quite a large amount of uncertainty of some experimental values used as model
819 parameters [cf. also with Fargue et al. (1998)]. In addition, a stronger contribution of the

820 Cahn-Hilliard contributions was registered, also because the mass fraction of the solute is
821 quite bigger than in the thermogravitational cell studied for the HDO-H₂O experiment.

822 For future research it could be interesting to employ the theoretical framework out-
823 lined in this paper to the thermodiffusion in physical systems for which an initial gradient
824 of mass fraction is present [cf., for example, Rowley and Horne (1980)]. Furthermore, also
825 the contribution provided by the Korteweg stress tensor to Darcy's law necessitates a
826 more thorough study.

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998 **List of tables**

Quantity	Units	HDO-H ₂ O	C ₂₄ H ₅₀ -C ₁₂ H ₂₆
L	m	$4.0 \cdot 10^{-1}$ [1]	$4.0 \cdot 10^{-1}$ [1]
H	m	$4.0 \cdot 10^{-3}$ [1]	$4.5 \cdot 10^{-3}$ [1]
ϕ	—	0.4 [1]	0.4 [1]
ρ_0	kg/m ³	989.10 [2]	758.30
c_0	—	$5.8 \cdot 10^{-6}$	0.15
T_{ref}	°C	47.5 [1]	48.5 [1]
ΔT	°C	19 [1]	25 [1]
β	1/K	$4.4 \cdot 10^{-4}$ [2]	—
γ	—	0	—
μ	Pa · s	$5.7 \cdot 10^{-4}$ [2]	$0.96 \cdot 10^{-3}$ [1]
$\bar{D} = D/\phi$	m ² /s	$2.09 \cdot 10^{-9}$ [2]	$6.5 \cdot 10^{-10}$ [1]
S_{st}	1/K	$6.3158 \cdot 10^{-5}$ [2]	$1 \cdot 10^{-3}$ [3]
C_{pf}	J/(kg · K)	4180.1 [2]	1094.7
C_{ps}	J/(kg · K)	1000.0 [4]	1000.0 [4]
κ	W/(m · K)	$\in [2.89, 9.27]$ [2]	≈ 13

Table 1: $\bar{D} = 6.5 \cdot 10^{-10}$ m²/s refers to C₂₄H₅₀. $S_{\text{st}} = 6.3158 \cdot 10^{-5}$ K⁻¹ is obtained by dividing $S = 1.2 \cdot 10^{-3}$ (Benano-Melly et al., 2001) by $\Delta T = 19$ K. [1] Jamet et al. (1992); [2] Benano-Melly et al. (2001); [3] Fargue et al. (1998); [4] Oldenburg and Pruess (1999).

Quantity	Units	C ₂₄ H ₅₀	C ₁₂ H ₂₆
True mass densities	kg/m ³	$\rho_1 = 799.1$	$\rho_2 = 751.1$
Initial concentrations	kg/m ³	$\chi_1 = 113.8$	$\chi_2 = 644.9$

Table 2: Experimental values taken from Jamet et al. (1992).

λ [m ⁴ /s ²]	S_{st} [1/K]	$S_{\text{eff,max}}$ [1/K]	$S_{\text{eff,min}}$ [1/K]
1.8	$3.5 \cdot 10^{-4}$	$6.39 \cdot 10^{-4}$	$2.13 \cdot 10^{-4}$
3.0	$2.0 \cdot 10^{-4}$	$5.73 \cdot 10^{-4}$	$6.81 \cdot 10^{-5}$
3.8	$1.2 \cdot 10^{-4}$	$5.04 \cdot 10^{-4}$	$7.14 \cdot 10^{-6}$

Table 3: Values corresponding to the curves in Figure 2d (cf. Fargue et al. (1998)).

999 **Figure Captions**

1000 Figure 1: (a) Isolines of the solute mass fraction during the time, from the early times (left)
 1001 to the steady state (right). The results are obtained for the HDO-H₂O mixture within the

1002 standard setting of thermodiffusion. The benchmark is taken from Benano-Melly et al.
 1003 (2001) and has been recomputed in the present paper with parameters $L = 0.02$ m,
 1004 $H = 0.004$ m, and permeability $k = 5 \cdot 10^{-12}$ m² (cf. Jamet et al. (1992)). (b) Spatial
 1005 Pattern of S_{CH} for $\lambda = 1.8$ m⁴/s² and $k = 5 \cdot 10^{-12}$ m², and the corresponding normalised
 1006 mass fraction at the steady state. (c) Spatial Pattern of S_{CH} for $\lambda = 1.8$ m⁴/s² and
 1007 $k = 1 \cdot 10^{-10}$ m², and its corresponding normalised mass fraction at the steady state.

1008

1009 Figure 2: (a) Separation ratio as a function of permeability for the HDO-H₂O mixture. (b)
 1010 Separation ratio as a function of permeability for the C₂₄H₅₀-C₁₂H₂₆ mixture. The results
 1011 are obtained within the standard setting of thermodiffusion, $\lambda = 0$ m⁴/s². (c) Mixture
 1012 HDO-H₂O: Results obtained with standard Soret coefficient equal to $S_{\text{st}} = 1.0 \cdot 10^{-5}$ 1/K.
 1013 (d) Mixture C₂₄H₅₀-C₁₂H₂₆: Results obtained for various values of λ and S_{st} . Best fit
 1014 obtained for $S_{\text{st}} = 2.55 \cdot 10^{-4}$ 1/K. Experimental data and analytical curves have been
 1015 recomputed and redrawn from Jamet et al. (1992) and Fargue et al. (1998).

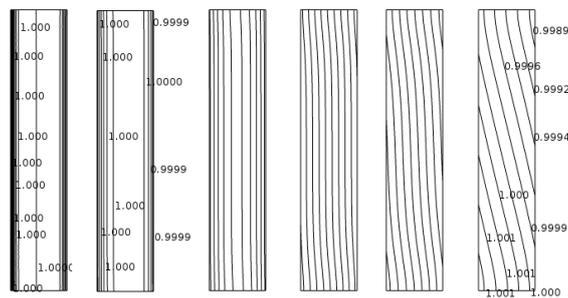
1016

1017 Figure 3: (a) Steady state separation ratio for different values of λ in the HDO-H₂O
 1018 mixture (see also Jamet et al. (1992) and Fargue et al. (1998) for comparison). The stan-
 1019 dard Soret coefficient, S_{st} , is defined in Table 1. (b) Time evolution of ε for $k = 8 \cdot 10^{-11}$ m².
 1020 (c) Dependence of ε on the permeability for some nonzero values of λ .

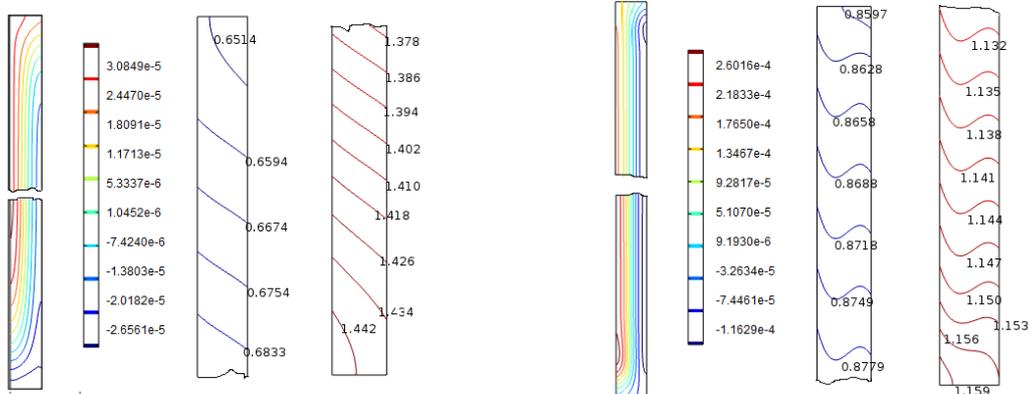
1021

1022 Figure 4: Mixture C₂₄H₅₀-C₁₂H₂₆. (a) Time behaviour of c_{B} (solid lines) and c_{T} (dashed
 1023 lines), starting from a non-uniform mass fraction. Circled lines correspond to simulations
 1024 involving $S_{\text{CH}} \neq 0$ ($\lambda = 3.8$ m⁴/s²) and $S_{\text{st}} = 0$. Lines with asterisks correspond to simu-
 1025 lations in which $S_{\text{st}} = 1.2 \cdot 10^{-4}$ 1/K and $S_{\text{CH}} = 0$. Lines with no markers correspond to
 1026 the case with no cross effects. (b) Initial mass fraction.

1027 **List of figures**



(a)



(b)

(c)

Figure 1

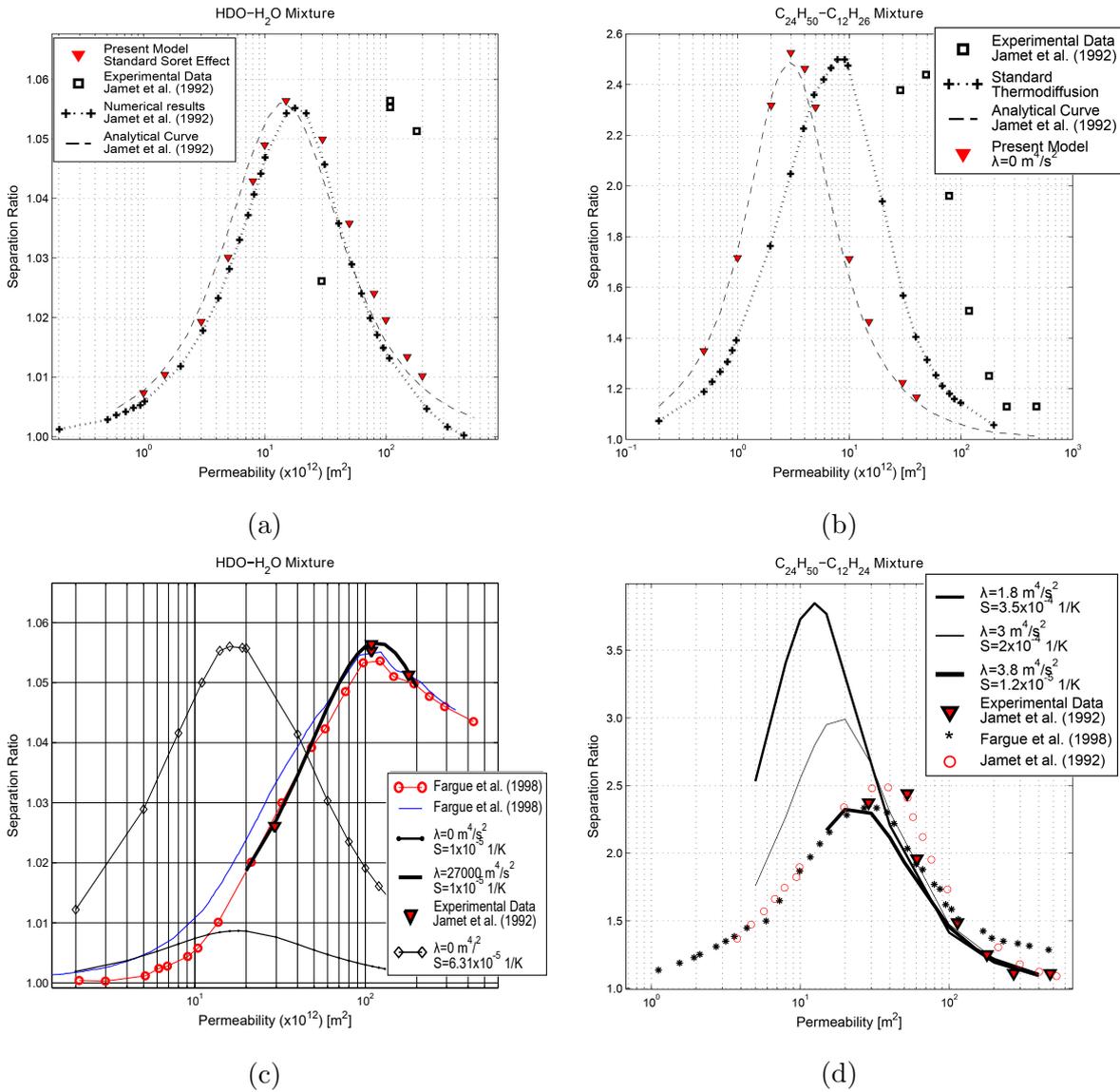
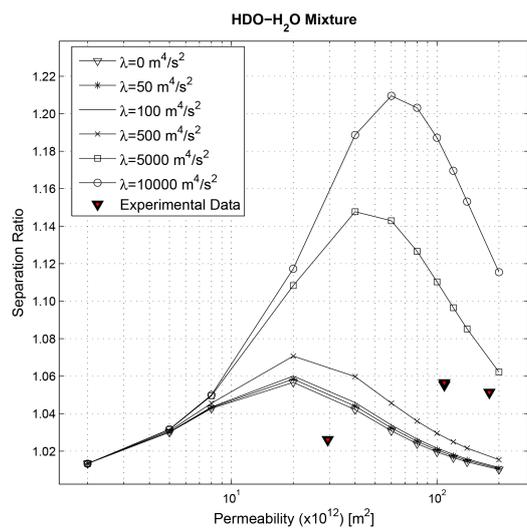
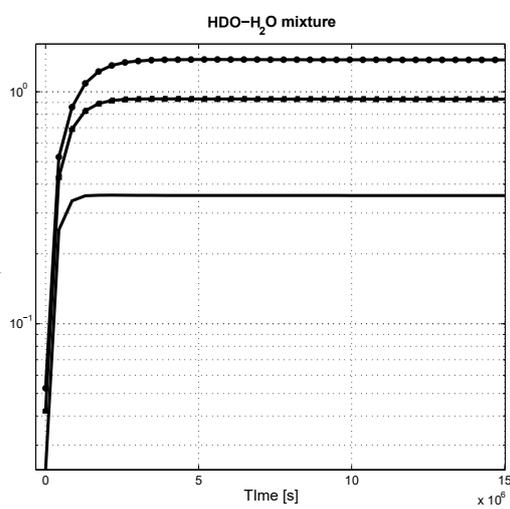


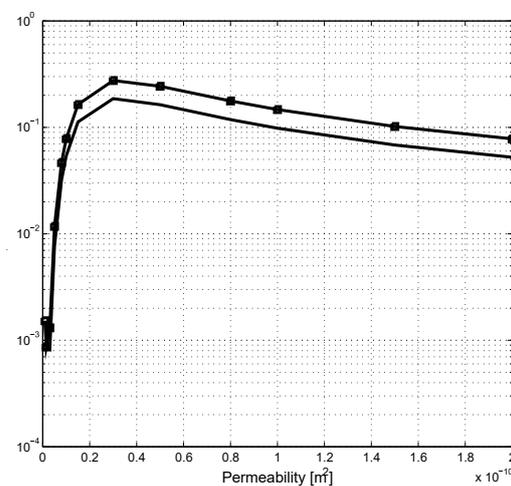
Figure 2



(a)

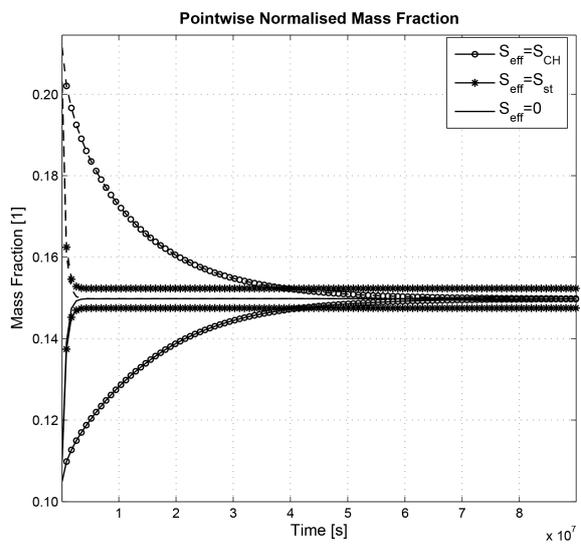


(b)

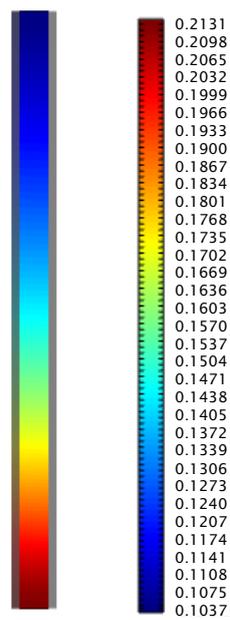


(c)

Figure 3



(a)



(b)

Figure 4