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# **A LOCAL THERMAL NON-EQUILIBRIUM MODEL FOR COUPLED HEAT AND MASS TRANSFER WITH DISPERSION AND THERMAL DIFFUSION IN POROUS MEDIA**

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**ABSTRACT:** A theoretical model is proposed to predict Darcy-scale mass transport in porous media coupled with non-equilibrium heat transfer and taking into account the thermal diffusion process. A volume-averaging technique was used with approximations leading to a two-equation or two-temperature model for the macro-scale energy balance equations. Because of the Soret effect, the concentration deviation with respect to the averaged value is a function of concentration and temperature gradients in the fluid phase, the temperature gradient in the solid phase, and the difference between the two averaged temperatures. The mapping between deviations and averages involves four closure problems for the mass transport equations: problems which were solved numerically over a two-dimensional periodic-unit cell for evaluation purposes. The results show that the effective coefficients depend strongly on the thermo-physical properties of the medium and the Péclet number. In particular, the effective-Soret coefficient in porous media changes with the Péclet number and the phases' thermal conductivity ratios.

**KEY WORDS:** Coupled phenomena, Soret effect, Numerical simulation, Upscaling, Volume averaging

## NOMENCLATURE

$\mathcal{A}_{\beta\sigma}$	Area of the $\beta$ - $\sigma$ interface contained within the macroscopic region, $\text{m}^2$	$\mathbf{S}_{T\beta\sigma}^*$	Effective Soret tensor associated with $\nabla\langle T_\sigma \rangle^\sigma$ in the $\beta$ -phase, $1/\text{K}$
$\mathcal{A}_{\beta e}$	Area of the entrances and exits of the $\beta$ - $\sigma$ phase associated with the macroscopic system, $\text{m}^2$	$s_\beta$	Scalar field that maps $\left(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma\right)$ onto $\tilde{T}_\beta$
$A_{\beta\sigma}$	Area of the $\beta$ - $\sigma$ interface within the averaging volume, $\text{m}^2$	$s_\sigma$	Scalar field that maps $\left(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma\right)$ onto $\tilde{T}_\sigma$
$\mathbf{b}_{C\beta}$	Mapping vector field for $\tilde{c}_\beta$ , $\text{m}$	$t$	Time, $\text{s}$
$\mathbf{b}_{S\beta}$	Mapping vector field for $\tilde{c}_\beta$ , $\text{m}$	$T_\beta$	Temperature of the $\beta$ -phase, $\text{K}$
$\mathbf{b}_{S\beta\beta}$	Vector field that maps $\nabla\langle T_\beta \rangle^\beta$ onto $\tilde{c}_\beta$ , $\text{m}$	$\langle T_\beta \rangle^\beta$	Intrinsic average temperature of the $\beta$ -phase, $\text{K}$
$\mathbf{b}_{S\beta\sigma}$	Vector field that maps $\nabla\langle T_\sigma \rangle^\sigma$ onto $\tilde{c}_\beta$ , $\text{m}$	$\tilde{T}_\beta$	Spatial deviation temperature in the $\beta$ -phase, $\text{K}$
$\mathbf{b}_{T\beta}$	Mapping vector field for $\tilde{T}_\beta$ , $\text{m}$	$T_\sigma$	Temperature of the $\sigma$ -phase, $\text{K}$
$\mathbf{b}_{T\sigma}$	Mapping vector field for $\tilde{T}_\sigma$ , $\text{m}$	$\langle T_\sigma \rangle^\sigma$	Intrinsic average temperature of the $\sigma$ -phase, $\text{K}$
$\mathbf{b}_{T\beta\beta}$	Vector field that maps $\nabla\langle T_\beta \rangle^\beta$ onto $\tilde{T}_\beta$ , $\text{m}$	$\tilde{T}_\sigma$	Spatial deviation temperature in the $\sigma$ -phase, $\text{K}$
$\mathbf{b}_{T\beta\sigma}$	Vector field that maps $\nabla\langle T_\sigma \rangle^\sigma$ onto $\tilde{T}_\beta$ , $\text{m}$	$\mathbf{u}_{C\beta}$	Mass convective vector associated with $\nabla\left(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma\right)$
$\mathbf{b}_{T\sigma\beta}$	Vector field that maps $\nabla\langle T_\beta \rangle^\beta$ onto $\tilde{T}_\sigma$ , $\text{m}$	$\mathbf{u}_{\beta\beta}$	Two-equation model heat convective vector associated with $\nabla\langle T_\beta \rangle^\beta$ in the $\beta$ -phase equation

$\mathbf{b}_{T\sigma\sigma}$	Vector field that maps $\nabla\langle T_\sigma \rangle^\sigma$ onto $\tilde{T}_\sigma$ , m	$\mathbf{u}_{\beta\sigma}$	Two-equation model heat convective vector associated with $\nabla\langle T_\sigma \rangle^\sigma$ in the $\beta$ -phase equation
$c_p$	Constant pressure heat capacity, J.kg/K	$\mathbf{u}_{\sigma\beta}$	Two-equation model heat convective vector associated with $\nabla\langle T_\beta \rangle^\beta$ in the $\sigma$ -phase equation
$c_\beta$	Total mass fraction in the $\beta$ -phase	$\mathbf{u}_{\sigma\sigma}$	Two-equation model heat convective vector associated with $\nabla\langle T_\sigma \rangle^\sigma$ in the $\sigma$ -phase equation
$\langle c_\beta \rangle^\beta$	Intrinsic average mass fraction in the $\beta$ -phase	$Pe_T$	Thermal cell Péclet number
$\tilde{c}_\beta$	Spatial deviation mass fraction in the $\beta$ -phase	$Pe_C$	Solutal cell Péclet number
$D_\beta$	Binary diffusion coefficient, m <sup>2</sup> /s	$r_0$	Radius of the averaging volume, m
$D_{T\beta}$	Thermal diffusion coefficient, m <sup>2</sup> /s.K	$\mathbf{v}_\beta$	Mass average velocity in the $\beta$ -phase, m/s
$\mathbf{D}_{T\beta\beta}^*$	Effective thermal diffusion tensor associated with $\nabla\langle T_\beta \rangle^\beta$ in the $\beta$ -phase	$\langle \mathbf{v}_\beta \rangle^\beta$	Intrinsic average mass average velocity in the $\beta$ -phase, m/s
$\mathbf{D}_{T\beta\sigma}^*$	Effective thermal diffusion tensor associated with $\nabla\langle T_\sigma \rangle^\sigma$ in the $\beta$ -phase	$\tilde{\mathbf{v}}_\beta$	Spatial deviation mass average velocity, m/s
$\mathbf{D}_\beta^*$	Total dispersion tensor, m <sup>2</sup> /s	$V_\beta$	Volume of the $\beta$ -phase contained within the averaging volume, m <sup>3</sup>
$\mathbf{g}$	Gravitational acceleration, m <sup>2</sup> /s	$V_\sigma$	Volume of the $\sigma$ -phase contained within the averaging volume, m <sup>3</sup>
$h_T$	Film heat transfer coefficient, J/m <sup>2</sup> .s.K	$\mathcal{V}$	Local averaging volume, m <sup>3</sup>
$\mathbf{I}$	Unit tensor	$x, y, z$	Cartesian coordinates, m
$k_\beta$	Thermal conductivity of the fluid phase, W/m.K	<i>Greek symbols</i>	
$k_\sigma$	Thermal conductivity of the solid phase,	$\varepsilon_\beta$	Volume fraction of the $\beta$ -phase or porosity

	W/m.K		
$\mathbf{K}_\beta$	Permeability tensor, $\text{m}^2$	$\varepsilon_\sigma$	Volume fraction of the $\sigma$ -phase
$\mathbf{k}_{\beta\beta}$	Two-equation model effective thermal conductivity tensor associated with $\nabla\langle T_\beta \rangle^\beta$ in the $\beta$ -phase equation, W/m.K	$\kappa$	$k_\sigma/k_\beta$ , thermal conductivity ratio
$\mathbf{k}_{\beta\sigma}$	Two-equation model effective thermal conductivity tensor associated with $\nabla\langle T_\sigma \rangle^\sigma$ in the $\sigma$ -phase equation, W/m.K	$\mu_\beta$	Dynamic viscosity for the $\beta$ -phase, Pa.s
$\mathbf{k}_{\sigma\beta}$	Two-equation model effective thermal conductivity tensor associated with $\nabla\langle T_\beta \rangle^\beta$ in the $\sigma$ -phase equation, W/m.K	$\rho_\beta$	Total mass density in the $\beta$ -phase, $\text{kg/m}^3$
$\mathbf{k}_{\sigma\sigma}$	Two-equation model effective thermal conductivity tensor associated with $\nabla\langle T_\sigma \rangle^\sigma$ in the $\sigma$ -phase equation, W/m.K	$\tau$	Scalar tortuosity factor
$\mathbf{k}^*$	One-equation total thermal conductivity tensor, W/m.K	$\varphi$	Arbitrary function
$\ell$	Characteristic length associated with the microscopic scale, m	<i>Subscripts, superscripts and other symbols</i>	
$\ell_{UC}$	Characteristic length associated with a unit cell, m	$\beta$	Fluid-phase
$\ell_\beta$	Characteristic length for the $\beta$ -phase, m	$\sigma$	Solid-phase
$L$	Characteristic length for macroscopic quantities, m	$\beta\sigma$	$\beta$ - $\sigma$ interphase
$\mathbf{n}_{\beta\sigma}$	Unit normal vector directed from the $\beta$ -phase toward the $\sigma$ -phase	$\beta e$	Fluid-phase entrances and exits
$p_\beta$	Pressure in the $\beta$ -phase, Pa	*	Effective quantity

$\langle p_\beta \rangle^\beta$	Intrinsic average pressure in the $\beta$ -phase, Pa	$\langle \rangle$	Spatial average
$\mathbf{r}$	Position vector, m	$\langle \rangle^\beta$	Intrinsic $\beta$ -phase average
$r_\beta$	Scalar field that maps $(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma)$ onto $\tilde{c}_\beta$	$( )_{xx}$	Longitudinal component of a tensor
$S_T$	Soret coefficient in free fluid, 1/K	$( )_x$	$x$ -component of a vector
$\mathbf{S}_{T\beta\beta}^*$	Effective Soret tensor associated with $\nabla \langle T_\beta \rangle^\beta$ in the $\beta$ -phase, 1/K		

## 1. INTRODUCTION

In many natural and industrial processes we must take into account the coupling between mass transport and temperature. When this occurs, an anti-diffusive mass flux can be generated in a fluid mixture under the existing temperature gradient, which tends to separate the species. This cross-effect phenomenon is known as the Soret effect or thermal diffusion. The term thermal diffusion, first used for gas mixtures, later came to refer to the phenomenon for all phase states. Thermal diffusion can occur in many processes involving coupled heat and mass transfer in porous media, for instance, in the chemical industry (Köhler and Morozov, 2016; Reddy et al., 2017), contaminant fate and transport and environmental processes (Beyer et al., 2016; Mon et al., 2016; Perrier et al., 2004; Ratchagar and Senthamilselvi, 2017), drying or vitrification processes (Dragun, 1991), and reservoir engineering (Firoozabadi, 1991; Galliéro et al., 2003; Vaerenbergh et al., 2006).

In a previous study (Davarzani et al., 2010a), a theoretical model was developed using the volume-averaging technique to predict coupled heat and mass transfer equations in porous media at the Darcy scale, in the case of local-equilibrium heat transfer (i.e., with a single temperature for all phases). The results revealed that in the macro-scale model the Soret coefficient, defined as the ratio of the thermal diffusion coefficient to the binary-diffusion coefficient, can be different from the free-liquid coefficients when convection is dominant. However, the Soret

coefficient was found to be the same in a free fluid and in a porous medium for a diffusion-dominated regime (Davarzani et al., 2010b; Platten and Costeseque, 2004). In all cases, the Soret coefficient in porous media is independent of the solid phase particle–particle contact or connectivity (Davarzani et al., 2011).

In a convection-dominant regime, the thermal conductivity ratio between fluid and solid plays an important role in determining the effective thermal diffusion coefficients (Davarzani et al., 2010a). The proposed theoretical model has been validated with experimental results for pure diffusion cases. A modified two-bulb method has been used to evaluate the free flow and effective diffusion as well as thermal diffusion coefficients in granular porous media (Davarzani et al., 2010b). This validated theoretical model can capture the coupled heat- and mass-transfer behaviors when the medium's thermo-physical contrasts are moderate, a situation that favors local equilibrium. However, when the thermo-physical contrast becomes high, the situation is much more complex and may lead to non-local thermal-equilibrium conditions, which is the focus of this paper.

Davarzani et al. (2010) compared averaged temperatures predicted from an upscaled macroscopic model and the results coming from the solution of microscopic pore-scale equations over a periodic array of disks. The results did indeed show that the theoretical local-equilibrium model can predict transport phenomena efficiently for moderate thermal-property contrasts. In this case, the results are less dependent on the boundary and initial conditions. For higher thermo-physical contrasts, they observed a significant difference between predicted temperature and the pore-scale averaged temperatures (solid and liquid phases) in the transient period. By contrast, at steady-state and for the considered initial boundary-value problem, the theoretical local-equilibrium model can again predict how the system will behave correctly (Davarzani



et al., 2010a). There is therefore an essential need to develop a local non-equilibrium model if the interest is in transient behaviors with higher phase-contrast properties. The main objective of this work was to develop such a complex and advanced model.

It is important to recognize that non-equilibrium conditions cannot be described in general by a single macro-scale model. Therefore, alternative models have been developed to take into account the local non-equilibrium problem. There are at least two different approaches to treat this problem: the two-equation model (also called dual-porosity or two-region model) and the hybrid (or mixed) model. These models are well known in petroleum engineering for the description of the fractured mediums, in chemical engineering, and hydrogeology (mobile-mobile and mobile-immobile systems). The two-equation model consists of two coupled Darcy-scale balance equations. These two equations are connected through an exchange term. The domains of validity of different models, including two-equation, one-equation local equilibrium, and one-equation time-asymptotic non-equilibrium models, which depend on the Péclet number and a characteristic time, have been explored by (Davit et al., 2010; Davit and Quintard, 2015a). While the one-equation local equilibrium model and the one-equation non-equilibrium asymptotic model are of great interest, it was shown in Davit et al. (2010) that they have limitations. In particular, it is impossible with these models to assess whether non-equilibrium conditions are or have been reached. It is clear that the local equilibrium model fails to represent actual fields in non-equilibrium conditions. Asymptotic conditions may have been reached, thus providing some justification for the use of the asymptotic model. However, these conditions cannot be verified with this model. In addition, if the quasi-steady solution reverts to local equilibrium, the asymptotic model yields too large an effective-thermal tensor and thus fails to capture actual fields. An example of such situations is given in Davarzani et al. (2010)

(Davarzani et al., 2010a).

Contrary to the traditional two-equation model where both equations for fluid and solid are written at the macro-scale, i.e., they come from the volume averaging, the mixed models couple the macroscopic description of one continuous phase for fluids with a pore-scale equation for the solid particles (Arbogast, 1989; de Swaan, 1976; Kazemi, 1969). It was found that the mixed model matches better the direct numerical simulation results compared to the two-equation model when the thermal conductivity of the solid phase is orders of magnitude lower than the thermal conductivity of the flowing fluid (there is also a condition often overlooked in the literature that volume fractions are not close to unity or zero. For instance, in the framework of asymptotic homogenization, it must be on the order of  $\varepsilon^2$  ( $\varepsilon$  being in the context of the length-scale ratio between the pore-scale and Darcy-scale). Recently, Xin et al., 2018 studied a mixed model for high permeability granular porous media with very low solid-phase thermal conductivity. As expected, they showed that the equilibrium time of the fluid-solid center is longer for the low thermal conductivity of the solid matrix. This equilibrium time is affected significantly by solid size and flow rate [Lu et al., 2018; Xin et al., 2018]. Mixed model validity is limited to high thermos-physical contrasts of phases (e.g., very low solid/fluid thermal conductivity ratios) encountered in mobile-immobile and dispersed solid-phase systems (Debenest and Quintard, 2008; Xin et al., 2018). Moreover, in the case where the local non-equilibrium situations come from the fluid phase (e.g., heat exchangers, impact of heat sources), the mixed model does not provide a suitable solution. Also, the computational time for a mixed model is relatively high because it involves pore-scale grids and can become close to the calculation time of the direct numerical simulations if more precision is needed (Debenest and Quintard, 2008) and if the population of grains inside the averaging volume cannot be replaced

by the dynamics of a single grain or another type of simplified volume. Therefore, special attention should be paid to select a suitable local non-equilibrium model according to the problem and its context.

While the development of the two-equation model is more complicated, in many applications it gives better and more robust results. The lower required computational time is also a good argument to use this model in many large-scale applications such as soil contamination and petroleum engineering. It also must be emphasized that transient closures, involving time convolution with effective properties coming from the unsteady-state version of the closure problems, provide an accurate transient behavior that does not suffer from the limitations of mixed models, while the implementation of time-convolution in the macro-scale numerical model is not straightforward (see (Chastanet and Wood, 2008; Davit and Quintard, 2015b)). Finally, transient closures can be used as a basis to generate multi-rate or N-equations models as discussed in (Davit et al., 2019; Davit and Quintard, 2015b; Haggerty and Gorelick, 1995), which provide an alternative to transient closure without the numerical implementation problems. Therefore, the most versatile model and easily implemented, valid but with a variable degree of accuracy for all range of parameters, is the two-equation model with steady-state closure. This must be the first choice when working on a system expecting a non-equilibrium behavior. Hence our motivation to develop such a model in the presence of thermal diffusion.

So far, no theoretical predictive model has been proposed to simulate macro-scale mass transfer with thermal diffusion in porous media, in the case of local thermal non-equilibrium. We propose such a model here by extending previous results obtained using a volume-averaging technique in the case of a local non-equilibrium heat-transfer situation with no Soret effect. First, we present the pore-scale equations with an introduction to the upscaling technique we used.

Then we recall the results (macro-scale equations, closure problems, and effective thermal conductivities) for the macro-scale energy equation in the case of local equilibrium and local non-equilibrium. Using these results, we develop the macro-scale equation for the heat and mass transport equations. Finally, we calculate the effective properties for simple representative-unit cells in order to investigate the impact of the pore-scale physical parameters on the effective properties.

## 2. GOVERNING MICROSCOPIC EQUATION

The problem under consideration corresponds to non-isothermal mass transport in a porous medium as represented schematically in Fig. 1. A binary-fluid mixture flows through a saturated porous medium subjected to a temperature gradient. For simplicity, we follow the same notation as in (Quintard et al., 1997) and (Davarzani et al., 2010a), where the fluid phase is represented by the  $\beta$ -phase and the porous medium solid phase is identified as the  $\sigma$ -phase.

The pore-scale energy balances for the fluid ( $\beta$ -phase) and solid ( $\sigma$ -phase) with their associated boundary conditions are introduced as

$$(\rho c_p)_\beta \frac{\partial T_\beta}{\partial t} + (\rho c_p)_\beta v_\beta \cdot \nabla T_\beta = \nabla \cdot (k_\beta \nabla T_\beta), \text{ in the } \beta\text{-phase} \quad (1)$$

$$\text{BC1: } T_\beta = T_\sigma, \text{ at } \mathcal{A}_{\beta\sigma} \quad (2)$$

$$\text{BC2: } \mathbf{n}_{\beta\sigma} \cdot (k_\beta \nabla T_\beta) = \mathbf{n}_{\beta\sigma} \cdot (k_\sigma \nabla T_\sigma), \text{ at } \mathcal{A}_{\beta\sigma} \quad (3)$$

$$(\rho c_p)_\sigma \frac{\partial T_\sigma}{\partial t} = \nabla \cdot (k_\sigma \nabla T_\sigma), \text{ in the } \sigma\text{-phase} \quad (4)$$

where  $T_\beta$  and  $T_\sigma$  are the temperature fields in the  $\beta$ - and  $\sigma$ -phases, respectively,  $k_\beta$  and  $k_\sigma$  are the fluid and solid thermal conductivity coefficients,  $\mathbf{n}_{\beta\sigma}$  is a unit normal vector directed from the fluid toward the solid phase, and  $\mathcal{A}_{\beta\sigma}$  is the area of the interface between the two phases ( $\beta$ - $\sigma$

interfaces).

In this study, thermal diffusion (or the Soret effect), i.e., mass transport caused by the thermal gradient, is taken into account. Therefore, the pore-scale mass balance equation and the interface-boundary condition can be presented as follows (Nield and Bejan, 2013)

$$\frac{\partial c_\beta}{\partial t} + \nabla \cdot (c_\beta \mathbf{v}_\beta) = \nabla \cdot (D_\beta \nabla c_\beta + D_{T\beta} \nabla T_\beta), \text{ in the } \beta\text{-phase} \quad (5)$$

$$\text{BC1: } \mathbf{n}_{\beta\sigma} \cdot (D_\beta \nabla c_\beta + D_{T\beta} \nabla T_\beta) = 0, \text{ at } \mathcal{A}_{\beta\sigma} \quad (6)$$

where  $c_\beta$  is the species mass concentration in the  $\beta$ -phase,  $D_\beta$  is the binary molecular diffusion, and  $D_{T\beta}$  is the thermal diffusion coefficient in the free fluid. Here, we have considered that the fluid-solid interface is inert and impervious. Therefore, we have neglected any solute accumulation and exchange phenomena (e.g., adsorption, dissolution, reaction) at the  $\beta$ - $\sigma$  interface.

We have not taken into account the Dufour effect in the energy equation here. This is generally an acceptable approximation. It has the fundamental advantage of decoupling the heat- and mass-transport problems, provided that fluid properties do not also depend on the concentration. Consequently, we treated the upscaling problem in a sequential manner: temperature first (This problem has received a considerable attention in the literature (Carbonell and Whitaker, 1984; Levec and Carbonell, 1985; Quintard, 1993; Quintard et al., 1997; Vortmeyer and Schaefer, 1974; Zanotti and Carbonell, 1984)) and then the mass-transfer problem, in which heat-transfer closure was already known.

In this study, we have assumed that density and viscosity are constant and independent of temperature and concentration, such that the momentum equations are not coupled with the energy and mass-conservation equations. In fact, it is sufficient that this approximation holds at

the REV-scale. In this case, variations of the fluid properties can be taken into account in the macro-scale equations. Therefore, the fluid velocity fields are presumed to be known beforehand when dealing with those equations.

### **3. UPSCALING TECHNIQUE**

There are usually computational limitations to simulating transport phenomena at the pore scale in a large porous-medium domain, due to the required computational memory and time. In practice, a homogenous-equivalent model can simplify modeling multi-phase transport in porous media (Brenner, 1980; Carbonell and Whitaker, 1984; Cushman et al., 2002; Mei, 1991). Several theoretical methods and techniques exist for developing such a model and moving through different scales (Cushman et al., 2002). The volume-averaging method (Carbonell and Whitaker, 1984) and homogenization techniques (Mei, 1991) are the most widely used techniques. They share some common principles, in particular the idea of looking at the pore-scale field in terms of a correction or deviation to the macro-scale field, as discussed in (Davit et al., 2013). Our paper is an extension of previous papers devoted to the development of local non-equilibrium heat-transfer models using the framework of a volume-averaging theory. We will follow these developments closely and emphasize the original points when the Soret effect plays a role. The volume-averaging technique consists of first producing the macro-scale equations from averaging the pore-scale equations; second, solving micro-scale problems over a unit cell to obtain the effective properties; and finally, solving the upscaled macro-scale model with calculated effective properties and specific initial and boundary conditions.

Our starting point in this paper, given the above arguments on the sequential coupling between the heat- and mass-transport problems, is the local non-equilibrium two-temperature model extensively studied in the literature, especially using the volume-averaging method

(DeGroot and Straatman, 2011; Puiroux et al., 2004; Quintard et al., 1997; Quintard and Whitaker, 1993). The method and its application to the heat-transfer problem will be described without all the mathematical developments, as a preliminary for the original part of the paper: the treatment of the mass-transport problem with the Soret effect and thermal non-equilibrium.

To obtain a Darcy-scale model for the coupled heat- and mass-transfer problem, the pore-scale equations must be integrated over a representative elementary volume,  $\mathcal{V}$  shown in Fig. 1. While a more general and accurate averaging procedure may be used ((Davit and Quintard, 2017; Quintard and Whitaker, 1994a; Quintard and Whitaker, 1994b; Quintard and Whitaker, 1994c; Quintard and Whitaker, 1994d; Quintard and Whitaker, 1994e)), the superficial and intrinsic averages associated with the phases are in the classical sense respectively defined for a field variable  $\phi_\beta$  as (Whitaker, 1999)

$$\langle \phi_\beta \rangle = \frac{1}{\mathcal{V}} \int_{V_\beta} \phi_\beta dV \quad (7)$$

$$\langle \phi_\beta \rangle^\beta = \frac{1}{V_\beta} \int_{V_\beta} \phi_\beta dV \quad (8)$$

where  $V_\beta$  is the volume of the  $\beta$ -phase in the averaging volume. The superficial and intrinsic averages are related by

$$\langle \phi_\beta \rangle = \varepsilon_\beta \langle \phi_\beta \rangle^\beta \quad (9)$$

where  $\varepsilon_\beta$  is the  $\beta$ -phase volume fraction that will be considered as a constant in this study.

The sum of the volume fractions of the two phases satisfies

$$\varepsilon_\beta + \varepsilon_\sigma = 1 \quad (10)$$

Pore-scale deviations are defined as the difference between the point microscopic values and intrinsic averaged values. These spatial decompositions can be defined in the  $\beta$ -phase and  $\sigma$  -

phase as

$$\varphi_\beta = \langle \varphi_\beta \rangle^\beta + \tilde{\varphi}_\beta \text{ and } \varphi_\sigma = \langle \varphi_\sigma \rangle^\sigma + \tilde{\varphi}_\sigma \quad (11)$$

As usual, we will make use of the following length-scale constraints.

$$\ell_\beta \ll r_0 \ll L \quad (12)$$

This hypothesis leads to many simplifications at different steps of the upscaling processes. Below the macroscopic-coupled models obtained from upscaling are presented. In section 4, numerical results for the effective-diffusion and thermal-diffusion coefficients will be presented and discussed.

### 3.1 Macroscopic Energy-Balance Equation

We remind the reader that, with the adopted assumptions as explained in Section 2, the heat-transfer problem is independent of the concentration problem (Carbonell and Whitaker, 1984; Levec and Carbonell, 1985; Quintard, 1993; Quintard et al., 1997; Vortmeyer and Schaefer, 1974; Zanotti and Carbonell, 1984). The theoretical model for temperature has received considerable attention in the literature (Carbonell and Whitaker, 1984; Levec and Carbonell, 1985; Quintard, 1993; Quintard et al., 1997; Vortmeyer and Schaefer, 1974; Zanotti and Carbonell, 1984). In this section, we review the previously described one- and two-equation models.

#### 3.1.1 One-Equation Model

The Darcy-scale model for the local heat-equilibrium case is written as (Nozad et al., 1985; Quintard, 1993; Quintard et al., 1997; Quintard and Whitaker, 1993; Whitaker, 1977)

$$\left( \varepsilon_\beta (\rho c_p)_\beta + \varepsilon_\sigma (\rho c_p)_\sigma \right) \frac{\partial}{\partial t} \langle T \rangle + (\rho c_p)_\beta \nabla \cdot \left( \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle T \rangle \right) = \nabla \cdot (\mathbf{k}^* \cdot \nabla \langle T \rangle) \quad (13)$$

where  $\langle T \rangle = \langle T_\beta \rangle^\beta = \langle T_\sigma \rangle^\sigma$  and  $\mathbf{k}^*$  is the effective thermal conductivity tensor defined by



$$\mathbf{k}^* = (\varepsilon_\beta k_\beta + \varepsilon_\sigma k_\sigma) \mathbf{I} + \frac{(k_\beta - k_\sigma)}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{T\beta} dA - (\rho c_p)_\beta \langle \tilde{\mathbf{v}}_\beta \mathbf{b}_{T\beta} \rangle \quad (14)$$

where  $\mathbf{b}_{T\beta}$  is a mapping variable described below.

In this development, the spatial temperature and velocity decompositions are introduced as

$$\tilde{T}_\beta = T_\beta - \langle T_\beta \rangle^\beta, \text{ in } V_\beta \text{ and } \tilde{T}_\sigma = T_\sigma - \langle T_\sigma \rangle^\sigma, \text{ in } V_\sigma \quad (15)$$

$$\tilde{\mathbf{v}}_\beta = \mathbf{v}_\beta - \langle \mathbf{v}_\beta \rangle^\beta, \text{ in } V_\beta \quad (16)$$

The spatial deviations of the temperatures and average fields can be related in the upscaling process by a linear relationship as (Carbonell and Whitaker, 1984)

$$\tilde{T}_\beta = \mathbf{b}_{T\beta} \cdot \nabla \langle T \rangle \quad (17)$$

$$\tilde{T}_\sigma = \mathbf{b}_{T\sigma} \cdot \nabla \langle T \rangle \quad (18)$$

where  $\mathbf{b}_{T\beta}$  and  $\mathbf{b}_{T\sigma}$  are the *closure variables* for temperature.

Finally, the closure problem with the boundary conditions at the interface of phases that must be solved numerically to find  $\mathbf{k}^*$  from Eq. (14) is written below (Davarzani et al., 2010a; Quintard, 1993; Whitaker, 1999)

**Problem I:**

$$(\rho c_p)_\beta \mathbf{v}_\beta \cdot \nabla \mathbf{b}_{T\beta} + (\rho c_p)_\beta \tilde{\mathbf{v}}_\beta = k_\beta \nabla^2 \mathbf{b}_{T\beta} \quad (19)$$

$$\text{BC1: } \mathbf{b}_{T\beta} = \mathbf{b}_{T\sigma}, \text{ at } A_{\beta\sigma} \quad (20)$$

$$\text{BC2: } -\mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{b}_{T\beta} = -\mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla \mathbf{b}_{T\sigma} + \mathbf{n}_{\beta\sigma} (k_\beta - k_\sigma), \text{ at } A_{\beta\sigma} \quad (21)$$

$$0 = k_\sigma \nabla^2 \mathbf{b}_{T\sigma} \quad (22)$$

$$\text{Periodicity: } \mathbf{b}_{T\beta}(\mathbf{r} + \ell_i) = \mathbf{b}_{T\beta}(\mathbf{r}) \text{ \& } \mathbf{b}_{T\sigma}(\mathbf{r} + \ell_i) = \mathbf{b}_{T\sigma}(\mathbf{r}), i=1,2,3 \quad (23)$$

$$\langle \mathbf{b}_T \rangle = \varepsilon_\beta \langle \mathbf{b}_{T\beta} \rangle^\beta + \varepsilon_\sigma \langle \mathbf{b}_{T\sigma} \rangle^\sigma = 0 \quad (24)$$

### 3.1.2 Two-Equation Model

We have not reproduced here details about the upscaling of local thermal non-equilibrium situations, i.e., situations for which the two averaged temperatures may differ significantly. Discussion of this subject can be found in (Davarzani et al., 2010a; Davit et al., 2010; Davit and Quintard, 2015a; Davit and Quintard, 2017; Davit et al., 2012; DeGroot and Straatman, 2011; Moyne, 1997; Quintard, 1993). Different models may be introduced and in this paper we present the simplest and more commonly used, namely the two-temperature model (Carbonell and Whitaker, 1984; Levec and Carbonell, 1985; Quintard, 1993; Quintard et al., 1997; Vortmeyer and Schaefer, 1974; Zanotti and Carbonell, 1984).

Because of scale limitations (time and length), the macroscopic behaviors of porous media cannot generally be represented by a one-equation model for two different phases. The two-equation model consists of separate heat-transport equations for both the  $\sigma$ - and  $\beta$ -phases. The dominant coupling between the two-phase energy equations is then represented by a flux between the phases that depends, in the simpler version, on an exchange coefficient and the difference between the temperatures of the two phases. The temperature spatial deviations in terms of the macroscopic source terms are approximated in this case as

$$\tilde{T}_\beta = \mathbf{b}_{T\beta\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \mathbf{b}_{T\beta\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma - s_\beta \left( \langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma \right) \quad (25)$$

$$\tilde{T}_\sigma = \mathbf{b}_{T\sigma\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \mathbf{b}_{T\sigma\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma - s_\sigma \left( \langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma \right) \quad (26)$$

In these equations,  $\mathbf{b}_{T\beta\beta}$ ,  $\mathbf{b}_{T\beta\sigma}$ ,  $\mathbf{b}_{T\sigma\beta}$ , and  $\mathbf{b}_{T\sigma\sigma}$  are mapping vectors;  $s_\beta$  and  $s_\sigma$  are mapping scalars. They can be obtained from the solution of pore-scale closure problems as detailed in Appendix A (Quintard et al., 1997). The resulting macroscopic equation for the  $\beta$ -phase can be

written as

$$\begin{aligned} & \varepsilon_\beta (\rho_p)_\beta \frac{\partial}{\partial t} \langle T_\beta \rangle^\beta + \varepsilon_\beta (\rho_p)_\beta \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle T_\beta \rangle^\beta - \mathbf{u}_{\beta\beta} \cdot \nabla \langle T_\beta \rangle^\beta - \mathbf{u}_{\beta\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma \\ & = \nabla \cdot (\mathbf{k}_{\beta\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \mathbf{k}_{\beta\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma) - h_T (\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma) \end{aligned} \quad (27)$$

Here,  $\mathbf{k}_{\beta\beta}$  and  $\mathbf{k}_{\beta\sigma}$  are the effective thermal conductivity tensors;  $\mathbf{u}_{\beta\beta}$ ,  $\mathbf{u}_{\beta\sigma}$  are the effective heat-convective vectors;  $h_T$  is the heat-transfer coefficient. They can be calculated from the solution of closure problems and using the equations (A. 25), (A. 26), (A. 29), (A. 30), and (A. 24), respectively.

The intrinsic average-temperature equation for the  $\sigma$ -phase can be written as

$$\begin{aligned} & \varepsilon_\sigma (\rho_p)_\sigma \frac{\partial}{\partial t} \langle T_\sigma \rangle^\sigma - \mathbf{u}_{\sigma\beta} \cdot \nabla \langle T_\beta \rangle^\beta - \mathbf{u}_{\sigma\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma \\ & = \nabla \cdot (\mathbf{k}_{\sigma\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \mathbf{k}_{\sigma\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma) + h_T (\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma) \end{aligned} \quad (28)$$

In this equation also,  $\mathbf{k}_{\sigma\beta}$ ,  $\mathbf{k}_{\sigma\sigma}$ ,  $\mathbf{u}_{\sigma\beta}$ , and  $\mathbf{u}_{\sigma\sigma}$  are effective tensors, obtained from the corresponding closure problems and expressions given in Appendix A. As mentioned in (Quintard et al., 1997; Quintard and Whitaker, 1993), the effective-thermal conductivity in the case of one-equation local equilibrium model can be calculated as a limit case of the effective thermal conductivity tensors of the two-equation model (Quintard et al., 1997; Quintard and Whitaker, 1993) by

$$\mathbf{k}^* = \mathbf{k}_{\beta\beta} + \mathbf{k}_{\beta\sigma} + \mathbf{k}_{\sigma\beta} + \mathbf{k}_{\sigma\sigma} \quad (29)$$

### 3.2 Macroscopic Transport Equations for Concentration

The major assumptions that allow us to treat the upscaling process for the mass-transport problem in a sequential manner (by first solving the problem for  $T_\beta$  and  $T_\sigma$  then the problem for  $c_\beta$ ) are:

- the Dufour effect is neglected
- the pore-scale physical properties such as viscosity, density, thermal conductivity, heat capacity, and diffusion coefficients do not depend on temperature or concentration.

Consequently,  $T_\beta$  and  $T_\sigma$  may be replaced in Eq. (5) by their averaged values and their deviations. Furthermore, those variables may be replaced by their representations, in Eqs (17) and (18), or (25) and (26). This can be used to extend the theory of dispersion to the case with thermal diffusion, and the result will depend on the choice of the closure for the heat-transfer problem.

The choice of Eqs (17) and (18), i.e., a local equilibrium theory, has already been explored in Davarzani et al. 2010 (Davarzani et al., 2010a). We briefly give the main findings below. In the subsequent section, the original theory of thermal diffusion is presented in the case of a two-equation heat transfer model.

### 3.2.1 Mass Transport Model for Local Thermal Equilibrium

Application of the volume-averaging theorems on equation (5) and the use of classical simplifications lead to (Davarzani et al., 2010a)

$$\begin{aligned}
\frac{\partial \langle c_\beta \rangle^\beta}{\partial t} + \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \langle c_\beta \rangle^\beta &= \nabla \cdot (D_\beta \nabla \langle c_\beta \rangle^\beta) + \varepsilon_\beta^{-1} \nabla \cdot \left( \frac{D_\beta}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{c}_\beta dA \right) \\
+ \varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot (D_\beta \nabla \langle c_\beta \rangle^\beta) &+ \nabla \cdot (D_{T\beta} \nabla \langle T_\beta \rangle^\beta) + \varepsilon_\beta^{-1} \nabla \cdot \left( \frac{D_{T\beta}}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{T}_\beta dA \right) \\
+ \varepsilon_\beta^{-1} \nabla \varepsilon_\beta \cdot (D_{T\beta} \nabla \langle T_\beta \rangle^\beta) &- \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{c}_\beta \tilde{\mathbf{v}}_\beta \rangle
\end{aligned} \tag{30}$$

in which the spatial deviation of the concentration is defined by

$$c_\beta = \langle c_\beta \rangle^\beta + \tilde{c}_\beta, \text{ in } V_\beta \tag{31}$$

The quasi-steady closure problem for the spatial-deviation concentration is obtained as

$$\mathbf{v}_\beta \cdot \nabla \tilde{c}_\beta + \tilde{\mathbf{v}}_\beta \cdot \nabla \langle c_\beta \rangle^\beta = \nabla \cdot (D_\beta \nabla \tilde{c}_\beta) + \nabla \cdot (D_{T\beta} \nabla \tilde{T}_\beta) \quad (32)$$

$$\text{BC1: } -\mathbf{n}_{\beta\sigma} \cdot (D_\beta \nabla \tilde{c}_\beta + D_{T\beta} \nabla \tilde{T}_\beta) = \mathbf{n}_{\beta\sigma} \cdot (D_\beta \nabla \langle c_\beta \rangle^\beta + D_{T\beta} \nabla \langle T \rangle^\beta), \text{ at } \mathcal{A}_{\beta\sigma} \quad (33)$$

$$\text{BC2: } \tilde{c}_\beta(\mathbf{r} + \ell_i) = \tilde{c}_\beta(\mathbf{r}), i=1, 2, 3 \quad (34)$$

Here, the point-concentration deviation is proportional to the macroscopic-average concentration and the temperature gradients through the closure variables  $\mathbf{b}_{c\beta}$  and  $\mathbf{b}_{s\beta}$  such that

$$\tilde{c}_\beta = \mathbf{b}_{c\beta} \cdot \nabla \langle c_\beta \rangle^\beta + \mathbf{b}_{s\beta} \cdot \nabla \langle T \rangle \quad (35)$$

These two closure variables are the solution of the two boundary value problems IIa and IIb presented below.

#### **Problem IIa**

$$\mathbf{v}_\beta \cdot \nabla \mathbf{b}_{c\beta} + \tilde{\mathbf{v}}_\beta = D_\beta \nabla^2 \mathbf{b}_{c\beta} \quad (36)$$

$$\text{BC: } -\mathbf{n}_{\beta\sigma} \cdot D_\beta \nabla \mathbf{b}_{c\beta} = \mathbf{n}_{\beta\sigma} \cdot D_\beta, \text{ at } \mathcal{A}_{\beta\sigma} \quad (37)$$

$$\text{Periodicity: } \mathbf{b}_{c\beta}(\mathbf{r} + \ell_i) = \mathbf{b}_{c\beta}(\mathbf{r}), i=1,2,3 \quad (38)$$

$$\text{Averages: } \langle \mathbf{b}_{c\beta} \rangle^\beta = 0 \quad (39)$$

#### **Problem IIb**

$$\mathbf{v}_\beta \cdot \nabla \mathbf{b}_{s\beta} = D_\beta \nabla^2 \mathbf{b}_{s\beta} + D_{T\beta} \nabla^2 \mathbf{b}_{T\beta} \quad (40)$$

$$\text{BC: } -\mathbf{n}_{\beta\sigma} \cdot (D_\beta \nabla \mathbf{b}_{s\beta} + D_{T\beta} \nabla \mathbf{b}_{T\beta}) = \mathbf{n}_{\beta\sigma} \cdot D_{T\beta}, \text{ at } \mathcal{A}_{\beta\sigma} \quad (41)$$

$$\text{Periodicity: } \mathbf{b}_{s\beta}(\mathbf{r} + \ell_i) = \mathbf{b}_{s\beta}(\mathbf{r}), i=1, 2, 3 \quad (42)$$

$$\text{Averages: } \langle \mathbf{b}_{s\beta} \rangle^\beta = 0 \quad (43)$$

We must note here that the closure problem for diffusion (Problem IIa) can be solved separately from the other closure problems. However, the closure problem for thermal diffusion

(Problem IIb) depends on the closure variable for temperature  $\mathbf{b}_{T\beta}$ .

The Darcy-scale mass balance equation with the thermal diffusion effect is then obtained as

$$\frac{\partial \langle \varepsilon_\beta c_\beta \rangle^\beta}{\partial t} + \nabla \cdot (\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_\beta \rangle^\beta) = \nabla \cdot (\varepsilon_\beta \mathbf{D}_\beta^* \cdot \nabla \langle c_\beta \rangle^\beta + \varepsilon_\beta \mathbf{D}_{T\beta}^* \cdot \nabla \langle T \rangle) \quad (44)$$

where the effective diffusion coefficients  $\mathbf{D}_\beta^*$  and effective thermal diffusion coefficients  $\mathbf{D}_{T\beta}^*$  are calculated from

$$\mathbf{D}_\beta^* = D_\beta \left( \mathbf{I} + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{c\beta} dA \right) - \langle \tilde{\mathbf{v}}_\beta \mathbf{b}_{c\beta} \rangle^\beta \quad (45)$$

$$\mathbf{D}_{T\beta}^* = D_\beta \left( \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{s\beta} dA \right) + D_{T\beta} \left( \mathbf{I} + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{T\beta} dA \right) - \langle \tilde{\mathbf{v}}_\beta \mathbf{b}_{s\beta} \rangle^\beta \quad (46)$$

### 3.2.2 Mass-Transport Model for Local Thermal Non-Equilibrium

Additional source terms in Eq. (35) must be taken into account in the case of local thermal non-equilibrium conditions. Following the approximations used before, we seek the concentration deviation under the form

$$\tilde{c}_\beta = \mathbf{b}_{c\beta} \cdot \nabla \langle c_\beta \rangle^\beta + \mathbf{b}_{s\beta\beta} \cdot \nabla \langle T_\beta \rangle^\beta + \mathbf{b}_{s\beta\sigma} \cdot \nabla \langle T_\sigma \rangle^\sigma - r_\beta (\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma) \quad (47)$$

Here, we have supposed that the concentration deviation with respect to the averaged value is a function of concentration and temperature gradients in the fluid phase, the temperature gradient in the solid phase, and also the difference between the two averaged temperatures.

By substituting this new concentration deviation, and the  $\beta$ -phase temperature deviation from Eq. (25), into the quasi-steady closure problem presented before in Eqs (32)-(34), we obtain the closure problems for coupled heat and mass transfer listed as follows

### Problem IIIa

$$\mathbf{v}_\beta \cdot \nabla \mathbf{b}_{C\beta} + \tilde{\mathbf{v}}_\beta = D_\beta \nabla^2 \mathbf{b}_{C\beta} \quad (48)$$

$$\text{BC: } -\mathbf{n}_{\beta\sigma} \cdot D_\beta \nabla \mathbf{b}_{C\beta} = \mathbf{n}_{\beta\sigma} D_\beta, \text{ at } A_{\beta\sigma} \quad (49)$$

$$\text{Periodicity: } \mathbf{b}_{C\beta}(\mathbf{r} + \ell_i) = \mathbf{b}_{C\beta}(\mathbf{r}), i=1, 2, 3 \quad (50)$$

$$\text{Averages: } \langle \mathbf{b}_{C\beta} \rangle^\beta = 0 \quad (51)$$

### Problem IIIb

$$\mathbf{v}_\beta \cdot \nabla \mathbf{b}_{S\beta\beta} = D_\beta \nabla^2 \mathbf{b}_{S\beta\beta} + D_{T\beta} \nabla^2 \mathbf{b}_{T\beta\beta} \quad (52)$$

$$\text{BC: } -\mathbf{n}_{\beta\sigma} \cdot (D_\beta \nabla \mathbf{b}_{S\beta\beta} + D_{T\beta} \nabla \mathbf{b}_{T\beta\beta}) = \mathbf{n}_{\beta\sigma} \cdot D_{T\beta}, \text{ at } A_{\beta\sigma} \quad (53)$$

$$\text{Periodicity: } \mathbf{b}_{S\beta\beta}(\mathbf{r} + \ell_i) = \mathbf{b}_{S\beta\beta}(\mathbf{r}), i=1, 2, 3 \quad (54)$$

$$\text{Averages: } \langle \mathbf{b}_{S\beta\beta} \rangle^\beta = 0 \quad (55)$$

### Problem IIIc

$$\mathbf{v}_\beta \cdot \nabla \mathbf{b}_{S\beta\sigma} = D_\beta \nabla^2 \mathbf{b}_{S\beta\sigma} + D_{T\beta} \nabla^2 \mathbf{b}_{T\beta\sigma} \quad (56)$$

$$\text{BC: } -\mathbf{n}_{\beta\sigma} \cdot (D_\beta \nabla \mathbf{b}_{S\beta\sigma} + D_{T\beta} \nabla \mathbf{b}_{T\beta\sigma}) = 0, \text{ at } A_{\beta\sigma} \quad (57)$$

$$\text{Periodicity: } \mathbf{b}_{S\beta\sigma}(\mathbf{r} + \ell_i) = \mathbf{b}_{S\beta\sigma}(\mathbf{r}), i=1, 2, 3 \quad (58)$$

$$\text{Averages: } \langle \mathbf{b}_{S\beta\sigma} \rangle^\beta = 0 \quad (59)$$

### Problem IIId

$$\mathbf{v}_\beta \cdot \nabla r_\beta = D_\beta \nabla^2 r_\beta + D_{T\beta} \nabla^2 s_\beta \quad (60)$$

$$\text{BC: } -\mathbf{n}_{\beta\sigma} \cdot (D_\beta \nabla r_\beta + D_{T\beta} \nabla s_\beta) = 0, \text{ at } A_{\beta\sigma} \quad (61)$$

$$\text{Periodicity: } r_\beta(\mathbf{r} + \ell_i) = r_\beta(\mathbf{r}), i=1, 2, 3 \quad (62)$$

$$\text{Averages: } \langle r_\beta \rangle^\beta = 0 \quad (63)$$

By substituting  $\tilde{c}_\beta$  and  $\tilde{T}_\beta$  from the decomposition given by Eqs (25) and (47) into Eq. (30), the Darcy-scale mass balance equation for the non-equilibrium two-equation temperature model case can be written

$$\begin{aligned} \frac{\partial \langle \varepsilon_\beta c_\beta \rangle^\beta}{\partial t} + \nabla \cdot \left( \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_\beta \rangle^\beta \right) - \nabla \cdot \left( \mathbf{u}_{C\beta} \left( \langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma \right) \right) = \\ \nabla \cdot \left( \varepsilon_\beta \left( \mathbf{D}_\beta^* \cdot \nabla \langle c_\beta \rangle^\beta + \mathbf{D}_{T\beta\beta}^* \cdot \nabla \langle T_\beta \rangle^\beta + \mathbf{D}_{T\beta\sigma}^* \cdot \nabla \langle T_\sigma \rangle^\sigma \right) \right) \end{aligned} \quad (64)$$

where the effective tensors are defined by

$$\mathbf{D}_\beta^* = D_\beta \left( \mathbf{I} + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{C\beta} dA \right) - \langle \tilde{\mathbf{v}}_\beta \mathbf{b}_{C\beta} \rangle^\beta \quad (65)$$

$$\mathbf{D}_{T\beta\beta}^* = D_\beta \left( \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{S\beta\beta} dA \right) + D_{T\beta} \left( \mathbf{I} + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{T\beta\beta} dA \right) - \langle \tilde{\mathbf{v}}_\beta \mathbf{b}_{S\beta\beta} \rangle^\beta \quad (66)$$

$$\mathbf{D}_{T\beta\sigma}^* = D_\beta \left( \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{S\beta\sigma} dA \right) + D_{T\beta} \left( \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{T\beta\sigma} dA \right) - \langle \tilde{\mathbf{v}}_\beta \mathbf{b}_{S\beta\sigma} \rangle^\beta \quad (67)$$

$$\mathbf{u}_{C\beta} = D_\beta \left( \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} r_\beta dA \right) + D_{T\beta} \left( \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} s_\beta dA \right) - \langle \tilde{\mathbf{v}}_\beta r_\beta \rangle^\beta \quad (68)$$

We need therefore to solve four closure problems for concentration (Problem IIIa through IIId) after three closure problems for the two temperatures (Problem A-I through A-II) to model, at the Darcy-scale, mass transport coupled with the local non-equilibrium model defined in Eqs (64), (27) and (28).

The problem for  $\mathbf{b}_{C\beta}$  is the same as the problem IIa for the thermal equilibrium one-equation model, as it does not depend on the temperature gradient, which is consistent with the fact that we should recover the classical dispersion case if the Soret effect is zero.



In the next section, effective mass-transport coefficients are computed for simple unit cells in the case of the proposed two-equation model.

#### 4. NUMERICAL RESULTS

Stokes equations are solved numerically over the unit cell shown in Fig. 2, representing the unit cell of a 2D periodic array of disks. The velocity field is generated by the introduction of an average pressure gradient along the  $x$ -axis. Given the velocity and deviation fields, the three closure problems for temperature can be solved independently from the mass-transport closure problems. As we have mentioned before, the closure problem for diffusion (problem IIIa) can also be solved independently.

The three remaining closure problems depend on the closure problems for temperature. Here, the solution of the closure problem IIIb depends on the solution of the closure problem A-I for  $\mathbf{b}_{T\beta\beta}$ ; the closure problem IIIc depends on  $\mathbf{b}_{T\beta\sigma}$ , which comes from the solution of the closure problem A-II; and, finally, the solution of the closure problem IIId depends on the solution of the closure problem A-III for the scalar value,  $s_\beta$ .

The closure problems have been solved numerically using COMSOL Multiphysics<sup>®</sup>, a commercial package that is based on the finite element method. We used Lagrange quadratic elements for the velocity and linear elements for the pressure (P2-P1) to discretize the Stokes equation by considering Galerkin Least Square (GLS) streamline stabilization method [Hauke and Hughes, 1994]. The closure problems (in a form of diffusion or diffusion-advection equations) were solved using a quadratic Lagrange scheme. The simulation domains were discretized by triangular meshes with a minimum of 2,780 elements. Local mesh refinement was applied at the fluid-solid interface. To ensure that the output results are independent of the mesh size and structure, several mesh-sensitivity simulations were performed. In this study, all results

are presented for a  $\beta$ -phase volume fraction,  $\varepsilon_\beta$ , equal to 0.80. This value was chosen to be comparable to the results for the effective thermal diffusion coefficients with local-thermal equilibrium (Davarzani et al., 2010a).

The results are expressed as a function of the pore-scale thermal and solutal cell Péclet numbers, which are defined respectively as

$$Pe_T = (\rho c_p)_\beta \frac{\langle v_\beta \rangle^\beta \ell_{UC}}{k_\beta} \quad (69)$$

$$Pe_C = \frac{\langle v_\beta \rangle^\beta \ell_{UC}}{D_\beta} \quad (70)$$

where  $\ell_{UC}$  is defined in Fig. 2.

#### 4.1 Mass-Dispersion Tensors

The most important mass-transport tensor in Eq. (64) is the well-known dispersion tensor  $\mathbf{D}_\beta^*$ . Problem IIIa has been solved numerically over the two-dimensional representative symmetric unit cell shown in Fig. 2 to give the mapping vector  $\mathbf{b}_{C\beta}$ . Then the dispersion tensors were calculated by using Equation (65), through the use of numerical integration on the fluid-solid interface and also the fluid subdomain. It is noteworthy to mention that, while the closure problems were solved in this section over a very simple symmetrical unit cell, the model introduced in this paper is valid for any kind of unit-cell geometry including non-symmetrical cells. Therefore, the proposed model can be applied, for example, to geometries coming from X-ray tomography using a suitable method to correctly capture the anisotropy (Guibert et al., 2016). Our goal here was to understand the impact of the various pore-scale parameters on the resulting effective properties and not to provide a series of exhaustive results for various types of porous materials.

The longitudinal mass-dispersion coefficient,  $(D_\beta^*)_{xx}$ , obtained for an averaged velocity along the  $x$ -axis, is shown in Fig. 3 as a function of the Péclet number. The dispersion tensor features the usual behavior with three different regimes: a diffusion-dominant regime for low Péclet numbers, a transition behavior for moderate Péclet numbers, and finally, a convection-dominant regime with a power-law trend.

Changes in the transverse component of the mass dispersion coefficient,  $(D_\beta^*)_{yy}$ , with the Péclet number is shown in Fig. 4. Given the symmetries of the unit cell, the transverse coefficient is equal to the longitudinal coefficient in the diffusive-dominant regime i.e., the medium is indeed isotropic. The transition regime for the transverse component occurs at a Péclet number greater than for the longitudinal component. For such a simple unit cell, the longitudinal components are much bigger than transverse components in the convective regime. Once again, a different behavior would be expected for a more disordered porous medium.

These dispersion curves can be represented as (Quintard and Whitaker, 1994) (while this formulation may lack accuracy in the transition regime)

$$(D_\beta^*)_{xx}/D_\beta = \frac{1}{\tau} + aPe_C^n \quad (71)$$

where, the tortuosity term is defined as

$$\frac{1}{\tau} \mathbf{I} = \mathbf{I} + \frac{1}{V_\beta} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{C\beta} dA \quad (72)$$

The exponent on the Péclet number,  $n$ , may vary between one for a linear-dispersive regime and a maximum value of two for a Taylor dispersion.

## 4.2 Thermal Diffusion Tensors

The closure problems IIIb and IIIc have been solved over the same symmetric unit cell to obtain the thermal diffusion tensors  $\mathbf{D}_{T\beta\beta}^*$  and  $\mathbf{D}_{T\beta\sigma}^*$  from the expressions presented in Eqs (66) and

(67).

The longitudinal component of the thermal diffusion tensor  $\mathbf{D}_{T\beta\beta}^*$  is plotted in Fig. 5 versus the Péclet number and for thermal conductivity ratio ranging from 0.01 to 100. To show the effective values in Fig. 5 for the diffusive regime more precisely, the results are subtracted from  $1/\tau = 1/1.20$ . This value corresponds to the ratio of the effective thermal diffusion (or diffusion) coefficients to the (pore-scale) binary coefficients in the diffusive regime. Therefore, as shown in Fig. 5, this term is approximately zero for low Péclet numbers. When the Péclet number is increased, this term decreases and then it becomes negative for high Péclet numbers. Similar behavior was also observed for the local-equilibrium case. (See thorough discussion in (Davarzani et al., 2010a)).

As can be seen in Fig. 5, the impact of the thermal conductivity ratio ( $\kappa = k_\sigma/k_\beta$ ) on the effective thermal diffusion is important only in the convective regime. The effects are more important for a low-thermal conductivity ratio between 0.1 and 10. Outside that range, the effective thermal diffusion coefficients are less affected by variations. This is coherent with how thermal-dispersion tensors change with the thermal conductivity ratio as shown in Fig. A1a of Appendix A. In fact, the variation of the second term of the right-hand side of equation (65) with the thermal conductivity ratio influences the effective thermal diffusion coefficient. We should note again that the two-equation model for temperature may not predict the temperature correctly when the solid/fluid conductivity ratio is very low and the solid diameter of porous media is large. In this case, we observe a difference between solid center and solid surface temperature (Debenest and Quintard, 2008; Xin et al., 2018). Therefore, a mixed model can also be used if more accuracy is required and if there is no restriction in the computational cost.

The transverse component of the thermal diffusion tensor  $\mathbf{D}_{T\beta\beta}^*$  is represented in Fig. 6

versus the Péclet number and also for different values of the thermal conductivity ratio. For this symmetric unit cell, the transverse component of the thermal diffusion coefficient  $(D_{T\beta\beta}^*)_{yy}$  is constant and equal to the longitudinal thermal diffusion coefficient,  $(D_{T\beta\beta}^*)_{xx}$ , in the diffusive regime. As expected, the results show that the transverse thermal diffusion coefficient is smaller than the longitudinal coefficient in the convective regime. Here also, like for the thermal-dispersion tensors, the variations of the thermal conductivity ratio change more considerably than the effective coefficients for moderate thermal conductivity ratios. The transverse thermal diffusion coefficient,  $(D_{T\beta\beta}^*)_{yy}$ , decreases with increasing Péclet number in the convective regime.

The second thermal diffusion tensor appearing in the macroscopic-mass transport, Eq. (64), is  $D_{T\beta\sigma}^*$ . The longitudinal component of this thermal diffusion tensor,  $(D_{T\beta\sigma}^*)_{xx}$ , is shown in Fig. 7 versus the Péclet number and for different thermal conductivity ratios. It is clear that for the diffusion-dominant regime, this effective thermal diffusion value is close to zero. Increasing the Péclet number increases the effective coefficient: lightly for the low thermal conductivity ratios and significantly for high thermal conductivity ratios. These results are also coherent, in terms of behavior, with the results for the effective thermal conductivity coefficient,  $(k_{\beta\sigma}^*)_{xx}$ , Fig. A1b, Appendix A. Contrary to  $(D_{T\beta\beta}^*)_{xx}$  and  $(D_{T\beta\beta}^*)_{yy}$ , the impact of the thermal conductivity ratio is greater for moderate and high thermal conductivity ratios (the change between the thermal conductivities of 10 and 100 is considerable in Fig. 7).

The transverse component of the thermal diffusion tensor  $(D_{T\beta\sigma}^*)_{yy}$  is plotted in Fig. 8 as a function of the Péclet number and for different thermal conductivity ratios. We see that this component also is equal to its longitudinal coefficient for low Péclet number, i.e., zero values for

the diffusion-dominant regime, and then that the effective values increase in the convection-dominant regime for the moderate and high thermal conductivity ratios. The effective values for the low contrast of phase-thermal conductivities are much less sensitive to changing Péclet number. The transverse effective values are lower than the longitudinal values, and the transition between diffusion- and convection-dominant regime occurs when the Péclet number is around 10. Here also, the behavior results are comparable with  $(k_{\beta\sigma}^*)_{yy}$  as shown in Fig. A1d of Appendix A.

We found from the numerical results that the thermal diffusion tensors come from the local thermal non-equilibrium,  $\mathbf{D}_{T\beta\beta}^*$  and  $\mathbf{D}_{T\beta\sigma}^*$ , and the thermal diffusion tensors obtained from the local thermal equilibrium,  $\mathbf{D}_{T\beta}^*$ , are related by

$$\mathbf{D}_{T\beta}^* = \mathbf{D}_{T\beta\beta}^* + \mathbf{D}_{T\beta\sigma}^* \quad (73)$$

for all ranges of the Péclet number and thermal conductivity ratio.

### 4.3 Mass-Convective Vector

Simulations of Problem IIIId have been obtained to calculate the vector  $\mathbf{u}_{c\beta}$  in Eq. (64), which was named “the mass-convective vector” to distinguish it from “the heat-convective vectors” presented in Appendix A for the heat-transfer non-equilibrium model. The solution of Problem IIIId for  $r_\beta$  depends on the mapping vector  $s_\beta$  of the thermal non-equilibrium closure problems. Therefore, Problem A-III must be solved before or simultaneously with Problem IIIId to obtain the mapping vector  $r_\beta$ . Then the mass-convective vector is calculated using the formula given in Eq. (68).

The  $x$ -component of vector  $\mathbf{u}_{c\beta}$  is plotted in Fig. 9. In this figure, the value  $(u_{c\beta})_x$  has been divided by the average velocity  $\langle v_\beta \rangle^\beta$ , to evaluate the significance of the mass-convective term

compared to the mass-transport-convective term. The mass-convective term versus Péclet number gives a reverse sigmoid curve. The results show a constant and negligible mass-transport-convective term for a low thermal conductivity ratio. The mass-conductive terms are constant in the diffusive regime and then decrease in the conductive regime. They are significant for moderate thermal conductivity ratios. However, increasing the thermal conductivity ratios has less effect on mass-transport-convective term for high thermal conductivity ratios.

#### 4.4 Soret Coefficients

To evaluate the importance of the effective thermal diffusion tensors, compared to dispersion, we rewrite Eq. (64) in term of Soret coefficients as

$$\begin{aligned} & \frac{\partial \langle \varepsilon_\beta c_\beta \rangle^\beta}{\partial t} + \nabla \cdot \left( \varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle c_\beta \rangle^\beta \right) - \nabla \cdot \left( \mathbf{u}_{c\beta} \cdot \left( \langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma \right) \right) = \\ & \nabla \cdot \left( \varepsilon_\beta \mathbf{D}_\beta^* \cdot \left( \nabla \langle c_\beta \rangle^\beta + \mathbf{S}_{T\beta\beta}^* \cdot \nabla \langle T_\beta \rangle^\beta + \mathbf{S}_{T\beta\sigma}^* \cdot \nabla \langle T_\sigma \rangle^\sigma \right) \right) \end{aligned} \quad (74)$$

where the Soret matrix coefficients can be defined as the ratio of the thermal diffusion tensors to the isothermal diffusion tensors ( $\mathbf{S}_{T\beta\beta}^* = \mathbf{D}_{T\beta\beta}^* \cdot \mathbf{D}_\beta^{*-1}$  and  $\mathbf{S}_{T\beta\sigma}^* = \mathbf{D}_{T\beta\sigma}^* \cdot \mathbf{D}_\beta^{*-1}$ ).

Fig. 10 and Fig. 11 represent the variations of these two Soret coefficients versus the Péclet number, for several thermal conductivity ratios. The ratios of the components of the effective-Soret coefficients  $\mathbf{S}_{T\beta\beta}^*$  versus the Soret coefficient in the free fluid,  $S_{T\beta} = D_{T\beta} / D_\beta$ , are plotted in Fig. 10, versus the Péclet number and for different thermal conductivity ratios.

The results for the longitudinal-Soret coefficient  $(S_{T\beta\beta})_{xx}$  are plotted in Fig. 10a. The longitudinal-Soret coefficient is obtained by dividing the longitudinal thermal diffusion coefficients,  $(D_{T\beta\beta}^*)_{xx}$ , presented in Fig. 3 by the longitudinal-dispersion coefficients,  $(D_\beta^*)_{xx}$ , given in Fig. 5. We obtained the same behavior as for the effective-Soret coefficient for the one-

equation temperature model, i.e., the effective-longitudinal-Soret coefficient in porous media  $(S_{T\beta\beta}^*)_{xx}$  is identical to the Soret coefficient in the free fluid, in the purely diffusive regime ( $(S_{T\beta\beta}^*)_{xx}/S_{T\beta} = 1$ ). However, this is no longer valid when convection becomes important. In that case, the Soret ratio decreases gradually with increasing Péclet number and then becomes negative with asymptotic behavior, for the convection-dominant regime. The impact of the thermal conductivity ratio is more important for moderate thermal conductivity ratios between 0.1 and 10. Similar to the longitudinal-mass dispersion, the transition between convective and diffusive regime occurs when the Péclet number is around one.

The results for the transverse-Soret coefficient,  $(S_{T\beta\beta}^*)_{yy}$ , shown in Fig. 10b, are quite similar. Here also, the effective-transverse-Soret coefficient in porous media  $(S_{T\beta\beta}^*)_{yy}$  is identical to the Soret coefficient in the free fluid, in the purely diffusive regime ( $(S_{T\beta\beta}^*)_{yy}/S_{T\beta} = 1$ ). Then the effective-Soret coefficient decreases with increasing Péclet number. The transition regime occurs when the Péclet number is around 1. No asymptotic behavior has been observed for high Péclet numbers, instead absolute minimum values were found for low thermal conductivity ratios. The effective-transverse-Soret coefficient  $(S_{T\beta\beta}^*)_{yy}$  has been obtained by dividing the effective transverse thermal-diffusion coefficients,  $(D_{T\beta\beta}^*)_{yy}$ , of Fig. 6 by the transverse-dispersion coefficient,  $(D_{\beta}^*)_{yy}$ , of Fig. 4.

Fig. 11 shows the ratio of the effective-Soret coefficients,  $\mathbf{S}_{T\beta\sigma}^*$ , versus the Soret coefficient in the free fluid,  $S_{T\beta}$ , as a function of the Péclet number and for different thermal conductivity ratios. The longitudinal-Soret coefficient  $(S_{T\beta\sigma}^*)_{xx}$  is plotted in Fig. 11a. It was obtained by dividing the longitudinal thermal diffusion coefficients,  $(D_{T\beta\sigma}^*)_{xx}$ , by the longitudinal-dispersion



coefficient,  $(D_{\beta}^*)_{xx}$ , given in Fig. 3 and Fig. 7, respectively.

For pure diffusion regimes the effective-longitudinal Soret coefficient in porous media,  $(S_{T\beta\sigma}^*)_{xx}$ , was close to zero. This coefficient then increased with increasing Péclet number up to a maximum point when the Péclet number was around 10. Finally, the effective value decreased with increasing Péclet number to again reach low values at sufficiently high Péclet numbers. The effective values for very low thermal conductivity ratios ( $<0.01$ ) were close to zero. The more the thermal conductivity ratios increase, the more the Péclet number changes the effective-longitudinal Soret coefficients, and consequently the maximum points.

The results for the transverse-Soret coefficient  $(S_{T\beta\sigma}^*)_{yy}$  are shown in Fig. 11b. The effective-transverse-Soret coefficient, which is obtained by dividing the  $(D_{T\beta\sigma}^*)_{yy}$  of Fig. 8 by the  $(D_{\beta}^*)_{yy}$  of Fig. 4, is close to zero for very small Péclet numbers. Then it increases with increasing Péclet numbers.

Finally, the relationship between the effective properties obtained from non-equilibrium and equilibrium models can be also expressed in term of the thermal-equilibrium Soret coefficients,  $\mathbf{S}_{T\beta}^*$ , and non-equilibrium Soret coefficients as

$$\mathbf{S}_{T\beta}^* = \mathbf{S}_{T\beta\beta}^* + \mathbf{S}_{T\beta\sigma}^* \quad (75)$$

## 5. CONCLUSIONS

We have developed a Darcy-scale theoretical model to predict coupled heat and mass transfer in porous media including the Soret cross-effect, for local thermal non-equilibrium regimes.

The porous-medium energy and mass-transfer equations were deduced using the volume-averaging upscaling method. The model equation for mass balance contains a dispersion tensor, two thermal diffusion tensors involving the gradient in the fluid and solid phase, and also a mass-

convective vector corresponding to the temperature gradient of the temperature difference between the two phases.

Effective Darcy-scale coefficients have been determined by solving the corresponding closure problems over a simple representative-unit cell. The results show that, except for pure diffusive cases where the Soret coefficients in the porous medium and the free fluid are the same, the effective-Soret coefficients are impacted by the fluid hydrodynamics and also depend significantly on the medium's thermo-physical properties, in particular, the phases' thermal conductivity contrasts.

When the conditions of local-thermal equilibrium are not satisfied, it may be more convenient and accurate to use the theoretical model proposed in this study for modeling coupled transfer in porous media with a thermal diffusion-cross effect, especially at large Péclet numbers. The proposed model is original and must be tested thoroughly; in particular, experimental studies must be developed to validate the theoretical model.

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## **APPENDIX A. THE CLOSURE PROBLEMS FOR THE LOCAL THERMAL NON-EQUILIBRIUM MODEL: EFFECTIVE CALCULATION RESULTS AND MODEL VALIDATION**

The closure problems for the two-temperature model have been already investigated (Carbonell and Whitaker, 1984; Levec and Carbonell, 1985; Quintard, 1993; Quintard et al., 1997; Vortmeyer and Schaefer, 1974; Zanotti and Carbonell, 1984). Here, we present these three closure problems and the corresponding macroscopic-effective coefficients needed to solve the Darcy-scale heat-transfer equations presented in Eqs (27) and (28).

The numerical results are obtained for the same unit cell as in Fig. 2. We followed the decomposition method proposed by (Quintard et al., 1997) to solve the integro-differential



closure problems for the thermal dispersion case. The three closure problems are listed below.

### Problem A-I

$$(\rho c_p)_\beta \mathbf{v}_\beta \cdot \nabla \mathbf{b}_{T\beta\beta} + (\rho c_p)_\beta \tilde{\mathbf{v}}_\beta = k_\beta \nabla^2 \mathbf{b}_{T\beta\beta} - \varepsilon_\beta^{-1} \mathbf{c}_{\beta\beta}, \text{ in } V_\beta \quad (\text{A. 1})$$

$$\text{BC1: } \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{b}_{T\beta\beta} = \mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla \mathbf{b}_{T\sigma\beta} - \mathbf{n}_{\beta\sigma} k_\beta, \text{ at } A_{\beta\sigma} \quad (\text{A. 2})$$

$$\text{BC2: } \mathbf{b}_{T\beta\beta} = \mathbf{b}_{T\sigma\beta}, \text{ at } A_{\beta\sigma} \quad (\text{A. 3})$$

$$0 = k_\sigma \nabla^2 \mathbf{b}_{T\sigma\beta} - \varepsilon_\sigma^{-1} \mathbf{c}_{\sigma\beta}, \text{ in } V_\sigma \quad (\text{A. 4})$$

$$\text{Periodicity: } \mathbf{b}_{T\beta\beta}(\mathbf{r} + \ell_i) = \mathbf{b}_{T\beta\beta}(\mathbf{r}) \text{ \& } \mathbf{b}_{T\sigma\beta}(\mathbf{r} + \ell_i) = \mathbf{b}_{T\sigma\beta}(\mathbf{r}), i=1, 2, 3 \quad (\text{A. 5})$$

$$\text{Averages: } \langle \mathbf{b}_{T\beta\beta} \rangle = 0 \text{ \& } \langle \mathbf{b}_{T\sigma\beta} \rangle = 0 \quad (\text{A. 6})$$

$$\mathbf{c}_{\beta\beta} = \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{b}_{T\beta\beta} dA \quad (\text{A. 7})$$

$$\mathbf{c}_{\sigma\beta} = \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta} \cdot k_\sigma \nabla \mathbf{b}_{T\sigma\beta} dA = -\mathbf{c}_{\beta\beta} \quad (\text{A. 8})$$

### Problem A-II

$$(\rho c_p)_\beta \mathbf{v}_\beta \cdot \nabla \mathbf{b}_{T\beta\sigma} = k_\beta \nabla^2 \mathbf{b}_{T\beta\sigma} - \varepsilon_\beta^{-1} \mathbf{c}_{\beta\sigma}, \text{ in } V_\beta \quad (\text{A. 9})$$

$$\text{BC1: } \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{b}_{T\beta\sigma} = \mathbf{n}_{\beta\sigma} \cdot k_\sigma \nabla \mathbf{b}_{T\sigma\sigma} + \mathbf{n}_{\beta\sigma} k_\sigma, \text{ at } A_{\beta\sigma} \quad (\text{A. 10})$$

$$\text{BC2: } \mathbf{b}_{T\beta\sigma} = \mathbf{b}_{T\sigma\sigma}, \text{ at } A_{\beta\sigma} \quad (\text{A. 11})$$

$$0 = k_\sigma \nabla^2 \mathbf{b}_{T\sigma\sigma} - \varepsilon_\sigma^{-1} \mathbf{c}_{\sigma\sigma}, \text{ in } V_\sigma \quad (\text{A. 12})$$

$$\text{Periodicity: } \mathbf{b}_{T\beta\sigma}(\mathbf{r} + \ell_i) = \mathbf{b}_{T\beta\sigma}(\mathbf{r}) \text{ \& } \mathbf{b}_{T\sigma\sigma}(\mathbf{r} + \ell_i) = \mathbf{b}_{T\sigma\sigma}(\mathbf{r}), i=1, 2, 3 \quad (\text{A. 13})$$

$$\text{Averages: } \langle \mathbf{b}_{T\beta\sigma} \rangle = 0 \text{ \& } \langle \mathbf{b}_{T\sigma\sigma} \rangle = 0 \quad (\text{A. 14})$$

$$\mathbf{c}_{\beta\sigma} = \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathbf{b}_{T\beta\sigma} dA \quad (\text{A. 15})$$

$$\mathbf{c}_{\sigma\sigma} = \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta} \cdot k_{\sigma} \nabla \mathbf{b}_{T\sigma\sigma} dA = -\mathbf{c}_{\beta\sigma} \quad (\text{A. 16})$$

### Problem A-III

$$(\rho c_p)_{\beta} \mathbf{v}_{\beta} \cdot \nabla s_{\beta} = k_{\beta} \nabla^2 s_{\beta} - \varepsilon_{\beta}^{-1} h_{\beta}, \text{ in } V_{\beta} \quad (\text{A. 17})$$

$$\text{BC1: } \mathbf{n}_{\beta\sigma} \cdot k_{\beta} \nabla s_{\beta} = \mathbf{n}_{\beta\sigma} \cdot k_{\sigma} \nabla s_{\sigma}, \text{ at } A_{\beta\sigma} \quad (\text{A. 18})$$

$$\text{BC2: } s_{\beta} = 1 + s_{\sigma}, \text{ at } A_{\beta\sigma} \quad (\text{A. 19})$$

$$0 = k_{\sigma} \nabla^2 s_{\sigma} + \varepsilon_{\sigma}^{-1} h_{\sigma}, \text{ in } V_{\sigma} \quad (\text{A. 20})$$

$$\text{Periodicity: } s_{\beta}(\mathbf{r} + \ell_i) = s_{\beta}(\mathbf{r}) \text{ \& } s_{\sigma}(\mathbf{r} + \ell_i) = s_{\sigma}(\mathbf{r}), i=1, 2, 3 \quad (\text{A. 21})$$

$$\text{Averages: } \langle s_{\beta} \rangle = 0 \text{ \& } \langle s_{\sigma} \rangle = 0 \quad (\text{A. 22})$$

$$h_{\beta} = \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_{\beta} \nabla s_{\beta} dA \quad (\text{A. 23})$$

$$h_{\sigma} = -\frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta} \cdot k_{\sigma} \nabla s_{\sigma} dA = h_{\beta} = h_T \quad (\text{A. 24})$$

We note that the volumetric heat-transfer coefficient,  $h_T$ , can be calculated from solving Problem A-III and using equation (A. 23) or (A. 24). The other effective coefficients are given below.

$$\mathbf{k}_{\beta\beta} = k_{\beta} \left( \varepsilon_{\beta} \mathbf{I} + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{T\beta\beta} dA \right) - (\rho c_p)_{\beta} \langle \tilde{\mathbf{v}}_{\beta} \mathbf{b}_{T\beta\beta} \rangle \quad (\text{A. 25})$$

$$\mathbf{k}_{\beta\sigma} = k_{\beta} \left( \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_{T\beta\sigma} dA \right) - (\rho c_p)_{\beta} \langle \tilde{\mathbf{v}}_{\beta} \mathbf{b}_{T\beta\sigma} \rangle \quad (\text{A. 26})$$

$$\mathbf{k}_{\sigma\beta} = k_{\sigma} \left( \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta} \mathbf{b}_{T\sigma\beta} dA \right) \quad (\text{A. 27})$$

$$\mathbf{k}_{\sigma\sigma} = k_{\sigma} \left( \varepsilon_{\sigma} \mathbf{I} + \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta} \mathbf{b}_{T\sigma\sigma} dA \right) \quad (\text{A. 28})$$

$$\mathbf{u}_{\beta\beta} = \mathbf{c}_{\beta\beta} - k_{\beta} \left( \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} s_{\beta} dA \right) + (\rho c_p)_{\beta} \langle \tilde{\mathbf{v}}_{\beta} s_{\beta} \rangle \quad (\text{A. 29})$$

$$\mathbf{u}_{\beta\sigma} = \mathbf{c}_{\beta\sigma} + k_{\beta} \left( \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} s_{\beta} dA \right) - (\rho c_p)_{\beta} \langle \tilde{\mathbf{v}}_{\beta} s_{\beta} \rangle \quad (\text{A. 30})$$

$$\mathbf{u}_{\sigma\sigma} = \mathbf{c}_{\sigma\sigma} + k_{\sigma} \left( \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta} s_{\sigma} dA \right) \quad (\text{A. 31})$$

$$\mathbf{u}_{\sigma\beta} = \mathbf{c}_{\sigma\beta} - k_{\sigma} \left( \frac{1}{\mathcal{V}} \int_{A_{\beta\sigma}} \mathbf{n}_{\sigma\beta} s_{\sigma} dA \right) \quad (\text{A. 32})$$

Numerical calculations were developed using COMSOL Multiphysics<sup>®</sup>, following the same numerical procedures outlined in Section 4. Longitudinal and transverse thermal-dispersion coefficients are plotted as a function of thermal Péclet number for  $\varepsilon_{\beta} = 0.80$  and for different thermal conductivity ratios in Fig. A1. They are calculated from the numerical solution of Problem A-I and A-II using Eqs (A. 25)-(A. 28).

The results of this model for  $\varepsilon_{\beta} = 0.38$  (results have not been presented in this study) and thermal-dispersion coefficients agree quite well with the results obtained in Quintard et al. (1997). Generally, the influence of the phases' thermal conductivity contrasts on the effective thermal-dispersion coefficients is greater for moderate-thermal conductivity ratios between 0.1 and 10. As mentioned before, this behavior can be related to corresponding thermal diffusion coefficients.

To calculate the convective heat vectors from Eqs (A. 29) to (A. 32) we must solve all three closure problems for thermal dispersion (A-I, A-II, and A-III). The results are shown in Fig. A2

as a function of Péclet number and for  $\varepsilon_\beta = 0.80$  and different thermal conductivity ratios. Except for the high Péclet numbers, the results agree with the results presented in Quintard et al. (1997) for  $\varepsilon_\beta = 0.38$ . Their results show an absolute maximum value around  $Pe=300$  followed by asymptotic behavior toward zero for Péclet numbers approaching infinity. By contrast, the convective vectors continue to increase in this study for both porosities ( $\varepsilon_\beta = 0.38$  and  $0.80$ ) without reaching an absolute maximum value. Below this Péclet number, the results agree with the results obtained in Quintard et al. (1997)<sup>†</sup>.

The results for the heat transfer coefficients are plotted in Fig. A3 as a function of Péclet number and for different thermal conductivity ratios are in good agreement with the ones published before in Quintard et al. (1997).

**FIG. 1:** Problem configuration

**FIG. 2:** Representative unit cell

**FIG. 3:** Longitudinal-mass dispersion  $(\mathbf{D}_\beta^*)_{xx}$  versus Péclet number for  $\varepsilon_\beta = 0.80$

**FIG. 4:** Transverse-mass dispersion  $(\mathbf{D}_\beta^*)_{yy}$  as a function of Péclet number for  $\varepsilon_\beta = 0.80$

**FIG. 5:** Longitudinal thermal diffusion coefficient  $(\mathbf{D}_{T\beta\beta}^*)_{xx}$  versus Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

**FIG. 6:** Transverse thermal diffusion coefficient,  $(\mathbf{D}_{T\beta\beta}^*)_{yy}$ , versus Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

**FIG. 7:** Longitudinal thermal diffusion coefficient  $(\mathbf{D}_{T\beta\sigma}^*)_{xx}$  versus Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

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<sup>†</sup>A minor error in the Fortran code (M. Quintard, personal communication) used to calculate the integrals giving these coefficients may explain these differences and suggests that these results should be considered instead of those in Quintard et al. (1997).

**FIG. 8:** Transverse thermal diffusion coefficient  $(\mathbf{D}_{T\beta\sigma}^*)_{yy}$  versus Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

**FIG. 9:**  $x$ -component of the mass-convective vector for thermal diffusion,  $(\mathbf{u}_{c\beta})_x$ , versus Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

**FIG. 10:** Longitudinal- and transverse-components of Soret coefficients  $\mathbf{S}_{T\beta\beta}^*$  a)  $(S_{T\beta\beta}^*)_{xx}$  and b)  $(S_{T\beta\beta}^*)_{yy}$  versus Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

**FIG. 11:** Longitudinal- and transverse-components of the Soret coefficients  $\mathbf{S}_{T\beta\sigma}^*$  a)  $(S_{T\beta\sigma}^*)_{xx}$  and b)  $(S_{T\beta\sigma}^*)_{yy}$  versus the Péclet number and for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

**FIG. A1:** Longitudinal and transverse thermal-dispersion coefficients a)  $(k_{\beta\beta})_{xx}$ , b)  $(k_{\beta\beta})_{yy}$ , c)  $(k_{\beta\sigma})_{xx}$ , d)  $(k_{\beta\sigma})_{yy}$ , and e)  $(k_{\sigma\sigma})_{xx}$  versus Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

**FIG. A2:**  $x$ -Component of heat convective vectors for thermal dispersion a)  $(u_{\beta\beta})_x$  b)  $(u_{\beta\sigma})_x$  c)  $(u_{\sigma\beta})_x$  versus Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$

**FIG. A3:** Heat-transfer coefficient  $h_T$  as a function of the Péclet number for different thermal conductivity ratios,  $\kappa$ , and  $\varepsilon_\beta = 0.80$























