Simplifications of macroscopic models for heat and mass transfer in porous media

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A B S T R A C T

When performing upscaling of transport phenomena in multiscale systems it is not uncommon that terms of different physical nature than those present at the underlying scale arise in the resulting averaged differential equations. For diffusive species mass transfer with heterogeneous reaction and conductive heat transfer, additional terms result from upscaling using the volume averaging method, which are classically discarded by means of orders of magnitude estimates. In this work, these two cases are revisited and it is shown that, for single and two-species diffusive mass transfer with heterogeneous nonlinear reaction, the additional term is exactly zero using Green's formula. This conclusion is shown to also be applicable when using the periodic homogenization method. Nevertheless, for heat conduction, with and without considering interfacial resistance, only the dominant conduction-corrective terms are shown to be zero also using Green's formula. In contrast, the contribution of the co-conduction-corrective terms may be relevant depending on the systems characteristics, the properties of the phases and the macroscopic boundary conditions. This is exemplified by performing numerical simulations in a non-symmetric unit cell.

1. Introduction

The study of transport phenomena in multiscale systems requires, in many practical situations, the use of upscaling methods that allow deriving the governing equations at the desired scale level. Nowadays, upscaling can be performed by multiple approaches as revised by Battiato et al. (2019), in order to capture the essential information at the microscale and bring it to the macroscale. While performing upscaling of transport phenomena in multiscale systems, it is not uncommon that additional terms arise in the macroscale models in contrast to those present at the microscale. An example is Eq. (6.12) in Wood and Valdés-Parada (2013), which is a somewhat general upscaled model resulting from volume-averaging a convection–diffusion equation with homogeneous and heterogeneous source/sink terms. In particular, for diffusive mas transfer with heterogeneous reaction, the reaction term is present in the upscaled differential equation, albeit it was absent in the governing balance equation at the microscale as reported in many works using both the volume averaging and homogenization methods (Ryan et al., 1980; Whitaker, 1999; Wood et al., 2007; Valdés-Parada et al., 2011, 2017; Bourbatache et al., 2020, 2021; Le et al., 2023; Bourbatache et al., 2023). This particular process is also interesting because a convective-like term was reported to arise by Whitaker (1999) (see, equation (1.4-64) therein). This term was shown to be exactly zero in symmetric unit cells and, when this is not the case, it was neglected on the basis of separation of length scales between the macroscale and the microscale. For this process, the macroscopic model obtained from the homogenization technique in the mass transfer-limited regime, *i.e.*, for a Damkhöler (or kinetic) number smaller than unity, does not include such a convective-like term (see, for example, section 2.3 in Gerisch et al., 2017). Out of this regime, however, some issues with the traditional use of homogenization have been recently discussed by Bourbatache et al. (2021) following Mauri (1991). A modification was introduced when the characteristic times of diffusion and reaction are comparable, making use of a spectral approach (Bourbatache et al., 2023; Le et al., 2023). This has been recently discussed in Valdés-Parada and Lasseux (2025).

For heat transfer with non-local thermal equilibrium, several additional terms have been kept in the macroscopic models (Quintard and Whitaker, 1993; Quintard et al., 1997) even if they were shown to be zero for particular microstructures having specific symmetry properties (Whitaker, 1999). Although the cited works result from using the volume averaging method, these additional terms can also arise in the homogenization approach. Indeed, with this technique, the

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information contained at different orders of magnitude of the scale ratio used as the small parameter for the asymptotic expansion is systematically captured. Therefore, it is possible that, at a given order of magnitude, some terms arise although they may actually cancel between each other. In the general case, it is unclear which ones are relevant and if some can be safely discarded. Furthermore, relating these terms to convection is misleading, in general, because they appear even in situations when there is no fluid flow. The motivation to further analyze the effective-medium coefficients stems from the possibility of clarifying whether some of them are actually zero or can be related to other terms. In both cases, this yields a reduction in the computational cost to use the upscaled model and also avoids associating a physical meaning to quantities that are potentially zero.

In this work, the additional terms involved in (single and two-species) mass transport with heterogeneous reaction and also in non-thermal equilibrium heat conduction (with or without interfacial heat transfer resistance) are physically re-interpreted and analyzed. The motivation for studying these two problems in specific is because they are archetypes for many applications of interest in porous media systems. For diffusive mass transfer with heterogeneous non-linear chemical reaction, it is found that the corrective term for diffusion is exactly zero using both the method of volume averaging and the homogenization technique. For conductive heat transfer, four corrective terms arise, two dominant conduction-corrective terms and two co-conduction-corrective terms. The first two are demonstrated to be exactly zero, but the last two are only zero in symmetric unit cells. This conclusion is applicable with and without considering interfacial heat transfer resistance. The outcome of the present work is relevant as it has consequences when it is not possible to neglect terms on the basis of orders of magnitude estimates as it is typically the case when using the volume averaging method. Some examples of this are the derivation of jump conditions (e.g. Valdés-Parada et al. (2006)), mass transfer and reaction near zones of intense chemical reaction (Battiato et al., 2009), heat transport processes with rapid changes in the macroscopic heat flux (Pietrzyk et al., 2023), among others.

The present analysis is organized as follows. In Section 2, the process of single species diffusion undergoing a nonlinear and heterogeneous chemical reaction is addressed. Only the key elements of the upscaling process using the volume averaging method are recalled here as they have been reported in detail in the literature (Ryan et al., 1981; Whitaker, 1999; Valdés-Parada et al., 2011, 2017). In this section, a new integral relationship between the two closure variables involved in the macroscale model is derived using Green's formula. In addition, it is shown that this simplification approach using Green's formula can also be used to simplify the upscaled model resulting from using periodic homogenization (Appendix A). This section is concluded with a discussion about the extensions to diffusion and convection (Appendix B) and to multispecies cases. Following the same approach, in Section 3, the upscaling process for non-thermal equilibrium is recalled and analyzed for the case in which there is no interfacial heat transfer resistance. Since the co-conduction-corrective terms are non-zero, in general, they are predicted by solving the associated closure problems and this is illustrated in a particular non-symmetric unit cell, together with the other effective-medium coefficients involved in the macroscale model. This is reported in Section 3.3. Furthermore, to assess the relevance of each term in the model, a case study is considered and analyzed in detail that clearly shows the relevance of these corrective terms. This analysis is extended to situations in which there is interfacial heat transfer resistance in Appendix E reaching similar conclusions as in the case discussed in Section 3. Finally, the corresponding conclusions are presented in Section 4.

2. Chemical species diffusion with heterogeneous non-linear reaction

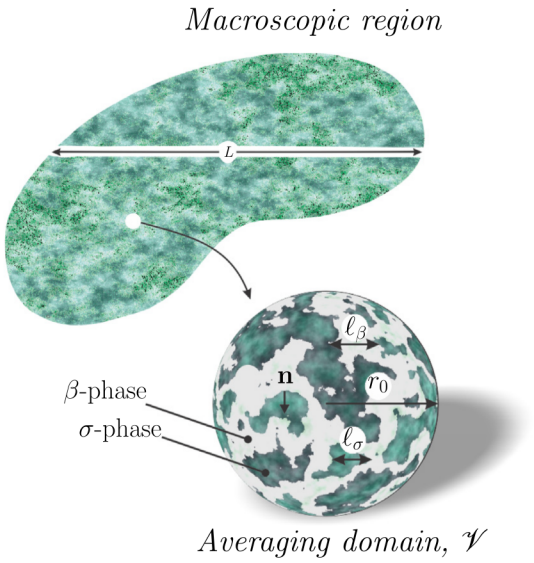

Fig. 1. Sketch of a porous medium saturated by a single fluid phase (the β-phase) and of a representative averaging domain, including the characteristic lengths associated to the macroscale (*i.e.*, L), the averaging domain (r_0) and the microscale (ℓ_β and ℓ_σ). Note that the unit normal vector $\mathbf{n}$ is directed from the fluid towards the solid phase.

2.1. Single chemical species

Consider a rigid and homogeneous porous medium (of characteristic length L) saturated by a single fluid phase (*i.e.*, the β-phase) as the one sketched in Fig. 1. The characteristic length scales associated to the fluid and solid phases at the microscale (*i.e.*, the pore-scale) are ℓ_β and ℓ_σ, respectively. The first case of interest in this work corresponds to diffusive mass transfer of a dilute chemical species in the fluid phase undergoing a nonlinear chemical reaction at the solid–fluid interface. Assuming that Fick's law is applicable, the governing differential equation and interfacial boundary condition, on a molar basis, can be written as follows

$$\frac{\partial c}{\partial t} = \nabla \cdot (\mathscr{D} \nabla c), \quad \text{in } \mathscr{V}_\beta, \tag{1a}$$

$$\text{B.C.} \quad -\mathbf{n} \cdot \mathscr{D} \nabla c = R, \quad \text{at } \mathscr{A}_{\beta\sigma}. \tag{1b}$$

Here c denotes the molar concentration of the chemical species, while $\mathscr{D}$ and R respectively denote the molecular diffusion coefficient and the heterogeneous reaction rate term. This term is assumed to be a known non-linear function of c and infinitely differentiable with respect to this variable. Note that this is a generic formulation that encompasses the classical case of a linear first-order reaction. Although these equations are applicable in the entire porous medium, they have been conveniently written in the space $\mathscr{V}_\beta$ (of volume V_β), occupied by the fluid phase within a representative averaging domain, $\mathscr{V}$ of volume V and size r_0 (see Fig. 1). In addition, $\mathscr{A}_{\beta\sigma}$ (of area $A_{\beta\sigma}$) represents the solid–fluid interface contained in the averaging domain. Finally, the nomenclature

$$\mathbf{n} \equiv \mathbf{n}_{\beta\sigma}, \tag{2}$$

is employed throughout this work to designate the unit normal vector at $\mathscr{A}_{\beta\sigma}$ directed from the β-phase towards the σ-phase.

Using the volume averaging method, the intrinsic averaging operator

$$\langle \cdot \rangle^\beta = \frac{1}{V_\beta} \int_{\mathscr{V}_\beta} \cdot \, dV, \tag{3}$$

is applied to Eq. (1a), along with the spatial averaging theorem (see, for instance, (Howes and Whitaker, 1985)), taking into account the

interfacial boundary condition given in Eq. (1b). This procedure leads to the following *unclosed* macroscale model (see details in Whitaker (1999), Valdés-Parada et al. (2011, 2017))

$$\frac{\partial\langle c\rangle^\beta}{\partial t} = \nabla\cdot\left[\mathscr{D}\left(\nabla\langle c\rangle^\beta + \underbrace{\frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\tilde{c}\,dA}_{\text{diffusive filter}}\right)\right] - \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} R\,dA. \tag{4}$$

To obtain this equation, the fact that average quantities (and/or their gradient) can be considered as constants within the averaging domain is used on the basis of the length-scale separation $\ell_\beta \ll r_0 \ll L$ inherent to any upscaling process. Note that in the interfacial integral term (*i.e.*, the diffusive filter of information from the microscale (Whitaker, 1999)), the pore-scale concentration was decomposed according to (Gray, 1975)

$$c = \langle c\rangle^\beta + \tilde{c}. \tag{5}$$

Moreover, the fact that the medium is spatially homogeneous was employed, implying $\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\,dA = \mathbf{0}$.

At this point, no simplification has been made regarding the nonlinear reaction term. One simple way to handle it is to follow Lugo-Méndez et al. (2015), and expand the reaction term using the following Taylor series about $\langle c\rangle^\beta$

$$R|_c = R|_{\langle c\rangle^\beta} + \left.\frac{\partial R}{\partial c}\right|_{\langle c\rangle^\beta}\tilde{c} + \dots, \tag{6a}$$

or,

$$R|_c = \mathcal{R} + \mathcal{R}'\tilde{c} + \dots, \tag{6b}$$

with the nomenclature

$$\mathcal{R} \equiv R|_{\langle c\rangle^\beta}, \tag{6c}$$

$$\mathcal{R}' \equiv \left.\frac{\partial R}{\partial c}\right|_{\langle c\rangle^\beta}. \tag{6d}$$

With the intention of keeping the model linear in $\tilde{c}$, only the first two terms in the above expansion are maintained, which constitutes a linear approximation. This is compliant with the idea that the overall closure development is carried out at the first order in $\tilde{c}$ (see Section 7 in Lugo-Méndez et al. (2015) for further details). Adopting this approximation, and considering the length scale constraint $\ell_\beta \ll L$, Eq. (4) takes the following form

$$\frac{\partial\langle c\rangle^\beta}{\partial t} = \nabla\cdot\left[\mathscr{D}\left(\nabla\langle c\rangle^\beta + \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\tilde{c}\,dA\right)\right] - \frac{a_v\mathcal{R}}{\phi} - \frac{\mathcal{R}'}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\tilde{c}\,dA. \tag{7}$$

Here $\phi \equiv \phi_\beta = V_\beta/V$ is the volume fraction of the β-phase within $\mathscr{V}$, which, in this case corresponds to the porosity. In addition, $a_v \equiv A_{\beta\sigma}/V$ is the interfacial area per unit volume in the averaging domain.

Note that $\mathcal{R}$ depends only on the macroscale space variable, $\mathbf{x}$, through $\langle c\rangle^\beta$. This type of linear approximation has been validated for both homogeneous (Lugo-Méndez et al., 2015) and heterogeneous (Lenne et al., 2024) reactions in porous media. Note that, in the particular case of first-order kinetics ($R = kc$), it follows that $\mathcal{R} = k\langle c\rangle^\beta$ and $\mathcal{R}' = k$ making the linearization exact.

Eq. (7) is classified as unclosed because it is written in terms of both $\langle c\rangle^\beta$ and $\tilde{c}$. The last term on the right-hand side was discarded by Whitaker (1999) under the assumption that $\tilde{c} \ll \langle c\rangle^\beta$, while considering a linear reaction rate. However, in this work, such assumption is not made so that the model has both diffusive and reactive filters of pore-scale information, as they are necessary for the rest of the derivations.

In order to close the model, it is necessary to perform a closure procedure that consists in: (1) Deriving and (when pertinent) simplifying the governing equations and boundary conditions for the deviation variable, (2) Finding the formal solution of the resulting problem for the deviation in a periodic unit cell, (3) Deriving the associated closure problems, and finally substitute the formal solution into the unclosed equation to obtain the macroscale balance equation. To perform step (1), the decomposition given in Eq. (5) is substituted into Eqs. (1) from which Eq. (7) is subtracted, to obtain

$$\frac{\partial\tilde{c}}{\partial t} = \mathscr{D}\nabla^2\tilde{c} - \nabla\cdot\left(\frac{\mathscr{D}}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\tilde{c}\,dA\right) + \frac{a_v\mathcal{R}}{\phi} + \frac{\mathcal{R}'}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\tilde{c}\,dA, \quad \text{in } \mathscr{V}_\beta. \tag{8}$$

To simplify this equation for $\tilde{c}$, it is assumed that the reference time, t_{ref}, at which the model is applicable is much larger than the one for pore-scale diffusion, *i.e.*, $t^d_{ref} = \ell^2_\beta/\mathscr{D} \ll t_{ref}$. With this constraint, the problem for $\tilde{c}$ remains quasi-steady. This means that the resulting upscaled model should not be expected to perform well at time scales smaller than t^d_{ref}. This claim may appear to be overly severe, as the model may still provide accurate results for time scales of $\mathbf{O}(t^d_{ref})$, especially if $\mathcal{R}' \gg \mathscr{D}/\ell_\beta$. In this case, the corresponding time-scale constraint is $\ell_\beta/\mathcal{R}' \ll t_{ref}$. In addition, the field of $\tilde{c}$ is determined within a periodic unit cell that is representative of the system (see an example in Fig. 2), so that $\tilde{c}$ is assumed to be periodic at the external boundaries of this unit cell. This means that, if both $\tilde{c}$ and the geometry are assumed to be periodic, then the integral terms containing $\tilde{c}$ and $\mathbf{n}\tilde{c}$ can be considered as constants at the unit cell level. It is pertinent to emphasize that the periodicity assumption is imposed here to provide a local description of the field of $\tilde{c}$. This does not imply that the resulting macroscale model is only applicable to periodic media.

On the basis of the above, the corresponding differential equation and boundary conditions for the concentration deviation can be written as follows (Valdés-Parada et al., 2011, 2017)

$$0 = \mathscr{D}\nabla^2\tilde{c} + \frac{a_v\mathcal{R}}{\phi} + \frac{\mathcal{R}'}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\tilde{c}\,dA, \quad \text{in } \mathscr{V}_\beta, \tag{9a}$$

$$\text{B.C.} \quad -\mathbf{n}\cdot\mathscr{D}\nabla\tilde{c} - \mathcal{R}'\tilde{c} = \mathbf{n}\cdot\mathscr{D}\nabla\langle c\rangle^\beta + \mathcal{R}, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{9b}$$

$$\tilde{c}(\mathbf{r}) = \tilde{c}(\mathbf{r}+\mathbf{l}_i), \quad i = 1,2,3, \tag{9c}$$

$$\langle\tilde{c}\rangle^\beta = 0. \tag{9d}$$

The boundary condition in Eq. (9b) results from substituting the decomposition given in Eq. (5) into Eq. (1b) together with the linearization of the reaction rate term. The average constraint in Eq. (9d) results from applying the intrinsic averaging operator to Eq. (5). It is necessary to well-pose the problem in the absence of chemical reaction.

The next step in the closure process is the formal solution of the problem given in Eqs. (9). This can be achieved by noticing that the problem for $\tilde{c}$ is linear and is made non-homogeneous by two sources (namely, $\mathcal{R}$ and $\nabla\langle c\rangle^\beta$), which are constant at the unit cell level. Therefore, the formal solution can be expressed under the form of a linear combination of these sources. The same result can be obtained by using Green's formula (Valdés-Parada, 2010). The resulting expression is

$$\tilde{c} = \mathbf{d}\cdot\nabla\langle c\rangle^\beta + s\mathcal{R}. \tag{10}$$

Here, $\mathbf{d}$ and $s \equiv (f-1)/\mathcal{R}'$ are closure variables that solve the following boundary-value problems in a periodic unit cell that is representative of the microscale, such as the one sketched in Fig. 2.

Problem $\mathbf{d}$

$$\mathbf{0} = \mathscr{D}\nabla^2\mathbf{d} + \frac{\mathcal{R}'}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{d}\,dA, \quad \text{in } \mathscr{V}_\beta, \tag{11a}$$

$$\text{B.C.} \quad -\mathbf{n}\cdot\mathscr{D}\nabla\mathbf{d} - \mathcal{R}'\mathbf{d} = \mathscr{D}\mathbf{n}, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{11b}$$

$$\mathbf{d}(\mathbf{r}) = \mathbf{d}(\mathbf{r}+\mathbf{l}_i), \quad i = 1,2,3, \tag{11c}$$

$$\langle\mathbf{d}\rangle^\beta = \mathbf{0}. \tag{11d}$$

Problem f

$$0 = \mathscr{D}\nabla^2 f + \frac{\mathcal{R}'}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} f\,dA, \quad \text{in } \mathscr{V}_\beta, \tag{12a}$$

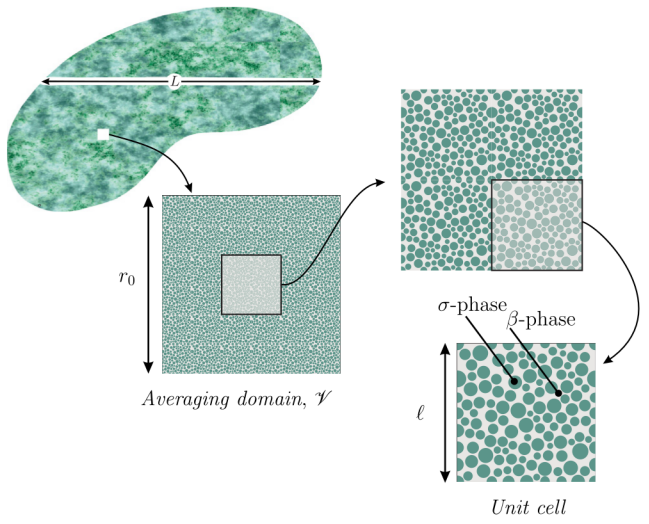

Fig. 2. Sketch of a two-dimensional periodic unit cell for the closure problems solution.

$$\text{B.C.} \quad -\mathbf{n}\cdot\mathscr{D}\nabla f = \mathcal{R}' f, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{12b}$$

$$f(\mathbf{r}) = f(\mathbf{r}+\mathbf{l}_i), \quad i=1,2,3, \tag{12c}$$

$$\langle f\rangle^{\beta} = 1. \tag{12d}$$

These problems are obtained by substituting the formal solution in the problem for $\tilde{c}$ and separating the contribution of each source. It is worth noting that the above problems depend on $\langle c\rangle^{\beta}$ due to the presence of $\mathcal{R}'$, except in the case of a first (or even zeroth)-order reaction. This situation can be handled by recursively solving the closure problems for a collection of values of a Damköhler number defined as $\mathcal{R}'\ell_{\beta}/\mathscr{D}$. With this information at hand, it is possible to determine the dependence of the effective-medium coefficients on this dimensionless number. This approach was used by Lugo-Méndez et al. (2015) to validate the resulting upscaled model while considering a homogeneous and nonlinear chemical reaction in the fluid phase saturating homogeneous porous medium.

Substitution of the formal solution given in Eq. (10) into the integral filters present in Eq. (7), leads to the following macroscale model (see Appendix C.1, for details)

$$\frac{\partial\langle c\rangle^{\beta}}{\partial t} = \nabla\cdot\left(\mathbf{D}_{effr}\cdot\nabla\langle c\rangle^{\beta}\right) - \frac{a_v\langle f\rangle_{\beta\sigma}}{\phi}\mathcal{R} + \left(\frac{\mathscr{D}}{V_{\beta}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}f\,dA\right)\cdot\frac{\nabla\mathcal{R}}{\mathcal{R}'} - \left(\frac{\mathcal{R}'}{V_{\beta}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{d}\,dA\right)\cdot\nabla\langle c\rangle^{\beta}. \tag{13}$$

In the above equation the effective diffusivity tensor $\mathbf{D}_{effr}$ is defined as

$$\mathbf{D}_{effr} = \mathscr{D}\left(\mathbf{I} + \frac{1}{V_{\beta}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\mathbf{d}\,dA\right), \tag{14}$$

and $\langle f\rangle_{\beta\sigma} = \frac{1}{A_{\beta\sigma}}\int_{\mathscr{A}_{\beta\sigma}} f\,dA$. As shown in Valdés-Parada and Lasseux (2025) (see Appendix C), $\mathbf{D}_{effr}$ is a symmetric positive tensor.

At this point, it is worth noting that, due to the chain rule

$$\frac{\nabla\mathcal{R}}{\mathcal{R}'} = \nabla\langle c\rangle^{\beta}, \tag{15}$$

so that Eq. (13) can be written as

$$\frac{\partial\langle c\rangle^{\beta}}{\partial t} = \nabla\cdot\left(\mathbf{D}_{effr}\cdot\nabla\langle c\rangle^{\beta}\right) - \frac{a_v\langle f\rangle_{\beta\sigma}}{\phi}\mathcal{R} + \mathscr{D}\mathbf{u}\cdot\nabla\langle c\rangle^{\beta}. \tag{16}$$

The effective-medium coefficient $\mathbf{u}$ is defined as follows:

$$\mathbf{u} = \frac{1}{V_{\beta}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}f\,dA - \frac{\mathcal{R}'}{\mathscr{D}}\frac{1}{V_{\beta}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{d}\,dA. \tag{17}$$

Note that $\mathbf{u}$ has the unit of the inverse of a length.

The first two terms on the right-hand side of Eq. (16) correspond to effective diffusion and effective reaction. The term *effective* is used here not only to make it clear that the model contains the necessary pore-scale information but also to emphasize that the apparent effective diffusion tensor, $\mathbf{D}_{effr}$ and the effective reaction rate coefficient, $\langle f\rangle_{\beta\sigma}\mathcal{R}$, depend, in general, on both diffusion and reaction processes at the microscale. Finally, the last term may be conceived as a diffusion-corrective term, although it has been referred to as "a convective transport term that is generated by the heterogeneous reaction" (Whitaker, 1999). However, it is physically misleading to consider this term as a convective one as there is no momentum transport associated to it. This term is usually neglected in comparison to the previous two other ones on the basis of orders of magnitude estimates relying on the separation of length scales between the microscale and the macroscale (Whitaker, 1999; Valdés-Parada et al., 2011, 2017). However, such arguments are not necessary as it will be shown below.

Special attention shall be dedicated to the situation where the characteristic time of diffusion t^{d}_{ref} is much smaller than the characteristic time of reaction, $t^{r}_{ref} = \ell_{\beta}/\mathcal{R}'$, which corresponds to a Damköler number, $Da = t^{d}_{ref}/t^{r}_{ref} = \ell_{\beta}\mathcal{R}'/\mathscr{D}$, much smaller than unity. In this particular case, the source $\langle c\rangle^{\beta}$ is no longer relevant in the deviation problem given in Eqs. (9). Therefore, $f=1$, and the effective diffusion coefficient is the same as in the absence of reaction. Moreover, $\mathbf{u}$ appears to be evanescent as it is proportional to Da. This explains why the macroscopic model obtained from asymptotic homogenization in this limit of Da does not include the corrective term $\mathscr{D}\mathbf{u}\cdot\nabla\langle c\rangle^{\beta}$ (see, for example, Chapter 2 in Gerisch et al., 2017). Nevertheless, using periodic homogenization for $Da = \mathbf{O}(\ell_{\beta}/L)$, it is possible to obtain an upscaled model with the same structure as the one given in Eq. (16), albeit the closure problems are different due to the constraint in the Damköhler number as shown in Appendix A for a first-order reaction. This model is different from the one reported by Bourbatache et al. (2021) because the time variable is not made dimensionless by the diffusion time but by the reaction time. The resulting model and closure problems correspond to those previously reported by Valdés-Parada et al. (2017) using the volume averaging method.

To further analyze the diffusion-corrective coefficient, $\mathbf{u}$, it is convenient to consider the following Green's formula that relates piece-wise continuous scalar, a, and vector, $\mathbf{a}$, fields that are periodic at the external boundaries of a unit cell (Polyanin and Manzhirov, 2006)

$$\int_{\mathscr{V}_{\beta}}\left(a\nabla^2\mathbf{a} - \nabla^2 a\,\mathbf{a}\right)dV = \int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\left(a\nabla\mathbf{a} - \nabla a\,\mathbf{a}\right)dA. \tag{18}$$

Note that periodicity reduces the area integral to $\mathscr{A}_{\beta\sigma}$ in this formula.

Setting $a = f$ and $\mathbf{a} = \mathbf{d}$ in the above equation leads, after substitution of the corresponding differential equations and boundary conditions, to

$$\frac{\mathcal{R}'}{\mathscr{D}}\frac{1}{V_{\beta}}\int_{\mathscr{V}_{\beta}}\left(f\int_{\mathscr{A}_{\beta\sigma}}\mathbf{d}\,dA - \mathbf{d}\int_{\mathscr{A}_{\beta\sigma}}f\,dA\right)dV = \int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}f\,dA. \tag{19}$$

Note that the area integral terms containing $\mathbf{d}$ and f on the left-hand side of the above equation are constants within $\mathscr{V}_{\beta}$ and can be safely taken out of the volume integral on the left hand side of Eq. (19). After dividing both sides of the resulting equation by V_{β} and recalling the average constraints given in Eqs. (11d) and (12d), the following result is obtained

$$\frac{\mathcal{R}'}{\mathscr{D}}\frac{1}{V_{\beta}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{d}\,dA = \frac{1}{V_{\beta}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}f\,dA. \tag{20}$$

Substituting this expression into Eq. (17) proves that $\mathbf{u}=\mathbf{0}$. In other words, there is no correction to diffusion resulting from the upscaling process and therefore, Eq. (16) can be simplified to

$$\phi\frac{\partial\langle c\rangle^{\beta}}{\partial t} = \nabla\cdot\left(\phi\mathbf{D}_{effr}\cdot\nabla\langle c\rangle^{\beta}\right) - a_v\langle f\rangle_{\beta\sigma}\mathcal{R}. \tag{21}$$

Note that this demonstration would not have been possible if the reactive filter in Eq. (7) is discarded as reported by Whitaker (1999). This means that, in the volume averaging method, it is more convenient to avoid making simplifications until reaching the derivation

of the deviation variables problem. In Appendix A it is shown that a similar simplification is applicable to the upscaled model resulting from periodic homogenization for a first-order heterogeneous reaction, despite the fact that the closure problems are different from the ones presented here because the model is constrained to $Da = \mathbf{O}(\ell_\beta/L)$. The extents and limitations of this particular upscaled model were studied by Valdés-Parada et al. (2017).

At this point, it is worth mentioning that if convection is present, then a convective filter appears in the unclosed model, which after substitution of the formal solution of the concentration deviations, leads to an effective velocity vector containing the diffusive, reactive and convective filters of microscale information (see Eq. (19a) in Valdés-Parada et al. (2020)). In this case, the simplification provided here does not apply and this is detailed in Appendix B where an alternative form of the expression of the effective convective velocity present in the macroscopic model is derived. Consequently, the macroscopic model reported in Eq. (20) in Valdés-Parada et al. (2020) is the pertinent one to use, in general. Nevertheless, in some situations, analyses based upon orders of magnitude estimates can help derive a simplified version of this model as reported in this reference.

2.2. Two-species diffusion and heterogeneous reaction

The analysis presented so far has been limited to the transport and reaction process of a single chemical species. However, many relevant processes of practical interest involve at least two chemical species and for this reason it has recently received considerable attention in the derivation of upscaled models (see, for example Qiu et al., 2017; Bourbatache et al., 2023; Pietrzyk and Battiato, 2023). A simple case consists in the diffusive transport of two chemical species undergoing a first-order reaction as studied by Qiu et al. (2017) using the volume averaging method, more recently by Bourbatache et al. (2023) using the homogenization technique, and in a broader context by Pietrzyk and Battiato (2023). Motivated by the above, consider the diffusion process of two chemical species (A and B of molar concentration c_A and c_B) undergoing nonlinear chemical reactions at the solid–fluid interface in a homogeneous porous medium. The governing differential equations for the chemical species are

$$\frac{\partial c_A}{\partial t} = \mathscr{D}\nabla^2 c_A, \quad \text{in } \mathscr{V}_\beta, \tag{22a}$$

$$\frac{\partial c_B}{\partial t} = \mathscr{D}\nabla^2 c_B, \quad \text{in } \mathscr{V}_\beta. \tag{22b}$$

Note that the molecular diffusion coefficient has been set to be the same for both chemical species, which is an assumption used by both Qiu et al. (2017) and Bourbatache et al. (2023). The interfacial boundary conditions are

$$\text{B.C.1}, \quad -\mathbf{n}\cdot\mathscr{D}\nabla c_A = R_A - R_B, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{22c}$$

$$\text{B.C.2}, \quad -\mathbf{n}\cdot\mathscr{D}\nabla c_B = R_B - R_A, \quad \text{at } \mathscr{A}_{\beta\sigma}. \tag{22d}$$

In the above equations, R_A and R_B are nonlinear functions of c_A and c_B. As in the previous case, a linearization scheme is proposed so that

$$R_A \approx \mathcal{R}_A + \mathcal{R}'_A \tilde{c}_A, \tag{23a}$$

$$R_B \approx \mathcal{R}_B + \mathcal{R}'_B \tilde{c}_B. \tag{23b}$$

Following Bourbatache et al. (2023), it is convenient to introduce the following changes of variables in order to decouple the problem

$$\xi = c_A + c_B, \tag{24a}$$

$$\zeta = \mathcal{R}'_A c_A - \mathcal{R}'_B c_B. \tag{24b}$$

The new variables ξ and ζ solve the following problems

$$\frac{\partial \xi}{\partial t} = \mathscr{D}\nabla^2 \xi, \quad \text{in } \mathscr{V}_\beta, \tag{25a}$$

$$\text{B.C.} \quad -\mathbf{n}\cdot\mathscr{D}\nabla\xi = 0, \quad \text{at } \mathscr{A}_{\beta\sigma}. \tag{25b}$$

$$\frac{\partial \zeta}{\partial t} = \mathscr{D}\nabla^2 \zeta, \quad \text{in } \mathscr{V}_\beta, \tag{26a}$$

$$\text{B.C.} \quad -\mathbf{n}\cdot\mathscr{D}\nabla\zeta = \mathcal{R}_+\mathcal{R}_- + \mathcal{R}_+\tilde{\xi}, \quad \text{at } \mathscr{A}_{\beta\sigma}. \tag{26b}$$

In this last equation, the following definitions were used:

$$\mathcal{R}_+ \equiv \mathcal{R}'_A + \mathcal{R}'_B, \tag{27a}$$

$$\mathcal{R}_- \equiv \mathcal{R}_A - \mathcal{R}_B. \tag{27b}$$

Details on the derivation of Eqs. (26) are available in Appendix C.2. The mathematical structure of the problem given in Eqs. (25) corresponds to passive diffusion in porous media and the upscaled model does not have a corrective term that is subject to simplifications using Green's formula. In contrast, the problem given in Eqs. (26) has the same mathematical structure as the one given in Eqs. (1) after substituting the linear approximation for R given in Eq. (6b) into the interfacial boundary condition. Hence a corrective term is obtained from the upscaling process but is indeed zero upon use of Green's formula as explained above.

3. Non-thermal equilibrium heat conduction

The second case of interest in the present study corresponds to heat transfer by conduction in a homogeneous porous medium under non-thermal equilibrium conditions. The upscaling process of this problem was reported by Quintard and Whitaker (1993), and later in Quintard et al. (1997) under convective conditions using the volume averaging method. The reader interested in the derivation using the homogenization method is directed to the monograph by Auriault et al. (2009).

3.1. Pore-scale model

Assuming that Fourier's law is applicable in both the β and σ phases, and neglecting interfacial resistance to heat transfer, as well as jump terms in the interfacial heat flux, the governing pore-scale equations and interfacial boundary conditions for this process can be written as

$$\rho_\beta c_{p\beta}\frac{\partial T_\beta}{\partial t} = \nabla\cdot\left(k_\beta\nabla T_\beta\right), \quad \text{in } \mathscr{V}_\beta, \tag{28a}$$

$$\text{B.C.1} \quad T_\beta = T_\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{28b}$$

$$\text{B.C.2} \quad -\mathbf{n}\cdot k_\beta\nabla T_\beta = -\mathbf{n}\cdot k_\sigma\nabla T_\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{28c}$$

$$\rho_\sigma c_{p\sigma}\frac{\partial T_\sigma}{\partial t} = \nabla\cdot\left(k_\sigma\nabla T_\sigma\right) + \varphi_\sigma, \quad \text{in } \mathscr{V}_\sigma. \tag{28d}$$

Here, T_α, ρ_α, $c_{p\alpha}$ and k_α ($\alpha = \beta, \sigma$) respectively denote the temperature, density, heat capacity and thermal conductivity of the α phase. As in the previous section, $\mathbf{n}$ is used to denote the unit normal vector at $\mathscr{A}_{\beta\sigma}$ directed from the β-phase towards the σ-phase. In the energy balance equation for the σ-phase, a constant source term, φ_σ is introduced with the idea that this term may play a significant role in triggering non thermal equilibrium effects. Such a situation may be envisaged, for instance, in a composite system (made of two solid phases) placed in a modulated electromagnetic field and for which the σ-phase has magnetic properties whereas the β-phase has not. This problem differs from the one studied by Whitaker (1999) (see Chapter 2 therein) and more recently by Davarzani et al. (2021) (to study thermo-diffusion in porous media) only due to the presence of the source term in the σ phase. Note that the structure of this problem resembles the one used to study single-phase flow in heterogeneous porous media (see equations (5.2–14)-(5.2–17) in Whitaker, 1999). Recently, Pietrzyk et al. (2023) used the software Symbolica to develop an upscaled model for a more general situation that incorporates another solid phase and heat transfer resistance at $\mathscr{A}_{\beta\sigma}$. Although this problem is more complicated than the one stated above, the procedure to simplify the resulting upscaled model is the same as for the problem discussed here. For the sake of brevity in presentation, the case in which interfacial heat transfer resistance is relevant is presented in Appendix E.

3.2. Upscaling

Following the volume averaging method, the intrinsic averaging operator corresponding to each phase is applied accordingly, along with the use of the spatial averaging theorem and the decomposition $T_\alpha = \langle T\rangle^\alpha + \tilde{T}_\alpha$ $(\alpha = \beta, \sigma)$. Recalling the separation of length scales allows regarding average quantities and their derivatives as constants within the integral filters. The resulting set of unclosed equations is given by

$$\rho_\beta c_{p\beta}\frac{\partial\langle T_\beta\rangle^\beta}{\partial t} = \nabla\cdot\left[k_\beta\left(\nabla\langle T_\beta\rangle^\beta + \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\tilde{T}_\beta\,dA\right)\right] + \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot k_\beta\nabla\tilde{T}_\beta\,dA, \tag{29a}$$

$$\rho_\sigma c_{p\sigma}\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} = \nabla\cdot\left[k_\sigma\left(\nabla\langle T_\sigma\rangle^\sigma - \frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\tilde{T}_\sigma\,dA\right)\right] - \frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot k_\sigma\nabla\tilde{T}_\sigma\,dA + \varphi_\sigma. \tag{29b}$$

To achieve a closed macroscopic model, a closure procedure is required, which follows the same steps and assumptions as those used in Section 2. Under quasi-steady conditions at the level of a unit cell, which can be assumed if the process is observed at the time scale t_{ref} such that $t_{ref} \gg \max\left[\frac{\rho_\beta c_{p\beta}\ell_\beta^2}{k_\beta}(1,\ \frac{\rho_\sigma c_{p\sigma}}{\rho_\beta c_{p\beta}}\frac{\ell_\sigma^2}{\ell_\beta^2}\frac{k_\beta}{k_\sigma})\right]$, the governing equations for the temperature deviations are (Whitaker, 1999, see Sec. 2.4 for details)

$$0 = k_\beta\nabla^2\tilde{T}_\beta - \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot k_\beta\nabla\tilde{T}_\beta\,dA, \quad \text{in } \mathscr{V}_\beta, \tag{30a}$$

$$\text{B.C.1}\ \tilde{T}_\beta = \tilde{T}_\sigma - \left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right), \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{30b}$$

$$\text{B.C.2}\ -\mathbf{n}\cdot k_\beta\nabla\tilde{T}_\beta = -\mathbf{n}\cdot k_\sigma\nabla\tilde{T}_\sigma + \mathbf{n}\cdot\left(k_\beta\nabla\langle T_\beta\rangle^\beta - k_\sigma\nabla\langle T_\sigma\rangle^\sigma\right), \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{30c}$$

$$0 = k_\sigma\nabla^2\tilde{T}_\sigma + \frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot k_\sigma\nabla\tilde{T}_\sigma\,dA, \quad \text{in } \mathscr{V}_\sigma, \tag{30d}$$

$$\tilde{T}_\alpha(\mathbf{r}) = \tilde{T}_\alpha(\mathbf{r}+\mathbf{l}_i), \quad i = 1,2,3, \alpha = \beta,\sigma, \tag{30e}$$

$$\langle\tilde{T}_\alpha\rangle^\alpha = 0, \quad \alpha = \beta,\sigma. \tag{30f}$$

Note that the temperature deviations are not influenced by the source term, nor by $\rho_\alpha c_{p\alpha}$ $(\alpha = \beta,\sigma)$. The former is a consequence of assuming that this source term is constant and the second stems from not including convective heat transport and restraining the analysis to quasi-steady conditions at the closure level. The latter implies that the resulting upscaled model should not be expected to perform well at *early times*, *i.e.*, at time scales below $\max\left(\frac{\rho_\beta c_{p\beta}\ell_\beta^2}{k_\beta}, \frac{\rho_\sigma c_{p\sigma}\ell_\sigma^2}{k_\sigma}\right)$. At these times scales, the values of $\rho_\alpha c_{p\alpha}$ $(\alpha = \beta,\sigma)$ should play a role in the values of the effective coefficients.

The problem given in Eqs. (30) is linear and has two source terms, namely, $\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma$ and $k_\beta\nabla\langle T_\beta\rangle^\beta - k_\sigma\nabla\langle T_\sigma\rangle^\sigma$. Therefore its solution can be expressed as follows

$$\tilde{T}_\beta = \frac{\mathbf{b}_\beta}{k_\beta}\cdot\left(k_\beta\nabla\langle T_\beta\rangle^\beta - k_\sigma\nabla\langle T_\sigma\rangle^\sigma\right) - s_\beta\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right), \tag{31a}$$

$$\tilde{T}_\sigma = -\frac{\mathbf{b}_\sigma}{k_\sigma}\cdot\left(k_\beta\nabla\langle T_\beta\rangle^\beta - k_\sigma\nabla\langle T_\sigma\rangle^\sigma\right) + s_\sigma\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right). \tag{31b}$$

Here, $\mathbf{b}_\alpha$ and s_α $(\alpha = \beta,\sigma)$ are closure variables that solve the following closure problems that are obtained from the substitution of the above formal solutions into the deviations problem given in Eqs. (30) and splitting according to each source

Problem ***b***

$$\mathbf{0} = \nabla^2\mathbf{b}_\beta - \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla\mathbf{b}_\beta\,dA, \quad \text{in } \mathscr{V}_\beta, \tag{32a}$$

$$\text{B.C.1}\ \mathbf{b}_\beta = -\frac{k_\beta}{k_\sigma}\mathbf{b}_\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{32b}$$

$$\text{B.C.2}\ -\mathbf{n}\cdot\nabla\mathbf{b}_\beta = \mathbf{n}\cdot\nabla\mathbf{b}_\sigma + \mathbf{n}, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{32c}$$

$$\mathbf{0} = \nabla^2\mathbf{b}_\sigma + \frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla\mathbf{b}_\sigma\,dA, \quad \text{in } \mathscr{V}_\sigma, \tag{32d}$$

$$\mathbf{b}_\alpha(\mathbf{r}) = \mathbf{b}_\alpha(\mathbf{r}+\mathbf{l}_i), \quad i = 1,2,3, \alpha = \beta,\sigma, \tag{32e}$$

$$\langle\mathbf{b}_\alpha\rangle^\alpha = \mathbf{0}, \quad \alpha = \beta,\sigma. \tag{32f}$$

Problem ***s***

$$0 = \nabla^2 s_\beta - \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla s_\beta\,dA, \quad \text{in } \mathscr{V}_\beta, \tag{33a}$$

$$\text{B.C.1}\ s_\beta = 1 - s_\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{33b}$$

$$\text{B.C.2}\ -\mathbf{n}\cdot k_\beta\nabla s_\beta = \mathbf{n}\cdot k_\sigma\nabla s_\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{33c}$$

$$0 = \nabla^2 s_\sigma + \frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla s_\sigma\,dA, \quad \text{in } \mathscr{V}_\sigma, \tag{33d}$$

$$s_\alpha(\mathbf{r}) = s_\alpha(\mathbf{r}+\mathbf{l}_i), \quad i = 1,2,3, \alpha = \beta,\sigma, \tag{33e}$$

$$\langle s_\alpha\rangle^\alpha = 0, \quad \alpha = \beta,\sigma. \tag{33f}$$

Substitution of the formal solution given in Eqs. (31) into the unclosed model (Eqs. (29)) yields the following macroscopic thermal energy balance equations

$$\rho_\beta c_{p\beta}\frac{\partial\langle T_\beta\rangle^\beta}{\partial t} = \nabla\cdot\left(\mathbf{K}_{\beta\beta}\cdot\nabla\langle T_\beta\rangle^\beta + \mathbf{K}_{\beta\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma\right) + \mathbf{u}_{\beta\beta}\cdot\nabla\langle T_\beta\rangle^\beta + \mathbf{u}_{\beta\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma - \frac{a_v h}{\phi_\beta}\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right), \tag{34a}$$

$$\rho_\sigma c_{p\sigma}\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} = \nabla\cdot\left(\mathbf{K}_{\sigma\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma + \mathbf{K}_{\sigma\beta}\cdot\nabla\langle T_\beta\rangle^\beta\right) + \mathbf{u}_{\sigma\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma + \mathbf{u}_{\sigma\beta}\cdot\nabla\langle T_\beta\rangle^\beta - \frac{a_v h}{\phi_\sigma}\left(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta\right) + \varphi_\sigma. \tag{34b}$$

Here, $\phi_\alpha = V_\alpha/V$ $(\alpha = \beta,\sigma)$ is the volume fraction of the α phase. In addition, the effective-medium coefficients present in the above two-equations macroscopic model are defined as

$$\mathbf{K}_{\beta\beta} = k_\beta\left(\mathbf{I} + \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\mathbf{b}_\beta\,dA\right), \tag{35a}$$

$$\mathbf{K}_{\beta\sigma} = -\frac{k_\sigma}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\mathbf{b}_\beta\,dA, \tag{35b}$$

$$\mathbf{K}_{\sigma\sigma} = k_\sigma\left(\mathbf{I} - \frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\mathbf{b}_\sigma\,dA\right), \tag{35c}$$

$$\mathbf{K}_{\sigma\beta} = \frac{k_\beta}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\mathbf{b}_\sigma\,dA, \tag{35d}$$

$$\mathbf{u}_{\beta\beta} = \frac{k_\beta}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\left(-\mathbf{I}s_\beta + \nabla\mathbf{b}_\beta\right)dA, \tag{35e}$$

$$\mathbf{u}_{\beta\sigma} = \frac{k_\beta}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\left(\mathbf{I}s_\beta - \frac{k_\sigma}{k_\beta}\nabla\mathbf{b}_\beta\right)dA, \tag{35f}$$

$$\mathbf{u}_{\sigma\sigma} = \frac{k_\sigma}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\left(\mathbf{I}s_\sigma - \nabla\mathbf{b}_\sigma\right)dA, \tag{35g}$$

$$\mathbf{u}_{\sigma\beta} = \frac{k_\sigma}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\left(-\mathbf{I}s_\sigma + \frac{k_\beta}{k_\sigma}\nabla\mathbf{b}_\sigma\right)dA, \tag{35h}$$

$$h = \frac{k_\beta}{A_{\beta\sigma}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla s_\beta\,dA = -\frac{k_\sigma}{A_{\beta\sigma}}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla s_\sigma\,dA. \tag{35i}$$

The coefficients $\mathbf{K}_{\alpha\kappa}$ $(\alpha,\kappa = \beta,\sigma)$ given in Eqs. (35a)–(35d) are the dominant $(\alpha = \kappa)$ and coupled $(\alpha \neq \kappa)$ heat diffusion (or conductivity) tensors. In Appendix D, these second-order tensors are shown to be symmetric (see also, Lasseux and Valdés-Parada, 2017, Sec. III A) and positive. It should be noted that the two coupled heat conductivity tensors are simply related to each other by

$$\phi_\beta\mathbf{K}_{\beta\sigma} = \phi_\sigma\mathbf{K}_{\sigma\beta} = \mathbf{K}_c, \tag{36a}$$

whereas the dominant ones are related by

$$\phi_\beta k_\sigma^2\left(\mathbf{K}_{\beta\beta} - k_\beta\mathbf{I}\right) = \phi_\sigma k_\beta^2\left(\mathbf{K}_{\sigma\sigma} - k_\sigma\mathbf{I}\right). \tag{36b}$$

In addition, $\mathbf{u}_{\alpha\kappa}$ $(\alpha,\kappa = \beta,\gamma)$ expressed in Eqs. (35e)–(35h) are the dominant conduction-corrective $(\alpha = \kappa)$ and co-conduction-corrective $(\alpha \neq \kappa)$ coefficients, whereas h in Eq. (35i) is the effective interfacial heat transfer coefficient. Consistently with the mass transfer case (see Appendix B), if convective heat transport is taking place, then no further simplifications of the corresponding model (see, for example, Quintard et al., 1997) are possible using Green's formula. Nevertheless, it is possible that in some situations the conduction and co-conduction-corrective terms may be discarded using orders of magnitude analyses.

At this point, it is convenient to reconsider Green's formula in the form given in Eq. (18) and use it in $\mathscr{V}_\beta$, setting $a = s_\beta$ and $\mathbf{a} = \mathbf{b}_\beta$. After substitution of the corresponding differential equations and boundary conditions along with the corresponding average constraints for the closure variables, the following integral relation results

$$\mathbf{0} = \int_{\mathscr{A}_{\beta\sigma}} \left(\mathbf{n}\cdot\nabla\mathbf{b}_\sigma s_\sigma - \mathbf{n}\cdot\nabla s_\sigma \mathbf{b}_\sigma\right) dA - \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla\mathbf{b}_\sigma\, dA + \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} s_\sigma\, dA. \tag{37}$$

To simplify the above equation, Green's formula in Eq. (18) is now applied over $\mathscr{V}_\sigma$, taking $a = s_\sigma$ and $\mathbf{a} = \mathbf{b}_\sigma$. Employing the same mathematical steps as those used in Section 2.1, the following equation results

$$\mathbf{0} = \int_{\mathscr{A}_{\beta\sigma}} \left(\mathbf{n}\cdot\nabla\mathbf{b}_\sigma s_\sigma - \mathbf{n}\cdot\nabla s_\sigma \mathbf{b}_\sigma\right) dA. \tag{38}$$

Consequently, Eq. (37) reduces to

$$\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} s_\sigma\, dA = \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla\mathbf{b}_\sigma\, dA. \tag{39a}$$

In addition, since all the equations in the closure problems satisfy reciprocity between the two phases, *i.e.*, are unchanged upon switching β and σ, the following result is straightforwardly obtained from the above relationship

$$\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} s_\beta\, dA = \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla\mathbf{b}_\beta\, dA. \tag{39b}$$

When these last two expressions are substituted back into Eqs. (35e) and (35g), one readily obtains

$$\mathbf{u}_{\beta\beta} = \mathbf{0}, \tag{40a}$$

$$\mathbf{u}_{\sigma\sigma} = \mathbf{0}. \tag{40b}$$

Furthermore, adding up Eqs. (35e) and (35f), on the one hand, and (35g) and (35h), on the other hand, yields

$$\mathbf{u}_{\beta\sigma} = \frac{k_\beta - k_\sigma}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} s_\beta\, dA = \frac{k_\beta - k_\sigma}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla\mathbf{b}_\beta\, dA, \tag{41a}$$

$$\mathbf{u}_{\sigma\beta} = \frac{k_\beta - k_\sigma}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} s_\sigma\, dA = \frac{k_\beta - k_\sigma}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla\mathbf{b}_\sigma\, dA. \tag{41b}$$

The boundary condition given in Eq. (32c) can now be substituted into the last expression of either $\mathbf{u}_{\beta\sigma}$ or $\mathbf{u}_{\sigma\beta}$, and, recalling the assumption of a spatially homogeneous medium, which implies $\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\, dA = \mathbf{0}$, this allows writing

$$\phi_\beta \mathbf{u}_{\beta\sigma} = -\phi_\sigma \mathbf{u}_{\sigma\beta}. \tag{42}$$

The conclusions reached here on the coefficients $\mathbf{u}_{\alpha\kappa}$ $(\alpha,\kappa = \beta,\sigma)$ confirm and clarify the result that $\phi_\beta(\mathbf{u}_{\beta\beta}+\mathbf{u}_{\beta\sigma})+\phi_\sigma(\mathbf{u}_{\sigma\sigma}+\mathbf{u}_{\sigma\beta}) = \mathbf{0}$, which corresponds to Eq. (150) in Quintard and Whitaker (1993). Finally, the macroscopic model for non-thermal equilibrium heat conduction in a homogeneous porous medium is given by

$$\phi_\beta\rho_\beta c_{p\beta}\frac{\partial\langle T_\beta\rangle^\beta}{\partial t} = \nabla\cdot\left(\phi_\beta\mathbf{K}_{\beta\beta}\cdot\nabla\langle T_\beta\rangle^\beta + \mathbf{K}_c\cdot\nabla\langle T_\sigma\rangle^\sigma\right) + (k_\beta - k_\sigma)\mathbf{u}_c\cdot\nabla\langle T_\sigma\rangle^\sigma - a_v h\left(\langle T_\beta\rangle^\beta - \langle T_\sigma\rangle^\sigma\right), \tag{43a}$$

$$\phi_\sigma\rho_\sigma c_{p\sigma}\frac{\partial\langle T_\sigma\rangle^\sigma}{\partial t} = \nabla\cdot\left(\phi_\sigma\mathbf{K}_{\sigma\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma + \mathbf{K}_c\cdot\nabla\langle T_\beta\rangle^\beta\right) + (k_\sigma - k_\beta)\mathbf{u}_c\cdot\nabla\langle T_\beta\rangle^\beta - a_v h\left(\langle T_\sigma\rangle^\sigma - \langle T_\beta\rangle^\beta\right) + \phi_\sigma\varphi_\sigma. \tag{43b}$$

In this two-equation (non-thermal equilibrium) model, $\mathbf{K}_c$ is the co-conductivity tensor defined in Eq. (36a) whereas $\mathbf{u}_c$ is the co-conduction-corrective coefficient that has units of the inverse of a length, and is defined as

$$(k_\beta - k_\sigma)\mathbf{u}_c = \phi_\beta\mathbf{u}_{\beta\sigma} = -\phi_\sigma\mathbf{u}_{\sigma\beta}. \tag{44}$$

The term $(k_\alpha - k_\kappa)\mathbf{u}_c\cdot\nabla\langle T_\kappa\rangle^\kappa$ $(\alpha,\kappa = \beta,\sigma,\ \alpha \neq \kappa)$ is a co-conduction-corrective term that is not zero in the general case. The exception is when the thermal conductivities in both phases are equal. Moreover, the ith component of the co-conduction coefficient is zero if the unit cell is symmetric in the ith direction, in accordance with the proof provided by Whitaker (1999).

This model shows that, when studying conductive heat transfer in porous media, it is not only necessary to consider heat exchange between the phases induced by their average temperature difference, but also co-conduction including the corrective term, the latter being triggered by the thermal conductivity contrast between the two phases. The last three terms on the right-hand side of Eq. (43a) are clearly the result of the upscaling process and they should all be considered, in general, when studying non-thermal equilibrium, *i.e.*, when $\langle T_\beta\rangle^\beta \neq \langle T_\sigma\rangle^\sigma$ and a similar conclusion applies to Eq. (43b). These conclusions are extensible to the case in which there is an interfacial heat transfer resistance as shown in Appendix E with the only exception that $\mathbf{K}_{\sigma\beta}$ and $\mathbf{K}_{\beta\sigma}$ are not symmetric tensors, in general. This case is a subset of the process investigated in Pietrzyk et al. (2023) and the results in Appendix E are in full agreement with what was reported in this reference. However, in their work, these authors kept the dominant conduction-corrective terms (which they refer to as "*effective advection terms*") and found them to be zero when the phase under concern has a circular shape, in agreement with the proof provided by Whitaker (1999). The results reported in Appendix E provide a systematic analysis of the coefficients that allows clarifying the upscaled model, and answer the remark in the above mentioned reference (end of section 4.2.2) as "*we suggest that further investigation could [...] provide simplifications of the effective velocities*".

For conditions in which the properties and sources of both phases are sufficiently similar, or when the volumetric fraction of one phase is much larger than the other, or when some length scale constraint is applicable (see an extensive discussion in chapter 2, section 2.3 in Whitaker, 1999, for details), it is reasonable to assume local thermal equilibrium, *i.e.*, $\langle T_\beta\rangle^\beta = \langle T_\sigma\rangle^\sigma = \langle T\rangle$. In this case, the macroscopic model results from adding up Eqs. (43a) and (43b), leading to an average thermal energy balance equation that simply reads

$$\langle\rho C_p\rangle\frac{\partial\langle T\rangle}{\partial t} = \nabla\cdot\left[\left(\phi_\beta\mathbf{K}_{\beta\beta} + 2\mathbf{K}_c + \phi_\sigma\mathbf{K}_{\sigma\sigma}\right)\cdot\nabla\langle T\rangle\right] + \phi_\sigma\varphi_\sigma, \tag{45}$$

with the following nomenclature

$$\langle\psi\rangle = \frac{1}{V}\left(\int_{\mathscr{V}_\beta}\psi_\beta\, dV + \int_{\mathscr{V}_\sigma}\psi_\sigma\, dV\right) = \phi_\beta\langle\psi_\beta\rangle^\beta + \phi_\sigma\langle\psi_\sigma\rangle^\sigma. \tag{46}$$

This last model is in agreement with the result reported by Whitaker (1999) and it does not involve any correction or exchange terms because they cancel in the summation operation (see also Section 4.2.2 in Auriault et al., 2009). Note that this equilibrium one-equation model is likely to be accurate when $\varphi_\sigma = 0$ and when the thermal properties between the two phases are not too contrasted.

3.3. Illustrative results

To illustrate about the non-zero nature of the co-conduction -corrective coefficient, $\mathbf{u}_c$, and the importance of the co-conduction-corrective term in the energy balance equation in each phase, a case example is studied numerically. This case corresponds to a macroscopic

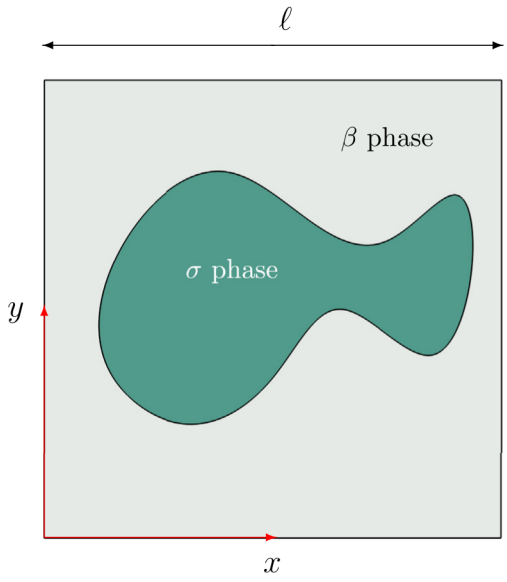

Fig. 3. Sketch of the periodic and non-symmetric unit cell used for the closure problem solution. In this geometry $\phi_\beta = 0.723$.

system for which the periodic non-symmetric unit cell is represented in Fig. 3 whose β-phase volume fraction is $\phi_\beta = 0.723$. To this end, the following procedure was carried out.

First, *Problem* ***b*** and *Problem s* were solved on the unit cell of Fig. 3, using Comsol Multiphysics 6.2, employing the heat transfer module and checking mesh convergence. Using the size of the unit cell, ℓ, as the reference length, all the dimensionless effective coefficients appearing in the macroscopic two-equation model were computed (the superscript * denotes dimensionless quantities), namely $\mathbf{K}^*_{\alpha\alpha} = \mathbf{K}_{\alpha\alpha}/k_\alpha$ $(\alpha = \beta, \sigma)$, $\mathbf{K}^*_c = \mathbf{K}_c/k_\sigma$, $\mathbf{u}^*_c = \ell \mathbf{u}_c = \frac{1}{V^*}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} s_\beta \, dA^*$, $h^* = h\ell/k_\beta$ and $a^*_v = \ell a_v$. Moreover, the thermal conductivity ratio is defined as $r = k_\sigma/k_\beta$.

Second, with the effective coefficients at hand, the macroscopic model given in Eqs. (43) was solved in its dimensionless form, taking a reference temperature, T_0, and assuming steady-state. The macroscopic domain under consideration is made of 20 unit cells in the x-direction and only one unit cell in the y-direction upon assuming the medium is y-periodic. The problem is therefore 1D (in the x-direction) only requiring the xx-components of $\mathbf{K}^*_{\alpha\alpha}$ $(\alpha = \beta, \sigma)$ and $\mathbf{K}^*_c$, as well as the x-component of $\mathbf{u}^*_c$. The dimensionless energy balance equations to be solved can therefore be written as

$$0 = \underbrace{\phi_\beta K^*_{\beta\beta xx} \frac{\partial^2 \langle T^*_\beta \rangle^\beta}{\partial x^{*2}}}_{M_{1\beta}} + \underbrace{K^*_{cxx} r \frac{\partial^2 \langle T^*_\sigma \rangle^\sigma}{\partial x^{*2}}}_{M_{2\beta}} + \underbrace{(1-r) u^*_{cx} \frac{\partial \langle T^*_\sigma \rangle^\sigma}{\partial x^*}}_{M_{3\beta}} \underbrace{- a^*_v h^* \left(\langle T^*_\beta \rangle^\beta - \langle T^*_\sigma \rangle^\sigma \right)}_{M_{4\beta}}, \tag{47a}$$

$$0 = \underbrace{\phi_\sigma K^*_{\sigma\sigma xx} \frac{\partial^2 \langle T^*_\sigma \rangle^\sigma}{\partial x^{*2}}}_{M_{1\sigma}} + \underbrace{K^*_{cxx} \frac{\partial^2 \langle T^*_\beta \rangle^\beta}{\partial x^{*2}}}_{M_{2\sigma}} + \underbrace{\left(1 - \frac{1}{r}\right) u^*_{cx} \frac{\partial \langle T^*_\beta \rangle^\beta}{\partial x^*}}_{M_{3\sigma}} \underbrace{- \frac{1}{r} a^*_v h^* \left(\langle T^*_\sigma \rangle^\sigma - \langle T^*_\beta \rangle^\beta \right)}_{M_{4\sigma}} + \phi_\sigma \varphi^*_\sigma, \tag{47b}$$

with $\varphi^*_\sigma = \frac{\varphi_\sigma \ell^2}{k_\sigma T_0}$. The associated boundary conditions are given by

$$\langle T^*_\alpha \rangle^\alpha = 1, \quad \text{at } x^* = 0, \ \alpha = \beta, \gamma, \tag{47c}$$

$$\langle T^*_\alpha \rangle^\alpha = 0, \quad \text{at } x^* = 20, \ \alpha = \beta, \gamma. \tag{47d}$$

Note that, although not restricted to a periodic system, the macroscopic model is not expected to be accurate at a distance from the macroscopic boundaries typically smaller than the size of one unit cell (see an illustration for a diffusion reaction problem in Valdés-Parada et al. (2017)). Moreover, $\phi_\sigma \varphi^*_\sigma$ was taken equal to 1000 with the intention of highlighting the contrast of heat transfer between the two phases.

The numerical solution of the above problem was carried out using Comsol Multiphysics 6.2 with the 1D mass transport module using sufficient discretization elements to ensure independence of this degree of freedom. In addition, a quintic discretization approach was used for both dependent variables in order to obtain accurate predictions of the second-order spatial derivatives.

3.3.1. *Effective coefficients*

Results on the xx-components of the dimensionless dominant conductivity ($K^*_{\alpha\alpha xx}$, $\alpha = \beta, \gamma$) and co-conductivity (K^*_{cxx}) tensors together with the x-component of the co-conduction-corrective coefficient, u^*_{cx}, and effective heat transfer coefficient (multiplied by a^*_v), $a^*_v h^*$, are reported in Fig. 4(a)–(d) for r ranging between 10^{-3} and 10^3. These results, obtained for the unit cell represented in Fig. 3, call upon the following comments

- $K^*_{\beta\beta xx}$ continuously increases with r between a finite value for $r = 10^{-3}$ to 1 for $r = 10^3$, with an asymptotic behavior in the limit of both large and small values of r (see Fig. 4(a)). The asymptotic value of 1 for large values of r is to be expected since, in this limit, the conductivity of the trapped phase (the σ-phase, see Fig. 3) is extremely large compared to that of the β-phase so that the effective heat conductivity of the later is not perturbed by that of the former.
- Conversely, $K^*_{\sigma\sigma xx}$ reaches an asymptotic value of 1 in both limits of extremely small and extremely large values of r (see Fig. 4(a)). It decreases and then increases with r, and reaches a minimum for $r \approx 1.6$.
- K^*_{cxx} reported in Fig. 4(b) shows a decreasing behavior when r increases and reaches a zero asymptotic value in the limit of large values of r. This indicates that, when the trapped (σ-) phase is much more conductive than the continuous (β-) phase, co-conduction is likely to be unimportant.
- The x-component of the co-conduction-corrective coefficient, u^*_{cx}, remains positive over the whole range of r and exhibits a bell shape with a maximum value for $r \approx 5.6$ and a zero asymptotic value in both limits of exceedingly large and exceedingly small values of r. For these two limits, the co-conduction-corrective term is hence expected to play a very minor role.
- Finally, the heat transfer coefficient, $a^*_v h^*$, represented in Fig. 4, is shown to remain positive. This coefficient exhibits a similar dependence on r as $K^*_{\beta\beta xx}$, *i.e.*, it increases with r between two finite values in the limits of extremely small and extremely large values of r, respectively.

From the above observations, it is clear that three ranges of r can be identified. For $r < 10^{-2}$, where the solid phase is much less conductive than the fluid phase, it is found that $K^*_{\beta\beta xx}$ and $a^*_v h^*$ acquire their minimal values, whereas the opposite happens for $K^*_{\sigma\sigma xx}$, u^*_{cx} and K^*_{cxx}. Then for $r^* \in (0.1, 10^2)$, u^*_{cx} exhibits a maximum, whereas a minimum is found for $K^*_{\sigma\sigma xx}$. Finally, for $r > 10^2$, the solid phase is much more conductive than the fluid and $K^*_{\sigma\sigma xx}$, $K^*_{\beta\beta xx}$ and $a^*_v h^*$ have their maximum values, whereas K^*_{cxx} and u^*_{cx} tend to zero. From here, it is evident that, depending on the values of the thermal conductivity ratio, some coefficients can become more active than others. However, at this stage, it is not clear how these changes in the values of the effective coefficients affect the terms in the upscaled model. For this reason, in the following paragraphs, the weight of each term is pondered for two values of r, one in which the co-conduction corrective coefficient has a vanishingly small value ($r^* = 0.1$) and another one where it is near its maximum value ($r^* = 10$).

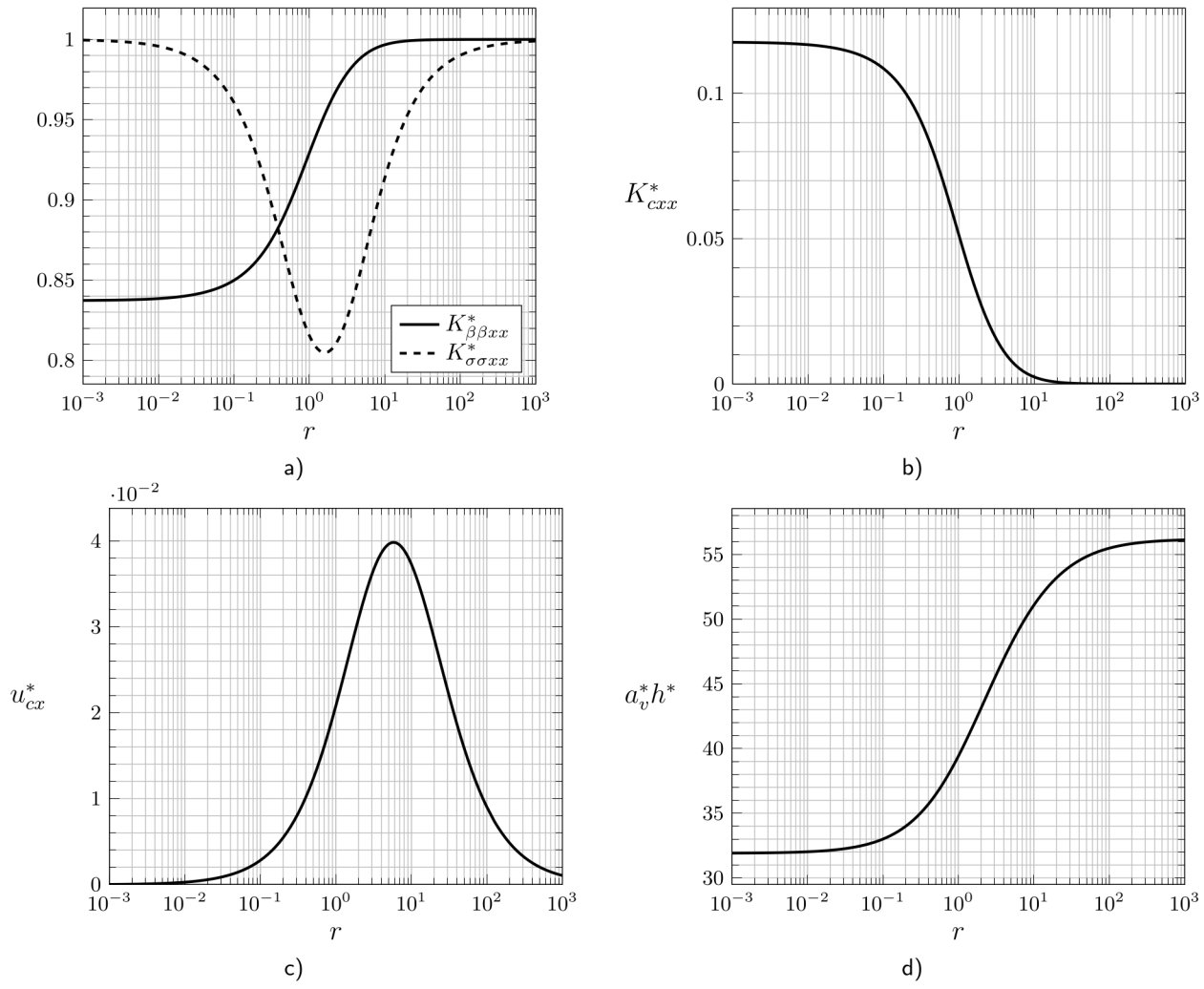

Fig. 4. Predictions of (a) the xx component of (a) the effective conductivity tensors $\mathbf{K}^*_{\alpha\alpha}$ ($\alpha = \beta, \sigma$), (b) the xx component of the co-conductivity tensor $\mathbf{K}^*_c$, (c) the x component of co-conduction corrective coefficient, $\mathbf{u}^*_c$ and (d) the exchange coefficient $a^*_v h^*$ as functions of the ratio of thermal conductivities $r = k_\sigma / k_\beta$. Results were obtained from solving *Problem* **b** and *Problem s* in the unit cell depicted in Fig. 3.

3.3.2. Terms in the energy balance equations

At this point, it is of interest to analyze the contribution of each of the terms identified as $M_{i\alpha}$ ($\alpha = \beta, \sigma$, $i = 1, \dots 4$) in Eqs. (47a) and (47b), with a special attention to those specific to the non-thermal equilibrium effect, namely $M_{2\alpha}$, $M_{3\alpha}$ and $M_{4\alpha}$ ($\alpha = \beta, \sigma$). For this purpose the four terms are represented versus $0 \leq x^* \leq 20$ for each phase (Figs. 5(a) and (c) for the β-phase and Figs. 5(b) and (d) for the σ-phase) considering two values of r, *i.e.*, $r = 0.1$ (Figs. 5(a) and (b)) and $r = 10$ (Figs. 5(c) and (d)). Since the macroscopic model is not supposed to provide accurate solutions close to the boundaries $x^* = 0$ and $x^* = 20$, the behavior of each term close to these locations, more specifically for $x^* < 1$ and $x^* > 19$, are not commented.

When the continuous phase is much more conductive than the trapped ($\sigma-$) phase ($r = 0.1$, Figs. 5(a) and (b)), it is observed that both the co-conduction ($M_{2\alpha}$) and co-conduction-corrective ($M_{3\alpha}$) terms ($\alpha = \beta, \sigma$) are not very significant. More specifically the co-conduction term remains smaller than the co-conduction-corrective one. The most important terms are the dominant conduction and heat exchange terms. Moreover, in this situation, the dominant conduction term is not varying significantly along the domain, whereas the heat exchange term slightly increases in magnitude along x^*. However, in the opposite situation with $r = 10$, a totally different behavior is obtained as shown in Figs. 5(c) and (d). Indeed, in that case, both the co-conduction-corrective and heat exchange terms are playing a major role in the energy balance in both phases. Note that, the co-conduction-corrective term increases with x^* in the β-phase, but decreases in the σ-phase. This can be explained by the prefactors $(1 - r)$ and $(1 - 1/r)$ in Eqs. (47a) and (47b), which change signs between the two phases. Moreover, the heat exchange terms exhibit the opposite behavior. In addition, the co-conduction term is the smallest one whereas the dominant conduction term remains almost constant along the domain. This example highlights the fact that, under certain circumstances, the co-conduction-corrective terms are crucial in the macroscopic heat balance equations.

4. Conclusions

The upscaling of diffusive mass transfer of single or two-species undergoing nonlinear heterogeneous chemical reactions and of two-phase heat conduction under non-local thermal equilibrium conditions, including interfacial heat transfer resistance or not, in homogeneous porous media is revisited in this work showing two important features. In the former case, the diffusion-corrective term resulting from upscaling is shown to be zero regardless the porous structure under

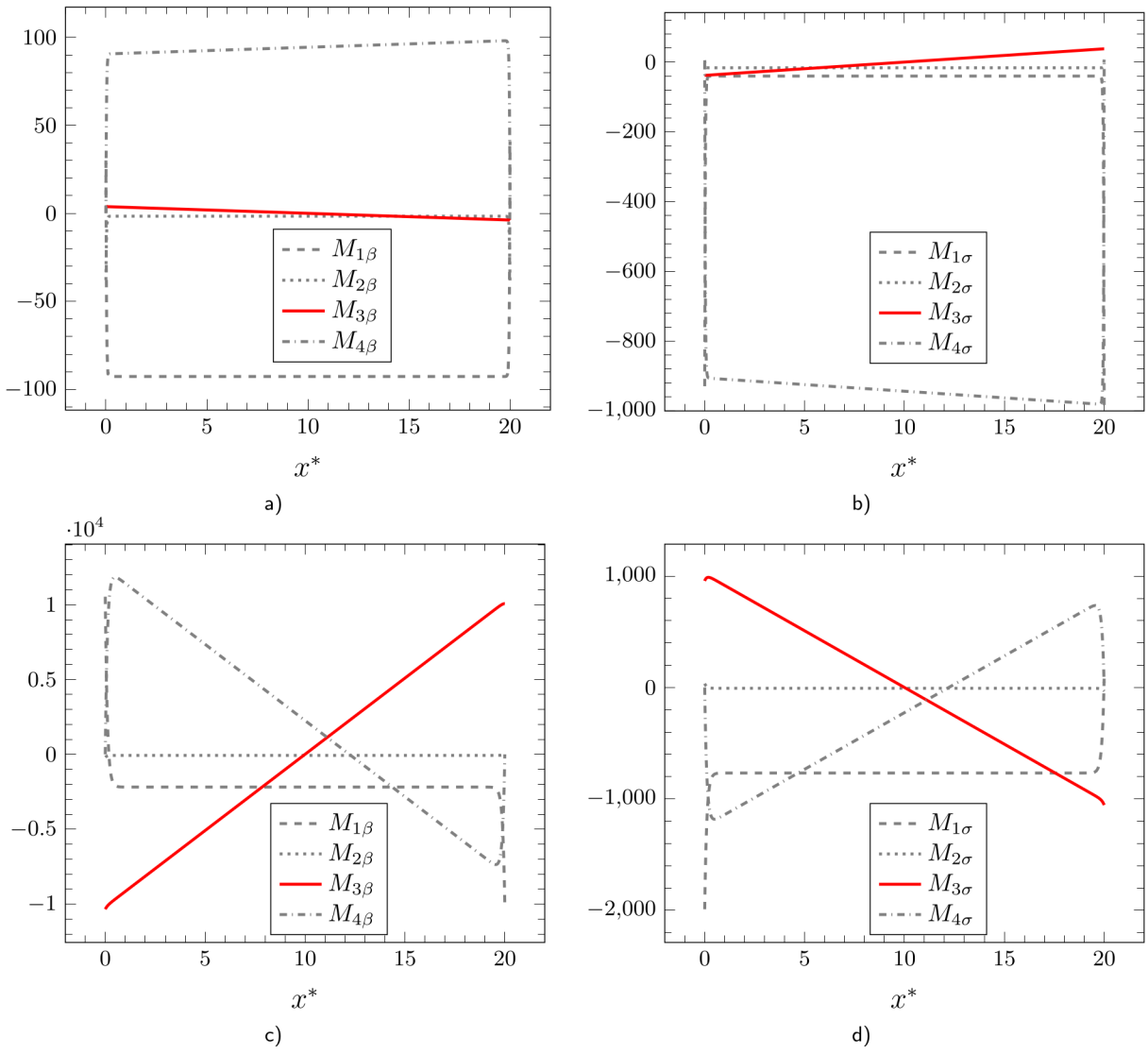

Fig. 5. Variation versus x^* of each term identified in Eq. (47a) (a) and (c) and Eq. (47b) (b) and (d) taking $r = 0.1$ (a) and (b) and $r = 10$ (c) and (d). In all the simulations $\phi_\sigma \varphi_\sigma^* = 1000$.

consideration and the Damköhler number value. This was made possible by using a linearization approximation of the reaction terms and a combination of the two closure variables involved in the macroscopic model using Green's formula. This clarifies the macroscopic models for which such physical processes are under concern (Ryan et al., 1981; Valdés-Parada et al., 2011; Whitaker, 1999). This simplification is shown to also apply to the upscaled model resulting from periodic homogenization corresponding to non exceedingly small values of the Damköhler number (see Appendix A). However, when mass is transported due to the combination of diffusion and convection, this simplification is no longer applicable, as shown in Appendix B.

In the case of conductive heat transfer under non-local thermal equilibrium, the dominant conduction-corrective coefficients induced by upscaling are shown to be zero, whereas a co-conduction-corrective coefficient remains in each phase, the two being related by a simple expression. This conclusion was shown to be applicable with and without considering interfacial heat transfer resistance. This result brings new light to the development reported by Quintard and Whitaker (1993) and more recently by Pietrzyk et al. (2023). When the (periodic) unit cell representative of the porous structure is symmetric in a given direction, the corresponding component of the co-conduction-corrective coefficient is zero. In the general case, this term should not be ignored as its contribution may not be negligible depending on the microstructure, thermal conductivity contrast between the two phases, the macroscopic system and macroscopic boundary conditions under consideration. This last point deserves a more extensive investigation depending on these parameters, an analysis that is, however, beyond the scope of the present study.

It is worth noting that in order for the simplifications resulting from the use of Green's formula to be applicable, it is convenient that the number of simplifications are kept to a minimum to derive the unclosed model in the volume averaging method. In other words, it is more convenient to not impose simplifications until the derivation of the problem for the deviations variables. Another relevant contribution from this work is that the corrective terms in the upscaled models for heat and mass transport in porous media are no longer interpreted as convective-like terms. This is because this terminology may be misleading. A clear evidence of this is heat transfer in a composite system where, at least, one of the two phases is a solid, where convection cannot be a transport mechanism.

As a final note, the results from this work suggest that it is advisable to use Green's formula to relate the closure variables involved in upscaled models, as, in some cases, this can lead to simplifications which have a formal exact basis that avoids using orders of magnitude

estimates. This conclusion is applicable to models resulting from both the volume averaging and the homogenization methods. Of course, if there is interest to further simplify an upscaled model, orders of magnitude estimates may be used with caution, and should be verified whenever possible (see, for example, Appendix A in Valdés-Parada et al., 2020). Finally, it is worth recalling that this work is constrained to the bulk of a homogeneous porous medium. In other words, if the porosity exhibits spatial variations, the conclusions reached here may be revisited.

CRediT authorship contribution statement

Didier Lasseux: Writing – review & editing, Writing – original draft, Methodology, Conceptualization. **Francisco J. Valdés-Parada:** Writing – review & editing, Writing – original draft, Software.

Declaration of competing interest

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

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Data reported in this manuscript are all available upon request to the authors.

Appendix A. Upscaling diffusion and reaction using periodic homogenization

The purpose of this appendix is to derive an upscaled model for diffusion and first-order heterogeneous reaction that is not limited to vanishingly small values of the Damköhler number using periodic homogenization. To this end reconsider the pore-scale problem given in Eqs. (1) in the main text, which can be rewritten in the following dimensionless form

$$\frac{Da}{\epsilon^2}\frac{\partial c^*}{\partial t^*} = \nabla^{*2} c^*, \quad \text{in } \mathscr{V}_\beta, \tag{A.1a}$$

$$\text{B.C.} \quad -\mathbf{n}\cdot\nabla^* c^* = \frac{Da}{\epsilon} c^*, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{A.1b}$$

using the following definitions

$$c^* = \frac{c}{c_{ref}}, \quad \nabla^* = L\nabla, \quad t^* = \frac{t}{t^r_{ref}}, \quad Da = \frac{k\ell_\beta}{\mathscr{D}},$$

$$\epsilon = \frac{\ell_\beta}{L}. \tag{A.2}$$

Note that, contrary to previous studies of homogenization of diffusion and heterogeneous reaction (Gerisch et al., 2017; Bourbatache et al., 2021), time was made dimensionless using the characteristic time for reaction. This is convenient since the interest lies in cases in which the characteristic time for diffusion is smaller than the characteristic time for reaction only by a factor of ϵ, this is, $Da = \epsilon$. Taking this estimate into account, Eqs. (A.1) can be further developed by substituting the following expansion for the dimensionless concentration

$$c^* = c_0^* + \epsilon c_1^* + \epsilon^2 c_2^* + \dots, \tag{A.3}$$

and the decomposition $\nabla^* = \nabla^*_{\mathbf{x}} + \epsilon^{-1}\nabla^*_{\mathbf{y}}$, in order to obtain the following set of equations

$$\frac{1}{\epsilon}\frac{\partial}{\partial t^*}(c_0^* + \epsilon c_1^* + \dots) = (\nabla^*_{\mathbf{x}} + \epsilon^{-1}\nabla^*_{\mathbf{y}})\cdot(\nabla^*_{\mathbf{x}} + \epsilon^{-1}\nabla^*_{\mathbf{y}})$$
$$(c_0^* + \epsilon c_1^* + \epsilon^2 c_2^* + \dots), \quad \text{in } \mathscr{V}_\beta, \tag{A.4a}$$

$$\text{B.C.} \quad -\mathbf{n}\cdot(\epsilon^{-1}\nabla^*_{\mathbf{x}} + \epsilon^{-2}\nabla^*_{\mathbf{y}})(c_0^* + \epsilon c_1^* + \epsilon^2 c_2^* + \dots) =$$
$$\epsilon^{-1}(c_0^* + \epsilon c_1^* + \epsilon^2 c_2^* + \dots), \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{A.4b}$$

$$c_j^*(\mathbf{r}^*) = c_j^*(\mathbf{r}^* + \mathbf{l}_i^*), \quad i = 1,2,3; j = 0,1,2,3,\dots. \tag{A.4c}$$

Note that the periodicity condition was incorporated in order to complete the problem statement. It is worth mentioning that the operator $\nabla^*_{\mathbf{x}}$ captures the spatial variations of slow-changing variables (such as macroscale variables), whereas the operator $\nabla^*_{\mathbf{y}}$ captures the spatial variations of rapid-changing variables (such as microscale variables). From the above problem, a series of boundary-value sub-problems can be extracted at the successive orders in ϵ. At the largest order (*i.e.*, at $\mathbf{O}(\epsilon^{-2})$), the resulting problem is

Problem at $\mathbf{O}(\epsilon^{-2})$

$$0 = \nabla^{*2}_{\mathbf{y}} c_0^*, \quad \text{in } \mathscr{V}_\beta, \tag{A.5a}$$

$$\text{B.C.} \quad -\mathbf{n}\cdot\nabla^*_{\mathbf{y}} c_0^* = 0, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{A.5b}$$

$$c_0^*(\mathbf{r}^*) = c_0^*(\mathbf{r}^* + \mathbf{l}_i^*), \quad i = 1,2,3. \tag{A.5c}$$

This problem leads to the conclusion that c_0^* is a macroscale variable, *i.e.*, $c_0^*(\mathbf{x}^*, \mathbf{y}^*, t^*) = c_0^*(\mathbf{x}^*, t^*)$. Moving on to the problem at the next order in ϵ, the following problem results

Problem at $\mathbf{O}(\epsilon^{-1})$

$$\frac{\partial c_0^*}{\partial t^*} = \nabla^*_{\mathbf{y}}\cdot(\nabla^*_{\mathbf{x}} c_0^* + \nabla^*_{\mathbf{y}} c_1^*), \quad \text{in } \mathscr{V}_\beta, \tag{A.6a}$$

$$\text{B.C.} \quad -\mathbf{n}\cdot(\nabla^*_{\mathbf{x}} c_0^* + \nabla^*_{\mathbf{y}} c_1^*) = c_0^*, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{A.6b}$$

$$c_1^*(\mathbf{r}^*) = c_1^*(\mathbf{r}^* + \mathbf{l}_i^*), \quad i = 1,2,3. \tag{A.6c}$$

At first glance, this problem has three source terms and the compatibility between the differential equation and the interfacial boundary condition does not seem obvious. The latter can be overcome by applying the intrinsic averaging operator to Eq. (A.6a), which, together with the divergence theorem and the boundary conditions, leads to

$$\frac{\partial c_0^*}{\partial t^*} = -\frac{A^*_{\beta\sigma} c_0^*}{V^*_\beta} = -\frac{a_v^* c_0^*}{\phi}. \tag{A.7}$$

Substitution of this result into Eq. (A.6a), yields

$$-\frac{a_v^* c_0^*}{\phi} = \nabla^*_{\mathbf{y}}\cdot(\nabla^*_{\mathbf{x}} c_0^* + \nabla^*_{\mathbf{y}} c_1^*), \quad \text{in } \mathscr{V}_\beta. \tag{A.8}$$

With this expression, it is now clear that the problem has only two source terms, namely c_0^* and $\nabla^*_{\mathbf{x}} c_0^*$, and the differential equation is compatible with the interfacial boundary condition. Since the problem is linear, its formal solution can be written as

$$c_1^*(\mathbf{x}^*, \mathbf{y}^*, t^*) = \mathbf{b}^*(\mathbf{y}^*)\cdot\nabla^*_{\mathbf{x}} c_0^*(\mathbf{x}^*, t^*) + s_1^*(\mathbf{y}^*) c_0^*(\mathbf{x}^*, t^*)$$
$$+ \langle c_1^*\rangle^\beta(\mathbf{x}^*, t^*). \tag{A.9}$$

Here, $\mathbf{b}^*$ and s_1^* are closure variables that solve the following problems

Problem $\mathbf{b}^*$

$$\mathbf{0} = \nabla^{*2}_{\mathbf{y}}\mathbf{b}^*, \quad \text{in } \mathscr{V}_\beta, \tag{A.10a}$$

$$-\mathbf{n}\cdot\left(\mathbf{I} + \nabla^*_{\mathbf{y}}\mathbf{b}^*\right) = \mathbf{0}, \quad \text{in } \mathscr{A}_{\beta\sigma}, \tag{A.10b}$$

$$\mathbf{b}^*(\mathbf{r}^*) = \mathbf{b}^*(\mathbf{r}^* + \mathbf{l}_i^*), \quad i = 1,2,3, \tag{A.10c}$$

$$\langle\mathbf{b}^*\rangle^\beta = \mathbf{0}. \tag{A.10d}$$

Problem s_1^*

$$\nabla^{*2}_{\mathbf{y}} s_1^* = -\frac{a_v^*}{\phi}, \quad \text{in } \mathscr{V}_\beta, \tag{A.11a}$$

$$-\mathbf{n}\cdot\nabla^*_{\mathbf{y}} s_1^* = 1, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{A.11b}$$

$$s_1^*(\mathbf{r}^*) = s_1^*(\mathbf{r}^* + \mathbf{l}_i^*), \quad i = 1,2,3, \tag{A.11c}$$

$$\langle s_1^* \rangle^\beta = 0. \tag{A.11d}$$

This last problem corresponds to the closure problem given in equations (81)–(84) in Valdés-Parada et al. (2017) for $j = 1$. In addition, *Problem* $\mathbf{b}^*$ is the dimensionless version of the closure problem for passive diffusion in homogeneous porous media (Whitaker, 1999).

Finally, the problem at order ϵ^0 is given by

Problem at $\mathbf{O}(\epsilon^0)$

$$\frac{\partial c_1^*}{\partial t^*} = \nabla_{\mathbf{y}}^* \cdot \left(\nabla_{\mathbf{x}}^* c_1^* + \nabla_{\mathbf{y}}^* c_2^* \right)$$
$$+ \nabla_{\mathbf{x}}^* \cdot \left(\nabla_{\mathbf{x}}^* c_0^* + \nabla_{\mathbf{y}}^* c_1^* \right), \quad \text{in } \mathscr{V}_\beta, \tag{A.12a}$$
$$- \mathbf{n} \cdot \left(\nabla_{\mathbf{x}}^* c_1^* + \nabla_{\mathbf{y}}^* c_2^* \right) = c_1^*, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{A.12b}$$
$$c_2^*(\mathbf{r}^*) = c_2^*(\mathbf{r}^* + \mathbf{l}_i^*), \quad i = 1, 2, 3. \tag{A.12c}$$

Application of the intrinsic averaging operator to Eq. (A.12a), using the divergence theorem and the corresponding boundary conditions, leads to

$$\frac{\partial \langle c_1^* \rangle^\beta}{\partial t^*} = \nabla_{\mathbf{x}}^* \cdot \left(\nabla_{\mathbf{x}}^* c_0^* + \langle \nabla_{\mathbf{y}}^* c_1^* \rangle^\beta \right) - \frac{1}{V_\beta^*} \int_{\mathscr{A}_{\beta\sigma}} c_1^* \, dA^*. \tag{A.13}$$

After substitution of the formal solution given in Eq. (A.9), this last equation yields

$$\frac{\partial \langle c_1^* \rangle^\beta}{\partial t^*} = \nabla_{\mathbf{x}}^* \cdot \left(\langle \mathbf{I} + \nabla_{\mathbf{y}}^* \mathbf{b}^* \rangle^\beta \cdot \nabla_{\mathbf{x}}^* c_0^* \right) - \frac{1}{V_\beta^*} \int_{\mathscr{A}_{\beta\sigma}} s_1^* \, dA^* c_0^*$$
$$- \frac{a_v^* \langle c_1^* \rangle^\beta}{\phi} + \left(\langle \nabla_{\mathbf{y}}^* s_1^* \rangle^\beta - \frac{1}{V_\beta^*} \int_{\mathscr{A}_{\beta\sigma}} \mathbf{b}^* \, dA^* \right) \cdot \nabla_{\mathbf{x}}^* c_0^*. \tag{A.14}$$

Defining $c^* = c_0^* + \epsilon c_1^* + \mathbf{O}(\epsilon^2)$, the macroscopic model, approximated at $\mathbf{O}(\epsilon^2)$, can be formed by adding the above equation, pre-multiplied by ϵ, to Eq. (A.7). The resulting equation can be written as

$$\frac{\partial \langle c^* \rangle^\beta}{\partial t^*} = \epsilon \nabla_{\mathbf{x}}^* \cdot \left(\mathbf{D}_{eff}^* \cdot \nabla_{\mathbf{x}}^* \langle c^* \rangle^\beta \right) - \frac{a_v^* k_{eff}^* \langle c^* \rangle^\beta}{\phi}$$
$$+ \epsilon \mathbf{u}^* \cdot \nabla_{\mathbf{x}}^* \langle c^* \rangle^\beta. \tag{A.15}$$

The dimensional version of the above equation has the same structure as the one given in Eq. (16) in the main text for a first-order reaction. In the above equation, the following definitions were employed

$$\mathbf{D}_{eff}^* = \frac{\mathbf{D}_{eff}}{\mathscr{D}} = \langle \mathbf{I} + \nabla_{\mathbf{y}}^* \mathbf{b}^* \rangle^\beta, \tag{A.16a}$$
$$k_{eff}^* = \frac{k_{eff}}{k} = 1 + \frac{\epsilon}{A_{\beta\sigma}^*} \int_{\mathscr{A}_{\beta\sigma}} s_1^* \, dA^*, \tag{A.16b}$$
$$\mathbf{u}^* = \frac{\mathbf{u}}{k} = \langle \nabla_{\mathbf{y}}^* s_1^* \rangle^\beta - \frac{1}{V_\beta^*} \int_{\mathscr{A}_{\beta\sigma}} \mathbf{b}^* \, dA^*. \tag{A.16c}$$

To simplify Eq. (A.15), Green's formula can be used in the form given in Eq. (18) taking $a = s_1^*$ and $\mathbf{a} = \mathbf{b}^*$. Performing the corresponding substitutions, it results that

$$\mathbf{0} = \int_{\mathscr{A}_{\beta\sigma}} (-\mathbf{n} s_1^* + \mathbf{b}^*) \, dA^*. \tag{A.17}$$

Use of the divergence theorem on the first term leads to the conclusion that $\mathbf{u}^* = \mathbf{0}$ and this allows simplifying Eq. (A.15) to

$$\frac{\partial \langle c^* \rangle^\beta}{\partial t^*} = \epsilon \nabla_{\mathbf{x}}^* \cdot \left(\mathbf{D}_{eff}^* \cdot \nabla_{\mathbf{x}}^* \langle c^* \rangle^\beta \right) - \frac{a_v^* k_{eff}^* \langle c^* \rangle^\beta}{\phi}. \tag{A.18}$$

The dimensional version of the above equation corresponds to Eq. (94) in Valdés-Parada et al. (2017) for $m = 1$.

Appendix B. Mass dispersion coupled to a linear first order heterogeneous reaction

In this appendix, the case of mass diffusion and advection of a single chemical species of local molar concentration c, coupled to a first-order linear heterogeneous reaction is reinspected. This problem has been explored in detail by Valdés-Parada et al. (2020) considering a Navier-type slip boundary condition at the solid–fluid interface and the macroscopic model in the general case takes the following form

$$\frac{\partial \langle c \rangle^\beta}{\partial t} + \mathbf{v}_{eff} \cdot \nabla \langle c \rangle^\beta = \mathbf{D}^* : \nabla \nabla \langle c \rangle^\beta - k_{eff} a_v \epsilon^{-1} \langle c \rangle^\gamma, \tag{B.1a}$$

where $\mathbf{D}^*$, $\mathbf{v}_{eff}$ and k_{eff} are the effective dispersion tensor, convective velocity and reaction rate respectively given by

$$\mathbf{D}^* = \mathscr{D} \left(\mathbf{I} + \frac{1}{V_\beta} \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} \mathbf{b} \, dA \right) - \langle \mathbf{v} \mathbf{b} \rangle^\beta, \tag{B.1b}$$
$$\mathbf{v}_{eff} = \langle \mathbf{v} \rangle^\beta + \langle \tilde{\mathbf{v}} s \rangle^\beta - \frac{\mathscr{D}}{V_\beta} \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} s \, dA + \frac{k}{V_\beta} \int_{\mathscr{A}_{\beta\sigma}} \mathbf{b} \, dA, \tag{B.1c}$$
$$k_{eff} = \frac{k}{A_{\beta\sigma}} \int_{\mathscr{A}_{\beta\sigma}} s \, dA, \tag{B.1d}$$

with k being the reaction rate at the pore scale. In these expressions, the vector $\mathbf{b}$ and scalar s are closure variables that solve the following closure problems

Problem $\mathbf{b}$

$$\tilde{\mathbf{v}} + \mathbf{v} \cdot \nabla \mathbf{b} = \mathscr{D} \nabla^2 \mathbf{b} + \frac{k}{V_\beta} \int_{\mathscr{A}_{\beta\sigma}} \mathbf{b} \, dA, \quad \text{in } \mathscr{V}_\beta, \tag{B.2a}$$
$$- \mathbf{n} \cdot \mathscr{D} \nabla \mathbf{b} - k \mathbf{b} = \mathbf{n} \mathscr{D}, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{B.2b}$$
$$\mathbf{b}(\mathbf{r} + \mathbf{l}_i) = \mathbf{b}(\mathbf{r}), \quad i = 1, 2, 3, \tag{B.2c}$$
$$\langle \mathbf{b} \rangle^\beta = \mathbf{0}. \tag{B.2d}$$

Problem s

$$\mathbf{v} \cdot \nabla s = \mathscr{D} \nabla^2 s + \frac{k}{V_\beta} \int_{\mathscr{A}_{\beta\sigma}} s \, dA, \quad \text{in } \mathscr{V}_\beta, \tag{B.2e}$$
$$- \mathbf{n} \cdot \mathscr{D} \nabla s = k s, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{B.2f}$$
$$s(\mathbf{r} + \mathbf{l}_i) = s(\mathbf{r}), \quad i = 1, 2, 3, \tag{B.2g}$$
$$\langle s \rangle^\beta = 1. \tag{B.2h}$$

When Green's formula given in Eq. (18) is employed, taking $a = s$ and $\mathbf{a} = \mathbf{b}$, making use of the differential equations and boundary conditions of *Problem* $\mathbf{b}$ and *Problem* s, and after division of the result by V_β, the following relationship is obtained

$$\langle \tilde{\mathbf{v}} s \rangle^\beta + \langle s \mathbf{v} \cdot \nabla \mathbf{b} \rangle^\beta - \langle \mathbf{v} \cdot \nabla s \, \mathbf{b} \rangle^\beta =$$
$$\frac{k}{V_\beta} \int_{\mathscr{A}_{\beta\sigma}} \mathbf{b} \, dA - \frac{\mathscr{D}}{V_\beta} \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n} s \, dA. \tag{B.3}$$

The last two terms on the left-hand side of the above equation can be related by noticing that

$$\langle \nabla \cdot (s \mathbf{v} \mathbf{b}) \rangle^\beta = \langle s \nabla \cdot \mathbf{v} \, \mathbf{b} \rangle^\beta + \langle \mathbf{v} \cdot \nabla s \, \mathbf{b} \rangle^\beta + \langle s \mathbf{v} \cdot \nabla \mathbf{b} \rangle^\beta. \tag{B.4}$$

Since flow in the β-phase is assumed incompressible, the first term on the right-hand side of this last equation is zero. Moreover, by making use of the divergence theorem and taking into account the fact that $\mathscr{A}_{\beta\sigma}$ is impervious and that $s\mathbf{v}\mathbf{b}$ is periodic, the left-hand side of this equation is also zero and, therefore,

$$\langle \mathbf{v} \cdot \nabla s \, \mathbf{b} \rangle^\beta = - \langle s \mathbf{v} \cdot \nabla \mathbf{b} \rangle^\beta. \tag{B.5}$$

When this result, together with Eq. (B.3), are substituted back into Eq. (B.1c), the expression of $\mathbf{v}_{eff}$ takes the following form

$$\mathbf{v}_{eff} = \langle \mathbf{v} \rangle^\beta + 2 \langle s \left(\tilde{\mathbf{v}} + \mathbf{v} \cdot \nabla \mathbf{b} \right) \rangle^\beta. \tag{B.6}$$

This alternative expression of $\mathbf{v}_{eff}$ shows that the effective convective velocity explicitly contains the influence of diffusion and reaction. In the absence of convection ($\mathbf{v} = \mathbf{0}$), $\mathbf{v}_{eff} = \mathbf{0}$, in agreement with the result developed in Section 2.1 (see Eq. (20) and the ensuing conclusion). In the absence of reaction ($k = 0$), the solution to the closure problem for s is $s = 1$. Consequently, since $\langle \tilde{\mathbf{v}} \rangle^\beta = \mathbf{0}$ and due to Eq. (B.2h), $\mathbf{v}_{eff} = \langle \mathbf{v} \rangle^\beta + 2 \langle \mathbf{v} \cdot \nabla \mathbf{b} \rangle^\beta$. However, $\langle \mathbf{v} \cdot \nabla \mathbf{b} \rangle^\beta = \langle \nabla \cdot (\mathbf{v} \mathbf{b}) \rangle^\beta = \mathbf{0}$, due the solenoidal character of $\mathbf{v}$, as well as the periodicity of the product $\mathbf{v}\mathbf{b}$ and the fact that $\mathscr{A}_{\beta\sigma}$ is impervious. Therefore, $\mathbf{v}_{eff} = \langle \mathbf{v} \rangle^\beta$ in the case of

dispersion without reaction, a result in agreement with the macroscopic model for this mass transfer process reported in the literature (see, for example Whitaker, 1999; Auriault et al., 2009).

Appendix C. Simplifications of the reaction rate for single and two-species transport

The purpose of this appendix is to provide some details of the simplifications involved in the treatment of the non-linear reaction rate term present in the analysis of single and two-species mass transport. The Taylor series expansion given in Eq. (6b) can be written as

$$R|_c = \mathcal{R} + \mathcal{R}'\tilde{c} + \mathbf{O}\left(\mathcal{R}''\tilde{c}^2\right), \tag{C.1}$$

with the definition $\mathcal{R}'' \equiv \left.\frac{\partial^2 R}{\partial c^2}\right|_{\langle c\rangle^\beta}$. A sufficient assumption to keep only the first two terms in the above expansion is the following one

$$\mathbf{O}\left(\mathcal{R}''\tilde{c}\right) \ll \mathcal{R}'. \tag{C.2}$$

In the applications considered in this work, it is reasonable to assume that $\tilde{c}$ is, at most, of the same order of magnitude as $\langle c\rangle^\beta$. Hence, the above expression can also be written as

$$\mathbf{O}\left(\mathcal{R}''\langle c\rangle^\beta\right) \ll \mathcal{R}', \tag{C.3}$$

in which the term in the left-hand side is probably overestimated. In the following paragraphs this information is used to make simplifications in the derivations used for single and two-species transport.

C.1. Single species mass transport

In the derivation of Eq. (13), the factor $\nabla(\mathcal{R}/\mathcal{R}')$ results, which can be developed as follows

$$\nabla\left(\frac{\mathcal{R}}{\mathcal{R}'}\right) = \frac{\nabla\mathcal{R}}{\mathcal{R}'} - \frac{\mathcal{R}}{\mathcal{R}'^2}\nabla\mathcal{R}'. \tag{C.4}$$

After using the chain rule of derivation, this can be written as

$$\nabla\left(\frac{\mathcal{R}}{\mathcal{R}'}\right) = \frac{\nabla\mathcal{R}}{\mathcal{R}'} - \frac{\mathcal{R}}{\mathcal{R}'^2}\mathcal{R}''\nabla\langle c\rangle^\beta. \tag{C.5}$$

To simplify this equation, the following orders of magnitude estimates are proposed:

$$\frac{\nabla\mathcal{R}}{\mathcal{R}'} = \mathbf{O}\left(\frac{\mathcal{R}}{L\mathcal{R}'}\right), \tag{C.6a}$$

$$\frac{\mathcal{R}}{\mathcal{R}'^2}\mathcal{R}''\nabla\langle c\rangle^\beta = \mathbf{O}\left(\frac{\mathcal{R}}{L\mathcal{R}'}\frac{\mathcal{R}''\langle c\rangle^\beta}{\mathcal{R}'}\right). \tag{C.6b}$$

Hence, on the basis of the assumption given in (C.3), it is reasonable to also assume that

$$\frac{\mathcal{R}}{\mathcal{R}'^2}\mathcal{R}''\nabla\langle c\rangle^\beta \ll \frac{\nabla\mathcal{R}}{\mathcal{R}'}, \tag{C.7}$$

and consequently simplify Eq. (C.5) to

$$\nabla\left(\frac{\mathcal{R}}{\mathcal{R}'}\right) = \frac{\nabla\mathcal{R}}{\mathcal{R}'}. \tag{C.8}$$

This result was considered in writing Eq. (13) in the main text.

C.2. Two-species mass transport

The derivation of Eqs. (26) commences by respectively multiplying Eq. (22a) by $\mathcal{R}'_A$ and Eq. (22b) by $\mathcal{R}'_B$. This is,

$$\mathcal{R}'_\alpha\frac{\partial c_\alpha}{\partial t} = \mathscr{D}\mathcal{R}'_\alpha\nabla^2 c_\alpha, \quad \text{in } \mathscr{V}_\beta, \quad \alpha = A, B. \tag{C.9}$$

Focusing for the moment on the accumulation term, the following identity is applicable

$$\mathcal{R}'_\alpha\frac{\partial c_\alpha}{\partial t} = \frac{\partial\mathcal{R}'_\alpha c_\alpha}{\partial t} - c_\alpha\frac{\partial\mathcal{R}'_\alpha}{\partial t}, \tag{C.10}$$

or, after using the chain rule of derivation,

$$\mathcal{R}'_\alpha\frac{\partial c_\alpha}{\partial t} = \frac{\partial\mathcal{R}'_\alpha c_\alpha}{\partial t} - c_\alpha\mathcal{R}''_\alpha\frac{\partial\langle c\rangle^\beta}{\partial t}, \tag{C.11}$$

where $\mathcal{R}''_\alpha \equiv \left.\frac{\partial^2 R_\alpha}{\partial c_\alpha^2}\right|_{\langle c_\alpha\rangle^\alpha}$. To simplify this equation, the following orders of magnitude estimates are proposed

$$\mathcal{R}'_\alpha\frac{\partial c_\alpha}{\partial t} = \mathbf{O}\left(\frac{\mathcal{R}'_\alpha c_\alpha}{t_c}\right), \tag{C.12a}$$

$$c_\alpha\mathcal{R}''_\alpha\frac{\partial\langle c\rangle^\beta}{\partial t} = \mathbf{O}\left(\frac{\mathcal{R}''_\alpha c_\alpha\langle c\rangle^\beta}{t_{\langle c\rangle^\beta}}\right). \tag{C.12b}$$

In the above expressions, $t_c = \mathbf{O}(\ell_\beta^2/\mathscr{D})$ and $t_{\langle c\rangle^\beta} = \mathbf{O}(L^2/\mathscr{D})$ respectively represent the characteristic times related to species mass transport at the microscale and macroscale. On the basis of the following inequality

$$\frac{\ell_\beta^2}{L^2}\mathcal{R}''_\alpha\langle c\rangle^\beta \ll \mathcal{R}'_\alpha, \tag{C.13}$$

it is reasonable to assume that

$$c_\alpha\mathcal{R}''_\alpha\frac{\partial\langle c\rangle^\beta}{\partial t} \ll \mathcal{R}'_\alpha\frac{\partial c_\alpha}{\partial t}, \tag{C.14}$$

and thus, simplify Eq. (C.11) to

$$\mathcal{R}'_\alpha\frac{\partial c_\alpha}{\partial t} = \frac{\partial\mathcal{R}'_\alpha c_\alpha}{\partial t}. \tag{C.15}$$

In this way, Eq. (C.9) takes the following form

$$\frac{\partial\mathcal{R}'_\alpha c_\alpha}{\partial t} = \mathscr{D}\mathcal{R}'_\alpha\nabla^2 c_\alpha, \quad \text{in } \mathscr{V}_\beta, \quad \alpha = A, B. \tag{C.16}$$

Directing now the attention to the diffusive transport term, the following identity applies

$$\mathscr{D}\mathcal{R}'_\alpha\nabla^2 c_\alpha = \mathscr{D}\left[\nabla^2(\mathcal{R}'_\alpha c_\alpha) - 2\nabla c_\alpha\cdot\nabla\mathcal{R}'_\alpha - c_\alpha\nabla^2\mathcal{R}'_\alpha\right]. \tag{C.17}$$

After using the chain's rule of derivation, this yields,

$$\begin{aligned}\mathscr{D}\mathcal{R}'_\alpha\nabla^2 c_\alpha = \mathscr{D}\Big[&\nabla^2(\mathcal{R}'_\alpha c_\alpha) - 2\mathcal{R}''_\alpha\nabla\langle c\rangle^\beta\cdot\nabla c_\alpha \\ &- c_\alpha\mathcal{R}''_\alpha\nabla^2\langle c\rangle^\beta - c_\alpha\mathcal{R}'''_\alpha\|\nabla\langle c\rangle^\beta\|^2\Big],\end{aligned} \tag{C.18}$$

To simplify this equation, the following orders of magnitude estimates are proposed

$$\mathscr{D}\mathcal{R}'_\alpha\nabla^2 c_\alpha = \mathbf{O}\left(\frac{\mathscr{D}\mathcal{R}'_\alpha c_\alpha}{\ell_\beta^2}\right), \tag{C.19a}$$

$$\mathscr{D}\mathcal{R}''_\alpha\nabla\langle c\rangle^\beta\cdot\nabla c_\alpha = \mathbf{O}\left(\frac{\mathscr{D}\mathcal{R}''_\alpha c_\alpha\langle c\rangle^\beta}{\ell_\beta L}\right), \tag{C.19b}$$

$$\mathscr{D}c_\alpha\mathcal{R}''_\alpha\nabla^2\langle c\rangle^\beta = \mathbf{O}\left(\frac{\mathscr{D}\mathcal{R}''_\alpha c_\alpha\langle c\rangle^\beta}{L^2}\right), \tag{C.19c}$$

$$\mathscr{D}c_\alpha\mathcal{R}'''_\alpha\|\nabla\langle c\rangle^\beta\|^2 = \mathbf{O}\left(\frac{\mathscr{D}\mathcal{R}'''_\alpha c_\alpha(\langle c\rangle^\beta)^2}{L^2}\right). \tag{C.19d}$$

Hence, on the basis of the following inequalities

$$\frac{\ell_\beta}{L}\mathcal{R}''_\alpha\langle c\rangle^\beta \ll \mathcal{R}'_\alpha, \tag{C.20a}$$

$$\frac{\ell_\beta^2}{L^2}\mathcal{R}'''_\alpha(\langle c\rangle^\beta)^2 \ll \mathcal{R}'_\alpha, \tag{C.20b}$$

Eq. (C.18) reduces to

$$\mathscr{D}\mathcal{R}'_\alpha\nabla^2 c_\alpha = \mathscr{D}\nabla^2(\mathcal{R}'_\alpha c_\alpha), \tag{C.21}$$

and thus Eq. (C.16) gives rise to the following balance equations

$$\frac{\partial\mathcal{R}'_A c_A}{\partial t} = \mathscr{D}\nabla^2(\mathcal{R}'_A c_A), \quad \text{in } \mathscr{V}_\beta, \tag{C.22a}$$

$$\frac{\partial\mathcal{R}'_B c_B}{\partial t} = \mathscr{D}\nabla^2(\mathcal{R}'_B c_B), \quad \text{in } \mathscr{V}_\beta. \tag{C.22b}$$

Subtracting Eq. (C.22b) to Eq. (C.22a), recalling the definition given in Eq. (24b), allows retrieving Eq. (26a) in the main text.

Finally, directing the attention to the interfacial boundary conditions, the expression resulting from adding Eq. (22c), premultiplied by $\mathcal{R}'_A$ and Eq. (22d), premultiplied by $-\mathcal{R}'_B$, taking into account the

approximations given in Eqs. (23b), can be written as

$$\text{B.C.,} -\mathbf{n}\cdot\mathscr{D}\left(\mathcal{R}'_A\nabla c_A-\mathcal{R}'_B\nabla c_B\right)=\mathcal{R}_+\mathcal{R}_-+\mathcal{R}_+\tilde{\zeta},\quad\text{at }\mathscr{A}_{\beta\sigma},\tag{C.23}$$

in which $\mathcal{R}_+$ and $\mathcal{R}_-$ are given by Eqs. (27), whereas $\tilde{\zeta}$ follows from the definition of ζ provided in Eq. (24b), *i.e.*, $\tilde{\zeta}=\mathcal{R}'_A\tilde{c}_A-\mathcal{R}'_B\tilde{c}_B$. To further simplify this result, it is convenient to note the following identity

$$\mathcal{R}'_\alpha\nabla c_\alpha=\nabla(\mathcal{R}'_\alpha c_\alpha)-c_\alpha\nabla\mathcal{R}'_\alpha,\tag{C.24}$$

or, after application of the chain rule of derivation,

$$\mathcal{R}'_\alpha\nabla c_\alpha=\nabla(\mathcal{R}'_\alpha c_\alpha)-c_\alpha\mathcal{R}''_\alpha\nabla\langle c\rangle^\beta.\tag{C.25}$$

At this point, the following order of magnitude estimates are proposed

$$\mathcal{R}'_\alpha\nabla c_\alpha=\mathbf{O}\left(\frac{\mathcal{R}'_\alpha c_\alpha}{\ell_\beta}\right),\tag{C.26a}$$

$$c_\alpha\mathcal{R}''_\alpha\nabla\langle c\rangle^\beta=\mathbf{O}\left(\frac{\mathcal{R}''_\alpha c_\alpha\langle c\rangle^\beta}{L}\right).\tag{C.26b}$$

Hence, on the basis of the constraint expressed in (C.20a), Eq. (C.24) reduces to

$$\mathcal{R}'_\alpha\nabla c_\alpha=\nabla(\mathcal{R}'_\alpha c_\alpha).\tag{C.27}$$

Consequently, Eq. (C.23) takes the form given in Eq. (26b) in the main text.

Appendix D. Symmetry and positiveness of the effective heat conduction tensors

This appendix is dedicated to the proof that the four effective heat conduction tensors given in Eqs. (35a) to (35b) are positive (and symmetric). To this aim, it is convenient to consider the following Green's formula that is written for any second order tensor $\mathbf{A}$ and vector $\mathbf{a}$, both being sufficiently regular and periodic over the outer boundaries of the volume under consideration

$$\int_{\mathscr{V}_\alpha}\left(\nabla\cdot\mathbf{A}\mathbf{a}+\mathbf{A}^T\cdot\nabla\mathbf{a}\right)dV=\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}_\alpha\cdot\mathbf{A}\mathbf{a}\,dA,\quad\alpha=\beta\text{ or }\sigma.\tag{D.1}$$

Here, $\mathscr{V}_\alpha$ is understood as the domain occupied by the α phase inside the unit cell in which the closure problem given in Eqs. (32) is defined, and $\mathbf{n}_\alpha$ is the unit normal vector at $\mathscr{A}_{\beta\sigma}$ pointing out of $\mathscr{V}_\alpha$.

Considering this formula in $\mathscr{V}_\beta$, taking $\mathbf{A}=\nabla\mathbf{b}_\beta$ and $\mathbf{a}=\mathbf{b}_\beta$, making use of Eqs. (32a), (32b) and (32c) and dividing the resulting equation by V leads to

$$\langle\nabla\mathbf{b}_\beta^T\cdot\nabla\mathbf{b}_\beta\rangle_\beta=\frac{k_\beta}{k_\sigma}\left(\frac{1}{V}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla\mathbf{b}_\sigma\mathbf{b}_\sigma\,dA+\frac{1}{V}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\mathbf{b}_\sigma\,dA\right).\tag{D.2}$$

Repeating the same operation in $\mathscr{V}_\sigma$ with $\mathbf{A}=\nabla\mathbf{b}_\sigma$ and $\mathbf{a}=\mathbf{b}_\sigma$ yields

$$\langle\nabla\mathbf{b}_\sigma^T\cdot\nabla\mathbf{b}_\sigma\rangle_\sigma=-\frac{1}{V}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla\mathbf{b}_\sigma\mathbf{b}_\sigma\,dA.\tag{D.3}$$

In the above two equations, the following definition was used for the superficial averaging operator

$$\langle\cdot\rangle_\alpha=\frac{1}{V}\int_{\mathscr{V}_\alpha}\cdot\,dV,\quad\alpha=\beta,\sigma.\tag{D.4}$$

Substituting Eq. (D.3) into Eq. (D.2), while noticing from the divergence theorem (taking into account the facts that the closure variable and the geometry are assumed periodic) that $\frac{1}{V}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\mathbf{b}_\sigma\,dA=-\langle\nabla\mathbf{b}_\sigma\rangle_\sigma$, and multiplying the result by $\frac{k_\sigma}{k_\beta}$ allows one to write

$$\frac{k_\sigma}{k_\beta}\langle\nabla\mathbf{b}_\beta^T\cdot\nabla\mathbf{b}_\beta\rangle_\beta+\langle\nabla\mathbf{b}_\sigma^T\cdot\nabla\mathbf{b}_\sigma\rangle_\sigma+\langle\nabla\mathbf{b}_\sigma\rangle_\sigma=\mathbf{0}.\tag{D.5}$$

Taking the transpose of the above and adding it to an alternative expression of $\mathbf{K}_{\sigma\sigma}$ which gives $\frac{\phi_\sigma}{k_\sigma}\mathbf{K}_{\sigma\sigma}=\langle\mathbf{I}+\nabla\mathbf{b}_\sigma\rangle_\sigma$, allows writing

$$\frac{\phi_\sigma}{k_\sigma}\mathbf{K}_{\sigma\sigma}=\left\langle\left(\nabla\mathbf{b}_\sigma^T+\mathbf{I}\right)\cdot\left(\nabla\mathbf{b}_\sigma+\mathbf{I}\right)\right\rangle_\sigma+\frac{k_\sigma}{k_\beta}\left\langle\nabla\mathbf{b}_\beta^T\cdot\nabla\mathbf{b}_\beta\right\rangle_\beta.\tag{D.6}$$

This expression clearly shows that $\mathbf{K}_{\sigma\sigma}$ is a symmetric tensor that is also positive since, for any arbitrary constant and non-zero vector λ, $\frac{\phi_\sigma}{k_\sigma}\lambda\cdot\mathbf{K}_{\sigma\sigma}\cdot\lambda=\left\langle\left(\left(\nabla\mathbf{b}_\sigma+\mathbf{I}\right)\cdot\lambda\right)^2\right\rangle_\sigma+\frac{k_\sigma}{k_\beta}\left\langle\left(\nabla\mathbf{b}_\beta\cdot\lambda\right)^2\right\rangle_\beta\geq 0$.

Furthermore, from Eq. (D.5), it is also deduced that

$$\frac{1}{V}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\mathbf{b}_\sigma\,dA=\frac{k_\sigma}{k_\beta}\langle\nabla\mathbf{b}_\beta^T\cdot\nabla\mathbf{b}_\beta\rangle_\beta+\langle\nabla\mathbf{b}_\sigma^T\cdot\nabla\mathbf{b}_\sigma\rangle_\sigma.\tag{D.7}$$

Since the terms on the right-hand side of this equation are symmetric and positive, it can be concluded, from Eq. (35d), that $\mathbf{K}_{\sigma\beta}$ is also symmetric and positive. The demonstrations of symmetry and positiveness for the remaining two effective conductivity tensors is straightforward due to reciprocity between the two phases.

Appendix E. Non-thermal equilibrium heat transfer with interfacial resistance

In this appendix, the problem analyzed in Section 3 is re-examined by considering interfacial heat transfer resistance. This means that the governing equations at the pore-scale (see Eqs. (28)) remain the same, except that Eq. (28b) is changed to

$$\text{B.C.1}\quad-\mathbf{n}\cdot k_\beta\nabla T_\beta=h_i(T_\beta-T_\sigma),\quad\text{at }\mathscr{A}_{\beta\sigma}.\tag{E.1}$$

Here h_i is the pore-scale interfacial heat transfer coefficient that should not be confused with its macroscale counterpart h.

Using the volume averaging method, the same unclosed model given in Eqs. (29) is obtained. Furthermore, the quasi-steady Eqs. (30) governing the fields of $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ are still valid under the same time-scale constraint expressed just before Eqs. (30), with the exception that Eq. (30b) is replaced by

$$\text{B.C.1}\quad-\mathbf{n}\cdot k_\beta\nabla\tilde{T}_\beta=h_i(\tilde{T}_\beta-\tilde{T}_\sigma)+\mathbf{n}\cdot k_\beta\nabla\langle T_\beta\rangle^\beta+h_i\left(\langle T_\beta\rangle^\beta-\langle T_\sigma\rangle^\sigma\right),\quad\text{at }\mathscr{A}_{\beta\sigma}.\tag{E.2}$$

Since there are now three source terms for the temperature deviations, the formal solution of the linear problem for $\tilde{T}_\beta$ and $\tilde{T}_\sigma$ is given by

$$\tilde{T}_\beta=\mathbf{b}_{\beta\beta}\cdot\nabla\langle T_\beta\rangle^\beta+\mathbf{b}_{\beta\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma-s_\beta\left(\langle T_\beta\rangle^\beta-\langle T_\sigma\rangle^\sigma\right),\tag{E.3a}$$

$$\tilde{T}_\sigma=\mathbf{b}_{\sigma\beta}\cdot\nabla\langle T_\beta\rangle^\beta+\mathbf{b}_{\sigma\sigma}\cdot\nabla\langle T_\sigma\rangle^\sigma+s_\sigma\left(\langle T_\beta\rangle^\beta-\langle T_\sigma\rangle^\sigma\right).\tag{E.3b}$$

The new closure variables $\mathbf{b}_{\alpha\alpha}$ and s_α ($\alpha=\beta,\sigma$) solve the following boundary-value problems in a periodic unit cell

Problem $\mathbf{b}_{\beta\beta}$, $\mathbf{b}_{\sigma\beta}$

$$\mathbf{0}=\nabla^2\mathbf{b}_{\beta\beta}-\frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla\mathbf{b}_{\beta\beta}\,dA,\quad\text{in }\mathscr{V}_\beta,\tag{E.4a}$$

$$\text{B.C.1}\quad-\mathbf{n}\cdot k_\beta\nabla\mathbf{b}_{\beta\beta}=h_i(\mathbf{b}_{\beta\beta}-\mathbf{b}_{\sigma\beta})+k_\beta\mathbf{n},\quad\text{at }\mathscr{A}_{\beta\sigma},\tag{E.4b}$$

$$\text{B.C.2}\quad-\mathbf{n}\cdot k_\beta\nabla\mathbf{b}_{\beta\beta}=-\mathbf{n}\cdot k_\sigma\nabla\mathbf{b}_{\sigma\beta}+k_\beta\mathbf{n},\quad\text{at }\mathscr{A}_{\beta\sigma},\tag{E.4c}$$

$$\mathbf{0}=\nabla^2\mathbf{b}_{\sigma\beta}+\frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla\mathbf{b}_{\sigma\beta}\,dA,\quad\text{in }\mathscr{V}_\sigma,\tag{E.4d}$$

$$\mathbf{b}_{\alpha\beta}(\mathbf{r})=\mathbf{b}_{\alpha\beta}(\mathbf{r}+\mathbf{l}_i),\quad i=1,2,3,\alpha=\beta,\sigma,\tag{E.4e}$$

$$\langle\mathbf{b}_{\alpha\beta}\rangle^\alpha=\mathbf{0},\quad\alpha=\beta,\sigma.\tag{E.4f}$$

Problem $\mathbf{b}_{\beta\sigma}$, $\mathbf{b}_{\sigma\sigma}$

$$\mathbf{0}=\nabla^2\mathbf{b}_{\beta\sigma}-\frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla\mathbf{b}_{\beta\sigma}\,dA,\quad\text{in }\mathscr{V}_\beta,\tag{E.5a}$$

$$\text{B.C.1}\quad-\mathbf{n}\cdot k_\beta\nabla\mathbf{b}_{\beta\sigma}=h_i(\mathbf{b}_{\beta\sigma}-\mathbf{b}_{\sigma\sigma}),\quad\text{at }\mathscr{A}_{\beta\sigma},\tag{E.5b}$$

$$\text{B.C.2}\quad-\mathbf{n}\cdot k_\beta\nabla\mathbf{b}_{\beta\sigma}=-\mathbf{n}\cdot k_\sigma\nabla\mathbf{b}_{\sigma\sigma}-k_\sigma\mathbf{n},\quad\text{at }\mathscr{A}_{\beta\sigma},\tag{E.5c}$$

$$\mathbf{0}=\nabla^2\mathbf{b}_{\sigma\sigma}+\frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}}\mathbf{n}\cdot\nabla\mathbf{b}_{\sigma\sigma}\,dA,\quad\text{in }\mathscr{V}_\sigma,\tag{E.5d}$$

$$\mathbf{b}_{\alpha\sigma}(\mathbf{r})=\mathbf{b}_{\alpha\sigma}(\mathbf{r}+\mathbf{l}_i),\quad i=1,2,3,\alpha=\beta,\sigma,\tag{E.5e}$$

$$\langle\mathbf{b}_{\alpha\sigma}\rangle^\alpha=\mathbf{0},\quad\alpha=\beta,\sigma.\tag{E.5f}$$

Problem s_β, s_σ

$$0 = \nabla^2 s_\beta - \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla s_\beta \, dA, \quad \text{in } \mathscr{V}_\beta, \tag{E.6a}$$

$$\text{B.C.1 } \mathbf{n}\cdot k_\beta \nabla s_\beta = h_i(1 - s_\beta - s_\sigma), \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{E.6b}$$

$$\text{B.C.2 } -\mathbf{n}\cdot k_\beta \nabla s_\beta = \mathbf{n}\cdot k_\sigma \nabla s_\sigma, \quad \text{at } \mathscr{A}_{\beta\sigma}, \tag{E.6c}$$

$$0 = \nabla^2 s_\sigma + \frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla s_\sigma \, dA, \quad \text{in } \mathscr{V}_\sigma, \tag{E.6d}$$

$$s_\alpha(\mathbf{r}) = s_\alpha(\mathbf{r} + \mathbf{l}_i), \quad i = 1,2,3, \alpha = \beta,\sigma, \tag{E.6e}$$

$$\langle s_\alpha \rangle^\alpha = 0, \quad \alpha = \beta,\sigma. \tag{E.6f}$$

Substitution of the formal solution given in Eqs. (E.3) into the unclosed model expressed in Eqs. (29) leads to a closed model that is exactly the same as that given in Eqs. (34), albeit the effective-medium coefficients are now defined as follows

$$\mathbf{K}_{\beta\beta} = k_\beta\left(\mathbf{I} + \frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\mathbf{b}_{\beta\beta}\, dA\right), \tag{E.7a}$$

$$\mathbf{K}_{\beta\sigma} = \frac{k_\beta}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\mathbf{b}_{\beta\sigma}\, dA, \tag{E.7b}$$

$$\mathbf{K}_{\sigma\sigma} = k_\sigma\left(\mathbf{I} - \frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\mathbf{b}_{\sigma\sigma}\, dA\right), \tag{E.7c}$$

$$\mathbf{K}_{\sigma\beta} = -\frac{k_\sigma}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\mathbf{b}_{\sigma\beta}\, dA, \tag{E.7d}$$

$$\mathbf{u}_{\beta\beta} = \frac{k_\beta}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\left(-\mathbf{I}s_\beta + \nabla\mathbf{b}_{\beta\beta}\right)\, dA, \tag{E.7e}$$

$$\mathbf{u}_{\beta\sigma} = \frac{k_\beta}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\left(\mathbf{I}s_\beta + \nabla\mathbf{b}_{\beta\sigma}\right)\, dA, \tag{E.7f}$$

$$\mathbf{u}_{\sigma\sigma} = -\frac{k_\sigma}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\left(-\mathbf{I}s_\sigma + \nabla\mathbf{b}_{\sigma\sigma}\right)\, dA, \tag{E.7g}$$

$$\mathbf{u}_{\sigma\beta} = -\frac{k_\sigma}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\left(\mathbf{I}s_\sigma + \nabla\mathbf{b}_{\sigma\beta}\right)\, dA, \tag{E.7h}$$

$$h = \frac{k_\beta}{A_{\beta\sigma}}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla s_\beta \, dA = -\frac{k_\sigma}{A_{\beta\sigma}}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot\nabla s_\sigma \, dA. \tag{E.7i}$$

At this point, it is of major interest to investigate the properties that these coefficients satisfy. This is done in the following paragraphs using the same methodology as that applied for the case in which there is no interfacial heat transfer resistance.

E.1. Conduction-corrective coefficients

To begin with, let the attention be focused on the conduction-corrective and co-conduction-corrective coefficients $\mathbf{u}_{\alpha\alpha}$ $(\alpha = \beta,\sigma)$. To do so, consider Green's formula in the form given in Eq. (18) in $\mathscr{V}_\beta$ and take $a = s_\beta$ and $\mathbf{a} = \mathbf{b}_{\beta\beta}$ to obtain, after substituting the corresponding differential equations and boundary conditions

$$\mathbf{0} = \int_{\mathscr{A}_{\beta\sigma}} \left[h_i(s_\beta \mathbf{b}_{\sigma\beta} + s_\sigma \mathbf{b}_{\beta\beta} - \mathbf{b}_{\beta\beta}) - k_\beta \mathbf{n} s_\beta\right]\, dA. \tag{E.8}$$

In addition, using once more Green's formula (Eq. (18)) in $\mathscr{V}_\sigma$ with $a = s_\sigma$ and $\mathbf{a} = \mathbf{b}_{\sigma\beta}$, and making the corresponding substitutions of the governing equations and boundary conditions, the following identity results

$$\int_{\mathscr{A}_{\beta\sigma}} h_i(s_\beta \mathbf{b}_{\sigma\beta} + s_\sigma \mathbf{b}_{\beta\beta})\, dA = \int_{\mathscr{A}_{\beta\sigma}} h_i \mathbf{b}_{\sigma\beta}\, dA. \tag{E.9}$$

Inserting this expression into Eq. (E.8) leads to

$$\int_{\mathscr{A}_{\beta\sigma}} h_i(\mathbf{b}_{\sigma\beta} - \mathbf{b}_{\beta\beta})\, dA = \int_{\mathscr{A}_{\beta\sigma}} k_\beta \mathbf{n} s_\beta \, dA, \tag{E.10}$$

or, after substitution of Eqs. (E.4b) and (E.4c), taking into account the spatial homogeneity assumption, *i.e.*, $\nabla\phi_\beta = -\nabla\phi_\sigma = -\frac{1}{V}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\, dA = \mathbf{0}$,

$$\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot k_\beta \nabla\mathbf{b}_{\beta\beta}\, dA = \int_{\mathscr{A}_{\beta\sigma}} k_\beta \mathbf{n} s_\beta \, dA = \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot k_\sigma \nabla\mathbf{b}_{\beta\sigma}\, dA. \tag{E.11}$$

From the first equality of the above expression and the definition of the dominant conduction-corrective coefficient provided in Eq. (E.7e), it is concluded that $\mathbf{u}_{\beta\beta} = \mathbf{0}$.

Following similar steps to relate the problems given in Eqs. (E.5) and (E.6), it results that

$$\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot k_\sigma \nabla\mathbf{b}_{\sigma\sigma}\, dA = \int_{\mathscr{A}_{\beta\sigma}} k_\sigma \mathbf{n} s_\sigma \, dA = \int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot k_\beta \nabla\mathbf{b}_{\beta\sigma}\, dA. \tag{E.12}$$

As before, substitution of the first equality into Eq. (E.7g) leads to conclude that $\mathbf{u}_{\sigma\sigma} = \mathbf{0}$. Finally, inserting the last equalities of the identities given in Eqs. (E.11) and (E.12), into Eqs. (E.7f) and (E.7h) leads to a relationship similar to that given in Eq. (42) in the main text when there is no interfacial heat transfer resistance, *i.e.*,

$$\phi_\beta \mathbf{u}_{\beta\sigma} = -\phi_\sigma \mathbf{u}_{\sigma\beta} = \frac{1}{V}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\left(k_\beta s_\beta + k_\sigma s_\sigma\right)\, dA. \tag{E.13}$$

E.2. Effective conductivity tensors

The analysis is now dedicated to the coefficients $\mathbf{K}_{\alpha\kappa}$ $(\alpha,\kappa = \beta,\sigma)$ considering Green's formula given by Eq. (D.1). First, let this formula be used in $\mathscr{V}_\beta$ with $\mathbf{A} = \nabla\mathbf{b}_{\beta\beta}$ and $\mathbf{a} = \mathbf{b}_{\beta\beta}$. Taking into account the corresponding differential equations and boundary conditions, in particular the one given by Eq. (E.4c), yields

$$k_\beta \int_{\mathscr{V}_\beta} \nabla\mathbf{b}_{\beta\beta}^T \cdot \nabla\mathbf{b}_{\beta\beta}\, dV = \int_{\mathscr{A}_{\beta\sigma}} \left(\mathbf{n}\cdot k_\sigma \nabla\mathbf{b}_{\sigma\beta} - k_\beta\mathbf{n}\right)\mathbf{b}_{\beta\beta}\, dA. \tag{E.14}$$

Similarly, the same Green's formula is now used in $\mathscr{V}_\sigma$ taking $\mathbf{A} = \nabla\mathbf{b}_{\sigma\beta}$ and $\mathbf{a} = \mathbf{b}_{\sigma\beta}$, leading to

$$k_\sigma \int_{\mathscr{V}_\beta} \nabla\mathbf{b}_{\sigma\beta}^T \cdot \nabla\mathbf{b}_{\sigma\beta}\, dV = -\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\cdot k_\sigma \nabla\mathbf{b}_{\sigma\beta}\mathbf{b}_{\sigma\beta}\, dA. \tag{E.15}$$

Adding the above two relationships, making use of the boundary conditions expressed in Eqs. (E.4b) and (E.4c), dividing the result by V_β and taking the transpose of the ensuing expression, allows writing

$$\begin{aligned}\mathbf{0} =& k_\beta\langle\nabla\mathbf{b}_{\beta\beta}^T\cdot\nabla\mathbf{b}_{\beta\beta}\rangle^\beta + k_\beta\langle\nabla\mathbf{b}_{\beta\beta}^T\rangle^\beta \\ &+ k_\sigma\frac{\phi_\sigma}{\phi_\beta}\langle\nabla\mathbf{b}_{\sigma\beta}^T\cdot\nabla\mathbf{b}_{\sigma\beta}\rangle^\sigma \\ &+ \frac{1}{h_i}\frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\left(\mathbf{n}\cdot k_\sigma\nabla\mathbf{b}_{\sigma\beta}\right)\left(\mathbf{n}\cdot k_\sigma\nabla\mathbf{b}_{\sigma\beta}\right)\, dA,\end{aligned} \tag{E.16}$$

in which it was made use of the fact that $\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\mathbf{b}_{\beta\beta}\, dA = \int_{\mathscr{V}_\beta} \nabla\mathbf{b}_{\beta\beta}\, dV$, as a result of the divergence theorem and periodicity of $\mathbf{b}_{\beta\beta}$. With the same last arguments, $\mathbf{K}_{\beta\beta}$ given in Eq. (E.7a) can alternatively be written as $\mathbf{K}_{\beta\beta} = k_\beta\langle\mathbf{I} + \nabla\mathbf{b}_{\beta\beta}\rangle^\beta$ and when added to Eq. (E.16), the following expression is obtained

$$\begin{aligned}\mathbf{K}_{\beta\beta} =& k_\beta\left\langle\left(\nabla\mathbf{b}_{\beta\beta}^T + \mathbf{I}\right)\cdot\left(\nabla\mathbf{b}_{\beta\beta} + \mathbf{I}\right)\right\rangle^\beta \\ &+ k_\sigma\frac{\phi_\sigma}{\phi_\beta}\langle\nabla\mathbf{b}_{\sigma\beta}^T\cdot\nabla\mathbf{b}_{\sigma\beta}\rangle^\sigma \\ &+ \frac{1}{h_i}\frac{1}{V_\beta}\int_{\mathscr{A}_{\beta\sigma}}\left(\mathbf{n}\cdot k_\sigma\nabla\mathbf{b}_{\sigma\beta}\right)\left(\mathbf{n}\cdot k_\sigma\nabla\mathbf{b}_{\sigma\beta}\right)\, dA.\end{aligned} \tag{E.17}$$

This result clearly indicates that $\mathbf{K}_{\beta\beta}$ is a symmetric positive tensor. Moreover, since all equations reported so far in this appendix satisfy reciprocity between the two phases β and σ, it can be readily concluded that $\mathbf{K}_{\sigma\sigma}$ has the same properties.

Finally, a relationship between $\mathbf{K}_{\beta\sigma}$ and $\mathbf{K}_{\sigma\beta}$ can now be derived, and for this purpose, it is convenient to introduce the following Green's formula between two arbitrary vector fields $\mathbf{u}$ and $\mathbf{v}$ with sufficient regularity and satisfying periodicity on the unit cell $\mathscr{V}$

$$\int_{\mathscr{V}_\alpha}\left(\nabla^2\mathbf{u}\,\mathbf{v} - \mathbf{u}\nabla^2\mathbf{v}\right)\, dV = \int_{\mathscr{A}_{\beta\sigma}}\left(\mathbf{n}_\alpha\cdot\nabla\mathbf{u}\,\mathbf{v} - \mathbf{u}\mathbf{n}_\alpha\cdot\nabla\mathbf{v}\right)\, dA. \tag{E.18}$$

Using this formula in $\mathscr{V}_\beta$ with $\mathbf{u} = k_\beta\mathbf{b}_{\beta\beta}$ and $\mathbf{v} = \mathbf{b}_{\beta\sigma}$, and employing the corresponding differential equations and boundary conditions, yields

$$\int_{\mathscr{A}_{\beta\sigma}} h_i\left(\mathbf{b}_{\sigma\beta}\mathbf{b}_{\beta\sigma} - \mathbf{b}_{\beta\beta}\mathbf{b}_{\sigma\sigma}\right)\, dA = \int_{\mathscr{A}_{\beta\sigma}} k_\beta\mathbf{n}\mathbf{b}_{\beta\sigma}\, dA. \tag{E.19a}$$

Repeating the same procedure, but this time in $\mathscr{V}_\sigma$, taking $\mathbf{u} = k_\sigma \mathbf{b}_{\sigma\beta}$ and $\mathbf{v} = \mathbf{b}_{\sigma\sigma}$, leads to

$$\int_{\mathscr{A}_{\beta\sigma}} h_i \left(\mathbf{b}_{\sigma\beta}\mathbf{b}_{\beta\sigma} - \mathbf{b}_{\beta\beta}\mathbf{b}_{\sigma\sigma}\right) dA = -\int_{\mathscr{A}_{\beta\sigma}} k_\sigma \mathbf{b}_{\sigma\beta}\mathbf{n}\, dA. \tag{E.19b}$$

The above two results and the definitions of $\mathbf{K}_{\beta\sigma}$ and $\mathbf{K}_{\sigma\beta}$ given in Eqs. (E.7b) and (E.7d) indicate that

$$\phi_\beta \mathbf{K}_{\beta\sigma} = \phi_\sigma \mathbf{K}_{\sigma\beta}^T. \tag{E.20}$$

Note that $\mathbf{K}_{\sigma\beta}$ is not a symmetric tensor when there is interfacial heat transfer resistance. To prove this point, commence with Eq. (E.16) and take into account the fact that $k_\beta \langle \nabla \mathbf{b}_{\beta\beta}^T \rangle^\beta$ is a symmetric tensor (this is due to the fact that $\mathbf{K}_{\beta\beta}$ is also a symmetric tensor), so that this equation can be rewritten, after multiplying it by ϕ_β/ϕ_σ, as

$$\begin{aligned}\mathbf{0} =& k_\beta \frac{\phi_\beta}{\phi_\sigma}\langle \nabla \mathbf{b}_{\beta\beta}^T \cdot \nabla \mathbf{b}_{\beta\beta}\rangle^\beta + \frac{k_\beta}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\mathbf{b}_{\beta\beta}\, dA \\ &+ k_\sigma \langle \nabla \mathbf{b}_{\sigma\beta}^T \cdot \nabla \mathbf{b}_{\sigma\beta}\rangle^\sigma \\ &+ \frac{1}{h_i}\frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \left(\mathbf{n}\cdot k_\sigma \nabla \mathbf{b}_{\sigma\beta}\right)\left(\mathbf{n}\cdot k_\sigma \nabla \mathbf{b}_{\sigma\beta}\right) dA. \end{aligned} \tag{E.21}$$

From the interfacial boundary conditions it results that, at $\mathscr{A}_{\beta\sigma}$, $\mathbf{b}_{\beta\beta} = -\mathbf{n}\cdot\frac{k_\sigma}{h_i}\nabla \mathbf{b}_{\sigma\beta} + \mathbf{b}_{\sigma\beta}$. Therefore, on the basis of the definition given in Eq. (E.7d), the following expression is obtained

$$\begin{aligned}\frac{k_\beta}{k_\sigma}\mathbf{K}_{\sigma\beta} =& k_\beta \frac{\phi_\beta}{\phi_\sigma}\langle \nabla \mathbf{b}_{\beta\beta}^T \cdot \nabla \mathbf{b}_{\beta\beta}\rangle^\beta - \frac{k_\beta k_\sigma}{h_i V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \mathbf{n}\mathbf{n}\cdot\nabla \mathbf{b}_{\sigma\beta}\, dA \\ &+ k_\sigma \langle \nabla \mathbf{b}_{\sigma\beta}^T \cdot \nabla \mathbf{b}_{\sigma\beta}\rangle^\sigma \\ &+ \frac{1}{h_i}\frac{1}{V_\sigma}\int_{\mathscr{A}_{\beta\sigma}} \left(\mathbf{n}\cdot k_\sigma \nabla \mathbf{b}_{\sigma\beta}\right)\left(\mathbf{n}\cdot k_\sigma \nabla \mathbf{b}_{\sigma\beta}\right) dA. \end{aligned} \tag{E.22}$$

Solving the closure problem given in Eqs. (E.4) in the periodic unit cell depicted in Fig. 3 indicates that the second term on the right-hand side is not symmetric. Certainly, this term can be ignored when there is no interfacial heat transfer resistance (*i.e.*, when $h_i \to \infty$), therefore leading to the conclusion reached in the last paragraph of Appendix D. Note, however, that the coupled heat conduction term, that writes $\mathbf{K}_{\alpha\kappa} : \nabla\nabla\langle T_\kappa\rangle^\kappa$, $(\alpha, \kappa = \beta\sigma,\ \alpha \neq \kappa)$, is such that the non-symmetric part of $\mathbf{K}_{\alpha\kappa}$ plays no role. This is due to the fact that $\nabla\nabla\langle T_\kappa\rangle^\kappa$ is a symmetric tensor.

Data availability

Data will be made available on request.

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