# Upscaling multi-component two-phase flow in porous media with partitioning coefficient

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A B S T R A C T

This paper deals with the upscaling of multicomponents two-phase flow in porous media. In this paper, chemical potential equilibrium at the interface between both phases is assumed to be described by a linear partitioning relationship such as Raoult or Henry's law. The resulting macro-scale dispersion model is a set of two equations related by a mass transfer coefficient and which involves several effective coefficients. These coefficients can be evaluated by solving closure problems over a representative unit-cell. The proposed model is successfully validated through direct analytical and numerical calculations.

*Keywords:*
Porous media
Volume averaging
Multicomponent
Dispersion
Partitioning law
Two-phase flow

## 1. Introduction

Two-phase flows in porous media with liquid–liquid or liquid–vapor phase exchange appear in a large number of situations such as chemical reactors, nuclear safety devices, transport in petroleum reservoirs, aquifer contamination, desalination processes by way of distillation.

In such a system, a liquid phase $\beta$ is in contact with another phase, referred to as the $\gamma$-phase. Molecules may be exchanged at the $\beta\gamma$-interface, and we will assume that, at this boundary, the phases are at thermodynamic equilibrium. This equilibrium generally leads to a concentration jump at the $\beta\gamma$-interface. Transfer in the interface neighborhood leads to concentration fields as schematically depicted in Fig. 1

In this paper we are interested in the macro-scale description of such flows in a porous medium, as represented in Fig. 2. More precisely, we will narrow our interests to the averaging of the mass transport equation for a given species *A*. A complete description would also requires to develop the macro-scale momentum balance equations, etc… We will assume that density and viscosity variations are small so the two-phase flow problem can be decoupled from the transport problem of the chosen chemical species, provided the change in saturation is very slow so a quasi-static analysis may be carried on for momentum transport. This two-phase flow problem has received a lot of attention in the literature, and we refer the reader to Whitaker (1986), Auriault (1987) for some indication on the averaging problem. At this point, we may focus our attention on the transport problem for a given species in order to develop a macro-scale dispersion equation taking into account the mass exchange at the interface. In a previous paper on such a problem (Quintard and Whitaker, 1994), we called it "active dispersion" by opposition to "passive dispersion" corresponding to the flow of a chemical species without exchange or reaction at the phase interface.

In the case of film flow, the mass transfer modelling at the interface liquid–gas has received a lot of attention. To characterize this mass transfer, the authors usually define local mass transfer resistances within each phase and an overall mass exchange coefficient (Taylor and Krishna, 1993). The latter is a combination of both local resistances according to an association in series. Numerous models evaluating the local resistance exist in the literature. Among the most widely used in chemical engineering, we can quote the Lewis and Whitman double film theory (Lewis and Whitman, 1924) who postulated that the local mass transfers occur in a thin layer on each side of the interface, the Higbie's penetration model (Higbie, 1935) or also the Danckwerts surface renewal theory (Danckwerts, 1970). In these two last models, the mass transfer is assumed to be controlled by the rate of surface renewal: after a time the surface elements are swept away and replaced by a fresh surface. Both models involve unsteady-state diffusion. These models are commonly used in

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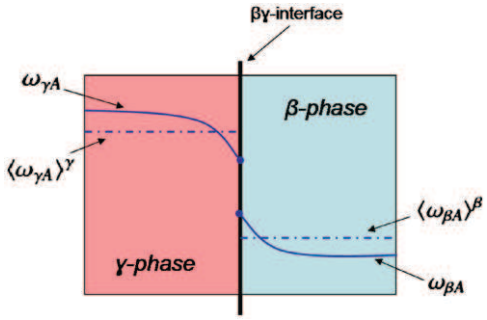


**Fig. 1.** Concentration field near the $\beta\gamma$-interface for species $A$.

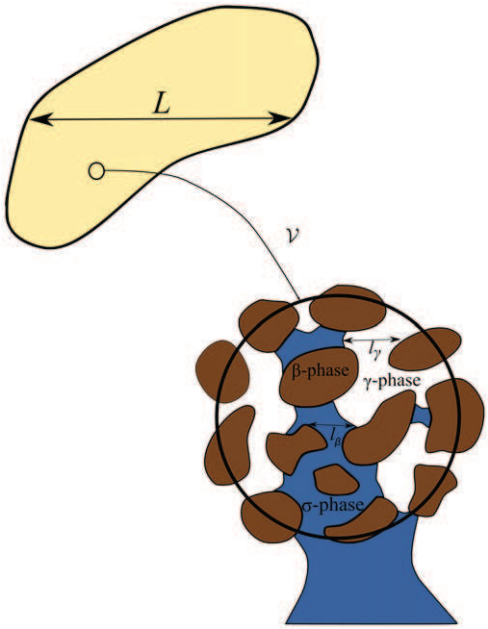


**Fig. 2.** Averaging volume.

regular engineering practice. They are even relatively accurate if the real conditions (especially geometry and flow parameters) are compatible with the film flow picture. However, in many complex geometries, it is impossible to predict an independent picture of the flow along the interfaces. The boundary layers, if this concept itself is relevant, are the results of a complex flow that must be solved accurately. Therefore, a porous medium theory cannot make the prior assumption that a simple film flow exists, or a simple boundary layer exists.

We will not make such assumptions here and will develop a more general theory in the continuity of the works of Quintard and Whitaker (1994) and of Coutelieris et al. (2006). In a sense it is also an extension of the paper by Bousquet-Melou et al. (2002) who studied active dispersion in mushy zones (in the case of the solidification of a binary mixture). We mention here that Bekri and Adler (2002) tackle the dispersion problem in multiphase flow with a different approach based on the combination of an Immiscible Lattice Boltzmann algorithm and random walks. In the first paper, a macroscopic model describing the flow of a two-phase, binary mixture was obtained from the pore-scale equations using a volume averaging upscaling method. Since thermodynamic equilibrium for a binary mixture forces the concentration at the interface to be a function of temperature and pressure only, and not of the composition, transport of species $A$ in one phase can be solved almost independently from the other phase problem. The resulting averaged equation is a dispersion equation with a mass exchange coefficient. The main effective parameters are the dispersion tensor and the mass-exchange coefficient. However, some additional terms such as velocity-like coefficients are also introduced in the macro-model. They suggest in particular that the macroscopic convective velocity is modified by the presence of the other phase. An important limitation of the model that we will try to overcome in this paper is that the development was limited to the case of a quasi-steady $\beta\gamma$-interface.

This theory was extended in the paper by Coutelieris et al. (2006) to multicomponent mixtures through the introduction of partitioning equilibrium condition at the $\beta\gamma$-interface, in the limited case of an immobile non-aqueous liquid phase and a flowing aqueous phase. Coutelieris et al. (2006) focused their attention on the mass exchange coefficient. It is calculated through a multi-region closure problem involving partitioning relationships at the interface of these regions. In both papers, one phase is treated as a rigid phase. In addition, the interface velocity is assumed to be very small and negligible so the flow of matter relative to the interface velocity may be neglected in comparison with the interfacial diffusive flux.

In the present paper, we extend these theoretical results to a more general case of two-phase multicomponent systems. The two phases are mobile, contrary to the above cited papers, and we fully develop the dispersion and the mass exchange effects. In addition, in the spirit of the work by Chella et al. (1998), the upscaling methodology is improved with respect to the interface movement, which is not neglected in the proposed full model.

The paper is organized as follows. The volume averaging method is applied to the microscopic, pore-scale equations that govern the system in order to develop a macro-scale model for a homogeneous porous medium. We consider that local mass non-equilibrium, i.e. averaged concentrations are not necessarily linked by the micro-scale equilibrium interface relationship. This results into two macroscopic equations involving dispersion tensors, additional convective transport terms and a mass exchange term; all these effective properties being influenced by the mass transfer process. These effective coefficients can entirely be determined by three closure problems defined over a unit-cell representative of the porous medium. A closed form of the total mass transfer rate is also proposed.

To better understand the results and validate the approach, in the last section we consider the case of the falling film along a vertical fixed wall. In this case, the closure problems can be solved analytically in the fully developed film regime. The obtained effective dispersion coefficients in the literature are in good agreement with the falling film theory results and the mass exchange coefficient corresponds to the Lewis and Whitman double film theory (Lewis and Whitman, 1924). Moreover, we compared with success the macro-scale model with a direct numerical simulation of the pore-scale model.

## 2. Pore scale problem

The pore-scale problem under consideration corresponds to the mass transfer of a component $A$ in a two-phase flow system. The two phases, $\beta$ and $\gamma$, flow through a porous medium (the $\sigma$-phase is the solid phase). The general problem is in fact composed of momentum equations, mass balance equations for each species and an energy equation. In principle there is a full coupling between these balance equations, especially through terms involving the velocity of the interface. One may imagine situations for which this coupling is very strong: for instance,

intense boiling of water in a nuclear debris bed with very rapid thermal transient is likely to produce a big rate of phase change that may corresponds to huge exchange of enthalpy and momentum between phases. To our knowledge this full problem has not been solved from an upscaling point of view. For instance, how the mass exchange rate affects the macro-scale momentum balance equation is an open question. However, there are also situations for which the interface may be quasi-static for the relaxation phenomena associated to momentum and energy exchanges. This is the case in distillation columns for which the industrial target tends to reach quasi-steady situations. In such cases, one may admit that:

1. the temperature is quasi-uniform over a representative unit-cell;
2. for a given interface position, the viscous relaxation of the velocity fields is rapid compared to the interface characteristic velocity.

As a consequence, the mass, momentum and energy equations may be solved in a sequential manner. In this case, the unit-cell velocity fields and the temperature are known input variables for the multicomponent mass balance problem. Therefore, the two velocity fields are supposed to be known in this section development and we will not consider the resolution of the two-phase flow problem. One can refer to Whitaker (1986, 1994), Auriault (1987), Lasseux et al. (1996) or Lasseux et al. (2008) for further details on the upscaling of two-phase flows in porous media with quasi-static interfaces. For small mass exchange rates as discussed above, the resulting equations, i.e. generalized Darcy's law and the various improvements, may be probably used as such. We leave open in this paper the upscaling in the case of big mass exchange rates.

The total mass transfer process is described by the following boundary value problem:

$$\frac{\partial \rho_\beta}{\partial t} + \nabla.(\rho_\beta \mathbf{v}_\beta) = 0 \text{ in } \mathcal{V}_\beta \tag{1}$$

$$\text{BC1 } \mathbf{v}_\beta = 0 \text{ at } \mathcal{A}_{\beta\sigma} \tag{2}$$

$$\text{BC2 } \mathbf{n}_{\beta\gamma}.(\rho_\beta(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma})) = \mathbf{n}_{\beta\gamma}.(\rho_\gamma(\mathbf{v}_\gamma - \mathbf{w}_{\beta\gamma})) \text{ at } \mathcal{A}_{\beta\gamma} \tag{3}$$

$$\text{BC3 } \mathbf{v}_\gamma = 0 \text{ at } \mathcal{A}_{\gamma\sigma} \tag{4}$$

$$\frac{\partial \rho_\gamma}{\partial t} + \nabla.(\rho_\gamma \mathbf{v}_\gamma) = 0 \text{ in } \mathcal{V}_\gamma \tag{5}$$

In this problem, we assume a no-slip boundary condition at the interface with the rigid porous structure. In these equations, $\mathbf{w}_{\beta\gamma}$ represents the velocity of $\mathcal{A}_{\beta\gamma}$, the interface between the $\beta$-phase and the $\gamma$-phase.

Many approaches can be found in the literature to model diffusion problems for multicomponent gas mixtures (Taylor and Krishna, 1993). Indeed, Maxwell–Stefan equations were used in a previous paper to deal with multicomponent "passive" dispersion in porous media (Quintard et al., 2006). As an intermediate step in the upscaling process, the diffusive fluxes were written under the form of generalized Fick's law, which may be obtained from Maxwell–Stefan equations (Taylor and Krishna, 1993; Quintard et al., 2006) but also from irreversible thermodynamics consideration (see for instance Giovangigli, 1999). However, the complexity of such equations make their resolution and their upscaling difficult in the perspective of this paper about two-phase flow situations. To avoid these difficulties, in this paper we will use an effective diffusivity method, which offers a good approximation in many situations of pratical interest. It consists in the definition of an effective diffusivity $D_{\beta A}$ such that the rate of diffusion $\mathbf{J}_{\beta A}$ of species $A$ in the $\beta$-phase depends on the species concentration gradients through the simple expression

$$\mathbf{J}_{\beta A} = -\rho_\beta D_{\beta A} \nabla \omega_{\beta A}; \quad A = 1, 2, 3 \ldots \tag{6}$$

where $D_{\beta A}$ is some characteristic diffusion coefficient of species $A$ in the $\beta$-phase mixture. Therefore, the transport of the component A is described by the following convection-diffusion problem:

$$\frac{\partial \rho_\beta \omega_{\beta A}}{\partial t} + \nabla.(\rho_\beta \omega_{\beta A} \mathbf{v}_\beta) = \nabla.(\rho_\beta D_{\beta A} \nabla \omega_{\beta A}) \text{ in } \mathcal{V}_\beta \tag{7}$$

$$\text{BC4 } \mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A} \nabla \omega_{\beta A} = 0 \text{ at } \mathcal{A}_{\beta\sigma} \tag{8}$$

$$\text{BC5 } \mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A} \nabla \omega_{\gamma A} = 0 \text{ at } \mathcal{A}_{\gamma\sigma} \tag{9}$$

$$\text{BC6 } \mathbf{n}_{\beta\gamma}.(\rho_\beta \omega_{\beta A}(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma}) - \rho_\beta D_{\beta A} \nabla \omega_{\beta A}) = \mathbf{n}_{\beta\gamma}.(\rho_\gamma \omega_{\gamma A}(\mathbf{v}_\gamma - \mathbf{w}_{\beta\gamma}) - \rho_\gamma D_{\gamma A} \nabla \omega_{\gamma A}) \text{ at } \mathcal{A}_{\beta\gamma} \tag{10}$$

$$\text{BC7 } \mu_{\beta A}(\omega_{\beta A}) = \mu_{\gamma A}(\omega_{\gamma A}) \text{ at } \mathcal{A}_{\beta\gamma} \tag{11}$$

$$\frac{\partial \rho_\gamma \omega_{\gamma A}}{\partial t} + \nabla.(\rho_\gamma \omega_{\gamma A} \mathbf{v}_\gamma) = \nabla.(\rho_\gamma D_{\gamma A} \nabla \omega_{\gamma A}) \text{ in } \mathcal{V}_\gamma \tag{12}$$

where $\mu_{\beta A}$ is the chemical potential associated to species $A$ in the $\beta$-phase. It is assumed in our development that the chemical potential equilibrium at the interface is linearized to a partitioning relationship (like for instance Henry's law or Raoult's law):

$$\omega_{\beta A} = H_A \omega_{\gamma A} \tag{13}$$

In this paper, the molecular effective diffusivity coefficients ($D_{\beta A}$ and $D_{\gamma A}$) and the partitioning coefficient ($H_A$) are considered constant in space and in time. This question (at least for the variation of the diffusion coefficients with composition) has been discussed in Quintard et al. (2006). Moreover, it is assumed that all the physical properties of the fluids do not change strongly with temperature. Therefore, the coupling with the energy equation is not discussed here and belongs to the sequential treatment outlined in the introduction of this section.

## 3. Volume averaging

In this paper, we follow the developments in Quintard and Whitaker (1994) and Coutelieris et al. (2006) who used the method of volume averaging (Whitaker, 1999) to derive the macro-scale equations. We recall in this section the main definitions and theorems necessary to develop the macroscopic model from the pore-scale equations. We consider the averaging volume as illustrated in Fig. 2.

For a function $\psi_\beta$ associated with the $\beta$-phase, we define the average as

$$\langle \psi_\beta \rangle = \frac{1}{\mathcal{V}} \int_{\mathcal{V}_\beta} \psi_\beta \, d\mathcal{V} \tag{14}$$

and the intrinsic phase average as

$$\langle \psi_\beta \rangle^\beta = \frac{1}{\mathcal{V}_\beta} \int_{\mathcal{V}_\beta} \psi_\beta \, d\mathcal{V} \tag{15}$$

Both are linked by

$$\langle \psi_\beta \rangle = \varepsilon_\beta \langle \psi_\beta \rangle^\beta \quad \text{with } \varepsilon_\beta = \frac{\mathcal{V}_\beta}{\mathcal{V}} \tag{16}$$

where $\mathcal{V}_\beta$ is the volume of the $\beta$-phase contained in the volume $\mathcal{V}$ and $\varepsilon_\beta$ is the volume fraction of the $\beta$-phase.

The phase variable $\psi_\beta$ can be expressed following Gray's decomposition (Gray, 1975) as

$$\psi_\beta = \langle \psi_\beta \rangle^\beta + \tilde{\psi}_\beta \tag{17}$$

The volume averaging theory requires the use of the following approximation:

$$\langle \tilde{\psi}_\beta \rangle = 0 \tag{18}$$

In order to get the macro-scale equations in terms of intrinsic phase averages, we will apply the following spatial and temporal averaging theorems

$$\langle \nabla \psi_\beta \rangle = \nabla \langle \psi_\beta \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \psi_\beta \, d\mathcal{A} + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma} \psi_\beta \, d\mathcal{A} \tag{19}$$

$$\left\langle \frac{\partial \psi_\beta}{\partial t} \right\rangle = \frac{\partial \langle \psi_\beta \rangle}{\partial t} - \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} . \mathbf{w}_{\beta\sigma} \psi_\beta \, d\mathcal{A} - \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma} . \mathbf{w}_{\beta\gamma} \psi_\beta \, d\mathcal{A} \tag{20}$$

The integrals in the equalities express the interfacial effects typical of porous media physics. The solid phase is considered to be inert in our analysis, therefore $\mathbf{w}_{\beta\sigma} = 0$. Moreover, applying the spatial averaging theorem (Eq. (19)) to $\psi_\beta = 1$ leads to the very useful lemma

$$\nabla \varepsilon_\beta = -\frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta \, d\mathcal{A} \tag{21}$$

Here, $\mathcal{A}_\beta$ denotes all the surfaces in contact with the $\beta$-phase (i.e. $\mathcal{A}_{\beta\sigma}$ and $\mathcal{A}_{\beta\gamma}$) and the normal $\mathbf{n}_\beta$ represents either $\mathbf{n}_{\beta\gamma}$ or $\mathbf{n}_{\beta\sigma}$. These notations will be adopted for the rest of this paper.

### 3.1. Total mass balance equations

The mere application of the volume averaging theorems to the continuity equations (Eq. (1)) and (Eq. (5)) leads to

$$\frac{\partial \langle \rho_\beta \rangle}{\partial t} + \nabla . (\langle \rho_\beta \mathbf{v}_\beta \rangle) + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma} . \rho_\beta (\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma}) \, d\mathcal{A} = 0 \text{ in } \mathcal{V}_\beta \tag{22}$$

$$\frac{\partial \langle \rho_\gamma \rangle}{\partial t} + \nabla . (\langle \rho_\gamma \mathbf{v}_\gamma \rangle) + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\gamma\beta} . \rho_\gamma (\mathbf{v}_\gamma - \mathbf{w}_{\beta\gamma}) \, d\mathcal{A} = 0 \text{ in } \mathcal{V}_\gamma \tag{23}$$

As indicated in the introduction, we suppose the fluid densities $\rho_\beta$ and $\rho_\gamma$ constant within the averaging volume $\mathcal{V}$ ($\rho_\beta = \langle \rho_\beta \rangle^\beta$ and $\rho_\gamma = \langle \rho_\gamma \rangle^\gamma$). It must be remembered that this does not mean that the fluid densities will not vary at the macroscale. Moreover, we define the total mass exchange rate $\dot{m}$ according to

$$\dot{m} = \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma} . \rho_\beta (\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma}) \, d\mathcal{A} \tag{24}$$

Hence, using the boundary condition (Eq. (3)), we obtain the following macroscopic form of the total mass transport equation

$$\frac{\partial \varepsilon_\beta \rho_\beta}{\partial t} + \nabla . (\rho_\beta \langle \mathbf{v}_\beta \rangle) = -\dot{m} \text{ in } \mathcal{V}_\beta \tag{25}$$

$$\frac{\partial \varepsilon_\gamma \rho_\gamma}{\partial t} + \nabla . (\rho_\gamma \langle \mathbf{v}_\gamma \rangle) = \dot{m} \text{ in } \mathcal{V}_\gamma \tag{26}$$

In the next sections, we will propose a closed form of the mass rate of evaporation $\dot{m}$.

### 3.2. Species mass balance equation

We will now form the average transport equation for Eq. (7) by successive applications of the volume averaging theorems. We have

$$\frac{\partial \rho_\beta \langle \omega_{\beta A} \rangle}{\partial t} + \nabla . (\rho_\beta \langle \omega_{\beta A} \mathbf{v}_\beta \rangle) + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma} . \rho_\beta \omega_{\beta A} (\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma}) \, d\mathcal{A}$$
$$= \nabla . \left( \rho_\beta D_{\beta A} \nabla \langle \omega_{\beta A} \rangle + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta \rho_\beta D_{\beta A} \omega_{\beta A} \, d\mathcal{A} \right)$$
$$+ \frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta . \rho_\beta D_{\beta A} \nabla \omega_{\beta A} \, d\mathcal{A} \tag{27}$$

We search a transport equation in terms of the intrinsic average mass fraction $\langle \omega_{\beta A} \rangle^\beta$. Using Gray's spatial decomposition for $\omega_{\beta A}$ and $\mathbf{v}_\beta$ and the definition $\langle \omega_{\beta A} \rangle = \varepsilon_\beta \langle \omega_{\beta A} \rangle^\beta$, one can eventually obtain for the left hand side of Eq. (27)

$$\frac{\partial \varepsilon_\beta \rho_\beta \langle \omega_{\beta A} \rangle^\beta}{\partial t} + \nabla . (\varepsilon_\beta \rho_\beta \langle \omega_{\beta A} \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta) + \nabla . (\rho_\beta \langle \tilde{\omega}_{\beta A} \tilde{\mathbf{v}}_\beta \rangle)$$
$$+ \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma} . \rho_\beta \omega_{\beta A} (\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma}) \, d\mathcal{A} \tag{28}$$

A similar operation for the right hand side leads to

$$\nabla . D_{\beta A} [\varepsilon_\beta \rho_\beta \nabla \langle \omega_{\beta A} \rangle^\beta + \rho_\beta \langle \omega_{\beta A} \rangle^\beta \nabla \varepsilon_\beta]$$
$$+ \nabla . D_{\beta A} \left[ \frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta \rho_\beta \langle \omega_{\beta A} \rangle^\beta \, d\mathcal{A} + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta \rho_\beta \tilde{\omega}_{\beta A} \, d\mathcal{A} \right]$$
$$+ \frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta . \rho_\beta D_{\beta A} \nabla \omega_{\beta A} \, d\mathcal{A} \tag{29}$$

Considering now the spatial lemma (Eq. (21)) and defining the mass transfer rate for the component A by

$$\dot{m}_A = \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma} . (\rho_\beta \omega_{\beta A} (\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma}) - \rho_\beta D_{\beta A} \nabla \omega_{\beta A}) \, d\mathcal{A} \tag{30}$$

The previous equation can be written as

$$\frac{\partial \varepsilon_\beta \rho_\beta \langle \omega_{\beta A} \rangle^\beta}{\partial t} + \nabla . (\varepsilon_\beta \rho_\beta \langle \omega_{\beta A} \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta) + \underbrace{\nabla . (\rho_\beta \langle \tilde{\omega}_{\beta A} \tilde{\mathbf{v}}_\beta \rangle)}_{\textit{dispersion term}}$$
$$= \nabla . \left( \varepsilon_\beta \rho_\beta D_{\beta A} \nabla \langle \omega_{\beta A} \rangle^\beta + \underbrace{\frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta \rho_\beta D_{\beta A} \tilde{\omega}_{\beta A} \, d\mathcal{A}}_{\textit{tortuosity term}} \right) - \dot{m}_A \tag{31}$$

A similar development for the convection-diffusion equation in the $\gamma$-phase gives

$$\frac{\partial \varepsilon_\gamma \rho_\gamma \langle \omega_{\gamma A} \rangle^\gamma}{\partial t} + \nabla . (\varepsilon_\gamma \rho_\gamma \langle \omega_{\gamma A} \rangle^\gamma \langle \mathbf{v}_\gamma \rangle^\gamma) + \nabla . (\rho_\gamma \langle \tilde{\omega}_{\gamma A} \tilde{\mathbf{v}}_\gamma \rangle)$$
$$= \nabla . \left( \varepsilon_\gamma \rho_\gamma D_{\gamma A} \nabla \langle \omega_{\gamma A} \rangle^\gamma + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_\gamma} \mathbf{n}_\gamma \rho_\gamma D_{\gamma A} \tilde{\omega}_{\gamma A} \, d\mathcal{A} \right) + \dot{m}_A \tag{32}$$

At this stage of the development, the averaged transport equations are not under a closed form since mass fraction deviations having microscopic length-scale are still present. The classical strategy is to derive a problem that governs the deviations, then to represent them in terms of average quantities (the so-called closure problem), and, finally, to insert these representations into the conservation equations (Eqs. (31) and (32)) to get the closed form of the averaged equations. In order to obtain a convenient form for the closure problem, we continue the development by the introduction of the Gray's decomposition of $\omega_{\beta A}$ in the

evaporation rate of species $A$. The right hand side of Eq. (31) becomes

$$\varepsilon_\beta \nabla.(D_{\beta A}\rho_\beta \nabla\langle\omega_{\beta A}\rangle^\beta)+(\nabla\varepsilon_\beta).\rho_\beta D_{\beta A}\nabla\langle\omega_{\beta A}\rangle^\beta + \nabla.\left[D_{\beta A}\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta\rho_\beta\tilde{\omega}_{\beta A}\,d\mathcal{A}\right]-\dot{m}\langle\omega_{\beta A}\rangle^\beta-(\nabla\varepsilon_\beta).\rho_\beta D_{\beta A}\nabla\langle\omega_{\beta A}\rangle^\beta - \frac{1}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\beta\gamma}.\rho_\beta\tilde{\omega}_{\beta A}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}+\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta.\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A}\,d\mathcal{A} \quad (33)$$

Using the macroscopic form of the continuity equation (Eq. (25)) in the left hand side of Eq. (31) leads to

$$\varepsilon_\beta\rho_\beta\frac{\partial\langle\omega_{\beta A}\rangle^\beta}{\partial t}+\varepsilon_\beta\rho_\beta\langle\mathbf{v}_\beta\rangle^\beta.\nabla\langle\omega_{\beta A}\rangle^\beta+\nabla.(\rho_\beta\langle\tilde{\omega}_{\beta A}\tilde{\mathbf{v}}_\beta\rangle)-\dot{m}\langle\omega_{\beta A}\rangle^\beta \quad (34)$$

Finally we obtain

$$\rho_\beta\frac{\partial\langle\omega_{\beta A}\rangle^\beta}{\partial t}+\rho_\beta\langle\mathbf{v}_\beta\rangle^\beta.\nabla\langle\omega_{\beta A}\rangle^\beta+\varepsilon_\beta^{-1}\nabla.(\rho_\beta\langle\tilde{\omega}_{\beta A}\tilde{\mathbf{v}}_\beta\rangle) = \nabla.(\rho_\beta D_{\beta A}\nabla\langle\omega_{\beta A}\rangle^\beta)+\varepsilon_\beta^{-1}\nabla.\left[D_{\beta A}\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta\rho_\beta\tilde{\omega}_{\beta A}\,d\mathcal{A}\right] - \frac{\varepsilon_\beta^{-1}}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\beta\gamma}.\rho_\beta\tilde{\omega}_{\beta A}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}+\frac{\varepsilon_\beta^{-1}}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta.\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A}\,d\mathcal{A} \quad (35)$$

## 4. Closure

The aim of this section is to develop the relationships between spatial deviations and average quantities in order to close the macroscopic model.

### 4.1. Differential equation for the concentration deviations

We are now ready to derive a governing differential equation for the deviations. We first recall the original convection-diffusion equation in a non-conservative form

$$\rho_\beta\frac{\partial\omega_{\beta A}}{\partial t}+\rho_\beta\mathbf{v}_\beta.\nabla\omega_{\beta A}=\nabla.(\rho_\beta D_{\beta A}\nabla\omega_{\beta A}) \quad (36)$$

By subtracting Eq. (35) from Eq. (36) and considering Gray's decomposition Eq. (17), we obtain the following equation for the spatial deviation of the mass fraction

$$\rho_\beta\frac{\partial\tilde{\omega}_{\beta A}}{\partial t}+\rho_\beta\mathbf{v}_\beta.\nabla\tilde{\omega}_{\beta A}+\rho_\beta\tilde{\mathbf{v}}_\beta.\nabla\langle\omega_{\beta A}\rangle^\beta-\varepsilon_\beta^{-1}\nabla.(\rho_\beta\langle\tilde{\omega}_{\beta A}\tilde{\mathbf{v}}_\beta\rangle) = \nabla.(\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A})-\varepsilon_\beta^{-1}\nabla.\left(\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta\rho_\beta D_{\beta A}\tilde{\omega}_{\beta A}\,d\mathcal{A}\right) + \frac{\varepsilon_\beta^{-1}}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\beta\gamma}.\rho_\beta\tilde{\omega}_{\beta A}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}-\frac{\varepsilon_\beta^{-1}}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta.\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A}\,d\mathcal{A} \quad (37)$$

When the pore scales and the macroscopic scales are separated, the classical following assumption is available

$$\nabla.\left(\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta\rho_\beta D_{\beta A}\tilde{\omega}_{\beta A}\,d\mathcal{A}\right)\ll\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A}\,d\mathcal{A} \quad (38)$$

Numerous other simplifications such as stationarity or the omission of the dispersion term are generally made in the literature. However, in our development, we will keep these terms and make assumptions later. Therefore, we consider the following differential equation for the $\beta$-phase :

$$\rho_\beta\frac{\partial\tilde{\omega}_{\beta A}}{\partial t}+\rho_\beta\mathbf{v}_\beta.\nabla\tilde{\omega}_{\beta A}+\overbrace{\rho_\beta\tilde{\mathbf{v}}_\beta.\nabla\langle\omega_{\beta A}\rangle^\beta}^{source} -\varepsilon_\beta^{-1}\nabla.(\rho_\beta\langle\tilde{\omega}_{\beta A}\tilde{\mathbf{v}}_\beta\rangle)-\nabla.(\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A}) = \frac{\varepsilon_\beta^{-1}}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\beta\gamma}.\rho_\beta\tilde{\omega}_{\beta A}\times(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}-\frac{\varepsilon_\beta^{-1}}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta.\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A}\,d\mathcal{A} \quad (39)$$

Similarly for the $\gamma$-phase, we have

$$\rho_\gamma\frac{\partial\tilde{\omega}_{\gamma A}}{\partial t}+\rho_\gamma\mathbf{v}_\gamma.\nabla\tilde{\omega}_{\gamma A}+\overbrace{\rho_\gamma\tilde{\mathbf{v}}_\gamma.\nabla\langle\omega_{\gamma A}\rangle^\gamma}^{source} -\varepsilon_\gamma^{-1}\nabla.(\rho_\gamma\langle\tilde{\omega}_{\gamma A}\tilde{\mathbf{v}}_\gamma\rangle)-\nabla.(\rho_\gamma D_{\gamma A}\nabla\tilde{\omega}_{\gamma A}) = \frac{\varepsilon_\gamma^{-1}}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\gamma\beta}.\rho_\gamma\tilde{\omega}_{\gamma A}\times(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}-\frac{\varepsilon_\gamma^{-1}}{\mathcal{V}}\int_{\mathcal{A}_\gamma}\mathbf{n}_\gamma.\rho_\gamma D_{\gamma A}\nabla\tilde{\omega}_{\gamma A}\,d\mathcal{A} \quad (40)$$

We can use the decomposition given by Eq. (17) with Eqs. (8), (9), (11) and (13) in order to develop the following boundary conditions for this deviation problem

$$\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A}=\underbrace{-\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla\langle\omega_{\beta A}\rangle^\beta}_{source}\ \text{at}\ \mathcal{A}_{\beta\sigma} \quad (41)$$

$$\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla\tilde{\omega}_{\gamma A}=\underbrace{-\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla\langle\omega_{\gamma A}\rangle^\gamma}_{source}\ \text{at}\ \mathcal{A}_{\gamma\sigma} \quad (42)$$

$$\tilde{\omega}_{\beta A}=H_A\tilde{\omega}_{\gamma A}+\underbrace{(H_A\langle\omega_{\gamma A}\rangle^\gamma}_{source}\underbrace{-\langle\omega_{\beta A}\rangle^\beta)}_{source}\ \text{at}\ \mathcal{A}_{\beta\gamma} \quad (43)$$

$$\mathbf{n}_{\beta\gamma}.\overbrace{(\beta\langle\omega_{\beta A}\rangle^\beta(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})}^{source}-\overbrace{\rho_\beta D_{\beta A}\nabla\langle\omega_{\beta A}\rangle^\beta)}^{source} +\mathbf{n}_{\beta\gamma}.(\rho_\beta\tilde{\omega}_{\beta A}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})-\rho_\beta D_{\beta A}\nabla\tilde{\omega}_{\beta A}) =\mathbf{n}_{\beta\gamma}.(\rho_\gamma\tilde{\omega}_{\gamma A}(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})-\rho_\gamma D_{\gamma A}\nabla\tilde{\omega}_{\gamma A}) +\mathbf{n}_{\beta\gamma}.(\underbrace{\rho_\gamma\langle\omega_{\gamma A}\rangle^\gamma(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})}_{source}\underbrace{-\rho_\gamma D_{\gamma A}\nabla\langle\omega_{\gamma A}\rangle^\gamma}_{source})\ \text{at}\ \mathcal{A}_{\beta\gamma} \quad (44)$$

In addition, we have the additional condition that the averages of the deviations must be zero

$$\langle\tilde{\omega}_{\beta A}\rangle^\beta=0;\quad\langle\tilde{\omega}_{\gamma A}\rangle^\gamma=0 \quad (45)$$

In order to solve the closure problem in a representative region of the porous medium instead of considering the entire macrostructure, we consider the model of a spatially periodic system. Hence, we add the following periodic conditions to this deviation problem

$$\tilde{\omega}_{\beta A}(r+l_i)=\tilde{\omega}_{\beta A}(r);\quad\tilde{\omega}_{\gamma A}(r+l_i)=\tilde{\omega}_{\gamma A}(r);\quad i=1,2,3 \quad (46)$$

At this point, it is important to remember that by comparison to the work by Coutelieris et al. (2006), we have kept the following important features:

- terms involving $(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})$ have been kept in the analysis,
- velocity in the $\gamma$-phase is not neglected.

### 4.2. Closure problems

There are four non-homogeneous terms ($\nabla\langle\omega_{\beta A}\rangle^\beta$, $\nabla\langle\omega_{\gamma A}\rangle^\gamma$, $\langle\omega_{\beta A}\rangle^\beta$ and $\langle\omega_{\gamma A}\rangle^\gamma$) in the previous equations. Following the work by Quintard and Whitaker (1994) and Coutelieris et al. (2006), it is possible to depict the mass fraction deviations in terms of a linear combination of these source terms thus

providing the following representation:

$$\tilde{\omega}_{\beta A} = \mathbf{b}_{\beta\beta}.\nabla\langle\omega_{\beta A}\rangle^{\beta} + \mathbf{b}_{\beta\gamma}.\nabla\langle\omega_{\gamma A}\rangle^{\gamma} + s_{\beta\beta}\langle\omega_{\beta A}\rangle^{\beta} + s_{\beta\gamma}\langle\omega_{\gamma A}\rangle^{\gamma} \tag{47}$$

$$\tilde{\omega}_{\gamma A} = \mathbf{b}_{\gamma\gamma}.\nabla\langle\omega_{\gamma A}\rangle^{\gamma} + \mathbf{b}_{\gamma\beta}.\nabla\langle\omega_{\beta A}\rangle^{\beta} + s_{\gamma\gamma}\langle\omega_{\gamma A}\rangle^{\gamma} + s_{\gamma\beta}\langle\omega_{\beta A}\rangle^{\beta} \tag{48}$$

where the closure variables $\mathbf{b}_{\beta\beta}$, $\mathbf{b}_{\beta\gamma}$, $\mathbf{b}_{\gamma\gamma}$, $\mathbf{b}_{\gamma\beta}$, $s_{\beta\beta}$, $s_{\beta\gamma}$, $s_{\gamma\gamma}$ and $s_{\gamma\beta}$ satisfy four closure problems.

The next step of our development is to establish the mathematical problems that will allow us to determine all the closure variables. These closure problems will be solved over a periodic representative unit-cell. They are found out by substituting the previous closure forms (Eqs. (47) and (48)) into the deviations problem of Section 4.1.

Here we focus on the treatment of the $\nabla.(\rho_\beta\langle\tilde{\omega}_{\beta A}\tilde{\mathbf{v}}_\beta\rangle)$ term. The insertion of the closure form of $\tilde{\omega}_{\beta A}$ in this term yields

$$\nabla.(\rho_\beta\langle\tilde{\omega}_{\beta A}\tilde{\mathbf{v}}_\beta\rangle) = \nabla.(\rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle\langle\omega_{\beta A}\rangle^{\beta}) + \nabla.(\rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\gamma}\rangle\langle\omega_{\gamma A}\rangle^{\gamma}) + \nabla.(\rho_\beta\langle\tilde{\mathbf{v}}_\beta\mathbf{b}_{\beta\beta}\rangle.\nabla\langle\omega_{\beta A}\rangle^{\beta}) + \nabla.(\rho_\beta\langle\tilde{\mathbf{v}}_\beta\mathbf{b}_{\gamma\beta}\rangle.\nabla\langle\omega_{\gamma A}\rangle^{\gamma}) \tag{49}$$

We notice that the first term of this sum be written as

$$\nabla.(\rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle\langle\omega_{\beta A}\rangle^{\beta}) = \rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle.\nabla\langle\omega_{\beta A}\rangle^{\beta} + \langle\omega_{\beta A}\rangle^{\beta}\nabla.(\rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle) \tag{50}$$

From the assumption of separation of scales one can deduce that

$$\langle\omega_{\beta A}\rangle^{\beta}\nabla.(\rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle) \ll \rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle.\nabla\langle\omega_{\beta A}\rangle^{\beta} \tag{51}$$

and

$$\nabla.(\rho_\beta\langle\tilde{\mathbf{v}}_\beta\mathbf{b}_{\beta\beta}\rangle.\nabla\langle\omega_{\beta A}\rangle^{\beta}) \ll \rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle.\nabla\langle\omega_{\beta A}\rangle^{\beta} \tag{52}$$

Finally, we can consider the following approximations:

$$\nabla.(\rho_\beta\langle\tilde{\omega}_{\beta A}\tilde{\mathbf{v}}_\beta\rangle) = \rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle.\nabla\langle\omega_{\beta A}\rangle^{\beta} + \rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\gamma}\rangle.\nabla\langle\omega_{\gamma A}\rangle^{\gamma} \tag{53}$$

$$\nabla.(\rho_\gamma\langle\tilde{\omega}_{\gamma A}\tilde{\mathbf{v}}_\gamma\rangle) = \rho_\gamma\langle\tilde{\mathbf{v}}_\gamma s_{\gamma\gamma}\rangle.\nabla\langle\omega_{\gamma A}\rangle^{\gamma} + \rho_\gamma\langle\tilde{\mathbf{v}}_\gamma s_{\gamma\beta}\rangle.\nabla\langle\omega_{\beta A}\rangle^{\beta} \tag{54}$$

The identification of each term involving $\nabla\langle\omega_{\beta A}\rangle^{\beta}$, $\nabla\langle\omega_{\gamma A}\rangle^{\gamma}$, $\langle\omega_{\beta A}\rangle^{\beta}$ and $\langle\omega_{\gamma A}\rangle^{\gamma}$ provides the four closure problems as developed in Appendix A.

At this point, we have achieved the following tasks:

- we have obtained macro-scale equations in which several properties appear which depend on some pore-scale closure problem,
- the closure problems allow to map the concentration deviations onto macro-scale concentrations and gradients (similar relations exist for the velocity deviations).

The closure problems are time-dependent because of the evolution of the interface (term involving $\mathbf{w}_{\beta\gamma}$ and $\mathcal{A}_{\beta\gamma}(x,t)$), and, also, because of the accumulation terms. Macro-scale equations and pore-scale closure problems are fully coupled, which in fact leads to memory (history) effects. Is it possible to simplify these closure problems in order to decouple macro and pore-scale problems? Considering that the diffusion term near the interface is dominant versus the flux proportional to $\mathbf{n}_{\beta\gamma}.(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma})$ and that the mass fraction field relaxes faster than the evolution of the interface, a first possibility could be to discard all terms involving $\mathbf{n}_{\beta\gamma}.(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma})$ and the accumulation term in the closure problems. The coupling between the macro and pore-scale equations remains through the evolution of the interface $\mathcal{A}_{\beta\gamma}(x,t)$. Therefore, even after having removed the $\mathbf{n}_{\beta\gamma}.(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma})$ and the accumulation terms, the effective properties are associated to a specific time and the underlying realisation of the pore-scale geometry. This way is a classical difficulty found in geochemistry, or for any other applications involving changing pore-scale geometry. However, if various positions of the interface can be identified in the process in an univoque manner, for instance as a function of the phase volume fractions, then the closure-problems can be solved independently from the macro-scale equations and the effective properties may be *tabulated* as a function of the volume fractions. In this way, the macro-scale equations can be solved using these correlations for the effective properties without the need for a fully coupled solution of the macro-scale equations and the micro-scale closure problems. This kind of development, which is the one practically usable, is detailed in the next section.

### 4.3. Simplified closure problems

For the moment, only few assumptions have been made. First, we have considered that the volume density of both $\beta$ and $\gamma$ phases does not vary within the representative volume $\mathcal{V}$. Then, according to the assumption of separation of scales, we simplified the differential equation for the mass fraction deviations considering Eq. (51).

We now consider additional assumptions in order to simplify the closure problems as described at the end of the preceding section. First, we neglect the spatial and temporal variations of the volume fractions. Then, since the time scales are also separated, it is convenient to consider quasi-steady closure problems. Moreover, in the closure problems flux terms involving $.(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma})$ are neglected in front of the diffusive fluxes. For instance, Eq. (A.28) in Problem III becomes

$$\mathbf{n}_{\beta\gamma}.\rho_\beta D_{\beta A}\nabla s_{\beta\beta} = \mathbf{n}_{\beta\gamma}.\rho_\gamma D_{\gamma A}\nabla s_{\gamma\beta} \text{ at } \mathcal{A}_{\beta\gamma} \tag{55}$$

According to this last hypothesis, the liquid–vapor mass exchange rate $\dot{m}$ is neglected in the closure problems. As an important consequence, Problems III and IV are identical with respect to the factor $H_A$. Therefore, we can easily demonstrate that

$$s_\beta = -s_{\beta\beta} = H_A^{-1}s_{\beta\gamma} \tag{56}$$

$$s_\gamma = H_A^{-1}s_{\gamma\gamma} = -s_{\gamma\beta} \tag{57}$$

we also have

$$\alpha_A = X_{\gamma\beta} = H_A^{-1}X_{\beta\gamma} \tag{58}$$

in which $\alpha_A$ will appear in the macro-scale equation as a *mass exchange coefficient*, as detailed in the next section. Because of the definition of $\alpha_A$, the problem defining the $s_\beta$ and $s_\gamma$ mapping variables involves integro-differential equations. To solve this kind of problem, it is convenient, following ideas put forth in Quintard and Whitaker (1994), to carry out the following decompositions:

$$s_\beta = 1 + s_\beta^0\alpha_A \tag{59}$$

$$s_\gamma = s_\gamma^0\alpha_A \tag{60}$$

The new variable $s_\beta^0$ and $s_\gamma^0$ satisfy the following Problem A

*Problem A*

$$\rho_\beta\mathbf{v}_\beta.\nabla s_\beta^0 = \nabla.(\rho_\beta D_{\beta A}\nabla s_\beta^0) + \varepsilon_\beta^{-1} \tag{61}$$

and

$$\rho_\gamma\mathbf{v}_\gamma.\nabla s_\gamma^0 = \nabla.(\rho_\gamma D_{\gamma A}\nabla s_\gamma^0) - \varepsilon_\gamma^{-1} \tag{62}$$

with the boundary conditions

$$\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla s_\beta^0 = 0 \text{ at } \mathcal{A}_{\beta\sigma} \tag{63}$$

$$\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla s_\gamma^0 = 0 \text{ at } \mathcal{A}_{\gamma\sigma} \tag{64}$$

$$s_\beta^0 = H_A s_\gamma^0 \text{ at } \mathcal{A}_{\beta\gamma} \tag{65}$$

$$\mathbf{n}_{\beta\gamma}.\rho_\beta D_{\beta A}\nabla s_\beta^0 = \mathbf{n}_{\beta\gamma}.\rho_\gamma D_{\gamma A}\nabla s_\gamma^0 \text{ at } \mathcal{A}_{\beta\gamma} \tag{66}$$

$$s_\beta^0(r+l_i) = s_\beta^0(r); \quad s_\gamma^0(r+l_i) = s_\gamma^0(r); \quad i=1,2,3 \tag{67}$$

$$\langle s_\beta^0\rangle^\beta = -\frac{1}{\alpha_A}; \quad \langle s_\gamma^0\rangle^\gamma = 0 \tag{68}$$

With the above assumptions, and considering that $\mathbf{v}_\gamma = 0$, we recover the problem studied by Coutelieris et al. (2006). The condition that the average of $s_\beta$ is zero allows to determine the mass exchange coefficient $\alpha_A$ (Eq. (68)).

A similar strategy is adopted for the $\mathbf{b}_{\beta\beta}$ and $\mathbf{b}_{\gamma\beta}$ fields by introducing the following decompositions in Problem I:

$$\mathbf{b}_{\beta\beta} = \mathbf{b}_{\beta\beta}^0 - \psi_{\beta\beta}\mathbf{u}_{\gamma\beta} \tag{69}$$

$$\mathbf{b}_{\gamma\beta} = \mathbf{b}_{\gamma\beta}^0 - \psi_{\gamma\beta}\mathbf{u}_{\gamma\beta} \tag{70}$$

We can easily verify that $\psi_{\beta\beta}$ and $\psi_{\gamma\beta}$ are solutions of the previous problem A and $\mathbf{b}_{\beta\beta}^0$ and $\mathbf{b}_{\gamma\beta}^0$ satisfy the following boundary value problem

*Problem B*:

$$\rho_\beta \mathbf{v}_\beta.\nabla\mathbf{b}_{\beta\beta}^0 - \nabla.(\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\beta}^0) + \rho_\beta\tilde{\mathbf{v}}_\beta = \rho_\beta\mathbf{v}_\beta + \rho_\beta\alpha_A\left(\mathbf{v}_\beta s_\beta^0 - \langle\tilde{\mathbf{v}}_\beta s_\beta^0\rangle^\beta\right) \tag{71}$$

and

$$\rho_\gamma \mathbf{v}_\gamma.\nabla\mathbf{b}_{\gamma\beta}^0 - \nabla.(\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\beta}^0) = \rho_\gamma\alpha_A(\mathbf{v}_\gamma s_\gamma^0 - \langle\tilde{\mathbf{v}}_\gamma s_\gamma^0\rangle^\gamma) \tag{72}$$

with the boundary conditions

$$\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\beta}^0 = -\mathbf{n}_{\beta\sigma}\rho_\beta D_{\beta A} \text{ at } \mathcal{A}_{\beta\sigma} \tag{73}$$

$$\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\beta}^0 = 0 \text{ at } \mathcal{A}_{\gamma\sigma} \tag{74}$$

$$\mathbf{b}_{\beta\beta}^0 = H_A\mathbf{b}_{\gamma\beta}^0 \text{ at } \mathcal{A}_{\gamma\beta} \tag{75}$$

$$\mathbf{n}_{\beta\gamma}.\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\beta}^0 - \mathbf{n}_{\beta\gamma}.\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\beta}^0 = -\mathbf{n}_{\beta\gamma}\rho_\beta D_{\beta A} \text{ at } \mathcal{A}_{\gamma\beta} \tag{76}$$

$$\langle\mathbf{b}_{\beta\beta}^0\rangle^\beta = -\frac{\mathbf{u}_{\gamma\beta}}{\alpha_A}; \quad \langle\mathbf{b}_{\gamma\beta}^0\rangle^\gamma = 0 \tag{77}$$

$$\mathbf{b}_{\beta\beta}^0(r+l_i) = \mathbf{b}_{\beta\beta}^0(r); \quad \mathbf{b}_{\gamma\beta}^0(r+l_i) = \mathbf{b}_{\gamma\beta}^0(r); \quad i=1,2,3 \tag{78}$$

Similarly, the following decomposition applied to Problem II:

$$\mathbf{b}_{\gamma\gamma} = \mathbf{b}_{\gamma\gamma}^0 + \psi_{\gamma\gamma}\mathbf{u}_{\beta\gamma} \tag{79}$$

$$\mathbf{b}_{\beta\gamma} = \mathbf{b}_{\beta\gamma}^0 + \psi_{\beta\gamma}\mathbf{u}_{\beta\gamma} \tag{80}$$

leads to the following problem.

*Problem C*:

$$\rho_\beta \mathbf{v}_\beta.\nabla\mathbf{b}_{\beta\gamma}^0 - \nabla.(\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\gamma}^0) = \rho_\beta H_A\alpha_A(\langle\tilde{\mathbf{v}}_\beta s_\beta^0\rangle^\beta - \mathbf{v}_\beta s_\beta^0) - \rho_\beta H_A\mathbf{v}_\beta \tag{81}$$

and

$$\rho_\gamma \mathbf{v}_\gamma.\nabla\mathbf{b}_{\gamma\gamma}^0 - \nabla.(\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\gamma}^0) + \rho_\gamma\tilde{\mathbf{v}}_\gamma = \rho_\gamma H_A\alpha_A(\langle\tilde{\mathbf{v}}_\gamma s_\gamma^0\rangle^\gamma - \mathbf{v}_\gamma s_\gamma^0) \tag{82}$$

with the boundary conditions

$$\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\gamma}^0 = 0 \text{ at } \mathcal{A}_{\beta\sigma} \tag{83}$$

$$\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\gamma}^0 = -\mathbf{n}_{\gamma\sigma}\rho_\gamma D_{\gamma A} \text{ at } \mathcal{A}_{\gamma\sigma} \tag{84}$$

$$\mathbf{b}_{\beta\gamma}^0 = H_A\mathbf{b}_{\gamma\gamma}^0 \text{ at } \mathcal{A}_{\gamma\beta} \tag{85}$$

$$\mathbf{n}_{\beta\gamma}.\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\gamma}^0 - \mathbf{n}_{\beta\gamma}.\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\gamma}^0 = -\mathbf{n}_{\beta\gamma}\rho_\gamma D_{\gamma A} \text{ at } \mathcal{A}_{\gamma\beta} \tag{86}$$

$$\langle\mathbf{b}_{\beta\gamma}^0\rangle^\beta = \frac{\mathbf{u}_{\beta\gamma}}{\alpha_A}; \quad \langle\mathbf{b}_{\gamma\gamma}^0\rangle^\gamma = 0 \tag{87}$$

$$\mathbf{b}_{\beta\gamma}^0(r+l_i) = \mathbf{b}_{\beta\gamma}^0(r); \quad \mathbf{b}_{\gamma\gamma}^0(r+l_i) = \mathbf{b}_{\gamma\gamma}^0(r); \quad i=1,2,3 \tag{88}$$

As previously, one can check that $\psi_{\beta\gamma}$ and $\psi_{\gamma\gamma}$ satisfy Problem A.

The constraints Eqs. (68), (77) and (87) in the previous problems allow the calculation of the mass exchange coefficient $\alpha$ and the velocity-like coefficients $\mathbf{u}_{\beta\gamma}$ and $\mathbf{u}_{\gamma\beta}$.

## 5. Closed form of the averaged equations

Given representations Eqs. (47) and (48) for the deviations $\tilde{\omega}_{\beta A}$ and $\tilde{\omega}_{\gamma A}$ and the above simplifications, we can now obtain a closed form of the macroscopic transport equations of the species *A*. For that purpose, we inject these representations in the Eqs. (31) and (32). In order to clarify the notations, the averaged quantities are denoted as $\Omega_{\beta A} = \langle\omega_{\beta A}\rangle^\beta$, $\Omega_{\gamma A} = \langle\omega_{\gamma A}\rangle^\gamma$, $\mathbf{V}_\beta = \langle\mathbf{v}_\beta\rangle$ and $\mathbf{V}_\gamma = \langle\mathbf{v}_\gamma\rangle$. The macroscopic $\beta$-phase equation in a conservative form is

$$\underbrace{\frac{\partial\varepsilon_\beta\rho_\beta\Omega_{\beta A}}{\partial t}}_{\text{accumulation}} + \underbrace{\nabla.(\rho_\beta\Omega_{\beta A}\mathbf{V}_\beta)}_{\text{convection}} + \underbrace{\nabla.(\varepsilon_\beta\rho_\beta\mathbf{E}_\beta^*(H_A\Omega_{\gamma A}-\Omega_{\beta A}))}_{\text{convection correction}}$$
$$= \underbrace{\nabla.(\varepsilon_\beta\rho_\beta\underline{\underline{\mathbf{D}}}_{\beta\beta}^*.\nabla\Omega_{\beta A})}_{\text{dispersion}} + \underbrace{\nabla.(\varepsilon_\beta\rho_\beta\underline{\underline{\mathbf{D}}}_{\beta\gamma}^*.\nabla\Omega_{\gamma A})}_{\text{dispersion correction}} - \underbrace{\dot{m}_A}_{\text{mass exchange}} \tag{89}$$

In this equation the velocity-like coefficient, $\mathbf{E}_\beta^*$, is defined by

$$\mathbf{E}_\beta^* = \langle\tilde{\mathbf{v}}_\beta s_\beta\rangle^\beta - \frac{1}{\mathcal{V}_\beta}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta D_{\beta A}s_\beta\, d\mathcal{A} \tag{90}$$

and the effective dispersion tensors take the following form

$$\underline{\underline{\mathbf{D}}}_{\beta\beta}^* = D_{\beta A}\mathbf{I} + \frac{1}{\mathcal{V}_\beta}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta D_{\beta A}\mathbf{b}_{\beta\beta}\, d\mathcal{A} - \langle\tilde{\mathbf{v}}_\beta\mathbf{b}_{\beta\beta}\rangle^\beta \tag{91}$$

$$\underline{\underline{\mathbf{D}}}_{\beta\gamma}^* = \frac{1}{\mathcal{V}_\beta}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta D_{\beta A}\mathbf{b}_{\beta\gamma}\, d\mathcal{A} - \langle\tilde{\mathbf{v}}_\beta\mathbf{b}_{\beta\gamma}\rangle^\beta \tag{92}$$

The closed form of the mass rate of evaporation of the A-component reads

$$\dot{m}_A = -\mathbf{u}_{\gamma\beta}.\nabla\Omega_{\beta A} + \mathbf{u}_{\beta\gamma}.\nabla\Omega_{\gamma A} + \alpha_A(H_A\Omega_{\gamma A} - \Omega_{\beta A}) \tag{93}$$

The establishment of this result will be detailed in the next section.

For the $\gamma$-phase, we obtain

$$\frac{\partial\varepsilon_\gamma\rho_\gamma\Omega_{\gamma A}}{\partial t} + \nabla.(\rho_\gamma\Omega_{\gamma A}\mathbf{V}_\gamma) + \nabla.(\varepsilon_\gamma\rho_\gamma\mathbf{E}_\gamma^*(H_A\Omega_{\gamma A}-\Omega_{\beta A}))$$
$$= \nabla.(\varepsilon_\gamma\rho_\gamma\underline{\underline{\mathbf{D}}}_{\gamma\gamma}^*.\nabla\Omega_{\gamma A}) + \nabla.(\varepsilon_\gamma\rho_\gamma\underline{\underline{\mathbf{D}}}_{\gamma\beta}^*.\nabla\Omega_{\beta A}) + \dot{m}_A \tag{94}$$

where

$$\mathbf{E}_\gamma^* = \langle\tilde{\mathbf{v}}_\gamma s_\gamma\rangle^\gamma - \frac{1}{\mathcal{V}_\gamma}\int_{\mathcal{A}_\gamma}\mathbf{n}_\gamma D_{\gamma A}s_\gamma\, d\mathcal{A} \tag{95}$$

$$\underline{\underline{\mathbf{D}}}_{\gamma\gamma}^* = D_{\gamma A}\mathbf{I} + \frac{1}{\mathcal{V}_\gamma}\int_{\mathcal{A}_\gamma}\mathbf{n}_\gamma D_{\gamma A}\mathbf{b}_{\gamma\gamma}\, d\mathcal{A} - \langle\tilde{\mathbf{v}}_\gamma\mathbf{b}_{\gamma\gamma}\rangle^\gamma \tag{96}$$

$$\underline{\underline{\mathbf{D}}}_{\gamma\beta}^* = \frac{1}{\mathcal{V}_\gamma}\int_{\mathcal{A}_\gamma}\mathbf{n}_\gamma D_{\gamma A}\mathbf{b}_{\gamma\beta}\, d\mathcal{A} - \langle\tilde{\mathbf{v}}_\gamma\mathbf{b}_{\gamma\beta}\rangle^\gamma \tag{97}$$

All these effective coefficients are entirely determined by the resolution of the three closure problems detailed in the previous section. Note that some cross terms appear in these macro-scale

equations. They suggest that the transport process in one phase is influenced by the presence of the other phase.

## 6. Closed form of the mass rate of evaporation

In this section, we develop a closed form of the mass rate of evaporation. We recall the definition of the mass exchange rate of species $A$

$$\dot{m}_A = \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma}.(\rho_\beta \omega_{\beta A}(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma}) - \rho_\beta D_{\beta A} \nabla \omega_{\beta A})\, d\mathcal{A} \tag{98}$$

We note that it can also be written as

$$\dot{m}_A = \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma}.\rho_\beta \omega_{\beta A}(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma})\, d\mathcal{A} - \frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta.\rho_\beta D_{\beta A} \nabla \omega_{\beta A}\, d\mathcal{A} \tag{99}$$

The insertion of Gray's decomposition in this relationship leads to

$$\dot{m}_A = \dot{m} \langle \omega_{\beta A} \rangle^\beta + \rho_\beta D_{\beta A} (\nabla \varepsilon_\beta).\nabla \langle \omega_{\beta A} \rangle^\beta + \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta\gamma}} \mathbf{n}_{\beta\gamma}.\rho_\beta \tilde{\omega}_{\beta A}(\mathbf{v}_\beta - \mathbf{w}_{\beta\gamma})\, d\mathcal{A} - \frac{1}{\mathcal{V}} \int_{\mathcal{A}_\beta} \mathbf{n}_\beta.\rho_\beta D_{\beta A} \nabla \tilde{\omega}_{\beta A}\, d\mathcal{A} \tag{100}$$

When we replace the deviations $\tilde{\omega}_{\beta A}$ and $\tilde{\omega}_{\gamma A}$ by their representations (Eqs. (47) and (48)) and by using the definition of $X_{\beta\beta}$, $X_{\beta\gamma}$, $\mathbf{u}_{\beta\beta}$ and $\mathbf{u}_{\beta\gamma}$ (see Appendix A) we have

$$\dot{m}_A = \dot{m} \langle \omega_{\beta A} \rangle^\beta + \rho_\beta D_{\beta A} (\nabla \varepsilon_\beta).\nabla \langle \omega_{\beta A} \rangle^\beta + \mathbf{u}_{\beta\beta}.\nabla \langle \omega_{\beta A} \rangle^\beta + \mathbf{u}_{\beta\gamma}.\nabla \langle \omega_{\gamma A} \rangle^\gamma + X_{\beta\beta} \langle \omega_{\beta A} \rangle^\beta + X_{\beta\gamma} \langle \omega_{\gamma A} \rangle^\gamma \tag{101}$$

Using the relations Eqs. (A.11) and (A.33) we finally get

$$\dot{m}_A = -\mathbf{u}_{\gamma\beta}.\nabla \langle \omega_{\beta A} \rangle^\beta + \mathbf{u}_{\beta\gamma}.\nabla \langle \omega_{\gamma A} \rangle^\gamma - X_{\gamma\beta} \langle \omega_{\beta A} \rangle^\beta + X_{\beta\gamma} \langle \omega_{\gamma A} \rangle^\gamma \tag{102}$$

It must be emphasized that this expression is the full expression that can be used if one wants to solve the coupled averaged equations/closure problems. If we now consider the simplifications previously discussed, the volume mass exchange rate of species $A$ becomes

$$\dot{m}_A = -\mathbf{u}_{\gamma\beta}.\nabla \Omega_{\beta A} + \mathbf{u}_{\beta\gamma}.\nabla \Omega_{\gamma A} + \alpha_A (H_A \Omega_{\gamma A} - \Omega_{\beta A}) \tag{103}$$

Here we see that the exchange term is not only calculated by the somehow classical term $\alpha_A(H_A\Omega_{\gamma A} - \Omega_{\beta A})$, but requires also the introduction of the extra convective terms. These terms are not necessarily negligible, especially for simple unit cells, as was illustrated by Golfier et al. (2002) in the case of flow in a capillary tube.

If necessary, we can calculate the total mass transfer rate, $\dot{m}$, by summing the mass exchange rate of all the species in the system

$$\dot{m} = \sum_A \dot{m}_A \tag{104}$$

## 7. Discussion

At this point, we have developed a comprehensive macro-scale model and the associated closure problems from the microscopic problem describing the transport of a chemical species in a two-phase system obeying a partitioning relationship. In fact two-models are available:

1. A fully macro-scale/micro-scale coupled model in which no particular assumption is made on the evolution of the $\beta\gamma$-interface. Of course, while solving these problems is a very complicated task, this result is of fundamental importance because it gives information on the potential impact of non-negligible interface movements on macro-scale transport equations. This represents an important extension of the work by Quintard and Whitaker (1994) and Coutelieris et al. (2006).
2. A simplified version in which this interface velocity terms have been discarded. The large-scale transport equation for species $A$ has the same structure as in the previous model. However, the macro-scale/micro-scale equations are somehow uncoupled this time, in the sense that effective properties may be calculated from the closure problem provided the position of the interface is know.

Concerning the comparison of this work with the results of Quintard and Whitaker (1994) and Coutelieris et al. (2006), we may add the following comments:

- Like in Coutelieris et al. (2006), the overall upscaling procedure yields two-macro scale equations linked by a mass exchange term. We developed a full closure to determine this term: it depends on a classical exchange term as pointed out by Coutelieris et al. (2006) and also on additional convective terms. The existence of such extra terms when dealing with active dispersion was already suggested in Quintard and Whitaker (1994). They indicate that the macroscopic convective velocity is modified by the presence of the other phase. In this work we have emphasized the importance of these extra terms in the mass rate of evaporation of each species and therefore in the overall mass transfer process.
- Moreover, the averaged equations involve dispersion cross terms, which were not present in the previous works.

## 8. Application to a two-phase film flow

In order to understand the implications of the theoretical developments presented in this paper from a quantitive point of view, we analyze below the classical film two-phase flow problem. Only the simplified version of the closure problems will be used here.

### 8.1. Analytical solutions of the closure problems

In this section we consider the 2D stratified flow of two phases as represented in Fig. 3. In this case, the velocity fields correspond to the classical Poiseuille two-phase flow. The unit-cell is simply a cross-section of the system, with the velocity fields perpendicular to the section and the three closure problems A, B and C can be solved analytically.

First we focus on the mass exchange coefficient $\alpha_A$. The resolution of Problem A gives the following relationship:

$$\frac{1}{\alpha_A} = \frac{L}{3}\left(\frac{H_A \varepsilon_\gamma L}{\rho_\gamma D_{\gamma A}} + \frac{\varepsilon_\beta L}{\rho_\beta D_{\beta A}}\right) \tag{105}$$

This result has to be compared to the overall mass exchange coefficient $K_{OV}$ for the interface transfer (Taylor and Krishna, 1993). It can be estimated as the association in series of the mass transfer coefficients $k_{\beta A}$ and $k_{\gamma A}$ in the $\beta$-phase and in the $\gamma$-phase

$$\frac{1}{K_{OV}} = \frac{H_A}{k_{\gamma A}} + \frac{1}{k_{\beta A}} \tag{106}$$

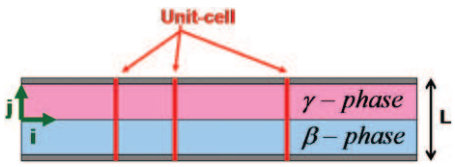


**Fig. 3.** Geometry.

The form of our mass transfer coefficient given by relation Eq. (105) is coherent with the Lewis and Whitman double film theory. Indeed, according to their theory, the resistance to the mass transfer is located in two films on each side of the interface where the thermodynamic equilibrium occurs. The thickness of each film is, respectively, $\delta_\gamma$ and $\delta_\beta$. They estimate the transfer coefficients $k_{\beta A}$ and $k_{\gamma A}$ by the following equations:

$$k_{\beta A}=\frac{\rho_\beta D_{\beta A}}{\delta_\beta};\quad k_{\gamma A}=\frac{\rho_\gamma D_{\gamma A}}{\delta_\gamma} \tag{107}$$

However, it must be noticed here that $\delta_\gamma$ and $\delta_\beta$ are not known a priori. They are in fact solutions of the transport problem. The advantage of the theory proposed in this paper is that the closure problems offer a way to incorporate the transport characteristics, for any unit-cell shape, without relying on a priori solutions like the ones postulated in many film theories.

Table 1 compares the mass transport coefficient obtained in the present case (Eq. (105)) with the ones found by Quintard and Whitaker (1994) and Coutelieris et al. (2006). Since the closure problem introduced by Quintard and Whitaker (1994) accounts for only one phase, the resulting coefficient is only a function of the mass transfer resistance within this phase. Moreover, we note that in this special configuration, the results are similar for the exchange coefficient calculated by Coutelieris et al. (2006) and the one given by Eq. (105). Indeed in this special case of a stratified unit-cell $\rho_\gamma \mathbf{v}_\gamma \cdot \nabla s_\gamma^0 = 0$ in Eq. (62), and, therefore both closure problems by Coutelieris et al. (2006) and Problem A are identical. We must emphasize that most of the time it is not the case.

Then, we solve Problems B and C in order to obtain analytical expressions for the dispersion tensors $\mathbf{D}^*_{\beta\beta}$, $\mathbf{D}^*_{\gamma\beta}$, $\mathbf{D}^*_{\beta\gamma}$ and $\mathbf{D}^*_{\gamma\gamma}$. The solution being very complex, we solve using Taylor's series expansions assuming that the thickness of the $\beta$-phase is very small in comparison with the one of the $\gamma$-phase. This simplification corresponds to the assumption of a $\beta$-phase film flow, i.e.

$$\varepsilon_\beta \ll \varepsilon_\gamma \tag{108}$$

We introduce the dimensionless parameter $\phi$ as

$$\phi=\frac{\rho_\gamma D_{\gamma A}}{\rho_\beta D_{\beta A}} \tag{109}$$

and the Péclet numbers of the $\beta$ and $\gamma$ phases as

$$Pe_\beta=\frac{\langle \mathbf{v}_\beta\rangle^\beta L}{D_{\beta A}};\quad Pe_\gamma=\frac{\langle \mathbf{v}_\gamma\rangle^\gamma L}{D_{\gamma A}} \tag{110}$$

We obtain, - $\mathbf{D}^*_{\beta\beta}$ :

$$\frac{\mathbf{i}.\mathbf{D}^*_{\beta\beta}.\mathbf{i}}{D_{\beta A}}=1+\frac{2}{105}Pe_\beta^2\varepsilon_\beta^2+O(\varepsilon_\beta^3) \tag{111}$$

$$\frac{\mathbf{i}.\mathbf{D}^*_{\beta\beta}.\mathbf{j}}{D_{\beta A}}=-\frac{1}{8}Pe_\beta\varepsilon_\beta+O(\varepsilon_\beta^2) \tag{112}$$

**Table 1**
Comparison of the mass exchange coefficient expression in the case of the stratified unit-cell.

| | Quintard and Whitaker (1994) | Coutelieris et al. (2006) | Present work |
|---|---|---|---|
| Coupled phase | No | Yes | Yes |
| $\gamma$-Phase mobile | No | No | Yes |
| $\frac{1}{\alpha_A}$ | $\frac{2L}{3}\frac{\varepsilon_\beta L}{\rho_\beta D_{\beta A}}$ | $\frac{L}{3}\left(\frac{H_A\varepsilon_\gamma L}{\rho_\gamma D_{\gamma A}}+\frac{\varepsilon_\beta L}{\rho_\beta D_{\beta A}}\right)$ | $\frac{L}{3}\left(\frac{H_A\varepsilon_\gamma L}{\rho_\gamma D_{\gamma A}}+\frac{\varepsilon_\beta L}{\rho_\beta D_{\beta A}}\right)$ |

$$\frac{\mathbf{j}.\mathbf{D}^*_{\beta\beta}.\mathbf{i}}{D_{\beta A}}=-\frac{7}{120}Pe_\beta\varepsilon_\beta+O(\varepsilon_\beta^2) \tag{113}$$

$$\frac{\mathbf{j}.\mathbf{D}^*_{\beta\beta}.\mathbf{j}}{D_{\beta A}}=\frac{3}{2}+O(\varepsilon_\beta) \tag{114}$$

Note that Eq. (111) is similar to the dispersion relationship calculated by Asbjørnsen (1973) and Prenosil (1973) in the case of the Taylor diffusion in falling liquid films. The additional dispersion tensors are given below.

- $\mathbf{D}^*_{\gamma\beta}$ :

$$\frac{\mathbf{i}.\mathbf{D}^*_{\gamma\beta}.\mathbf{i}}{D_{\gamma A}}=\frac{7\varepsilon_\beta^2}{4800H_A}\left(9Pe_\beta^2\left(\frac{D_{\beta A}}{D_{\gamma A}}\right)-2Pe_\beta Pe_\gamma\right)+O(\varepsilon_\beta^3) \tag{115}$$

$$\frac{\mathbf{i}.\mathbf{D}^*_{\gamma\beta}.\mathbf{j}}{D_{\gamma A}}=-\frac{\varepsilon_\beta}{120H_A}\left(9Pe_\beta\left(\frac{D_{\beta A}}{D_{\gamma A}}\right)-2Pe_\gamma\right)+O(\varepsilon_\beta^2) \tag{116}$$

$$\frac{\mathbf{j}.\mathbf{D}^*_{\gamma\beta}.\mathbf{i}}{D_{\gamma A}}=\frac{7\varepsilon_\beta^2}{\varepsilon_\gamma 80H_A}Pe_\beta+O(\varepsilon_\beta^3) \tag{117}$$

$$\frac{\mathbf{j}.\mathbf{D}^*_{\gamma\beta}.\mathbf{j}}{D_{\gamma A}}=-\frac{\varepsilon_\beta}{\varepsilon_\gamma 2H_A}+O(\varepsilon_\beta^2) \tag{118}$$

- $\mathbf{D}^*_{\beta\gamma}$ :

$$\frac{\mathbf{i}.\mathbf{D}^*_{\beta\gamma}.\mathbf{i}}{D_{\beta A}}=\frac{7\varepsilon_\gamma\varepsilon_\beta}{4800\phi^{-1}}\left(58Pe_\beta Pe_\gamma-51Pe_\beta^2\left(\frac{D_{\beta A}}{D_{\gamma A}}\right)\right)+O(\varepsilon_\beta^2) \tag{119}$$

$$\frac{\mathbf{i}.\mathbf{D}^*_{\beta\gamma}.\mathbf{j}}{D_{\beta A}}=-\frac{7\varepsilon_\beta}{120\phi^{-1}}Pe_\beta+O(\varepsilon_\beta^2) \tag{120}$$

$$\frac{\mathbf{j}.\mathbf{D}^*_{\beta\gamma}.\mathbf{i}}{D_{\beta A}}=\frac{\varepsilon_\gamma}{80\phi^{-1}}\left(58Pe_\gamma-51Pe_\beta\left(\frac{D_{\beta A}}{D_{\gamma A}}\right)\right)+O(\varepsilon_\beta) \tag{121}$$

$$\frac{\mathbf{j}.\mathbf{D}^*_{\beta\gamma}.\mathbf{j}}{D_{\beta A}}=-\frac{1}{2\phi^{-1}}+O(\varepsilon_\beta^2) \tag{122}$$

- $\mathbf{D}^*_{\gamma\gamma}$ :

$$\frac{\mathbf{i}.\mathbf{D}^*_{\gamma\gamma}.\mathbf{i}}{D_{\gamma A}}=1-\frac{\varepsilon_\gamma^2}{11200}\left(1444Pe_\gamma^2-2049\left(\frac{D_{\beta A}}{D_{\gamma A}}\right)^2Pe_\beta^2-704\left(\frac{D_{\beta A}}{D_{\gamma A}}\right)Pe_\beta Pe_\gamma\right)+O(\varepsilon_\beta) \tag{123}$$

$$\frac{\mathbf{i}.\mathbf{D}^*_{\gamma\gamma}.\mathbf{j}}{D_{\gamma A}}=-\frac{\phi}{120H_A}\varepsilon_\beta\left(-9Pe_\beta\left(\frac{D_{\beta A}}{D_{\gamma A}}\right)+2Pe_\gamma\right)+O(\varepsilon_\beta^2) \tag{124}$$

$$\frac{\mathbf{j}.\mathbf{D}^*_{\gamma\gamma}.\mathbf{i}}{D_{\gamma A}}=-\frac{1}{80}\varepsilon_\gamma\left(-179Pe_\beta\left(\frac{D_{\beta A}}{D_{\gamma A}}\right)+182Pe_\gamma\right)+O(\varepsilon_\beta) \tag{125}$$

$$\frac{\mathbf{j}.\mathbf{D}^*_{\gamma\gamma}.\mathbf{j}}{D_{\gamma A}}=1+\frac{\phi}{\varepsilon_\gamma 2H_A}\varepsilon_\beta+O(\varepsilon_\beta^2) \tag{126}$$

### 8.2. Numerical validation

In this section we control the validity of the approach developed in this paper by a comparison between our macro-scale model and a direct numerical simulation (DNS) of the pore-scale model. For our simulations, we used the COMSOL Multiphysics™3.5a finite elements toolbox. First, we consider the geometry depicted in Fig. 3. The unit-cells are the vertical cross-section of this geometry. We consider an established two-phase flow, and the $\beta\gamma$-interface is assumed to be motionless. Initially, the mass

fractions are equal to zero. The boundary conditions are

- at the inlet: $\omega_{\beta A} = 0.2$ and $\omega_{\gamma A} = 0.15$,
- at the outlet: a convective flux condition,
- at the wall: a zero flux condition.

In these numerical simulations, the velocity field and the mass fraction fields are, respectively, computed by solving the steady-state Navier–Stokes equations (using quadratic Lagrange elements for the velocities and linear for pressure) and the pore-scale problem (Eqs. (7)– (12)). The advection-diffusion equations are solved using a quadratic Lagrange element formulation. The linear systems are solved using the direct solver UMFPACK based on the Unsymmetric MultiFrontal method. The resulting fields are plotted in Fig. 4 for the steady state and particular choices of various parameters. One may identify here two regions: one entrance region near the inlet where the concentration field evolution is rapid, with a characteristic length-scale smaller than the unit-cell characteristic length. Elsewhere, one see a much smoother solutions which is more appropriate for the periodicity boundary conditions used in the closure problems. This point will be discussed again later, when comparing the macro-scale predictions.

The fields are averaged over cross-sections to provide the 1D evolution of macro-scale mass fractions. These averaged fields are then compared to the ones obtained from the macro-scale model. Before solving the macro-scale equations, we solved the closure problems on a unit-cell as described in Fig. 3.

First, we have investigated the dispersion value $\mathbf{i}.\mathbf{D}^*_{\beta\beta}.\mathbf{i}/D_{\beta A}$ according to the $\beta$-phase thickness by solving the closure problems for different Péclet numbers. Results are plotted in Fig. 5. They are compared to the analytical formula obtained in the previous section (Eq. (111)) and to the Taylor-Aris dispersion coefficient when the phases are treated separately (Quintard and Whitaker, 1994). As was expected for small liquid-phase thicknesses, the analytical result and the simulations fit well.

Then, since all the effective properties are known, we can finally solve the macro-scale equations over a 1D geometry with the same length and boundary conditions as the one of the DNS geometry. For the first simulation, the Péclet numbers considered are, respectively, $Pe_\beta = 1.2$ and $Pe_\gamma = 11.2$. The mass fractions along the $x$-axis when the steady state is reached are plotted in Figs. 6 and 7 is an elution curve in both DNS and macro-model cases.

The actual (DNS) and theoretically predicted mass fraction fields are in very good agreement.

We redo the same operations for higher Péclet number ($Pe_\beta = 12$ and $Pe_\gamma = 112$). Simulation results are exposed in Figs. 8 and 9.

While the overall agreement is fairly good, one sees an increasing discrepancy between the theoretical model and the DNS results, for the phase at high Péclet numbers, and near the domain entrance. These phenomena suggest the following remarks:

1. It is well known that the mass exchange coefficient calculated from DNS varies sharply near the entrance to reach a constant value after a characteristics length depending on the Péclet number,
2. Using periodicity conditions for the closure problems implies that we are working in the established regime. The resulting constant effective properties do not catch the effects occuring near the entrance region. Indeed, by definition, the volume averaging procedure assumes slow variation of the averaged properties which is definitely not the case in such area. Better approximation of the macro-scale mass fraction field in the

**Fig. 4.** Direct numerical simulation at steady-state for $H_A = 1.0$, $Pe_\beta = 3.8$, $Pe_\gamma = 35$.

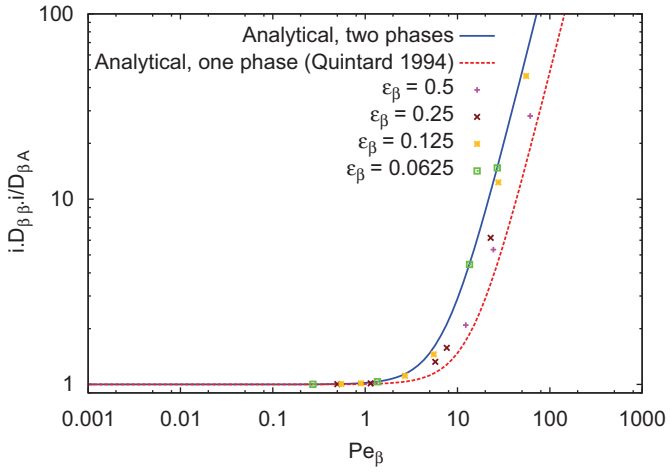


**Fig. 5.** Dispersion coefficient in the $\beta$-phase.

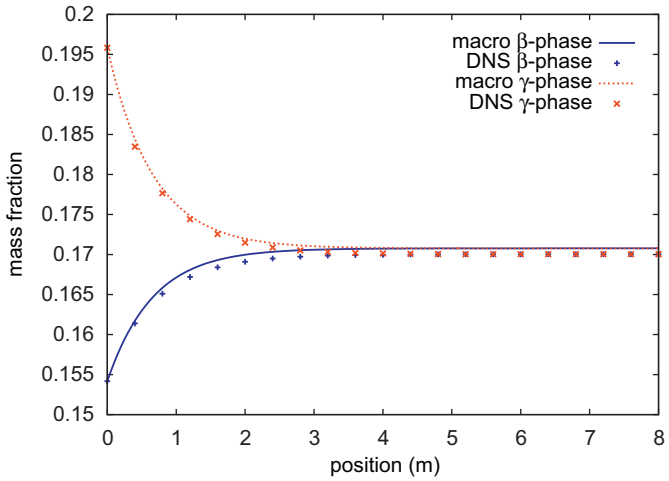


**Fig. 6.** Concentration profiles along the tube at steady state ($H_A = 1.0$, $Pe_\beta = 1.2$, $Pe_\gamma = 11.2$).

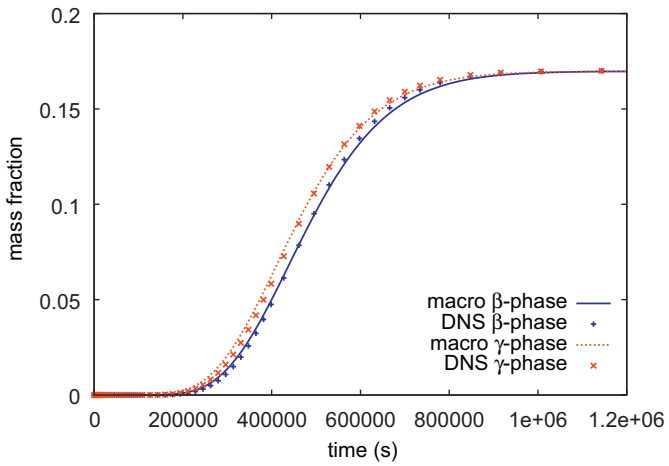


**Fig. 7.** Elution curve ($H_A = 1.0$, $Pe_\beta = 1.2$, $Pe_\gamma = 11.2$).

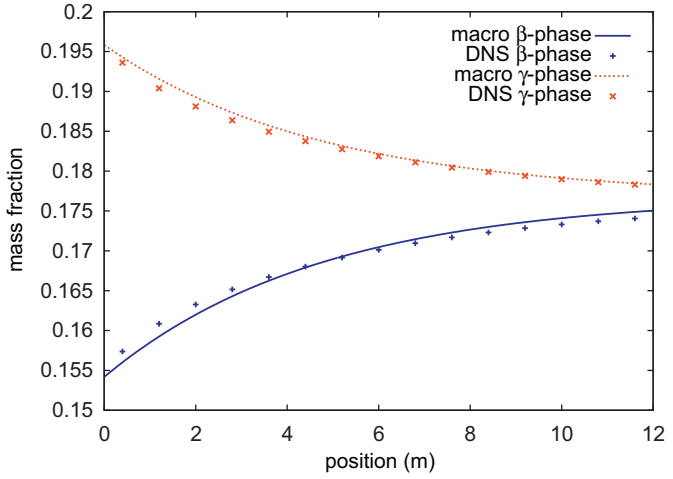


**Fig. 8.** Concentration profiles along the tube at steady state ($H_A = 1.0$, $Pe_\beta = 12$, $Pe_\gamma = 112$).

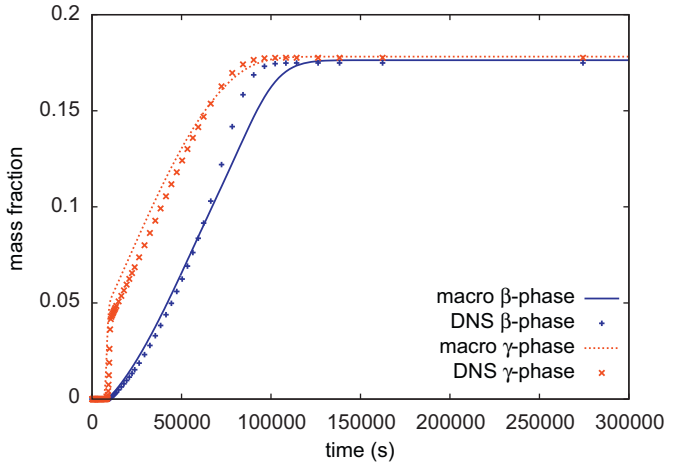


**Fig. 9.** Elution curve ($H_A = 1.0$, $Pe_\beta = 12$, $Pe_\gamma = 112$).

entrance region would require introducing some *non-local theory* that would express the mass exchange coefficient (and possibly change the other effective properties) as a function of the distance from the inlet boundary. For instance this kind of approach has been developed in Kechagia et al. (2002). An alternate solution could be to keep a micro-scale description in the entrance area coupled to the macro-scale model far enough from the entrance boundary (see an example for heat transfer in Batsale et al., 1996). Another approach could be to modify the entrance boundary condition to reflect the impact of the entrance boundary. In this latter example the macro-scale concentration field in the entrance region is less accurate than with the two others proposed techniques.

3. In terms of time evolution, it is well known that a first-order two-equation model has some limitations and that it does not catch all the characteristic times of the real flow. A more thorough discussion of these questions can be found in Davit et al. (2010).

## 9. Conclusion

At this point, we have developed a comprehensive macro-scale model with closure for the general case of the multicomponent flow of two phases in a porous medium, with the restriction that equilibrium is described by a partitioning coefficient. The initial structure of the coupled macro/micro problems has been obtained with a minimum of assumptions, in particular retaining transient terms and terms involving the velocity of the interface. Decoupled solutions were obtained by specifically neglecting these terms. These results represent a generalization of the work by Quintard and Whitaker (1994) and Coutelieris et al. (2006). Moreover, the present model takes into account the motion of both phases. In addition, some new effective terms appear in the macro-scale equations.

The theory was successfully tested against pore-scale DNS results for the simplified case of a stratified two-phase flows in a 2D tube and we have recovered some classical laws used in chemical engineering.

However, all the developments made in this work used the underlying assumptions that the flow regime is laminar. We know that turbulent regimes could modify the results obtained herein. We could tackle this problem using the ideas put forth in Cherblanc et al. (2007) and Pinson et al. (2007), who include turbulence effects inside a non-linear dispersion coefficient. This will be done later in a forthcoming paper where closure problems will be solved on more realistic pore scale geometries. Moreover, it should be interesting to confront the present upscaling process with a case involving a moving interface.

## Nomenclature

| | |
|---|---|
| $\langle \cdot \rangle^i$ | intrisic average for the $i$-phase |
| $\langle \cdot \rangle$ | superficial average |
| $\varepsilon_i$ | volume fraction of the $i$-phase |
| $\mathcal{V}$ | volume defining the unit-cell ($m^3$) |
| $\mathcal{V}_i$ | volume of the $i$-phase within the unit-cell ($m^3$) |
| $\mathbf{J}_{iA}$ | rate of diffusion of species $A$ in the $i$-phase ($kg/m^2/s$) |
| $D_{iA}$ | diffusion coefficient of specie A in the $i$-phase mixture ($m^2/s$) |
| $\omega_{iA}$ | mass fraction of specie A in the $i$-phase mixture |
| $\langle \omega_{iA} \rangle$ | superficial spatial average of $\omega_{iA}$ |
| $\langle \omega_{iA} \rangle^i$, $\Omega_{iA}$ | intrinsic spatial average of $\omega_{iA}$ |
| $\tilde{\omega}_{iA}$ | spatial deviation of $\omega_{iA}$ |
| $\rho_i$ | density in the $i$-phase ($kg/m^3$) |
| $\mathbf{v}_i$ | velocity of the $i$-phase (m/s) |
| $\langle \mathbf{v}_i \rangle^i$ | intrisic spatial average of $\mathbf{v}_i$ (m/s) |
| $\langle \mathbf{v}_i \rangle$, $\mathbf{V}_i$ | superficial spatial average of $\mathbf{v}_i$ (m/s) |
| $\tilde{\mathbf{v}}_i$ | spatial deviation of $\mathbf{v}_i$ (m/s) |
| $\mathbf{w}_{\beta\gamma}$ | velocity of the $\beta\gamma$-interface (m/s) |
| $\mu_{iA}$ | chemical potential of species $A$ in the $i$-phase |
| $H_A$ | partitioning coefficient of species $A$ |
| $\dot{m}$ | overall mass rate of evaporation ($kg/m^3/s$) |
| $\dot{m}_A$ | mass transfer rate for species $A$ ($kg/m^3/s$) |
| $\mathbf{b}_{i\beta}$ | closure variables mapping $\nabla\langle \omega_\beta \rangle^\beta$ (m) |
| $\mathbf{b}_{i\gamma}$ | closure variables mapping $\nabla\langle \omega_\gamma \rangle^\gamma$ (m) |
| $s_{i\beta}$ | closure variables mapping $\langle \omega_\beta \rangle^\beta$ |
| $s_{i\gamma}$ | closure variables mapping $\langle \omega_\gamma \rangle^\gamma$ |
| $s_i$, $s_i^0$, $\psi_{ij}$ | closure variables |
| $\alpha_A$ | exchange coefficient for species $A$ (kg/s) |
| $K_{OV}$ | exchange coefficient for species $A$ (kg/s) |
| $X_{ij}$ | exchange coefficient for species $A$ (kg/s) |
| $\mathbf{u}_{ij}$ | velocity-like coefficient for species $A$ (m/s) |
| $k_{\iota A}$ | mass transfer resistance of species $A$ in the $i$-phase (kg/s) |
| $\mathbf{D}_{ij}^*$ | dispersion tensors for species $A$ ($m^2/s$) |

| | |
|---|---|
| $\mathbf{E}_i^*$ | velocity-like coefficients for species $A$ (m/s) |
| $Pe_i$ | Péclet number in the $i$-phase |
| $\delta_i$ | film thickness in the $i$-phase (m) |
| $L$ | length of the unit-cell (m) |
| $\phi$ | dimensionless parameter defined as $\rho_\gamma D_{\gamma A}/\rho_\beta D_{\beta A}$ |

## Appendix A. Full closure problems

The mass fraction deviations mapping described by Eqs. (47) and (48) leads to four closure problems. They are simplified in Section 4.3.

*Problem I* (mapping onto $\nabla\langle\omega_{\beta A}\rangle^\beta$) :

$$\rho_\beta\frac{\partial\mathbf{b}_{\beta\beta}}{\partial t}+\rho_\beta\mathbf{v}_\beta.\nabla\mathbf{b}_{\beta\beta}+\rho_\beta\mathbf{v}_\beta s_{\beta\beta}-\rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\beta}\rangle^\beta+\rho_\beta\tilde{\mathbf{v}}_\beta = \nabla.(\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\beta})+\varepsilon_\beta^{-1}\mathbf{u}_{\beta\beta} \tag{A.1}$$

$$\rho_\gamma\frac{\partial\mathbf{b}_{\gamma\beta}}{\partial t}+\rho_\gamma\mathbf{v}_\gamma.\nabla\mathbf{b}_{\gamma\beta}+\rho_\gamma\mathbf{v}_\gamma s_{\gamma\beta}-\rho_\gamma\langle\tilde{\mathbf{v}}_\gamma s_{\gamma\beta}\rangle^\gamma=\nabla.(\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\beta})+\varepsilon_\gamma^{-1}\mathbf{u}_{\gamma\beta} \tag{A.2}$$

with the boundary conditions

$$\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\beta}=-\mathbf{n}_{\beta\sigma}\rho_\beta D_{\beta A}\text{ at }\mathcal{A}_{\beta\sigma} \tag{A.3}$$

$$\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\beta}=0\text{ at }\mathcal{A}_{\gamma\sigma} \tag{A.4}$$

$$\mathbf{b}_{\beta\beta}=H_A\mathbf{b}_{\gamma\beta}\text{ at }\mathcal{A}_{\beta\gamma} \tag{A.5}$$

$$-\mathbf{n}_{\beta\gamma}\rho_\beta D_{\beta A}+\mathbf{n}_{\beta\gamma}.(\rho_\beta\mathbf{b}_{\beta\beta}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})-\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\beta}) = \mathbf{n}_{\beta\gamma}.(\rho_\gamma\mathbf{b}_{\gamma\beta}(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})-\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\beta})\text{ at }\mathcal{A}_{\beta\gamma} \tag{A.6}$$

$$\langle\mathbf{b}_{\beta\beta}\rangle^\beta=0;\quad\langle\mathbf{b}_{\gamma\beta}\rangle^\gamma=0 \tag{A.7}$$

$$\mathbf{b}_{\beta\beta}(r+l_i)=\mathbf{b}_{\beta\beta}(r);\quad\mathbf{b}_{\gamma\beta}(r+l_i)=\mathbf{b}_{\gamma\beta}(r);\quad i=1,2,3 \tag{A.8}$$

and

$$\mathbf{u}_{\beta\beta}=\frac{1}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\beta\gamma}.\rho_\beta\mathbf{b}_{\beta\beta}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}-\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta.\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\beta}\,d\mathcal{A} \tag{A.9}$$

$$\mathbf{u}_{\gamma\beta}=\frac{1}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\gamma\beta}.\rho_\gamma\mathbf{b}_{\gamma\beta}(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}-\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\gamma}\mathbf{n}_\gamma.\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\beta}\,d\mathcal{A} \tag{A.10}$$

The integration of the $\beta\gamma$-interface boundary conditions Eq. (A.6) results in

$$-\mathbf{u}_{\gamma\beta}=\mathbf{u}_{\beta\beta}+\rho_\beta D_{\beta A}\nabla\varepsilon_\beta \tag{A.11}$$

*Problem II* (mapping onto $\nabla\langle\omega_{\gamma A}\rangle^\gamma$):

$$\rho_\beta\frac{\partial\mathbf{b}_{\beta\gamma}}{\partial t}+\rho_\beta\mathbf{v}_\beta.\nabla\mathbf{b}_{\beta\gamma}+\rho_\beta\mathbf{v}_\beta s_{\beta\gamma}-\rho_\beta\langle\tilde{\mathbf{v}}_\beta s_{\beta\gamma}\rangle^\beta=\nabla.(\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\gamma})+\varepsilon_\beta^{-1}\mathbf{u}_{\beta\gamma} \tag{A.12}$$

and

$$\rho_\gamma\frac{\partial\mathbf{b}_{\gamma\gamma}}{\partial t}+\rho_\gamma\mathbf{v}_\gamma.\nabla\mathbf{b}_{\gamma\gamma}+\rho_\gamma\mathbf{v}_\gamma s_{\gamma\gamma}-\rho_\gamma\langle\tilde{\mathbf{v}}_\gamma s_{\gamma\gamma}\rangle^\gamma+\rho_\gamma\tilde{\mathbf{v}}_\gamma=\nabla.(\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\gamma})+\varepsilon_\gamma^{-1}\mathbf{u}_{\gamma\gamma} \tag{A.13}$$

with the boundary conditions

$$\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\gamma}=0\text{ at }\mathcal{A}_{\beta\sigma} \tag{A.14}$$

$$\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\gamma}=-\mathbf{n}_{\gamma\sigma}\rho_\gamma D_{\gamma A}\text{ at }\mathcal{A}_{\gamma\sigma} \tag{A.15}$$

$$\mathbf{b}_{\beta\gamma}=H_A\mathbf{b}_{\gamma\gamma}\text{ at }\mathcal{A}_{\gamma\beta} \tag{A.16}$$

$$\mathbf{n}_{\gamma\beta}\rho_\gamma D_{\gamma A}+\mathbf{n}_{\gamma\beta}.(\rho_\gamma\mathbf{b}_{\gamma\gamma}(\mathbf{v}_\gamma-\mathbf{w}_{\gamma\beta})-\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\gamma}) = \mathbf{n}_{\gamma\beta}.(\rho_\beta\mathbf{b}_{\beta\gamma}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})-\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\gamma})\text{ at }\mathcal{A}_{\gamma\beta} \tag{A.17}$$

$$\langle\mathbf{b}_{\beta\gamma}\rangle^\beta=0;\quad\langle\mathbf{b}_{\gamma\gamma}\rangle^\gamma=0 \tag{A.18}$$

$$\mathbf{b}_{\beta\gamma}(r+l_i)=\mathbf{b}_{\beta\gamma}(r);\quad\mathbf{b}_{\gamma\gamma}(r+l_i)=\mathbf{b}_{\gamma\gamma}(r);\quad i=1,2,3 \tag{A.19}$$

and

$$\mathbf{u}_{\beta\gamma}=\frac{1}{\mathcal{V}}\int_{\mathcal{A}_{\gamma\beta}}\mathbf{n}_{\beta\gamma}.\rho_\beta\mathbf{b}_{\beta\gamma}(\mathbf{v}_\beta-\mathbf{w}_{\gamma\beta})\,d\mathcal{A}-\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta.\rho_\beta D_{\beta A}\nabla\mathbf{b}_{\beta\gamma}\,d\mathcal{A} \tag{A.20}$$

$$\mathbf{u}_{\gamma\gamma}=\frac{1}{\mathcal{V}}\int_{\mathcal{A}_{\gamma\beta}}\mathbf{n}_{\gamma\beta}.\rho_\gamma\mathbf{b}_{\gamma\gamma}(\mathbf{v}_\gamma-\mathbf{w}_{\gamma\beta})\,d\mathcal{A}-\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\gamma}\mathbf{n}_\gamma.\rho_\gamma D_{\gamma A}\nabla\mathbf{b}_{\gamma\gamma}\,d\mathcal{A} \tag{A.21}$$

The integration of the $\beta\gamma$-interface boundary conditions Eq. (A.17) results in

$$-\mathbf{u}_{\beta\gamma}=\mathbf{u}_{\gamma\gamma}+\rho_\gamma D_{\gamma A}\nabla\varepsilon_\gamma \tag{A.22}$$

*Problem III* (mapping onto $\langle\omega_{\beta A}\rangle^\beta$):

$$\rho_\beta\frac{\partial s_{\beta\beta}}{\partial t}+\rho_\beta\mathbf{v}_\beta.\nabla s_{\beta\beta}=\nabla.(\rho_\beta D_{\beta A}\nabla s_{\beta\beta})+\varepsilon_\beta^{-1}X_{\beta\beta} \tag{A.23}$$

and

$$\rho_\gamma\frac{\partial s_{\gamma\beta}}{\partial t}+\rho_\gamma\mathbf{v}_\gamma.\nabla s_{\gamma\beta}=\nabla.(\rho_\gamma D_{\gamma A}\nabla s_{\gamma\beta})+\varepsilon_\gamma^{-1}X_{\gamma\beta} \tag{A.24}$$

with the boundary conditions

$$\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla s_{\beta\beta}=0\text{ at }\mathcal{A}_{\beta\sigma} \tag{A.25}$$

$$\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla s_{\gamma\beta}=0\text{ at }\mathcal{A}_{\gamma\sigma} \tag{A.26}$$

$$s_{\beta\beta}=H_A s_{\gamma\beta}-1\text{ at }\mathcal{A}_{\beta\gamma} \tag{A.27}$$

$$\mathbf{n}_{\beta\gamma}.\rho_\beta(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})+\mathbf{n}_{\beta\gamma}.(\rho_\beta s_{\beta\beta}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})-\rho_\beta D_{\beta A}\nabla s_{\beta\beta}) = \mathbf{n}_{\beta\gamma}.(\rho_\gamma s_{\gamma\beta}(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})-\rho_\gamma D_{\gamma A}\nabla s_{\gamma\beta})\text{ at }\mathcal{A}_{\beta\gamma} \tag{A.28}$$

$$\langle s_{\beta\beta}\rangle^\beta=0;\quad\langle s_{\gamma\beta}\rangle^\gamma=0 \tag{A.29}$$

$$s_{\beta\beta}(r+l_i)=s_{\beta\beta}(r);\quad s_{\gamma\beta}(r+l_i)=s_{\gamma\beta}(r);\quad i=1,2,3 \tag{A.30}$$

and

$$X_{\beta\beta}=\frac{1}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\beta\gamma}.\rho_\beta s_{\beta\beta}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}-\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\beta}\mathbf{n}_\beta.\rho_\beta D_{\beta A}\nabla s_{\beta\beta}\,d\mathcal{A} \tag{A.31}$$

$$X_{\gamma\beta}=\frac{1}{\mathcal{V}}\int_{\mathcal{A}_{\beta\gamma}}\mathbf{n}_{\gamma\beta}.\rho_\gamma s_{\gamma\beta}(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})\,d\mathcal{A}-\frac{1}{\mathcal{V}}\int_{\mathcal{A}_\gamma}\mathbf{n}_\gamma.\rho_\gamma D_{\gamma A}\nabla s_{\gamma\beta}\,d\mathcal{A} \tag{A.32}$$

The integration of the $\beta\gamma$-interface boundary conditions Eq. (A.28) results in

$$-X_{\gamma\beta}=X_{\beta\beta}+\dot{m} \tag{A.33}$$

*Problem IV* (mapping onto $\langle\omega_{\gamma A}\rangle^\gamma$) :

$$\rho_\beta\frac{\partial s_{\beta\gamma}}{\partial t}+\rho_\beta\mathbf{v}_\beta.\nabla s_{\beta\gamma}=\nabla.(\rho_\beta D_{\beta A}\nabla s_{\beta\gamma})+\varepsilon_\beta^{-1}X_{\beta\gamma} \tag{A.34}$$

and

$$\rho_\gamma\frac{\partial s_{\gamma\gamma}}{\partial t}+\rho_\gamma\mathbf{v}_\gamma.\nabla s_{\gamma\gamma}=\nabla.(\rho_\gamma D_{\gamma A}\nabla s_{\gamma\gamma})+\varepsilon_\gamma^{-1}X_{\gamma\gamma} \tag{A.35}$$

with the boundary conditions

$$\mathbf{n}_{\beta\sigma}.\rho_\beta D_{\beta A}\nabla s_{\beta\gamma}=0\text{ at }\mathcal{A}_{\beta\sigma} \tag{A.36}$$

$$\mathbf{n}_{\gamma\sigma}.\rho_\gamma D_{\gamma A}\nabla s_{\gamma\gamma}=0\text{ at }\mathcal{A}_{\gamma\sigma} \tag{A.37}$$

$$s_{\gamma\gamma}=H_A^{-1}s_{\beta\gamma}-1\text{ at }\mathcal{A}_{\beta\gamma} \tag{A.38}$$

$$\mathbf{n}_{\gamma\beta}.\rho_\gamma(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})+\mathbf{n}_{\gamma\beta}.(\rho_\gamma s_{\gamma\gamma}(\mathbf{v}_\gamma-\mathbf{w}_{\beta\gamma})-\rho_\gamma D_{\gamma A}\nabla s_{\gamma\gamma}) = \mathbf{n}_{\gamma\beta}.(\rho_\beta s_{\beta\gamma}(\mathbf{v}_\beta-\mathbf{w}_{\beta\gamma})-\rho_\beta D_{\beta A}\nabla s_{\beta\gamma})\text{ at }\mathcal{A}_{\beta\gamma} \tag{A.39}$$

$$\langle s_{\gamma\gamma} \rangle^{\gamma} = 0; \quad \langle s_{\beta\gamma} \rangle^{\beta} = 0 \tag{A.40}$$

$$s_{\gamma\gamma}(r+l_i) = s_{\gamma\gamma}(r); \quad s_{\beta\gamma}(r+l_i) = s_{\beta\gamma}(r); \quad i = 1,2,3 \tag{A.41}$$

and

$$X_{\gamma\gamma} = \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\gamma\beta}} \mathbf{n}_{\gamma\beta}.\rho_{\gamma} s_{\gamma\gamma}(\mathbf{v}_{\gamma} - \mathbf{w}_{\gamma\beta})\, d\mathcal{A} - \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\gamma}} \mathbf{n}_{\gamma}.\rho_{\gamma} D_{\gamma A} \nabla s_{\gamma\gamma}\, d\mathcal{A} \tag{A.42}$$

$$X_{\beta\gamma} = \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\gamma\beta}} \mathbf{n}_{\beta\gamma}.\rho_{\beta} s_{\beta\gamma}(\mathbf{v}_{\beta} - \mathbf{w}_{\gamma\beta})\, d\mathcal{A} - \frac{1}{\mathcal{V}} \int_{\mathcal{A}_{\beta}} \mathbf{n}_{\beta}.\rho_{\beta} D_{\beta A} \nabla s_{\beta\gamma}\, d\mathcal{A} \tag{A.43}$$

The integration of the $\beta\gamma$-interface boundary conditions Eq. (A.39) results in

$$X_{\beta\gamma} = -X_{\gamma\gamma} + \dot{m} \tag{A.44}$$

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