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Advection-diffusion in porous media with low scale separation: modelling via higher-order asymptotic homogenisation

Pascale Royer

Abstract

Asymptotic multiple scale homogenisation allows to determine the effective behaviour of a porous medium by starting from the pore-scale description, when there is a large separation between the pore-scale and the macroscopic scale. When the scale ratio is “small but not too small,” the standard approach based on first-order homogenisation may break down since additional terms need to be taken into account in order to obtain an accurate picture of the overall response of the medium. The effect of low scale separation can be obtained by exploiting higher order equations in the asymptotic homogenisation procedure. The aim of the present study is to investigate higher-order terms up to the third order of the advective-diffusive model to describe advection-diffusion in a macroscopically homogeneous porous medium at low scale separation. The main result of the study is that the low separation of scales induces dispersion effects. In particular, the second-order model is similar to the most currently used phenomenological model of dispersion: it is characterised by a dispersion tensor which can be decomposed into a purely diffusive component and a mechanical dispersion part, whilst this property is not verified in the homogenised dispersion model (obtained at higher Péclet number). The third-order description contains second and third concentration gradient terms, with a fourth order tensor of diffusion and with a third-order and an additional second-order tensors of dispersion. The analysis of the macroscopic fluxes shows that the second and the third order macroscopic fluxes are distinct from the volume averages of the corresponding local fluxes and allows to determine expressions of the non-local effects.

1 Introduction

Most studies in the theory of flow and transport in porous media are based on the exploitation of the continuum theory implying that the original heterogeneous medium behaves like a homogeneous one characterised by macroscopic fluid flow and transport equations with certain effective properties. Such an approach requires that the condition of separation of scales be fulfilled: the microscopic size l of heterogeneities must be essentially smaller than the macroscopic characteristic length L : $l \ll L$. In this definition, length L represents either the size of the whole sample, or a macroscopic characteristic length of the phenomenon, which means that the condition of separation

of scales must be fulfilled geometrically and also and with respect to loading conditions.

The multiple-scale asymptotic homogenisation method which can be traced to Sanchez-Palencia (1980), Bensoussan et al. (1978), and Bakhvalov and Panasenko (1989) can be used as a systematic tool of averaging so as to derive such continuum models: first-order models obtained by asymptotic homogenisation are thus accurate for media with large scale separation between the pore scale and the macroscale. But when the ratio l/L is “small but not too small“, microstructural scale effects may occur which result in specific non-local phenomena. Then, the “local action” assumption of classical continuum mechanics, which postulates that the current state of the medium at a given point is only affected by its immediate neighbours and that there are no physical mechanisms that produce action at a distance, is no longer satisfied. Consequently, additional terms need to be taken into account in order to obtain an accurate picture of the overall response of the medium, which cannot be predicted in the frame of first-order homogenisation theory. Thus, the study of so-called higher order or non-local effects in the overall behaviour of heterogeneous media is motivated by the need to account for the scale effects observed in the behaviour of multiple-scale heterogeneous media where the scales are separated widely but not “too widely”, and these scale effects can be systematically analysed by considering higher-order correctors in the asymptotic homogenisation method.

Mathematical aspects of higher-order homogenisation have been developed in Smyshlyaev and Cherednichenko (2000), Cherednichenko and Smyshlyaev (2004). The role of higher order terms has been investigated for heat conduction in heterogeneous materials in Boutin (1995) and for elastic composite materials subjected to static loading in Gambin and Kroner (1989), Boutin (1996). In these studies, it is shown that the heterogeneity of the medium causes non-local effects on a macrolevel: instead of the homogenised equilibrium equations of continuum mechanics, new equilibrium equations are obtained that involve higher-order spatial derivatives and thus represent the influence of the microstructural heterogeneity on the macroscopic behaviour of the material. In dynamic problems, application of higher-order homogenisation provides a long-wave approach valid in the low-frequency range (Boutin and Auriault, 1993; Fish and Chen, 2001; Bakhvalov and Eglit, 2005; Chen and Fish, 200; Andrianov et al., 2008). In Boutin and Auriault (1993), it is demonstrated that higher-order terms successively introduce effects of polarization, dispersion and attenuation.

Transport in porous media with low scale separation has thus far received relatively little attention. However, two important works on fluid flow have been performed. In Goyeau et al. (1997, 1999), the authors investigate the permeability in a dendritic mushy zone, which is generally a nonhomogeneous porous structure. They make use of the volume averaging method to obtain corrector terms to Darcy’s law. In Auriault et al. (2005), the validity of Darcy’s law is investigated by higher-order asymptotic homogenisation up to the third order.

The focus of the present study is on solute transport by advection-diffusion in porous media with low scale separation, which can occur in the two following situations (Auriault et al., 2005): i) when large gradients of concentration are applied to macroscopically homogeneous porous media; ii) when the porous medium is macroscopically heterogeneous and the macroscopic characteristic length L associated to the

macroscopic heterogeneities is not “very” large compared to the characteristic length l of the pores. The scope of the present work is to derive higher-order homogenised models of advection-diffusion in macroscopically homogeneous porous media and is therefore aimed at describing the situations where large concentration gradients are applied. This may for example happen during soil-column experiments, where soil samples are necessarily limited in size and are subjected to large concentration gradients, especially at early stages of the tests. In these situations the macroscopic characteristic length $L \approx C/|\vec{\nabla}C|$ associated to this gradient of concentration is not “very” large compared to l (Auriault and Lewandowska, 1997). Homogenisation of convection-diffusion equations on the pore scale leads to three macroscopic transport models, accordingly to the order of magnitude of the Péclet number (Auriault and Adler, 1995): i) a diffusion model; ii) an advection-diffusion model; iii) an advection-dispersion model. Whilst the first two models are first-order models, the dispersive model requires to account for the first corrector. The purpose of the present work is to derive the second and third order homogenised models in the case where the model of advection diffusion is obtained at the first order.

The paper is organised as follows. Section 2 presents the existing phenomenological and homogenised macro-models and their properties for describing solute transport in rigid porous media. The input transport problem is formulated in Section 3: the medium geometry is described in §3.1 and the pore-scale governing equations for fluid flow and solute transport are then presented and nondimensionalised in §3.2. The results from Auriault et al. (2005) for higher-order homogenisation up to the third order of the fluid flow equations, and which are required for the developments that follow, are briefly summarised in Section 4. Section 5 is devoted to higher-order homogenisation up to the third order of solute transport equations in the advective-diffusive macro-regime. The physical meaning of the volume averages of local fluxes which arise with the homogenisation procedure is analysed in Section 6 and the writing of the second and third order homogenised models in terms of the macroscopic fluxes provides expressions of the non-local effects. Finally, Section 7, presents a summary of the main theoretical results contained in this work and highlights conclusive remarks.

2 About phenomenological and homogenised models of solute transport in porous media

2.1 Phenomenological macro-models

Let consider a rigid porous medium saturated by an incompressible Newtonian fluid. When the fluid is at rest, transient solute transport within the medium is described by the model of diffusion:

$$\phi \frac{\partial C}{\partial t} - \vec{\nabla} \cdot (\bar{\bar{D}}^{\text{eff}} \vec{\nabla} C) = 0, \quad (2.1)$$

in which ϕ denotes the porosity, C represents the concentration and $\bar{\bar{D}}^{\text{eff}}$ is the tensor of effective diffusive. When the fluid is in motion, solute transport may either be described

by the model of advection-diffusion

$$\phi \frac{\partial C}{\partial t} - \vec{\nabla} \cdot (\bar{D}^{\text{eff}} \vec{\nabla} C - C \vec{V}) = 0, \quad (2.2)$$

or by the model of advection-dispersion

$$\phi \frac{\partial C}{\partial t} - \vec{\nabla} \cdot (\bar{D}^{\text{disp}} \vec{\nabla} C - C \vec{V}) = 0. \quad (2.3)$$

In both models, \vec{V} denotes the macroscopic fluid velocity and verifies:

$$\begin{cases} \vec{V} = -\frac{\bar{K}}{\mu} \vec{\nabla} P, & \text{(Darcy's law)} \\ \vec{\nabla} \cdot \vec{V} = 0, \end{cases} \quad (2.4)$$

$$(2.5)$$

where \bar{K} denotes the tensor of permeability, μ is the fluid viscosity and P represents the fluid pressure. For the sake of simplicity, gravity is neglected in Eq. (2.4). Tensor \bar{D}^{disp} in model Eq. (2.3) is the tensor of hydrodynamic dispersion: it depends on the fluid velocity. In the most currently used model of dispersion (Bear, 1972; Bear and Bachmat, 1990), the tensor of dispersion is decomposed into the sum of a diffusive term and a term of mechanical dispersion which depends on the fluid velocity:

$$\bar{D}^{\text{disp}} = \bar{D}^{\text{eff}} + \bar{D}^{\text{mech disp}}. \quad (2.6)$$

Whilst the regime of advection-diffusion is rarely mentioned in the geosciences literature, it is of particular relevance for modelling electro-chemio-mechanical coupling in swelling porous media (Moyné and Murad, 2006). Advection-diffusion is furthermore the usual transport regime observed in biological tissues (Becker and Kuznetsov, 2013; Ambard and Swider, 2006; Swider et al., 2010; Lemaire and Naili, 2013).

2.2 Homogenised models

Homogenisation of the convection-diffusion equations on the pore scale allows to find the three above-mentioned transport regimes (Auriault and Adler, 1995) and to give their respective range of validity by means of the order of magnitude of the Péclet number

$$\text{Pe} = \frac{v_c L}{D_c}, \quad (2.7)$$

where L denotes the characteristic macroscopic length, and where v_c and D_c are characteristic values of the local fluid velocity and of the coefficient of molecular diffusion. The results of Auriault and Adler (1995) are the following:

$$\begin{cases} \text{Pe} \leq \mathcal{O}(\varepsilon) : & \text{Regime of diffusion} \\ \text{Pe} = \mathcal{O}(\varepsilon^0) & \text{Regime of advection-diffusion} \\ \text{Pe} = \mathcal{O}(\varepsilon^{-1}) & \text{Regime of advection-dispersion} \\ \text{Pe} \geq \mathcal{O}(\varepsilon^{-2}) & \text{No continuum macro-model,} \end{cases}$$

where $\varepsilon = l/L$, with l being the pore-scale characteristic length, is the small parameter of the asymptotic homogenisation method and where a parameter \mathbb{P} is said to be of order ε^p , $\mathbb{P} = \mathcal{O}(\varepsilon^p)$, when

$$\varepsilon^{p+1} \ll \mathbb{P} \ll \varepsilon^{p-1}. \quad (2.8)$$

The homogenised models of diffusion and of advection-diffusion are first-order models and are rigorously identical to models Eqs. (2.1)-(2.2). On the other hand however, the homogenised model of advection-dispersion is different from the classical phenomenological model Eq. (2.3). It is a second-order model, which in particular implies that Darcy's law is no longer valid (Auriault et al., 2005). Furthermore, the homogenised tensor of dispersion does not verify relationship Eq. (2.6) and is not symmetric (Auriault and Adler, 1995; Auriault et al., 2010). At high Péclet number, $\mathbb{P}e \geq \mathcal{O}(\varepsilon^{-2})$, the problem becomes dependent upon the macroscopic boundary-conditions. Consequently, there exists no continuum macro-model to describe solute transport within this regime.

3 Problem statement for homogenisation of solute transport within the advective-diffusive regime

3.1 Geometry

Consider a rigid porous medium with connected pores. We assume it to be periodic with period $\hat{\Omega}$. The fluid occupies the pores $\hat{\Omega}_p$, and $\hat{\Gamma}$ represents the surface of the solid matrix $\hat{\Omega}_s$. We denote as \hat{l} and \hat{L} the characteristic length of the pores and the macroscopic length (Fig. 1). We assume the scales to be separated and we define

$$\varepsilon = \frac{\hat{l}}{\hat{L}} \ll 1. \quad (3.1)$$

Using the two characteristic lengths, \hat{l} and \hat{L} , two dimensionless space variables are

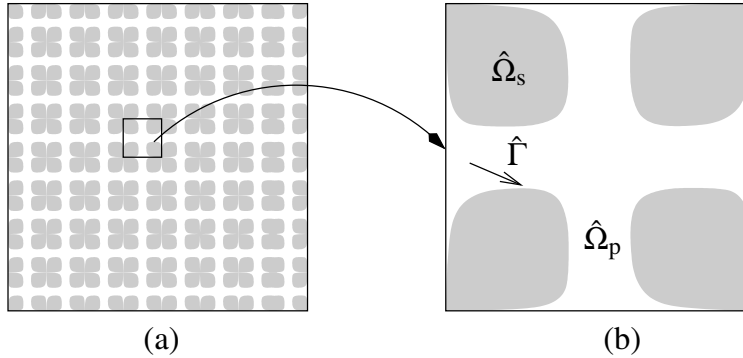


Figure 1: *Periodic porous medium : (a) Macroscopic sample ; (b) Periodic cell $\hat{\Omega}$.*

defined

$$\vec{y} = \frac{\vec{X}}{\hat{l}} \quad \text{which describes variations on the microscopic scale,} \quad (3.2)$$

$$\vec{x} = \frac{\vec{X}}{\hat{L}} \quad \text{which describes variations on the macroscopic scale,} \quad (3.3)$$

where \vec{X} is the physical spatial variable. Invoking the differentiation rule of multiple variables, the gradient operator with respect to \vec{X} is written as

$$\vec{\nabla}_{\vec{X}} = \frac{1}{\hat{l}} \vec{\nabla}_y + \frac{1}{\hat{L}} \vec{\nabla}_x, \quad (3.4)$$

where $\vec{\nabla}_y$ and $\vec{\nabla}_x$ are the gradient operators with respect to \vec{y} and \vec{x} , respectively.

3.2 Governing equations on the pore scale and estimates

The pores are saturated with a viscous, incompressible and Newtonian fluid containing a low concentration of solute \hat{c} . The fluid is in slow steady-state isothermal flow, so that the solute is transported by diffusion and convection.

3.2.1 Fluid flow

The equations governing velocity \vec{v} and pressure \hat{p} of an incompressible viscous fluid of viscosity $\hat{\mu}$ in slow steady-state flow within the pores are the following:

- Stokes equation

$$\hat{\mu} \Delta_{\vec{X}} \vec{v} - \vec{\nabla}_{\vec{X}} \hat{p} = \vec{0} \quad \text{within } \hat{\Omega}_p, \quad (3.5)$$

- the conservation of mass

$$\vec{\nabla}_{\vec{X}} \cdot \vec{v} = 0 \quad \text{within } \hat{\Omega}_p, \quad (3.6)$$

- the no-slip condition

$$\vec{v} = \vec{0} \quad \text{over } \hat{\Gamma}. \quad (3.7)$$

3.2.2 Solute transport

The transport of solute by diffusion-convection in the pore domain is described by conservation of mass

$$\frac{\partial \hat{c}}{\partial \hat{t}} - \vec{\nabla}_{\vec{X}} \cdot (\hat{D}_0 \vec{\nabla}_{\vec{X}} \hat{c} - \hat{c} \vec{v}) = 0 \quad \text{within } \hat{\Omega}_p, \quad (3.8)$$

and the no-flux boundary condition

$$(\hat{D}_0 \vec{\nabla}_{\vec{X}} \hat{c} - \hat{c} \vec{v}) \cdot \vec{n} = (\hat{D}_0 \vec{\nabla}_{\vec{X}} \hat{c}) \cdot \vec{n} = 0 \quad \text{over } \hat{\Gamma}, \quad (3.9)$$

where \hat{c} is the solute concentration (mass of solute per unit volume of fluid), \hat{t} is the time, \hat{D}_0 denotes the coefficient of molecular diffusion and \vec{n} is the unit vector giving the normal to $\hat{\Gamma}$ exterior to $\hat{\Omega}_p$.

3.2.3 Nondimensionalisation and estimates

Introducing into Eqs. (3.5)-(3.9)

$$\begin{aligned}\vec{\nabla}_{\hat{x}} &= 1/L \vec{\nabla}, & \Delta_{\hat{x}} &= 1/L^2 \Delta, \\ \hat{t} &= t_c t, & \partial/\partial \hat{t} &= 1/t_c \partial/\partial t, \\ \vec{v} &= v_c \vec{v}, & \hat{p} &= p_c p, & \hat{c} &= c_c c, \\ \hat{\mu} &= \mu_c \mu, & \hat{D}_0 &= D_c D_0,\end{aligned}$$

where quantities with subscript c denote characteristic quantities, we can write the microscopic description in dimensionless form as

$$\left\{ \begin{array}{l} \mathbb{F} \mu \Delta \vec{v} - \vec{\nabla} p = \vec{0} \quad \text{within } \Omega_p, \\ \vec{\nabla} \cdot \vec{v} = 0 \quad \text{within } \Omega_p, \\ \mathbb{N} \frac{\partial c}{\partial t} - \vec{\nabla} \cdot (D_0 \vec{\nabla} c - \mathbb{P}e c \vec{v}) = 0 \quad \text{within } \Omega_p, \\ \vec{v} = \vec{0} \quad \text{over } \Gamma, \\ (D_0 \vec{\nabla} c) \cdot \vec{n} = 0 \quad \text{over } \Gamma, \end{array} \right. \quad \begin{array}{l} (3.10) \\ (3.11) \\ (3.12) \\ (3.13) \\ (3.14) \end{array}$$

with

$$\mathbb{F} = \frac{\mu_c v_c}{L p_c}; \quad \mathbb{N} = \frac{L^2}{t_c D_c}; \quad \mathbb{P}e = \frac{v_c L}{D_c}.$$

In the above writing, the dimensionless counterpart of any dimensional quantity $\hat{\Psi}$ is $\Psi = \hat{\Psi}/\Psi_c$. In particular, the characteristic time t_c is the time over which we intend to describe the solute transport: it is the characteristic time of the observation. We have arbitrarily chosen the macroscopic length \hat{L} as the reference length for normalising the gradient operator. Consequently, according to Eq. (3.4), the corresponding dimensionless gradient operator reads

$$\vec{\nabla} = L \vec{\nabla}_{\hat{x}} = \varepsilon^{-1} \vec{\nabla}_y + \vec{\nabla}_x. \quad (3.15)$$

We may now estimate the three dimensionless parameters, \mathbb{F} , \mathbb{N} and the Péclet number $\mathbb{P}e$, with respect to powers of the small parameter ε and for this purpose we shall apply the rule defined by Eq. (2.8). Parameter \mathbb{F} , which arises from Stokes equation Eq. (3.10), is the ratio of the viscous term to the pressure gradient. We shall consider the case where homogenisation of Stokes equations leads to Darcy's law on the sample scale. As shown in Auriault (1991), this happens when the local flow is balanced by a macroscopic pressure gradient, which in an order-of-magnitude sense reads

$$\frac{\mu_c v_c}{l^2} = \mathcal{O}\left(\frac{p_c}{L}\right), \quad (3.16)$$

and yields

$$\mathbb{F} = \frac{\mu_c v_c}{L p_c} = \mathcal{O}(\varepsilon^2). \quad (3.17)$$

The order-of-magnitude of the Péclet number $\mathbb{P}e$ characterises the regime of solute transport. Indeed, it is the ratio of characteristic times of diffusion and convection

$$\mathbb{P}e = \frac{t^{\text{diff}}}{t^{\text{conv}}}, \quad (3.18)$$

where

$$\left\{ \begin{array}{l} t^{\text{diff}} = \frac{L^2}{D_c} \quad (\text{macroscopic characteristic time of diffusion}), \end{array} \right. \quad (3.19)$$

$$\left\{ \begin{array}{l} t^{\text{conv}} = \frac{L}{v_c} \quad (\text{macroscopic characteristic time of convection}). \end{array} \right. \quad (3.20)$$

We consider

$$\mathbb{P}e = \frac{v_c L}{D_c} = \mathcal{O}(\varepsilon^0), \quad (3.21)$$

which leads to the homogenised advective-diffusive model at the first order (Cf. §2.2). The dimensionless number \mathbb{N} is such that:

$$\mathbb{N} = \frac{t^{\text{diff}}}{t_c}. \quad (3.22)$$

Since $\mathbb{P}e = \mathcal{O}(\varepsilon^0)$ means that $t^{\text{diff}} = t^{\text{conv}}$, we take $t_c = t^{\text{diff}} = t^{\text{conv}}$, which yields

$$\mathbb{N} = \mathcal{O}(\varepsilon^0). \quad (3.23)$$

Note that taking $t_c = t^{\text{diff}} = t^{\text{conv}}$ ensures a macroscopic transient regime, while $t_c > t^{\text{diff}}$ would lead to a macroscopic steady-state regime and that when $t_c < t^{\text{diff}}$, the transport mechanism is not sufficiently developed for its evolution be described by means of a continuum model.

4 Higher-order homogenisation of fluid flow

Homogenisation of the fluid flow equations has been performed up to the third order in Auriault et al. (2005). Equations Eqs. (3.10)-(3.13) are considered with Eq. (3.17), which leads to the following set of flow equations

$$\left\{ \begin{array}{l} \varepsilon^2 \mu \Delta \vec{v} - \vec{\nabla} p = \vec{0} \quad \text{within } \Omega_p, \end{array} \right. \quad (4.1)$$

$$\left\{ \begin{array}{l} \vec{\nabla} \cdot \vec{v} = 0 \quad \text{within } \Omega_p, \end{array} \right. \quad (4.2)$$

$$\left\{ \begin{array}{l} \vec{v} = \vec{0} \quad \text{over } \Gamma, \end{array} \right. \quad (4.3)$$

where

$$\vec{\nabla} = \varepsilon^{-1} \vec{\nabla}_y + \vec{\nabla}_x. \quad (4.4)$$

The homogenisation procedure consists in looking for the pressure and the velocity in the form of asymptotic expansions in powers of ε (Bensoussan et al., 1978; Sanchez-Palencia, 1980):

$$\left\{ \begin{array}{l} p(\vec{y}, \vec{x}) = p^0(\vec{y}, \vec{x}) + \varepsilon p^1(\vec{y}, \vec{x}) + \varepsilon p^2(\vec{y}, \vec{x}) + \dots \\ \vec{v}(\vec{y}, \vec{x}) = \vec{v}^0(\vec{y}, \vec{x}) + \varepsilon \vec{v}^1(\vec{y}, \vec{x}) + \varepsilon^2 \vec{v}^2(\vec{y}, \vec{x}) + \dots \end{array} \right.$$

For a macroscopically homogeneous medium, the results can be summarised as follows

$$\frac{\partial}{\partial x_i} \langle v_i^n \rangle = 0 \quad (n = 0, 1, 2), \quad (4.5)$$

with

$$\left\{ \begin{array}{l} \langle v_i^0 \rangle = -\frac{K_{ij}}{\mu} \frac{\partial p^0}{\partial x_j}, \end{array} \right. \quad (4.6)$$

$$\left\{ \begin{array}{l} \langle v_i^1 \rangle = -\frac{N_{ijk}}{\mu} \frac{\partial^2 p^0}{\partial x_j \partial x_k} - \frac{K_{ij}}{\mu} \frac{\partial \bar{p}^1}{\partial x_j}, \end{array} \right. \quad (4.7)$$

$$\left\{ \begin{array}{l} \langle v_i^2 \rangle = -\frac{P_{ijkl}}{\mu} \frac{\partial^3 p^0}{\partial x_j \partial x_k \partial x_l} - \frac{N_{ijk}}{\mu} \frac{\partial^2 \bar{p}^1}{\partial x_j \partial x_k} - \frac{K_{ij}}{\mu} \frac{\partial \bar{p}^2}{\partial x_j}, \end{array} \right. \quad (4.8)$$

where $\langle . \rangle$ denotes the volume average and is defined by

$$\langle . \rangle = \frac{1}{|\Omega|} \int_{\Omega_p} . d\Omega. \quad (4.9)$$

The third order tensor N_{ijk} is symmetric with respect to its last two indices and anti-symmetric with respect to its first two indices. Then, since N_{ijk} is symmetrical with respect to its last two indices, it is equal to zero when the medium is isotropic.

Functions p^0 , p^1 and p^2 are such that

$$\left\{ \begin{array}{l} p^0 = p^0(\vec{x}), \end{array} \right. \quad (4.10)$$

$$\left\{ \begin{array}{l} p^1 = -a_j(\vec{y}) \frac{\partial p^0}{\partial x_j} + \bar{p}^1(\vec{x}), \end{array} \right. \quad (4.11)$$

$$\left\{ \begin{array}{l} p^2 = -d_{jk}(\vec{y}) \frac{\partial^2 p^0}{\partial x_j \partial x_k} - a_j(\vec{y}) \frac{\partial \bar{p}^1}{\partial x_j} + \bar{p}^2(\vec{x}). \end{array} \right. \quad (4.12)$$

Note that functions \bar{p}^1 and \bar{p}^2 , which appear in Eqs. (4.7) and (4.8), are particular solutions involved in the definitions of p^1 and p^2 , Eqs. (4.11) and (4.12), respectively. Combining Eq. (4.5) with the averaged velocities, the second-gradient terms vanish as a result of the antisymmetry of N_{ijk} . Thus, the following flow descriptions are obtained

$$\left\{ \begin{array}{l} \text{(First order)} \quad \frac{\partial}{\partial x_i} \left(K_{ij} \frac{\partial p^0}{\partial x_j} \right) = 0, \end{array} \right. \quad (4.13)$$

$$\left\{ \begin{array}{l} \text{(Second order)} \quad \frac{\partial}{\partial x_i} \left(K_{ij} \frac{\partial \bar{p}^1}{\partial x_j} \right) = 0, \end{array} \right. \quad (4.14)$$

$$\left\{ \begin{array}{l} \text{(Third order)} \quad \frac{\partial}{\partial x_i} \left(P_{ijkl} \frac{\partial^3 p^0}{\partial x_j \partial x_k \partial x_l} + K_{ij} \frac{\partial \bar{p}^2}{\partial x_j} \right) = 0. \end{array} \right. \quad (4.15)$$

5 Higher-order homogenisation of solute transport in the advective-diffusive regime

5.1 Local dimensionless description

We consider Eq. (3.12) with estimates Eq. (3.21) and Eq. (3.23), and boundary conditions Eqs. (3.13)-(3.14). This leads to the following set of equations:

$$\begin{cases} \frac{\partial c}{\partial t} - \vec{\nabla} \cdot (D_0 \vec{\nabla} c - c \vec{v}) = 0 & \text{within } \Omega_p, \\ \vec{v} = \vec{0} & \text{over } \Gamma, \\ (D_0 \vec{\nabla} c) \cdot \vec{n} = 0 & \text{over } \Gamma. \end{cases} \quad (5.1)$$

$$\vec{v} = \vec{0} \quad \text{over } \Gamma, \quad (5.2)$$

$$(D_0 \vec{\nabla} c) \cdot \vec{n} = 0 \quad \text{over } \Gamma. \quad (5.3)$$

We look for solutions to the unknowns c and \vec{v} of the form:

$$\begin{cases} c(\vec{y}, \vec{x}) = c^0(\vec{y}, \vec{x}) + \varepsilon c^1(\vec{y}, \vec{x}) + \varepsilon^2 c^2(\vec{y}, \vec{x}) + \dots \\ \vec{v}(\vec{y}, \vec{x}) = \vec{v}^0(\vec{y}, \vec{x}) + \varepsilon \vec{v}^1(\vec{y}, \vec{x}) + \varepsilon^2 \vec{v}^2(\vec{y}, \vec{x}) + \dots \end{cases}$$

where functions $c^n(\vec{y}, \vec{x})$ and $\vec{v}^n(\vec{y}, \vec{x})$ are Ω -periodic in \vec{y} . Furthermore, because of the two spatial variables \vec{x} and $\vec{y} = \varepsilon^{-1} \vec{x}$, the spatial derivation takes the form Eq. (4.4). The homogenisation technique involves the introduction of these expansions into the dimensionless equations Eqs. (5.1)-(5.3) and the identification of the powers of ε .

5.2 First-order homogenisation

5.2.1 Boundary value problem for c^0

At the first order, the boundary value problem Eqs. (5.1)-(5.3) leads to:

$$\begin{cases} \frac{\partial}{\partial y_i} \left(D_0 \frac{\partial c^0}{\partial y_i} \right) = 0 & \text{in } \Omega_p, \\ D_0 \frac{\partial c^0}{\partial y_i} n_i = 0 & \text{over } \Gamma, \\ c^0 : \text{periodic in } \vec{y}, \end{cases} \quad (5.4)$$

$$D_0 \frac{\partial c^0}{\partial y_i} n_i = 0 \quad \text{over } \Gamma, \quad (5.5)$$

$$c^0 : \text{periodic in } \vec{y}, \quad (5.6)$$

from which it is clear that the concentration c^0 is constant over the period

$$c^0 = c^0(\vec{x}, t). \quad (5.7)$$

5.2.2 Boundary value problem for c^1

We now consider the second order of Eqs. (5.1)-(5.3). Then, noticing that (see Eq. (4.2))

$$\frac{\partial v_i^0}{\partial y_i} = 0, \quad (5.8)$$

we obtain the following boundary value problem for c^1 :

$$\begin{cases} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^1}{\partial y_i} + \frac{\partial c^0}{\partial x_i} \right) \right] = 0 & \text{within } \Omega_p, \\ \left[D_0 \left(\frac{\partial c^1}{\partial y_i} + \frac{\partial c^0}{\partial x_i} \right) \right] n_i = 0 & \text{over } \Gamma, \\ c^1 : \text{periodic in } \vec{y}. \end{cases} \quad (5.9)$$

$$\left[D_0 \left(\frac{\partial c^1}{\partial y_i} + \frac{\partial c^0}{\partial x_i} \right) \right] n_i = 0 \quad \text{over } \Gamma, \quad (5.10)$$

$$c^1 : \text{periodic in } \vec{y}. \quad (5.11)$$

By virtue of linearity, the solution reads:

$$c^1 = \chi_j(\vec{y}) \frac{\partial c^0}{\partial x_j} + \bar{c}^1(\vec{x}, t), \quad (5.12)$$

where $\bar{c}^1(\vec{x}, t)$ is an arbitrary function. The exact definition of the vector $\vec{\chi}$ is reported in Appendix A.1. Note that, to render the solution unique, we impose that $\vec{\chi}$ is average to zero (Bensoussan et al., 1978; Sanchez-Palencia, 1980; Mei and Vernescu, 2010):

$$\langle \vec{\chi} \rangle = \frac{1}{|\Omega|} \int_{\Omega_p} \vec{\chi} d\Omega = \vec{0}. \quad (5.13)$$

Note further that, since we are considering a macroscopically homogeneous medium, $\vec{\chi}$ doesn't depend on variable \vec{x} : $\vec{\chi} = \vec{\chi}(\vec{y})$.

5.2.3 Derivation of the first-order macroscopic description

Let consider the boundary value problem Eqs. (5.1)-(5.3) at the third order:

$$\begin{cases} \frac{\partial c^0}{\partial t} - \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) - c^0 v_i^1 - c^1 v_i^0 \right] \\ - \frac{\partial}{\partial x_i} \left[D_0 \left(\frac{\partial c^1}{\partial y_i} + \frac{\partial c^0}{\partial x_i} \right) - c^0 v_i^0 \right] = 0 & \text{within } \Omega_p, \\ v_i^0 = v_i^1 = 0 & \text{over } \Gamma, \\ \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) \right] n_i = 0 & \text{over } \Gamma. \end{cases} \quad (5.14)$$

$$v_i^0 = v_i^1 = 0 \quad \text{over } \Gamma, \quad (5.15)$$

$$\left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) \right] n_i = 0 \quad \text{over } \Gamma. \quad (5.16)$$

The homogenisation procedure consists now in integrating Eq. (5.14) over Ω_p . This leads to the so called compatibility condition, which is a necessary and sufficient condition for the existence of solutions. Furthermore, it represents the first-order macroscopic description. Invoking Gauss' theorem, the integration yields:

$$\begin{aligned} & \frac{1}{|\Omega|} \int_{\Omega_p} \frac{\partial c^0}{\partial t} d\Omega - \frac{1}{|\Omega|} \int_{\delta\Omega_p} \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) - c^0 v_i^1 - c^1 v_i^0 \right] n_i dS \\ & - \frac{1}{|\Omega|} \int_{\Omega_p} \frac{\partial}{\partial x_i} \left[D_0 \left(\frac{\partial c^1}{\partial y_i} + \frac{\partial c^0}{\partial x_i} \right) - c^0 v_i^0 \right] d\Omega = 0, \end{aligned} \quad (5.17)$$

where $\delta\Omega_p = \Gamma \cup (\delta\Omega \cap \delta\Omega_p)$ denotes the bounding surface of Ω_p . The second term of Eq. (5.17) is thus the sum of two surface integrals and it actually cancels out: the

integral over the surface Γ vanishes because of boundary conditions Eqs. (5.15)-(5.16), while the integral over the cell boundary, $\delta\Omega \cap \delta\Omega_p$, vanishes by periodicity. Hence, Eq. (5.17) reduces to

$$\phi \frac{\partial c^0}{\partial t} - \frac{\partial}{\partial x_i} \langle D_0 \left(\frac{\partial c^1}{\partial y_i} + \frac{\partial c^0}{\partial x_i} \right) - c^0 v_i^0 \rangle = 0, \quad (5.18)$$

where

$$\phi = \frac{|\Omega_p|}{|\Omega|} \quad (5.19)$$

denotes the porosity. Using Eq. (5.12), we can write:

$$\frac{\partial c^1}{\partial y_i} + \frac{\partial c^0}{\partial x_i} = \gamma_{ij}^0 \frac{\partial c^0}{\partial x_j}, \quad (5.20)$$

where

$$\gamma_{ij}^0 = \frac{\partial \chi_j}{\partial y_i} + \delta_{ij}. \quad (5.21)$$

Taking Eq. (4.5) into account, Eq. (5.18) can be rewritten as follows:

$$\phi \frac{\partial c^0}{\partial t} - \frac{\partial}{\partial x_i} (D_{ij} \frac{\partial c^0}{\partial x_j}) + \langle v_i^0 \rangle \frac{\partial c^0}{\partial x_i} = 0, \quad (5.22)$$

where

$$D_{ij} = \frac{1}{|\Omega|} \int_{\Omega_p} D_0 \left(\frac{\partial \chi_j}{\partial y_i} + \delta_{ij} \right) d\Omega = \frac{1}{|\Omega|} \int_{\Omega_p} D_0 \gamma_{ij}^0 d\Omega \quad (5.23)$$

is the tensor of effective diffusion. It can be shown that the second-order tensor D_{ij} is positive and symmetric (Cf. Appendix A.2).

Defining the first-order macroscopic concentration and average fluid velocity by

$$\begin{cases} \langle c \rangle = \langle c^0 \rangle + \mathcal{O}(\varepsilon \langle c \rangle), \\ \langle \vec{v} \rangle = \langle \vec{v}^0 \rangle + \mathcal{O}(\varepsilon \langle \vec{v} \rangle), \end{cases} \quad (5.24)$$

$$\quad (5.25)$$

the first-order macroscopic description thus reads

$$\phi \frac{\partial \langle c \rangle}{\partial t} - \frac{\partial}{\partial x_i} (D_{ij} \frac{\partial \langle c \rangle}{\partial x_j}) + \langle v_i \rangle \frac{\partial \langle c \rangle}{\partial x_i} = \mathcal{O}(\varepsilon \phi \frac{\partial \langle c \rangle}{\partial t}). \quad (5.26)$$

In dimensional variables, it becomes

$$\phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} - \frac{\partial}{\partial \hat{X}_i} (\hat{D}_{ij}^{\text{diff}} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{X}_j}) + \langle \hat{v}_i \rangle \frac{\partial \langle \hat{c} \rangle}{\partial \hat{X}_i} = \mathcal{O}(\varepsilon \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}}), \quad (5.27)$$

where

$$\hat{D}_{ij}^{\text{diff}} = D_c D_{ij} \quad (5.28)$$

is the tensor of effective diffusion. The fluid velocity verifies (Cf. Section 4):

$$\left\{ \begin{array}{l} \langle \hat{v}_i \rangle = -\frac{\hat{K}_{ij}^{\text{eff}}}{\hat{\mu}} \frac{\partial \langle \hat{p} \rangle}{\partial \hat{X}_j} + \mathcal{O}(\varepsilon \langle \hat{v}_i \rangle), \\ \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i} = \mathcal{O}(\varepsilon \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i}). \end{array} \right. \quad (5.29)$$

$$\left\{ \begin{array}{l} \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i} = \mathcal{O}(\varepsilon \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i}). \end{array} \right. \quad (5.30)$$

The first-order behaviour is thus described by the classical advection-diffusion transport equation, in which the fluid velocity verifies Darcy's law.

5.3 Second-order homogenisation

5.3.1 Boundary value problem for c^2

The third-order boundary value given by Eqs. (5.14)-(5.16), can be transformed (Cf. Appendix B.1) so as to obtain the following boundary value problem for c^2 :

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \chi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^1}{\partial x_i} \right) \right] = \\ \left(\frac{1}{\phi} D_{ij} - D_0 \gamma_{ij}^0 \right) \frac{\partial^2 c^0}{\partial x_i \partial x_j} + (v_i^0 \gamma_{ij}^0 - \frac{1}{\phi} \langle v_j^0 \rangle) \frac{\partial c^0}{\partial x_j} \quad \text{within } \Omega_p, \\ \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \chi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^1}{\partial x_i} \right) \right] n_i = 0 \quad \text{over } \Gamma. \end{array} \right. \quad (5.31)$$

$$\left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \chi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^1}{\partial x_i} \right) \right] n_i = 0 \quad \text{over } \Gamma. \quad (5.32)$$

We observe that the solution must depend on three forcing terms, which are associated with $\partial^2 c^0 / \partial x_j \partial x_k$, $\partial c^0 / \partial x_j$ and $\partial \bar{c}^1 / \partial x_j$, respectively. By virtue of linearity, the solution is a linear combination of particular solutions associated with each of the three forcing terms. Note that the problem linked to $\partial \bar{c}^1 / \partial x_j$ is identical to that observed at the first order for $\partial c^0 / \partial x_j$ in the boundary value problem which defines c^1 (Eqs. (5.9)-(5.10)). Therefore, the solution reads

$$c^2 = \eta_{jk}(\vec{y}) \frac{\partial^2 c^0}{\partial x_j \partial x_k} + \pi_j(\vec{y}) \frac{\partial c^0}{\partial x_j} + \chi_j(\vec{y}) \frac{\partial \bar{c}^1}{\partial x_j} + \bar{c}^2(\vec{x}, t), \quad (5.33)$$

where $\bar{c}^2(\vec{x}, t)$ is an arbitrary function and where

$$\left\{ \begin{array}{l} \langle \eta_{jk} \rangle = 0, \\ \langle \pi_j \rangle = 0. \end{array} \right. \quad (5.34)$$

$$\left\{ \begin{array}{l} \langle \eta_{jk} \rangle = 0, \\ \langle \pi_j \rangle = 0. \end{array} \right. \quad (5.35)$$

The detailed definitions of η_{jk} and π_j are reported in Appendix B.2.

5.3.2 Derivation of the first corrector

At the fourth order, the boundary-value problem made of Eqs. (5.1)-(5.3) yields:

$$\begin{cases} \frac{\partial c^1}{\partial t} - \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^3}{\partial y_i} + \frac{\partial c^2}{\partial x_i} \right) - c^0 v_i^2 - c^1 v_i^1 - c^2 v_i^0 \right] \\ - \frac{\partial}{\partial x_i} \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) - c^0 v_i^1 - c^1 v_i^0 \right] = 0 \quad \text{within } \Omega_p, \end{cases} \quad (5.36)$$

$$v_i^0 = v_i^1 = v_i^2 = 0 \quad \text{over } \Gamma, \quad (5.37)$$

$$\left[D_0 \left(\frac{\partial c^3}{\partial y_i} + \frac{\partial c^2}{\partial x_i} \right) \right] n_i = 0 \quad \text{over } \Gamma. \quad (5.38)$$

The first corrector of the macroscopic description is obtained by integrating Eq. (5.36) over Ω_p . This leads to

$$\phi \frac{\partial \bar{c}^1}{\partial t} - \frac{\partial}{\partial x_i} \langle D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) \rangle + \frac{\partial}{\partial x_i} \langle c^0 v_i^1 + c^1 v_i^0 \rangle = 0. \quad (5.39)$$

Using the expressions obtained for c^1 and c^2 , Eqs. (5.12) and (5.33), we get

$$\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} = \gamma_{ijk}^1 \frac{\partial^2 c^0}{\partial x_j \partial x_k} + \frac{\partial \pi_j}{\partial y_i} \frac{\partial c^0}{\partial x_j} + \gamma_{ij}^0 \frac{\partial \bar{c}^1}{\partial x_j}, \quad (5.40)$$

with

$$\gamma_{ijk}^1 = \frac{\partial \eta_{jk}}{\partial y_i} + \chi_i \delta_{jk}. \quad (5.41)$$

Then, noticing that

$$\frac{\partial}{\partial x_i} \langle c^0 v_i^1 + c^1 v_i^0 \rangle = \langle v_i^1 \rangle \frac{\partial c^0}{\partial x_i} + \frac{\partial}{\partial x_i} \left[\langle v_i^0 \chi_j \rangle \frac{\partial c^0}{\partial x_j} \right] + \langle v_i^0 \rangle \frac{\partial \bar{c}^1}{\partial x_i}, \quad (5.42)$$

Eq. (5.39) becomes:

$$\phi \frac{\partial \bar{c}^1}{\partial t} - \frac{\partial}{\partial x_i} \left(E_{ijk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} + D'_{ij} \frac{\partial c^0}{\partial x_j} + D_{ij} \frac{\partial \bar{c}^1}{\partial x_j} \right) + \langle v_i^1 \rangle \frac{\partial c^0}{\partial x_i} + \langle v_i^0 \rangle \frac{\partial \bar{c}^1}{\partial x_i} = 0, \quad (5.43)$$

where

$$\begin{cases} E_{ijk} = \langle D_0 \left(\frac{\partial \eta_{jk}}{\partial y_i} + \chi_i \delta_{jk} \right) \rangle = \langle D_0 \gamma_{ijk}^1 \rangle, \end{cases} \quad (5.44)$$

$$\begin{cases} D'_{ij} = \langle D_0 \frac{\partial \pi_j}{\partial y_i} - v_i^0 \chi_j \rangle. \end{cases} \quad (5.45)$$

The third-order tensor E_{ijk} is symmetric with respect to its last two indices and anti-symmetric with respect to its first two indices (Cf. Appendix B.3). Note further that E_{ijk} can be determined from vector χ_i , without determining tensor η_{jk} (Cf. Appendix

B.3). As a result of the antisymmetry property of E_{ijk} , the second-order gradient term of Eq. (5.43) vanishes. Thus, the first corrector finally reads:

$$\phi \frac{\partial \bar{c}^1}{\partial t} - \frac{\partial}{\partial x_i} (D'_{ij} \frac{\partial c^0}{\partial x_j} + D_{ij} \frac{\partial \bar{c}^1}{\partial x_j}) + \langle v_i^1 \rangle \frac{\partial c^0}{\partial x_i} + \langle v_i^0 \rangle \frac{\partial \bar{c}^1}{\partial x_i} = 0. \quad (5.46)$$

From its definition Eq. (5.45), we see that the second-order tensor D'_{ij} contains a convective term: it is therefore a dispersion tensor. It is a non-symmetric tensor which can be decomposed into a symmetric and an antisymmetric parts (Cf. Appendix B.4). Furthermore, it can be determined from vectors v_i^0 and χ_j , without solving boundary value problem Eqs. (5.36)-(5.38) (Cf. Appendix B.4).

5.3.3 Second-order macroscopic description

Let add Eq. (5.22) to Eq. (5.46) multiplied by ε . We get:

$$\begin{cases} \phi \frac{\partial}{\partial t} (c^0 + \varepsilon \bar{c}^1) - \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial}{\partial x_j} (c^0 + \varepsilon \bar{c}^1) + \varepsilon D'_{ij} \frac{\partial c^0}{\partial x_j} \right] \\ + (\langle v_i^0 \rangle + \varepsilon \langle v_i^1 \rangle) \frac{\partial c^0}{\partial x_i} + \varepsilon \langle v_i^0 \rangle \frac{\partial \bar{c}^1}{\partial x_i} = 0. \end{cases} \quad (5.47)$$

Defining the second-order macroscopic concentration and average fluid velocity by

$$\begin{cases} \langle c \rangle = \langle c^0 \rangle + \varepsilon \bar{c}^1 + \mathcal{O}(\varepsilon^2 \langle c \rangle), \\ \langle \vec{v} \rangle = \langle \vec{v}^0 \rangle + \varepsilon \langle \vec{v}^1 \rangle + \mathcal{O}(\varepsilon^2 \langle \vec{v} \rangle), \end{cases} \quad (5.48)$$

$$\quad (5.49)$$

the second-order macroscopic description is written as follows

$$\begin{cases} \phi \frac{\partial \langle c \rangle}{\partial t} - \frac{\partial}{\partial x_i} \left[(D_{ij} + \varepsilon D'_{ij}) \frac{\partial \langle c \rangle}{\partial x_j} \right] + \langle v_i \rangle \frac{\partial \langle c \rangle}{\partial x_i} \\ = \mathcal{O}(\varepsilon^2 \phi \frac{\partial \langle c \rangle}{\partial t}). \end{cases} \quad (5.50)$$

When cast in dimensional variables, Eq. (5.50) becomes

$$\begin{cases} \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} - \frac{\partial}{\partial X_i} \left[(\hat{D}_{ij}^{\text{diff}} + \hat{D}_{ij}^{\text{eff}}) \frac{\partial \langle \hat{c} \rangle}{\partial X_j} \right] + \langle \hat{v}_i \rangle \frac{\partial \langle \hat{c} \rangle}{\partial X_i} \\ = \mathcal{O}(\varepsilon^2 \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}}), \end{cases} \quad (5.51)$$

where

$$\hat{D}_{ij}^{\text{eff}} = D_c \varepsilon D'_{ij}. \quad (5.52)$$

The second-order fluid velocity is such that (Cf. Section 4):

$$\begin{cases} \langle \hat{v}_i \rangle = -\frac{\hat{N}_{ijk}^{\text{eff}}}{\hat{\mu}} \frac{\partial^2 \langle \hat{p} \rangle}{\partial \hat{X}_j \partial \hat{X}_k} - \frac{\hat{K}_{ij}^{\text{eff}}}{\hat{\mu}} \frac{\partial \langle \hat{p} \rangle}{\partial \hat{X}_j} + \mathcal{O}(\varepsilon^2 \langle \hat{v}_i \rangle), \\ \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i} = \mathcal{O}(\varepsilon^2 \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i}). \end{cases} \quad (5.53)$$

$$\quad (5.54)$$

Note that combining both above equations leads to:

$$\frac{\partial}{\partial \hat{X}_i} \left(\frac{\hat{K}_{ij}^{\text{eff}}}{\hat{\mu}} \frac{\partial \langle \hat{p} \rangle}{\partial \hat{X}_j} \right) = \mathcal{O}(\varepsilon^2 \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i}). \quad (5.55)$$

Therefore, the second-order macroscopic transport description is a model of advection-dispersion, in which the tensor of dispersion is non-symmetric (*Cf.* Appendix B.4) and follows property Eq. (2.6) of the phenomenological model of dispersion. The fluid velocity verifies a second-order law Eq. (5.53), which reduces to Darcy's law in case of an isotropic medium. In other words, the second-order macroscopic transport model is similar to the phenomenological dispersion transport equation Eq. (2.3).

5.4 Third-order homogenisation

5.4.1 Boundary value problem for c^3

The fourth-order boundary value problem, Eqs. (5.36)-(5.38), can be transformed into the following boundary value problem for c^3 (*Cf.* Appendix C.1):

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^3}{\partial y_i} + \eta_{jk} \frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} + \pi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \chi_j \frac{\partial^2 \bar{c}^1}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^2}{\partial x_i} \right) \right] = \\ \left(\frac{1}{\phi} \chi_i D_{jk} - D_0 \gamma_{ijk}^1 \right) \frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} \\ + (v_i^0 \gamma_{ijk}^1 - D_0 \frac{\partial \pi_k}{\partial y_j} + \frac{1}{\phi} D'_{jk} - \frac{1}{\phi} \chi_j \langle v_k^0 \rangle) \frac{\partial^2 c^0}{\partial x_j \partial x_k} \\ + \left(\frac{1}{\phi} D_{ij} - D_0 \gamma_{ij}^0 \right) \frac{\partial^2 \bar{c}^1}{\partial x_i \partial x_j} \\ + (v_i^0 \frac{\partial \pi_j}{\partial y_i} + v_i^1 \gamma_{ij}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_j^0 \rangle}{\partial x_i} - \frac{1}{\phi} \langle v_j^1 \rangle) \frac{\partial c^0}{\partial x_j} \\ + (v_i^0 \gamma_{ij}^0 - \frac{1}{\phi} \langle v_j^0 \rangle) \frac{\partial \bar{c}^1}{\partial x_j} \quad \text{in } \Omega_p, \\ \left[D_0 \left(\frac{\partial c^3}{\partial y_i} + \eta_{jk} \frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} + \pi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \chi_j \frac{\partial^2 \bar{c}^1}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^2}{\partial x_i} \right) \right] n_i = 0 \\ \text{on } \Gamma. \end{array} \right. \quad (5.56)$$

From the above boundary value problem and its variational formulation (*Cf.* Appendix C.2), it can be seen that the solution must depend on the following forcing terms: $\partial^3 c^0 / \partial x_j \partial x_k \partial x_l$, $\partial^2 c^0 / \partial x_k \partial x_l$, $\partial^2 \bar{c}^1 / \partial x_k \partial x_l$, $\partial c^0 / \partial x_j$, $\partial \bar{c}^1 / \partial x_j$ and $\partial \bar{c}^2 / \partial x_j$. We note that the problem linked to $\partial \bar{c}^2 / \partial x_j$ is identical to that associated with $\partial c^0 / \partial x_j$ in the boundary value problem for c^1 Eqs. (5.9)-(5.10). Furthermore, the problem associated with $\partial \bar{c}^1 / \partial x_j$ is identical to that linked to $\partial c^0 / \partial x_j$ in the boundary value problem for c^2 , Eqs. (5.31)-(5.32), and the problem linked to $\partial^2 \bar{c}^1 / \partial x_k \partial x_l$ is identical to that obtained for $\partial^2 c^0 / \partial x_k \partial x_l$ in the boundary value problem for c^2 . Consequently,

the solution reads:

$$c^3 = \xi_{jkl}(\vec{y}) \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} + \tau_{kl}(\vec{y}) \frac{\partial^2 c^0}{\partial x_k \partial x_l} + \eta_{kl}(\vec{y}) \frac{\partial^2 \bar{c}^1}{\partial x_k \partial x_l} + \theta_j(\vec{y}) \frac{\partial c^0}{\partial x_j} + \pi_j(\vec{y}) \frac{\partial \bar{c}^1}{\partial x_j} + \chi_j(\vec{y}) \frac{\partial \bar{c}^2}{\partial x_j} + \bar{c}^3(\vec{x}, t), \quad (5.58)$$

where $\bar{c}^3(\vec{x}, t)$ is an arbitrary function, and where

$$\begin{cases} \langle \xi_{jkl} \rangle = 0, & (5.59) \\ \langle \tau_{kl} \rangle = 0, & (5.60) \\ \langle \theta_j \rangle = 0. & (5.61) \end{cases}$$

The exact definitions of ξ_{jkl} , τ_{kl} and θ_j are reported in Appendices C.3, C.4 and C.5, respectively. Let us recall that χ_j is related to the definition of c^1 Eq. (5.12), while η_{jk} and π_j have been introduced in the definition of c^2 Eq. (5.33). Note that in expression Eq. (5.58), ξ_{jkl} , η_{jk} , χ_j are only related to the diffusion mechanism, while τ_{kl} , θ_j and π_j contain both diffusive and convective terms.

5.4.2 Derivation of the second corrector

Let now consider the boundary-value problem Eqs. (5.1)-(5.3) at the fifth order:

$$\begin{cases} \frac{\partial c^2}{\partial t} - \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^4}{\partial y_i} + \frac{\partial c^3}{\partial x_i} \right) - c^0 v_i^3 - c^1 v_i^2 - c^2 v_i^1 - c^3 v_i^0 \right] \\ - \frac{\partial}{\partial x_i} \left[D_0 \left(\frac{\partial c^3}{\partial y_i} + \frac{\partial c^2}{\partial x_i} \right) - c^0 v_i^2 - c^1 v_i^1 - c^2 v_i^0 \right] = 0 \quad \text{within } \Omega_p, & (5.62) \end{cases}$$

$$\begin{cases} \left[D_0 \left(\frac{\partial c^4}{\partial y_i} + \frac{\partial c^3}{\partial x_i} \right) \right] n_i = 0 \quad \text{over } \Gamma. & (5.63) \end{cases}$$

Integrating Eq. (5.62) over Ω_p , we get:

$$\phi \frac{\partial \bar{c}^2}{\partial t} - \frac{\partial}{\partial x_i} \langle D_0 \left(\frac{\partial c^3}{\partial y_i} + \frac{\partial c^2}{\partial x_i} \right) \rangle + \frac{\partial}{\partial x_i} \langle c^0 v_i^2 + c^1 v_i^1 + c^2 v_i^0 \rangle = 0. \quad (5.64)$$

Using Eqs. (5.33) and (5.58), we deduce that

$$\begin{cases} \frac{\partial c^3}{\partial y_i} + \frac{\partial c^2}{\partial x_i} = \gamma_{ijkl}^2 \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} \\ + \left(\frac{\partial \tau_{jk}}{\partial y_i} + \pi_i \delta_{jk} \right) \frac{\partial^2 c^0}{\partial x_j \partial x_k} + \gamma_{ijk}^1 \frac{\partial^2 \bar{c}^1}{\partial x_j \partial x_k} \\ + \frac{\partial \theta_j}{\partial y_i} \frac{\partial c^0}{\partial x_j} + \frac{\partial \pi_j}{\partial y_i} \frac{\partial \bar{c}^1}{\partial x_j} + \gamma_{ij}^0 \frac{\partial \bar{c}^2}{\partial x_j}, & (5.65) \end{cases}$$

where

$$\gamma_{ijkl}^2 = \frac{\partial \xi_{jkl}}{\partial y_i} + \eta_{ij} \delta_{kl}. \quad (5.66)$$

Then, noticing that:

$$\left\{ \begin{array}{l} \frac{\partial}{\partial x_i} \langle c^0 v_i^2 + c^1 v_i^1 + c^2 v_i^0 \rangle = \\ \frac{\partial}{\partial x_i} \left[\langle v_i^0 \eta_{jk} \rangle \frac{\partial^2 c^0}{\partial x_j \partial x_k} + \langle v_i^1 \chi_j + v_i^0 \pi_j \rangle \frac{\partial c^0}{\partial x_j} + \langle v_i^0 \chi_j \rangle \frac{\partial \bar{c}^1}{\partial x_j} \right] \\ + \langle v_i^2 \rangle \frac{\partial c^0}{\partial x_i} + \langle v_i^1 \rangle \frac{\partial \bar{c}^1}{\partial x_i} + \langle v_i^0 \rangle \frac{\partial \bar{c}^2}{\partial x_i}, \end{array} \right. \quad (5.67)$$

Eq. (5.64) becomes:

$$\left\{ \begin{array}{l} \phi \frac{\partial \bar{c}^2}{\partial t} - \frac{\partial}{\partial x_i} \left[F_{ijkl} \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} + E'_{ijk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} + E_{ijk} \frac{\partial^2 \bar{c}^1}{\partial x_j \partial x_k} \right. \\ \left. + D''_{ij} \frac{\partial c^0}{\partial x_j} + D'_{ij} \frac{\partial \bar{c}^1}{\partial x_j} + D_{ij} \frac{\partial \bar{c}^2}{\partial x_j} \right] \\ \left. + \langle v_i^2 \rangle \frac{\partial c^0}{\partial x_i} + \langle v_i^1 \rangle \frac{\partial \bar{c}^1}{\partial x_i} + \langle v_i^0 \rangle \frac{\partial \bar{c}^2}{\partial x_i} = 0, \end{array} \right. \quad (5.68)$$

where

$$\left\{ \begin{array}{l} F_{ijkl} = \langle D_0 \frac{\partial \xi_{jkl}}{\partial y_i} + \eta_{ij} \delta_{kl} \rangle, \quad (5.69) \\ E'_{ijk} = \langle D_0 \frac{\partial \tau_{jk}}{\partial y_i} - v_i^0 \eta_{jk} \rangle, \quad (5.70) \\ D''_{ij} = \langle D_0 \frac{\partial \theta_j}{\partial y_i} - v_i^1 \chi_j - v_i^0 \pi_j \rangle. \quad (5.71) \end{array} \right.$$

Tensor F_{ijkl} is a fourth-order tensor of diffusion. It can be calculated from vector $\vec{\chi}$ and tensor $\vec{\eta}$, without solving the boundary-value problem Eqs. (5.56)-(5.57) (Cf. Appendix C.8). The third-order tensor E'_{ijk} and the second-order tensor D''_{ij} are tensors of dispersion. They can also be determined without solving the boundary-value problem Eqs. (5.56)-(5.57) (Cf. Appendices C.6 and C.7). Finally, we conclude that the second corrector can be determined from $\vec{\eta}$, $\vec{\chi}$, $\vec{\pi}$, \vec{v}^0 and \vec{v}^1 .

5.4.3 Third-order macroscopic description

Let add Eq. (5.47) to Eq. (5.68) multiplied by ε^2 :

$$\left\{ \begin{array}{l} \phi \frac{\partial}{\partial t} (c^0 + \varepsilon \bar{c}^1 + \varepsilon^2 \bar{c}^2) \\ - \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial}{\partial x_j} (c^0 + \varepsilon \bar{c}^1 + \varepsilon^2 \bar{c}^2) + \varepsilon D'_{ij} \frac{\partial}{\partial x_j} (c^0 + \varepsilon \bar{c}^1) + \varepsilon^2 D''_{ij} \frac{\partial c^0}{\partial x_j} \right. \\ \left. + \varepsilon^2 E'_{ijk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} + \varepsilon^2 F_{ijkl} \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} \right] \\ + (\langle v_i^0 \rangle + \varepsilon \langle v_i^1 \rangle + \varepsilon^2 \langle v_i^2 \rangle) \frac{\partial c^0}{\partial x_i} \\ + \varepsilon (\langle v_i^0 \rangle + \varepsilon \langle v_i^1 \rangle) \frac{\partial \bar{c}^1}{\partial x_i} + \varepsilon^2 \langle v_i^0 \rangle \frac{\partial \bar{c}^2}{\partial x_i} = 0. \end{array} \right. \quad (5.72)$$

Defining the third-order macroscopic concentration and fluid velocity by

$$\left\{ \begin{array}{l} \langle c \rangle = \langle c^0 \rangle + \varepsilon \bar{c}^1 + \varepsilon^2 \bar{c}^2 + \mathcal{O}(\varepsilon^3 \langle c \rangle), \\ \langle \vec{v} \rangle = \langle \vec{v}^0 \rangle + \varepsilon \langle \vec{v}^1 \rangle + \varepsilon^2 \langle \vec{v}^2 \rangle + \mathcal{O}(\varepsilon^3 \langle \vec{v} \rangle), \end{array} \right. \quad (5.73)$$

$$\left\{ \begin{array}{l} \langle c \rangle = \langle c^0 \rangle + \varepsilon \bar{c}^1 + \varepsilon^2 \bar{c}^2 + \mathcal{O}(\varepsilon^3 \langle c \rangle), \\ \langle \vec{v} \rangle = \langle \vec{v}^0 \rangle + \varepsilon \langle \vec{v}^1 \rangle + \varepsilon^2 \langle \vec{v}^2 \rangle + \mathcal{O}(\varepsilon^3 \langle \vec{v} \rangle), \end{array} \right. \quad (5.74)$$

the third-order macroscopic description is written as follows

$$\left\{ \begin{array}{l} \phi \frac{\partial \langle c \rangle}{\partial t} - \frac{\partial}{\partial x_i} \left[(D_{ij} + \varepsilon D'_{ij} + \varepsilon^2 D''_{ij}) \frac{\partial \langle c \rangle}{\partial x_j} \right] \\ - \frac{\partial}{\partial x_i} \left[\varepsilon^2 E'_{ijk} \frac{\partial^2 \langle c \rangle}{\partial x_j \partial x_k} + \varepsilon^2 F_{ijkl} \frac{\partial^3 \langle c \rangle}{\partial x_j \partial x_k \partial x_l} \right] \\ + \langle v_i \rangle \frac{\partial \langle c \rangle}{\partial x_i} = \mathcal{O}(\varepsilon^3 \phi \frac{\partial \langle c \rangle}{\partial t}). \end{array} \right. \quad (5.75)$$

In dimensional variables, we get:

$$\left\{ \begin{array}{l} \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} - \frac{\partial}{\partial X_i} \left[(\hat{D}_{ij}^{\text{diff}} + \hat{D}_{ij}^{\text{disp}} + \hat{D}_{ij}^{\prime\prime \text{disp}}) \frac{\partial \langle \hat{c} \rangle}{\partial X_j} \right] \\ - \frac{\partial}{\partial X_i} \left[\hat{E}_{ijk}^{\prime \text{disp}} \frac{\partial^2 \langle \hat{c} \rangle}{\partial X_j \partial X_k} + \hat{F}_{ijkl}^{\text{diff}} \frac{\partial^3 \langle \hat{c} \rangle}{\partial X_j \partial X_k \partial X_l} \right] \\ + \langle \hat{v}_i \rangle \frac{\partial \langle \hat{c} \rangle}{\partial X_i} = \mathcal{O}(\varepsilon^3 \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}}), \end{array} \right. \quad (5.76)$$

where

$$\left\{ \begin{array}{l} \hat{D}_{ij}^{\prime\prime \text{disp}} = D_c \varepsilon^2 D''_{ij}, \end{array} \right. \quad (5.77)$$

$$\left\{ \begin{array}{l} \hat{E}_{ijk}^{\prime \text{disp}} = \varepsilon l D_c E'_{ijk}, \end{array} \right. \quad (5.78)$$

$$\left\{ \begin{array}{l} \hat{F}_{ijkl}^{\text{diff}} = l^2 D_c F_{ijkl}. \end{array} \right. \quad (5.79)$$

The third-order fluid velocity verifies (Cf. Section 4):

$$\left\{ \begin{array}{l} \langle \hat{v}_i \rangle = -\frac{\hat{P}_{ijkl}^{\text{eff}}}{\hat{\mu}} \frac{\partial^2 \langle \hat{p} \rangle}{\partial \hat{X}_j \partial \hat{X}_k \partial \hat{X}_l} - \frac{\hat{N}_{ijk}^{\text{eff}}}{\hat{\mu}} \frac{\partial^2 \langle \hat{p} \rangle}{\partial \hat{X}_j \partial \hat{X}_k} - \frac{\hat{K}_{ij}^{\text{eff}}}{\hat{\mu}} \frac{\partial \langle \hat{p} \rangle}{\partial \hat{X}_j} + \mathcal{O}(\varepsilon^3 \langle \hat{v}_i \rangle) \\ \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i} = \mathcal{O}(\varepsilon^3 \frac{\partial \langle \hat{v}_i \rangle}{\partial \hat{X}_i}). \end{array} \right. \quad (5.80)$$

Note that when combining both above equations, the second-gradient term vanishes, due the antisymmetry property of tensor $\hat{N}_{ijk}^{\text{eff}}$.

The third-order transport model Eq. (5.76) introduces a fourth-order tensor of diffusion, and a third-order and an additional second-order tensors of dispersion.

6 Macroscopic fluxes

6.1 Volume vs surface averages

With the homogenisation averaging procedure, macroscopic descriptions are expressed in terms of variables which are systematically defined as volume averages. Specifying the meaning of the macroscopic variables, *i.e.* determining whether the use of volume averages is appropriate or not is thus an important issue (Hassanizadeh, 1979; Costanzo et al., 2005; Hill, 1972). In the particular context of solute transport in porous media, since a solute flux is physically defined over a specific area, macroscopic fluxes should thus be defined as surface averages.

6.2 Writing of local and homogenised equations in terms of fluxes

In order to address the above described issue, we may rewrite the local and the homogenised equations in terms of fluxes. We shall thus rewrite Eq. (5.1) as follows

$$\frac{\partial c}{\partial t} + \vec{\nabla} \cdot \vec{q} = 0 \quad \text{within } \Omega_p, \quad (6.1)$$

where the local flux \vec{q} is defined by

$$\vec{q} = -D_0 \vec{\nabla} c + c \vec{v}. \quad (6.2)$$

The no-flux boundary condition now reads

$$\vec{q} \cdot \vec{n} = 0 \quad \text{over } \Gamma. \quad (6.3)$$

Flux \vec{q} is looked for in the form of the following asymptotic expansion in powers of ε

$$\vec{q} = \vec{q}^0(\vec{y}, \vec{x}) + \varepsilon \vec{q}^1(\vec{y}, \vec{x}) + \varepsilon^2 \vec{q}^2(\vec{y}, \vec{x}) + \dots \quad (6.4)$$

This leads to the following perturbations equations for Eqs. (6.1)-(6.2) at the successive orders of powers of ε :

$$\left\{ \begin{array}{l} \vec{q}^0 = -D_0(\vec{\nabla}_y c^1 + \vec{\nabla}_x c^0) + c^0 \vec{v}^0 \\ \vec{q}^1 = -D_0(\vec{\nabla}_y c^2 + \vec{\nabla}_x c^1) + c^0 \vec{v}^1 + c^1 \vec{v}^0 \\ \vec{q}^2 = -D_0(\vec{\nabla}_y c^3 + \vec{\nabla}_x c^2) + c^0 \vec{v}^2 + c^1 \vec{v}^1 + c^2 \vec{v}^0 \end{array} \right. \quad (6.5)$$

$$\vec{q}^1 = -D_0(\vec{\nabla}_y c^2 + \vec{\nabla}_x c^1) + c^0 \vec{v}^1 + c^1 \vec{v}^0 \quad (6.6)$$

$$\vec{q}^2 = -D_0(\vec{\nabla}_y c^3 + \vec{\nabla}_x c^2) + c^0 \vec{v}^2 + c^1 \vec{v}^1 + c^2 \vec{v}^0 \quad (6.7)$$

and

$$\begin{cases} \vec{\nabla}_y \cdot \vec{q}^0 = 0 & (6.8) \\ \frac{\partial c^0}{\partial t} + \vec{\nabla}_y \cdot \vec{q}^1 + \vec{\nabla}_x \cdot \vec{q}^0 = 0 & (6.9) \\ \frac{\partial c^1}{\partial t} + \vec{\nabla}_y \cdot \vec{q}^2 + \vec{\nabla}_x \cdot \vec{q}^1 = 0 & (6.10) \end{cases}$$

As for the homogenised equations at the first three orders, Eqs. (5.18), (5.46) and (5.68), they are re-expressed as follows

First-order

$$\begin{cases} \phi \frac{\partial c^0}{\partial t} + \frac{\partial \langle q_i^0 \rangle}{\partial x_i} = 0 & (6.11) \\ \langle q_i^0 \rangle = -D_{ij} \frac{\partial c^0}{\partial x_j} + c^0 \langle v_i^0 \rangle & (6.12) \end{cases}$$

Second-order corrector

$$\begin{cases} \phi \frac{\partial \bar{c}^1}{\partial t} + \frac{\partial \langle q_i^1 \rangle}{\partial x_i} = 0 & (6.13) \\ \langle q_i^1 \rangle = -E_{ijk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} - D'_{ij} \frac{\partial c^0}{\partial x_j} - D_{ij} \frac{\partial \bar{c}^1}{\partial x_j} + c^0 \langle v_i^1 \rangle + \bar{c}^1 \langle v_i^0 \rangle & (6.14) \end{cases}$$

Third-order corrector

$$\begin{cases} \phi \frac{\partial \bar{c}^2}{\partial t} + \frac{\partial \langle q_i^2 \rangle}{\partial x_i} = 0 & (6.15) \\ \langle q_i^2 \rangle = -F_{ijkl} \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} - E'_{ijk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} - E_{ijk} \frac{\partial^2 \bar{c}^1}{\partial x_j \partial x_k} \\ - D''_{ij} \frac{\partial c^0}{\partial x_j} - D'_{ij} \frac{\partial \bar{c}^1}{\partial x_j} - D_{ij} \frac{\partial \bar{c}^2}{\partial x_j} + c^0 \langle v_i^2 \rangle + c^1 \langle v_i^1 \rangle + c^2 \langle v_i^0 \rangle & (6.16) \end{cases}$$

To analyse whether volume averages of local fluxes have the properties of macroscopic fluxes, we consider the following identity to transform volume averages into surface averages (Auriault et al., 2005)

$$\frac{\partial}{\partial y_i} (y_j q_i) \equiv y_j \frac{\partial q_i}{\partial y_i} + q_j. \quad (6.17)$$

6.3 First-order macroscopic flux

Let take $q_i = q_i^0$ in Eq. (6.17) and then integrate over Ω_p . Since by Eq. (6.8) q_i^0 is solenoidal according to $\vec{\nabla}_y$, it reduces to

$$\frac{1}{|\Omega|} \int_{\Omega_p} \frac{\partial}{\partial y_i} (y_j q_i^0) d\Omega = \langle q_j^0 \rangle. \quad (6.18)$$

Applying the divergence theorem and the no-flux boundary condition Eq. (6.3) of order ε^0 , leads to:

$$\frac{1}{|\Omega|} \int_{\delta\Omega_p \cap \delta\Omega} y_j q_i^0 n_i dS = \langle q_j^0 \rangle. \quad (6.19)$$

Let l_i be the dimensionless length of the period along the y_i axis. We denote by Σ_i^0 and

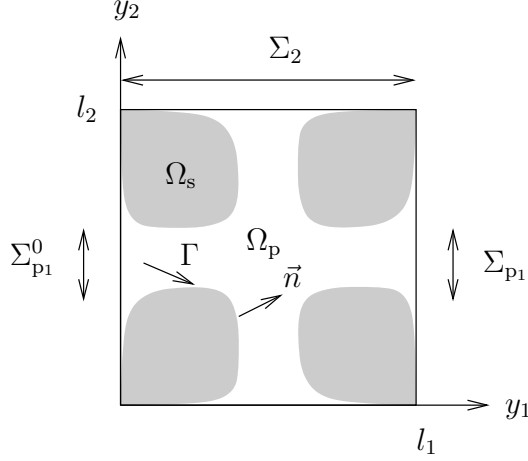


Figure 2: Two-dimensional periodic cell Ω .

Σ_i the cross-sections of the period at $y = 0$ and $y_i = l_i e_i$, respectively. $\Sigma_{p_i}^0$ and Σ_{p_i} are the fluid parts of Σ_i^0 and Σ_i , respectively (Cf. Fig.2). We firstly note that $y_j q_i^0$ is Ω -periodic in the y_k ($k \neq j$) direction. Consequently, only integrals over boundaries Σ_j^0 and Σ_j (where the normal unit vectors are $\pm e_j$) remain, the others cancel out. Furthermore, $y_j q_i^0 = 0$ for $y_j = 0$. Therefore, the integral over Σ_j^0 is zero. We are left with

$$\frac{1}{|\Omega|} \int_{\delta\Omega_p \cap \delta\Omega} y_j q_i^0 n_i dS = \frac{1}{|\Omega|} \int_{\Sigma_{p_j}} l_j q_i^0 dS = \frac{1}{|\Sigma_j|} \int_{\Sigma_{p_j}} q_j^0 dS, \quad (6.20)$$

(without summation over j), and we define

$$\langle q_j^0 \rangle_{\Sigma_i} = \frac{1}{|\Sigma_j|} \int_{\Sigma_{p_j}} q_j^0 dS. \quad (6.21)$$

Hence, we have

$$\langle q_j^0 \rangle = \langle q_j^0 \rangle_{\Sigma_j}, \quad (6.22)$$

which means that the volume average of q_j^0 is equal to a surface average. Therefore, $\langle q_j^0 \rangle$ has the properties of a macroscopic flux. As a consequence, from the expression of \vec{q}^0 , Eq. (6.5), we deduce that

$$\langle v_j^0 \rangle = \langle v_j^0 \rangle_{\Sigma_j}, \quad (6.23)$$

which means that the volume average of \vec{v}^0 has the properties of a Darcy's velocity. Note that the equalities between volume averages and surface averages of q_j^0 and v_j^0 are consequences of the solenoidal character of \vec{q}^0 and \vec{v}^0 , according to variable \vec{y} . Therefore, Eqs. (6.11)-(6.12) can be rewritten as

$$\left\{ \begin{array}{l} \phi \frac{\partial c^0}{\partial t} + \frac{\partial \langle q_i^0 \rangle_{\Sigma_{p_i}}}{\partial x_i} = 0, \end{array} \right. \quad (6.24)$$

$$\left\{ \begin{array}{l} \langle q_i^0 \rangle_{\Sigma_{p_i}} = -D_{ij} \frac{\partial c^0}{\partial x_j} + c^0 \langle v_i^0 \rangle_{\Sigma_{p_i}}, \end{array} \right. \quad (6.25)$$

and the first-order macroscopic description Eq. (5.26) can be expressed as

$$\left\{ \begin{array}{l} \phi \frac{\partial \langle c \rangle}{\partial t} + \frac{\partial \langle q_i \rangle_{\Sigma_{p_i}}}{\partial x_i} = \mathcal{O}(\varepsilon \phi \frac{\partial \langle c \rangle}{\partial t}), \end{array} \right. \quad (6.26)$$

$$\left\{ \begin{array}{l} \langle q_i \rangle_{\Sigma_{p_i}} = -D_{ij} \frac{\partial \langle c \rangle}{\partial x_j} + \langle c \rangle \langle v_i \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon \langle q_i \rangle_{\Sigma_{p_i}}), \end{array} \right. \quad (6.27)$$

where the first-order macroscopic solute flux and fluid velocity are defined by

$$\left\{ \begin{array}{l} \langle q_i \rangle_{\Sigma_{p_i}} = \langle q_i^0 \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon \langle q_i \rangle_{\Sigma_{p_i}}), \end{array} \right. \quad (6.28)$$

$$\left\{ \begin{array}{l} \langle v_i \rangle_{\Sigma_{p_i}} = \langle v_i^0 \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon \langle v_i \rangle_{\Sigma_{p_i}}). \end{array} \right. \quad (6.29)$$

Finally, in dimensional variables the first-order transport model read

$$\left\{ \begin{array}{l} \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} + \frac{\partial \langle \hat{q}_i \rangle_{\hat{\Sigma}_{p_i}}}{\partial \hat{X}_i} = \mathcal{O}(\varepsilon \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}}), \end{array} \right. \quad (6.30)$$

$$\left\{ \begin{array}{l} \langle \hat{q}_i \rangle_{\hat{\Sigma}_{p_i}} = -\hat{D}_{ij}^{\text{eff}} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{X}_j} + \langle \hat{c} \rangle \langle \hat{v}_i \rangle_{\hat{\Sigma}_{p_i}} + \mathcal{O}(\varepsilon \langle \hat{q}_i \rangle_{\hat{\Sigma}_{p_i}}). \end{array} \right. \quad (6.31)$$

6.4 Second-order macroscopic flux

To analyse the volume average of \vec{q}^1 , let consider identity Eq. (6.17) with $q_i = q_i^1$ and integrate over Ω_p . This yields

$$\langle q_i^1 \rangle_{\Sigma_{p_i}} = \langle y_i \frac{\partial q_j^1}{\partial y_j} \rangle + \langle q_i^1 \rangle. \quad (6.32)$$

Now, by Eq. (6.9), we get that \vec{q}^1 is non-solenoidal

$$\frac{\partial q_j^1}{\partial y_j} = -\frac{\partial q_j^0}{\partial x_j} - \frac{\partial c^0}{\partial t}. \quad (6.33)$$

Consequently, the volume average of \vec{q}^1 is not equal to its surface average

$$\langle q_i^1 \rangle_{\Sigma_{p_i}} \neq \langle q_i^1 \rangle, \quad (6.34)$$

which means that $\langle \bar{q}^1 \rangle$ is not a macroscopic flux.

By starting from Eq. (6.32) and then using Eq. (6.33) to get the term $\langle y_i \partial q_j^1 / \partial y_j \rangle$, we obtain the following expression for $\langle \bar{q}^1 \rangle_{\Sigma_{p_i}}$ (Cf. Appendix D.1):

$$\left\{ \begin{array}{l} \langle q_i^1 \rangle_{\Sigma_{p_i}} = -(E_{ijk} - E_{ijk}^\Sigma) \frac{\partial^2 c^0}{\partial x_j \partial x_k} \\ -(D'_{ij} - D'_{ij}^\Sigma) \frac{\partial c^0}{\partial x_j} - D_{ij} \frac{\partial \bar{c}^1}{\partial x_j} \\ + c^0 \langle v_i^1 \rangle_{\Sigma_{p_i}} + \bar{c}^1 \langle v_i^0 \rangle_{\Sigma_{p_i}}, \end{array} \right. \quad (6.35)$$

where

$$\left\{ \begin{array}{l} E_{ijk}^\Sigma = \langle D_0 y_i \gamma_{jk}^0 - \frac{1}{\phi} y_i D_{jk} \rangle, \\ D'_{ij}^\Sigma = \langle y_i (\frac{1}{\phi} \langle v_j^0 \rangle - v_j^0) \rangle. \end{array} \right. \quad (6.36)$$

$$\left\{ \begin{array}{l} D'_{ij}^\Sigma = \langle y_i (\frac{1}{\phi} \langle v_j^0 \rangle - v_j^0) \rangle. \end{array} \right. \quad (6.37)$$

Using Eq. (6.32), the first corrector of the macroscopic description, Eq. (6.13), can be rewritten in terms of the second-order macroscopic flux as follows:

$$\phi \frac{\partial \bar{c}^1}{\partial t} + \frac{\partial}{\partial x_i} (\langle q_i^1 \rangle_{\Sigma_{p_i}}) = \frac{\partial}{\partial x_i} (\langle y_i \frac{\partial q_j^1}{\partial y_j} \rangle). \quad (6.38)$$

Then, using Eqs. (D.4), (D.9), (6.36), (6.37), it becomes

$$\left\{ \begin{array}{l} \phi \frac{\partial \bar{c}^1}{\partial t} + \frac{\partial}{\partial x_i} (\langle q_i^1 \rangle_{\Sigma_{p_i}}) = \\ \frac{\partial}{\partial x_i} [E_{ijk}^\Sigma \frac{\partial^2 c^0}{\partial x_j \partial x_k} + D'_{ij}^\Sigma \frac{\partial c^0}{\partial x_j} - c^0 (\langle v_i^1 \rangle - \langle v_i^1 \rangle_{\Sigma_{p_i}})]. \end{array} \right. \quad (6.39)$$

Now, in order to obtain the corresponding second-order macroscopic description, let firstly add Eq. (6.24) to Eq. (6.39) multiplied by ε . We get

$$\left\{ \begin{array}{l} \phi \frac{\partial \langle c \rangle}{\partial t} + \frac{\partial \langle q_i \rangle_{\Sigma_{p_i}}}{\partial x_i} = \\ \frac{\partial}{\partial x_i} \left[\varepsilon E_{ijk}^\Sigma \frac{\partial^2 \langle c \rangle}{\partial x_j \partial x_k} + \varepsilon D'_{ij}^\Sigma \frac{\partial \langle c \rangle}{\partial x_j} - \langle c \rangle (\langle v_i \rangle - \langle v_i \rangle_{\Sigma_{p_i}}) \right] \\ + \mathcal{O}(\varepsilon^2 \phi \frac{\partial \langle c \rangle}{\partial t}). \end{array} \right. \quad (6.40)$$

Next, we add Eq. (6.25) to Eq. (6.35) multiplied ε , and we obtain

$$\left\{ \begin{array}{l} \langle q_i \rangle_{\Sigma_{p_i}} = -\varepsilon (E_{ijk} - E_{ijk}^\Sigma) \frac{\partial^2 \langle c \rangle}{\partial x_j \partial x_k} \\ -(D_{ij} + \varepsilon D'_{ij} - \varepsilon D'_{ij}^\Sigma) \frac{\partial \langle c \rangle}{\partial x_j} \\ + \langle c \rangle \langle v_i \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon^2 \langle q_i \rangle_{\Sigma_{p_i}}). \end{array} \right. \quad (6.41)$$

In the above equations, the second-order macroscopic solute flux and fluid velocity are defined by

$$\begin{cases} \langle q_i \rangle_{\Sigma_{p_i}} = \langle q_i^0 \rangle_{\Sigma_{p_i}} + \varepsilon \langle q_i^1 \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon^2 \langle q_i \rangle_{\Sigma_{p_i}}), & (6.42) \\ \langle v_i \rangle_{\Sigma_{p_i}} = \langle v_i^0 \rangle_{\Sigma_{p_i}} + \varepsilon \langle v_i^1 \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon^2 \langle v_i \rangle_{\Sigma_{p_i}}), & (6.43) \end{cases}$$

respectively. In dimensional variables, Eqs. (6.40) and (6.41) read

$$\begin{cases} \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} + \frac{\partial \langle \hat{q}_i \rangle_{\hat{\Sigma}_{p_i}}}{\partial \hat{X}_i} = \\ \frac{\partial}{\partial \hat{X}_i} \left[\hat{E}_{ijk}^{\Sigma} \frac{\partial^2 \langle \hat{c} \rangle}{\partial X_j \partial X_k} + \hat{D}'_{ij}{}^{\Sigma} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{X}_j} - \langle \hat{c} \rangle (\langle \hat{v}_i \rangle - \langle \hat{v}_i \rangle_{\hat{\Sigma}_{p_i}}) \right] \\ + \mathcal{O}(\varepsilon^2 \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}}), & (6.44) \\ \langle \hat{q}_i \rangle_{\Sigma_{p_i}} = -(\hat{E}_{ijk}^{\text{diff}} - \hat{E}_{ijk}^{\Sigma}) \frac{\partial^2 \langle \hat{c} \rangle}{\partial X_j \partial X_k} - (\hat{D}_{ij}^{\text{diff}} + \hat{D}_{ij}^{\text{disp}} - \hat{D}_{ij}'^{\Sigma}) \frac{\partial \langle \hat{c} \rangle}{\partial X_j} \\ + \langle \hat{c} \rangle \langle \hat{v}_i \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon^2 \langle \hat{q}_i \rangle_{\Sigma_{p_i}}), & (6.45) \end{cases}$$

where

$$\begin{cases} \hat{E}_{ijk}^{\text{diff}} = lD_c E_{ijk}, & (6.46) \end{cases}$$

$$\begin{cases} \hat{E}_{ijk}^{\Sigma} = lD_c E_{ijk}^{\Sigma}, & (6.47) \end{cases}$$

$$\begin{cases} \hat{D}_{ij}'^{\Sigma} = \varepsilon D_c D_{ij}'^{\Sigma}. & (6.48) \end{cases}$$

6.5 Third-order macroscopic flux

Proceeding in the same manner as in §6.4, we also conclude that

$$\langle \vec{q}^2 \rangle \neq \langle \vec{q}^2 \rangle_{\Sigma_{p_i}}, \quad (6.49)$$

and we show that in dimensional variables, the third-order transport model expressed in terms of the macroscopic flux reads (Cf. Appendix D.2):

$$\left\{ \begin{aligned} & \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} + \frac{\partial}{\partial X_i} (\langle q_i \rangle_{\Sigma_{p_i}}) = \\ & \frac{\partial}{\partial X_i} \left[\hat{F}_{ijkl}^{\Sigma} \frac{\partial^3 \langle c \rangle}{\partial X_j \partial X_k \partial X_l} + (\hat{E}_{ijk}^{\Sigma} + \hat{E}'_{ijk}{}^{\Sigma}) \frac{\partial^2 \langle c \rangle}{\partial X_j \partial X_k} \right. \\ & \left. + (\hat{D}'_{ij}{}^{\Sigma} + \hat{D}''_{ij}{}^{\Sigma}) \frac{\partial \langle c \rangle}{\partial X_j} + \langle c \rangle (\langle v_i \rangle - \langle v_i \rangle_{\Sigma_{p_i}}) \right] \\ & + \mathcal{O}(\varepsilon^3 \phi \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}}). \end{aligned} \right. \quad (6.50)$$

$$\left\{ \begin{aligned} & \langle \hat{q}_i \rangle_{\Sigma_{p_i}} = -(\hat{F}_{ijkl}^{\text{diff}} - \hat{F}_{ijk}^{\Sigma}) \frac{\partial^3 \langle c \rangle}{\partial X_j \partial X_k \partial X_l} \\ & - (\hat{E}_{ijk}^{\text{diff}} - \hat{E}_{ijk}^{\Sigma} + \hat{E}'_{ijk}{}^{\Sigma} - \hat{E}'_{ijk}{}^{\Sigma}) \frac{\partial^2 \langle c \rangle}{\partial X_j \partial X_k} \\ & - (\hat{D}_{ij} + \hat{D}'_{ij} - \hat{D}'_{ij}{}^{\Sigma} + \hat{D}''_{ij} - \hat{D}''_{ij}{}^{\Sigma}) \frac{\partial \langle c \rangle}{\partial X_j} \\ & + \langle \hat{c} \rangle \langle \hat{v}_i \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon^3 \langle \hat{q}_i \rangle_{\Sigma_{p_i}}) \end{aligned} \right. \quad (6.51)$$

where (Cf. Appendix D.2)

$$\left\{ \begin{aligned} & \hat{F}_{ijkl}^{\Sigma} = l^2 D_c F_{ijkl}^{\Sigma}, \end{aligned} \right. \quad (6.52)$$

$$\left\{ \begin{aligned} & \hat{E}'_{ijk}{}^{\Sigma} = \varepsilon l D_c E'_{ijk}{}^{\Sigma}, \end{aligned} \right. \quad (6.53)$$

$$\left\{ \begin{aligned} & \hat{D}''_{ij}{}^{\Sigma} = \varepsilon^2 D_c D''_{ij}{}^{\Sigma}. \end{aligned} \right. \quad (6.54)$$

Since $\langle \hat{q}_i \rangle_{\Sigma_{p_i}}$ has the properties of a macroscopic flux, the right-hand-sides of the mass-balance equations, Eq. (6.44) and Eq. (6.50), represent source terms, which are actually expressions of the second-order and third-order non-local effects, respectively.

7 Conclusions

In the present paper, higher-order asymptotic homogenisation up to the third order of solute transport in the advective-diffusive regime is performed. The main result of the study is that low scale separation induces dispersion effects. At the second order, the transport model is similar to the classical model of dispersion: the dispersion tensor is the sum of the diffusion tensor and a mechanical dispersion tensor, while this property is not verified in the homogenised dispersion model obtained at higher Péclet number. The velocity is governed by a second-order law which reduces to Darcy's law in case of isotropy. Thus, the second-order model of advection-diffusion is similar to the phenomenological model of dispersion. The third-order description contains second and third concentration gradient terms, with a fourth order tensor of diffusion and with a third-order and an additional second-order tensors of dispersion. Hence, these results show that when employing the first order model while ε is not "very" small would, for

example, lead to a wrong estimate of the tensor of effective diffusion from experimental data. We generally admit that a first-order model, whose degree of precision is $\mathcal{O}(\varepsilon)$, is valid for a value of ε up to $\varepsilon \approx 0.1$. Consequently, we may estimate that the p -order model is required when $\varepsilon^p \approx 0.1$. The analysis of the macroscopic fluxes shows that the second and the third order macroscopic fluxes are distinct from the volume averages of the corresponding local fluxes. From the writing of the second and third order models in terms of the macroscopic fluxes arise expressions of the non-local effects. All these results are valid for macroscopically homogeneous media and macroscopic heterogeneity would lead to stronger non-local effects.

The results at Péclet number $\mathcal{O}(\varepsilon)$ can quite easily be deduced from the above analysis. This leads to the model of diffusion at the first order, the model of advection-diffusion at the second order and dispersion effects appear at the third order. Eventually, we may conclude that scale separation is a crucial issue whenever the fluid is in motion, since low scale separation induces a modification of the apparent transport regime (Royer, 2018).

An important property of higher-order homogenised models is that edge effects are induced: the boundary layer created by the heterogeneity may affect the homogenised solution inside the domain in higher orders with respect to ε . Numerical simulations of the above derived effective higher-order equations thus requires a specific treatment of these edge effects (Smyshlyaev and Cherednichenko, 2000; Buannic and Cartaud, 2001; Dumontet, 1990). A discussion on that topic is complex and beyond the scope of this paper.

Since the advection-diffusion equation is a Fokker-Planck type equation, the higher-order transport homogenised equations may appear to be similar to a generalised Fokker-Planck equation (Risken, 1989). Such equation, which describes the time evolution of a probability density function is obtained by a Kramers–Moyal expansion which transforms an integro differential master equation. Pawula (1967) has proved that finite truncations of the generalised Fokker-Planck equation at any order greater than the second leads to a logical inconsistency, as the function must then have negative values at least for sufficiently small times and in isolated regions. This argument may be used to put into question the validity of higher-order homogenised transport models (Mauri, 1991). In this regard the work of van Kampen (1981) provides the framework for the introduction of a small parameter which allows for the construction of a modified Kramers-Moyal expansion. Then, one can approximate the expansion by a finite number of terms which involves derivatives of order higher than two, using an appropriate perturbation technique. In this case, the contribution from higher-order terms diminishes, because of their order in the small parameter. Such an expansion is admittedly questionable in view of Pawula’s theorem, but can be controlled when manipulated with care (Popescu and Lipan, 2015). Thus, the theorem of Pawula does not necessarily restrict the truncation of higher order terms, when we can formally obtain high-order perturbative equations (Kanasava, 2017) and nonvanishing higher-order coefficients have been observed in various systems (Anvari et al., 2016; Friedrich et al., 2011; Prusseit and Lehnertz, 2007; Tutkun and Mydlarski, 2004; Kim et al., 2008; Petelczyc et al., 2009, 2015). Therefore, though higher-order perturbative models might, in some cases, have negative values at some isolated times and positions, this does not invalidate the models derived in the study, which are valid only in zones where large

concentration gradients are applied.

Appendices

A First-order homogenisation

A.1 Definition of vector χ_j

Let multiply the local problem defined by Eqs. (5.9)-(5.10) by a test function α satisfying the condition of having zero average, and then, let integrate over Ω_p . We obtain the following variational formulation

$$\int_{\Omega_p} D_0 \frac{\partial \alpha}{\partial y_i} \frac{\partial c^1}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \alpha}{\partial y_i} d\Omega \frac{\partial c^0}{\partial x_i}. \quad (\text{A.1})$$

Vector χ_j is the solution for c^1 when $\partial c^0 / \partial x_i = \delta_{ij}$. Therefore, the variational formulation associated with χ_j is

$$\int_{\Omega_p} D_0 \frac{\partial \alpha}{\partial y_i} \frac{\partial \chi_j}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \alpha}{\partial y_j} d\Omega, \quad (\text{A.2})$$

and χ_j must satisfy

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial \chi_j}{\partial y_i} + \delta_{ij} \right) \right] = 0 \quad \text{in } \Omega_p, \\ \left[D_0 \left(\frac{\partial \chi_j}{\partial y_i} + \delta_{ij} \right) \right] n_i = 0 \quad \text{on } \Gamma, \\ \langle \chi_j \rangle = 0, \\ \vec{\chi}: \text{periodic in } \vec{y}. \end{array} \right. \quad (\text{A.3})$$

A.2 Symmetry of tensor D_{ij}

To demonstrate the symmetry of D_{ij} , we firstly take

$$\left\{ \begin{array}{l} \alpha = \chi_q, \\ c^1 = \chi_p, \frac{\partial c^0}{\partial x_i} = \delta_{ip}, \end{array} \right. \quad (\text{A.4})$$

into Eq. (A.1). This leads to:

$$\int_{\Omega_p} D_0 \frac{\partial \chi_q}{\partial y_i} \frac{\partial \chi_p}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \chi_q}{\partial y_p} d\Omega. \quad (\text{A.5})$$

Next, we consider

$$\left\{ \begin{array}{l} \alpha = \chi_p, \\ c^1 = \chi_q, \frac{\partial c^0}{\partial x_i} = \delta_{iq}, \end{array} \right. \quad (\text{A.6})$$

into Eq. (A.1), which leads to:

$$\int_{\Omega_p} D_0 \frac{\partial \chi_p}{\partial y_i} \frac{\partial \chi_q}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \chi_p}{\partial y_q} d\Omega. \quad (\text{A.7})$$

By Eqs. (A.5) and (A.7), we deduce that:

$$\int_{\Omega_p} \frac{\partial \chi_q}{\partial y_p} d\Omega = \int_{\Omega_p} \frac{\partial \chi_p}{\partial y_q} d\Omega. \quad (\text{A.8})$$

Consequently, we have:

$$D_{qp} = D_{pq}, \quad (\text{A.9})$$

which proves the symmetry of \bar{D} .

B Second-order homogenisation

B.1 Boundary value problem for c^2

The third-order boundary value given by Eqs. (5.14) and (5.16) can be written as follows:

$$\begin{cases} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) \right] - \frac{\partial}{\partial y_i} (c^0 v_i^1) - \frac{\partial}{\partial y_i} (c^1 v_i^0) = \\ \frac{\partial c^0}{\partial t} - \frac{\partial}{\partial x_i} \left[D_0 \left(\frac{\partial c^1}{\partial y_i} + \frac{\partial c^0}{\partial x_i} \right) \right] + \frac{\partial}{\partial x_i} (c^0 v_i^0) & \text{within } \Omega_p, \\ \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) \right] n_i = 0 & \text{over } \Gamma. \end{cases} \quad (\text{B.1})$$

Now, using Eq. (5.8), and the second order of Eq. (4.2)

$$\frac{\partial v_i^1}{\partial y_i} + \frac{\partial v_i^0}{\partial x_i} = 0, \quad (\text{B.3})$$

while bearing in mind Eq. (5.7), the second and the third terms of the left hand side of Eq. (B.1) can be transformed as follows:

$$\begin{cases} \frac{\partial}{\partial y_i} (c^0 v_i^1) = -c^0 \frac{\partial v_i^0}{\partial x_i}, \\ \frac{\partial}{\partial y_i} (c^1 v_i^0) = v_i^0 \frac{\partial c^1}{\partial y_i}. \end{cases} \quad (\text{B.4})$$

Next, using Eq. (5.22) we get

$$\frac{\partial c^0}{\partial t} = \frac{1}{\phi} D_{ij} \frac{\partial^2 c^0}{\partial x_i \partial x_j} - \frac{1}{\phi} \langle v_i^0 \rangle \frac{\partial c^0}{\partial x_i}, \quad (\text{B.6})$$

and from Eq. (5.12), we obtain

$$\frac{\partial c^1}{\partial x_i} = \chi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^1}{\partial x_i}. \quad (\text{B.7})$$

Substituting Eqs. (B.4) to (B.7) into Eqs. (B.1)-(B.2), and then using the expression Eq. (5.20), we get the boundary value problem Eqs. (5.31)-(5.32).

B.2 Definitions of tensor η_{jk} and vector π_j

By multiplying the local problem Eqs. (5.31)-(5.32) by a test function α of zero average, and then integrating over Ω_p , we obtain its variational formulation:

$$\begin{aligned} \int_{\Omega_p} \frac{\partial \alpha}{\partial y_i} [D_0 (\frac{\partial c^2}{\partial y_i} + \chi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^1}{\partial x_i})] d\Omega = \\ \int_{\Omega_p} \alpha D_0 \gamma_{ij}^0 \frac{\partial^2 c^0}{\partial x_i \partial x_j} d\Omega - \int_{\Omega_p} \alpha v_i^0 \gamma_{ij}^0 \frac{\partial c^0}{\partial x_j} d\Omega. \end{aligned} \quad (\text{B.8})$$

n_{lm} is the particular solution for c^2 when

$$\begin{cases} \frac{\partial^2 c^0}{\partial x_i \partial x_j} = \delta_{il} \delta_{jm}, \\ \frac{\partial c^0}{\partial x_i} = \frac{\partial \bar{c}^1}{\partial x_i} = 0. \end{cases}$$

Therefore, the variational formulation associated with n_{jk} reads

$$\int_{\Omega_p} \frac{\partial \alpha}{\partial y_i} D_0 (\frac{\partial n_{lm}}{\partial y_i} + \chi_m \delta_{il}) d\Omega = \int_{\Omega_p} \alpha D_0 \gamma_{lm}^0 d\Omega, \quad (\text{B.9})$$

and n_{jk} must satisfy

$$\begin{cases} \frac{\partial}{\partial y_i} (D_0 (\frac{\partial \eta_{lm}}{\partial y_i} + \chi_m \delta_{il})) = \frac{1}{\phi} D_{lm} - D_0 \gamma_{lm}^0 & \text{within } \Omega_p, \\ (D_0 (\frac{\partial \eta_{lm}}{\partial y_i} + \chi_m \delta_{il})) n_i = 0 & \text{over } \Gamma, \\ \langle \eta_{lm} \rangle = 0, \\ \eta_{lm}: \Omega\text{-periodic in variable } \vec{y}. \end{cases} \quad (\text{B.10})$$

From its definition, we see that η_{lm} is a parameter related to the diffusion mechanism.

π_k is the solution for c^2 when

$$\begin{cases} \frac{\partial c^0}{\partial x_j} = \delta_{jk}, \\ \frac{\partial \bar{c}^1}{\partial x_i} = \frac{\partial^2 c^0}{\partial x_i \partial x_j} = 0. \end{cases}$$

The variational formulation associated with π_k is thus

$$\int_{\Omega_p} \frac{\partial \alpha}{\partial y_i} D_0 \frac{\partial \pi_k}{\partial y_i} d\Omega = - \int_{\Omega_p} \alpha v_i^0 \gamma_{ik}^0 d\Omega, \quad (\text{B.11})$$

and π_k must satisfy

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i} (D_0 \frac{\partial \pi_k}{\partial y_i}) = \gamma_{ik}^0 v_i^0 - \frac{1}{\phi} \langle v_k^0 \rangle \quad \text{within } \Omega_p, \\ (D_0 \frac{\partial \pi_k}{\partial y_i}) n_i = 0 \quad \text{over } \Gamma, \\ \langle \pi_k \rangle = 0, \\ \pi_k: \Omega\text{-periodic in variable } \vec{y}. \end{array} \right. \quad (\text{B.12})$$

From the above definition it is clear that vector $\vec{\pi}$ depends on both the diffusive and the convective phenomena, which characterises the presence of dispersive effects.

B.3 Properties of the third-order tensor E_{ijk}

B.3.1 Symmetry by construction of a third-order tensor with respect to its last two indices

By construction, E_{ijk} is symmetric with respect its last two indices:

$$E_{ijk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} = E_{ijk} \frac{\partial^2 c^0}{\partial x_k \partial x_j} = E_{ikj} \frac{\partial^2 c^0}{\partial x_k \partial x_j} = E_{ikj} \frac{\partial^2 c^0}{\partial x_j \partial x_k}. \quad (\text{B.13})$$

Consequently:

$$E_{ijk} = E_{ikj}. \quad (\text{B.14})$$

In case of isotropy, third-order tensors are scalar multiples of the permutation tensor

$$E_{ijk} = E \varepsilon_{ijk} \quad \varepsilon_{ijk} : \text{permutation tensor}. \quad (\text{B.15})$$

Since $\varepsilon_{ijk} = -\varepsilon_{ikj}$, Eq. (B.14) induces that: $E = 0$. Thus, any third-order tensor which is symmetric with respect to its last two indices is equal to zero in case of isotropy.

B.3.2 Antisymmetry with respect to the first two indices

Let take $\alpha = \eta_{lm}$ in the variational formulation associated with functions χ_j Eq. (A.2). We obtain

$$\int_{\Omega_p} D_0 \frac{\partial \eta_{lm}}{\partial y_i} \frac{\partial \chi_j}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \eta_{lm}}{\partial y_j} d\Omega. \quad (\text{B.16})$$

Let now take $\alpha = \chi_j$ in the variational formulation associated with η_{lm} Eq. (B.9). We get

$$\begin{aligned} \int_{\Omega_p} D_0 \frac{\partial \eta_{lm}}{\partial y_i} \frac{\partial \chi_j}{\partial y_i} d\Omega = \\ - \int_{\Omega_p} D_0 \chi_m \frac{\partial \chi_j}{\partial y_l} d\Omega + \int_{\Omega_p} D_0 \chi_j \frac{\partial \chi_m}{\partial y_l} d\Omega. \end{aligned} \quad (\text{B.17})$$

From Eqs. (B.16) and (B.17), we deduce

$$\int_{\Omega_p} D_0 \left(\frac{\partial \eta_{lm}}{\partial y_j} + \chi_j \delta_{lm} \right) d\Omega = \int_{\Omega_p} D_0 \chi_m \frac{\partial \chi_j}{\partial y_l} d\Omega - \int_{\Omega_p} D_0 \chi_j \frac{\partial \chi_m}{\partial y_l} d\Omega. \quad (\text{B.18})$$

Thus, from the definition of E_{jlm} Eq. (5.44), we have

$$E_{jlm} = \frac{1}{|\Omega|} \int_{\Omega_p} D_0 \chi_m \frac{\partial \chi_j}{\partial y_l} d\Omega - \frac{1}{|\Omega|} \int_{\Omega_p} D_0 \chi_j \frac{\partial \chi_m}{\partial y_l} d\Omega, \quad (\text{B.19})$$

and

$$\begin{aligned} E_{ljm} &= \frac{1}{|\Omega|} \int_{\Omega_p} D_0 \chi_m \frac{\partial \chi_l}{\partial y_j} d\Omega - \frac{1}{|\Omega|} \int_{\Omega_p} D_0 \chi_l \frac{\partial \chi_m}{\partial y_j} d\Omega = \\ &= \frac{1}{|\Omega|} \int_{\Omega_p} D_0 \chi_j \frac{\partial \chi_m}{\partial y_l} d\Omega - \frac{1}{|\Omega|} \int_{\Omega_p} D_0 \chi_m \frac{\partial \chi_j}{\partial y_l} d\Omega. \end{aligned} \quad (\text{B.20})$$

Therefore

$$E_{jlm} = -E_{ljm}. \quad (\text{B.21})$$

Since the medium is macroscopically homogeneous, E_{ijk} does not depend on the macroscopic variable \vec{x} . Consequently, the antisymmetry with respect to the two first indices implies that

$$\frac{\partial}{\partial x_i} (E_{ijk} \frac{\partial^2 c^0}{\partial x_j \partial x_k}) = 0. \quad (\text{B.22})$$

From Eq. (B.19), we further note that tensor E_{jlm} can be determined from vector $\vec{\chi}$.

B.4 Properties of tensor D'_{ij}

Let take $c^2 = \pi_k$ and $\alpha = \chi_l$ in the variational formulation of the second-order local problem Eq. (B.8). We obtain

$$\int_{\Omega_p} \frac{\partial \chi_l}{\partial y_i} D_0 \frac{\partial \pi_k}{\partial y_i} d\Omega = - \int_{\Omega_p} \chi_l \frac{\partial \chi_k}{\partial y_i} v_i^0 d\Omega - \int_{\Omega_p} \chi_l v_k^0 d\Omega. \quad (\text{B.23})$$

Now, by taking $c^1 = \chi_l$ and $\alpha = \pi_k$ in the variational formulation of the first-order problem Eq. (A.1), we get

$$\int_{\Omega_p} \frac{\partial \pi_k}{\partial y_i} D_0 \frac{\partial \chi_l}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \pi_k}{\partial y_l} d\Omega. \quad (\text{B.24})$$

From Eqs. (B.23) and (B.24), we deduce

$$\int_{\Omega_p} D_0 \frac{\partial \pi_k}{\partial y_l} d\Omega = \int_{\Omega_p} \chi_l \frac{\partial \chi_k}{\partial y_i} v_i^0 d\Omega + \int_{\Omega_p} \chi_l v_k^0 d\Omega. \quad (\text{B.25})$$

Now, by considering the definition of \bar{D}' , Eq. (5.45), with the above expression, it comes

$$D'_{lk} = \langle D_0 \frac{\partial \pi_k}{\partial y_l} - v_l^0 \chi_k \rangle = \langle \chi_l v_k^0 \rangle + \langle \chi_l \frac{\partial \chi_k}{\partial y_i} v_i^0 \rangle - \langle \chi_k v_l^0 \rangle, \quad (\text{B.26})$$

from which we deduce

$$D'_{lk} - D'_{kl} = 2(\langle \chi_l v_k^0 \rangle - \langle \chi_k v_l^0 \rangle) \neq 0. \quad (\text{B.27})$$

Therefore, \bar{D}' is not symmetric:

$$D'_{lk} \neq D'_{kl}. \quad (\text{B.28})$$

From Eq. (B.26), tensor \bar{D}' can be decomposed as

$$D'_{lk} = {}^s D'_{lk} + {}^a D'_{lk}, \quad (\text{B.29})$$

where

$${}^s D'_{lk} = \langle \chi_l \frac{\partial \chi_k}{\partial y_i} v_i^0 \rangle \quad (\text{B.30})$$

is symmetric and where

$${}^a D'_{lk} = \langle \chi_l v_k^0 \rangle - \langle \chi_k v_l^0 \rangle \quad (\text{B.31})$$

is antisymmetric.

Furthermore, from Eq. (B.26), it can be seen that tensor D'_{lk} can be determined from vectors $\vec{\chi}$ and \vec{v}^0 .

C Third order homogenisation

C.1 Boundary value problem for c^3

From Eqs. (5.36)-(5.38), we get the following boundary value problem for c^3 :

$$\begin{cases} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^3}{\partial y_i} + \frac{\partial c^2}{\partial x_i} \right) \right] - \frac{\partial}{\partial y_i} (c^0 v_i^2) - \frac{\partial}{\partial y_i} (c^1 v_i^1) - \frac{\partial}{\partial y_i} (c^2 v_i^0) = \\ \frac{\partial c^1}{\partial t} - \frac{\partial}{\partial x_i} \left[D_0 \left(\frac{\partial c^2}{\partial y_i} + \frac{\partial c^1}{\partial x_i} \right) \right] + \frac{\partial}{\partial x_i} (c^0 v_i^1) + \frac{\partial}{\partial x_i} (c^1 v_i^0) \text{ in } \Omega_p, \\ \left[D_0 \left(\frac{\partial c^3}{\partial y_i} + \frac{\partial c^2}{\partial x_i} \right) \right] n_i = 0 \text{ over } \Gamma. \end{cases} \quad (\text{C.1})$$

Using Eq. (5.8) and Eq. (B.3), and Eq. (4.2) at the third order

$$\frac{\partial v_i^2}{\partial y_i} + \frac{\partial v_i^1}{\partial x_i} = 0, \quad (\text{C.3})$$

we deduce that

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i}(c^0 v_i^2) = -c^0 \frac{\partial v_i^1}{\partial x_i}, \end{array} \right. \quad (\text{C.4})$$

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i}(c^1 v_i^1) = -c^1 \frac{\partial v_i^0}{\partial x_i} + \frac{\partial c^1}{\partial y_i} v_i^1, \end{array} \right. \quad (\text{C.5})$$

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i}(c^2 v_i^0) = \frac{\partial c^2}{\partial y_i} v_i^0, \end{array} \right. \quad (\text{C.6})$$

$$\left\{ \begin{array}{l} \frac{\partial}{\partial x_i}(c^0 v_i^1) = c^0 \frac{\partial v_i^1}{\partial x_i} + \frac{\partial c^0}{\partial x_i} v_i^1, \end{array} \right. \quad (\text{C.7})$$

$$\left\{ \begin{array}{l} \frac{\partial}{\partial x_i}(c^1 v_i^0) = c^1 \frac{\partial v_i^0}{\partial x_i} + \frac{\partial c^1}{\partial x_i} v_i^0. \end{array} \right. \quad (\text{C.8})$$

Then, substituting Eqs. (C.4)-(C.8) into Eq. (C.1), while using Eqs. (5.20) and (5.40) yields

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial c^3}{\partial y_i} + \frac{\partial c^2}{\partial x_i} \right) \right] = -D_0 \gamma_{ijk}^1 \frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} \\ + (v_i^0 \gamma_{ijk}^1 - D_0 \frac{\partial \pi_k}{\partial y_j}) \frac{\partial^2 c^0}{\partial x_j \partial x_k} - D_0 \gamma_{ij}^0 \frac{\partial^2 \bar{c}^1}{\partial x_i \partial x_j} \\ + (v_i^0 \frac{\partial \pi_j}{\partial y_i} + v_i^1 \gamma_{ij}^0) \frac{\partial c^0}{\partial x_j} + v_i^0 \gamma_{ij}^0 \frac{\partial \bar{c}^1}{\partial x_j} + \frac{\partial c^1}{\partial t}. \end{array} \right. \quad (\text{C.9})$$

We may now determine an expression for $\partial c^1 / \partial t$. From the definition of c^1 (Eq. (5.12)), we have

$$\frac{\partial c^1}{\partial t} = \chi_i \frac{\partial}{\partial t} \left(\frac{\partial c^0}{\partial x_i} \right) + \frac{\partial \bar{c}^1}{\partial t} = \chi_i \frac{\partial}{\partial x_i} \left(\frac{\partial c^0}{\partial t} \right) + \frac{\partial \bar{c}^1}{\partial t}. \quad (\text{C.10})$$

Now, using the expression of $\partial c^0 / \partial t$ (Eq. (B.6)) and deducing $\partial \bar{c}^1 / \partial t$ from Eq. (5.46), the above equation finally becomes

$$\left\{ \begin{array}{l} \frac{\partial c^1}{\partial t} = \frac{1}{\phi} \chi_i D_{jk} \frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} \\ + \frac{1}{\phi} (D'_{ij} - \chi_i \langle v_j^0 \rangle) \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \frac{1}{\phi} D_{ij} \frac{\partial^2 \bar{c}^1}{\partial x_i \partial x_j} \\ - \frac{1}{\phi} \left(\chi_i \frac{\partial \langle v_j^0 \rangle}{\partial x_i} + \langle v_j^1 \rangle \right) \frac{\partial c^0}{\partial x_j} - \frac{1}{\phi} \langle v_i^0 \rangle \frac{\partial \bar{c}^1}{\partial x_i}. \end{array} \right. \quad (\text{C.11})$$

Then, from the expression obtained for c^2 , Eq. (5.33), we get

$$\frac{\partial c^2}{\partial x_i} = \eta_{jk} \frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} + \pi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \chi_j \frac{\partial^2 \bar{c}^1}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^2}{\partial x_i}. \quad (\text{C.12})$$

Finally, substituting Eqs. (C.11) and (C.12) into Eq. (C.9), we get Eq. (5.56), and the boundary condition Eq. (C.2) over Γ becomes Eq. (5.57).

C.2 Variational formulation of the local boundary value problem

The variational formulation of the the local problem defined by Eqs. (5.56) and (5.57) is obtained by multiplying both equations by a test function α of zero average and by integrating over Ω_p :

$$\left\{ \begin{array}{l} \int_{\Omega_p} \frac{\partial \alpha}{\partial y_i} [D_0 (\frac{\partial c^3}{\partial y_i} + \eta_{jk} \frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} + \pi_j \frac{\partial^2 c^0}{\partial x_i \partial x_j} + \chi_j \frac{\partial^2 \bar{c}^1}{\partial x_i \partial x_j} + \frac{\partial \bar{c}^2}{\partial x_i})] d\Omega = \\ - \int_{\Omega_p} \alpha (\frac{1}{\phi} \chi_i D_{jk} - D_0 \gamma_{ijk}^1) d\Omega \frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} \\ - \int_{\Omega_p} \alpha (v_i^0 \gamma_{ijk}^1 - D_0 \frac{\partial \pi_k}{\partial y_j} - \frac{1}{\phi} \chi_j \langle v_k^0 \rangle) d\Omega \frac{\partial^2 c^0}{\partial x_j \partial x_k} \\ + \int_{\Omega_p} \alpha D_0 \gamma_{ij}^0 d\Omega \frac{\partial^2 \bar{c}^1}{\partial x_i \partial x_j} \\ - \int_{\Omega_p} \alpha (v_i^0 \frac{\partial \pi_j}{\partial y_i} + v_i^1 \gamma_{ij}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_j^0 \rangle}{\partial x_i}) d\Omega \frac{\partial c^0}{\partial x_j} \\ - \int_{\Omega_p} \alpha v_i^0 \gamma_{ij}^0 d\Omega \frac{\partial \bar{c}^1}{\partial x_j}. \end{array} \right. \quad (C.13)$$

C.3 Definition of the third-order tensor ξ_{lmp}

ξ_{lmp} is the solution for c^3 when

$$\frac{\partial^3 c^0}{\partial x_i \partial x_j \partial x_k} = \delta_{il} \delta_{jm} \delta_{kp},$$

while the other forcing terms are set to zero. Thus, ξ_{lmp} must satisfy

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial \xi_{lmp}}{\partial y_i} + \eta_{mp} \delta_{il} \right) \right] = \frac{1}{\phi} \chi_l D_{mp} - D_0 \gamma_{lmp}^1 \quad \text{within } \Omega_p, \\ \left[D_0 \left(\frac{\partial \xi_{lmp}}{\partial y_i} + \eta_{mp} \delta_{il} \right) \right] n_i = 0 \quad \text{over } \Gamma, \\ \langle \xi_{lmp} \rangle = 0, \\ \xi_{lmp}: \Omega\text{-periodic.} \end{array} \right. \quad (C.14)$$

From Eq. (C.13), we deduce the corresponding variational formulation:

$$\int_{\Omega_p} \frac{\partial \alpha}{\partial y_i} \left[D_0 \left(\frac{\partial \xi_{lmp}}{\partial y_i} + \eta_{mp} \delta_{il} \right) \right] d\Omega = - \int_{\Omega_p} \alpha \left(\frac{1}{\phi} \chi_l D_{mp} - D_0 \gamma_{lmp}^1 \right) d\Omega. \quad (C.15)$$

C.4 Definition of the second-order tensor τ_{lm}

τ_{lm} is the solution for c^3 when

$$\frac{\partial^2 c^0}{\partial x_i \partial x_j} = \delta_{il} \delta_{jm}.$$

Thus, it is the solution to

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i} \left[D_0 \left(\frac{\partial \tau_{lm}}{\partial y_i} + \pi_m \delta_{il} \right) \right] = \\ v_i^0 \gamma_{ilm}^1 - D_0 \frac{\partial \pi_m}{\partial y_l} + \frac{1}{\phi} D'_{lm} - \frac{1}{\phi} \chi_l \langle v_m^0 \rangle \quad \text{within } \Omega_p, \\ \left[D_0 \left(\frac{\partial \tau_{lm}}{\partial y_i} + \pi_m \delta_{il} \right) \right] n_i = 0 \quad \text{over } \Gamma, \\ \langle \tau_{lm} \rangle = 0, \\ \bar{\tau}: \Omega\text{-periodic,} \end{array} \right. \quad (\text{C.16})$$

and the associated variational formulation reads

$$\int_{\Omega_p} \frac{\partial \alpha}{\partial y_i} \left[D_0 \left(\frac{\partial \tau_{lm}}{\partial y_i} + \pi_m \delta_{il} \right) \right] d\Omega = - \int_{\Omega_p} \alpha \left(v_i^0 \gamma_{ilm}^1 - D_0 \frac{\partial \pi_m}{\partial y_l} - \frac{1}{\phi} \chi_l \langle v_m^0 \rangle \right) d\Omega. \quad (\text{C.17})$$

C.5 Definition of vector θ_k

θ_k is the solution for c^3 when

$$\frac{\partial c^0}{\partial x_j} = \delta_{jk}.$$

Therefore, it must satisfy

$$\left\{ \begin{array}{l} \frac{\partial}{\partial y_i} \left(D_0 \frac{\partial \theta_k}{\partial y_i} \right) = v_i^0 \frac{\partial \pi_k}{\partial y_i} + v_i^1 \gamma_{ik}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_k^0 \rangle}{\partial x_i} - \frac{1}{\phi} \langle v_k^1 \rangle \quad \text{within } \Omega_p, \\ \left(D_0 \frac{\partial \theta_k}{\partial y_i} \right) n_i = 0 \quad \text{over } \Gamma, \\ \langle \theta_k \rangle = 0, \\ \bar{\theta}: \Omega\text{-periodic.} \end{array} \right. \quad (\text{C.18})$$

The corresponding variational formulation is

$$\int_{\Omega_p} \frac{\partial \alpha}{\partial y_i} D_0 \frac{\partial \theta_k}{\partial y_i} d\Omega = - \int_{\Omega_p} \alpha \left(v_i^0 \frac{\partial \pi_k}{\partial y_i} + v_i^1 \gamma_{ik}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_k^0 \rangle}{\partial x_i} \right) d\Omega. \quad (\text{C.19})$$

C.6 Properties of the second-order tensor D''_{jk}

By taking $\alpha = \theta_k$ in the variational formulation associated with $\bar{\chi}$ (Eq. (A.2)), we get:

$$\int_{\Omega_p} \frac{\partial \theta_k}{\partial y_i} D_0 \frac{\partial \chi_j}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \theta_k}{\partial y_j} d\Omega. \quad (\text{C.20})$$

Next, we consider $\alpha = \chi_j$ in the variational formulation associated with $\vec{\theta}$ (Eq. (C.19)):

$$\int_{\Omega_p} \frac{\partial \chi_j}{\partial y_i} D_0 \frac{\partial \theta_k}{\partial y_i} d\Omega = - \int_{\Omega_p} \chi_j (v_i^0 \frac{\partial \pi_k}{\partial y_i} + v_i^1 \gamma_{ik}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_k^0 \rangle}{\partial x_i}) d\Omega. \quad (C.21)$$

Then, from Eqs. (C.20)-(C.21), we deduce that:

$$\int_{\Omega_p} D_0 \frac{\partial \theta_k}{\partial y_j} d\Omega = \int_{\Omega_p} \chi_j (v_i^0 \frac{\partial \pi_k}{\partial y_i} + v_i^1 \gamma_{ik}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_k^0 \rangle}{\partial x_i}) d\Omega. \quad (C.22)$$

From the above relationship and from the expression of D''_{jk} , Eq. (5.71), we get:

$$D''_{jk} = \langle \chi_j (v_i^0 \frac{\partial \pi_k}{\partial y_i} + v_i^1 \gamma_{ik}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_k^0 \rangle}{\partial x_i}) \rangle - \langle v_j^1 \chi_k + v_j^0 \pi_k \rangle, \quad (C.23)$$

from which we see that D''_{jk} can be determined from $\vec{\chi}$, $\vec{\pi}$, \vec{v}^0 and \vec{v}^1 .

C.7 Properties of the third-order tensor E'_{jlm}

Let us consider $\alpha = \tau_{lm}$ in the variational formulation associated with $\vec{\chi}$ (Eq. (A.2)):

$$\int_{\Omega_p} \frac{\partial \tau_{lm}}{\partial y_i} D_0 \frac{\partial \chi_j}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \tau_{lm}}{\partial y_j} d\Omega. \quad (C.24)$$

We may now take $\alpha = \chi_j$ in the variational formulation associated with $\vec{\tau}$ (Eq. (C.17)):

$$\begin{aligned} \int_{\Omega_p} \frac{\partial \tau_{lm}}{\partial y_i} D_0 \frac{\partial \chi_j}{\partial y_i} d\Omega &= \\ - \int_{\Omega_p} \frac{\partial \chi_j}{\partial y_i} D_0 \tau_m \delta_{il} d\Omega & \quad (C.25) \\ - \int_{\Omega_p} \chi_j (v_i^0 \frac{\partial \pi_k}{\partial y_i} + v_i^1 \gamma_{ik}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_k^0 \rangle}{\partial x_i}) d\Omega. & \end{aligned}$$

From the above two equations, we get:

$$\int_{\Omega_p} D_0 \frac{\partial \tau_{lm}}{\partial y_j} d\Omega = \int_{\Omega_p} D_0 \frac{\partial \chi_l}{\partial y_j} \tau_m d\Omega + \int_{\Omega_p} \chi_j (v_i^0 \frac{\partial \pi_k}{\partial y_i} + v_i^1 \gamma_{ik}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_k^0 \rangle}{\partial x_i}) d\Omega. \quad (C.26)$$

From the definition of E'_{jlm} , Eq. (5.70), and the above relationship, we finally obtain:

$$E'_{jlm} = \langle D_0 \frac{\partial \chi_l}{\partial y_j} \tau_m \rangle + \langle \chi_j (v_i^0 \frac{\partial \pi_k}{\partial y_i} + v_i^1 \gamma_{ik}^0 - \frac{1}{\phi} \chi_i \frac{\partial \langle v_k^0 \rangle}{\partial x_i}) \rangle - \langle v_i^0 \eta_{jk} \rangle. \quad (C.27)$$

Therefore, tensor E'_{jlm} can be determined from $\vec{\chi}$, $\vec{\pi}$, $\vec{\eta}$, \vec{v}^0 and \vec{v}^1 .

C.8 Properties of the fourth-order tensor F_{jlmnp}

Let firstly take $\alpha = \xi_{lmnp}$ in the variational formulation associated with $\overline{\chi}$ (Eq. (A.2)):

$$\int_{\Omega_p} D_0 \frac{\partial \xi_{lmnp}}{\partial y_i} \frac{\partial \chi_j}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \xi_{lmnp}}{\partial y_j} d\Omega. \quad (C.28)$$

Next, by considering $\alpha = \chi_j$ in the variational formulation associated with $\overline{\xi}$ (Eq. (C.15)), we get:

$$\int_{\Omega_p} D_0 \frac{\partial \xi_{lmnp}}{\partial y_i} \frac{\partial \chi_j}{\partial y_i} d\Omega = - \int_{\Omega_p} D_0 \frac{\partial \chi_j}{\partial y_i} \eta_{mp} \delta_{il} d\Omega - \frac{1}{\phi} \int_{\Omega_p} D_{mp} \chi_j \chi_l d\Omega + \int_{\Omega_p} \chi_j \gamma_{lmnp}^1 d\Omega. \quad (C.29)$$

From the above two relationships, and from the definition of F_{jlmnp} (Eq. (5.69)), we deduce that:

$$F_{jlmnp} = \langle D_0 \eta_{mp} \frac{\partial \chi_l}{\partial y_j} \rangle - \langle \chi_j \gamma_{lmnp}^1 \rangle + \frac{1}{\phi} \langle \chi_j \chi_l D_{mp} \rangle + \langle \eta_{ji} \delta_{mp} \rangle, \quad (C.30)$$

which shows that F_{jlmnp} is determined from $\overline{\chi}$ and $\overline{\eta}$.

D Macroscopic fluxes

D.1 Derivation of $\langle q_i^1 \rangle_{\Sigma_{p_i}}$

To determine $\langle q_i^1 \rangle_{\Sigma_{p_i}}$, we see from Eq. (6.32), that the term $\langle y_i \partial q_j^1 / \partial y_j \rangle$ must be determined. This can be done by starting from Eq. (6.33). By Eq. (6.5), we firstly deduce that

$$\frac{\partial q_j^0}{\partial x_j} = -D_0 \gamma_{jk}^0 \frac{\partial^2 c^0}{\partial x_j \partial x_k} + v_j^0 \frac{\partial c^0}{\partial x_j} + c^0 \frac{\partial v_j^0}{\partial x_j}, \quad (D.1)$$

and then from Eq. (5.22), we get

$$\frac{\partial c^0}{\partial t} = \frac{1}{\phi} D_{jk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} - \frac{1}{\phi} \langle v_j^0 \rangle \frac{\partial c^0}{\partial x_j}. \quad (D.2)$$

Reporting expressions Eqs. (D.1) and (D.2) into Eq. (6.33), we get:

$$\frac{\partial q_j^1}{\partial y_j} = (D_0 \gamma_{jk}^0 - \frac{1}{\phi} D_{jk}) \frac{\partial^2 c^0}{\partial x_j \partial x_k} - (v_j^0 - \frac{1}{\phi} \langle v_j^0 \rangle) \frac{\partial c^0}{\partial x_j} - c^0 \frac{\partial v_j^0}{\partial x_j}, \quad (D.3)$$

from which we deduce

$$\langle y_i \frac{\partial q_j^1}{\partial y_j} \rangle = \langle D_0 y_i \gamma_{jk}^0 - \frac{1}{\phi} y_i D_{jk} \rangle \frac{\partial^2 c^0}{\partial x_j \partial x_k} - \langle y_i (v_j^0 - \frac{1}{\phi} \langle v_j^0 \rangle) \rangle \frac{\partial c^0}{\partial x_j} - c^0 \langle y_i \frac{\partial v_j^0}{\partial x_j} \rangle. \quad (D.4)$$

Now, reporting the above expression together with Eq. (6.14) into Eq. (6.32), we obtain the following expression for the surface average of q_i^1 :

$$\left\{ \begin{array}{l} \langle q_i^1 \rangle_{\Sigma_{p_i}} = -(E_{ijk} - \langle D_0 y_i \gamma_{jk}^0 - \frac{1}{\phi} y_i D_{jk} \rangle) \frac{\partial^2 c^0}{\partial x_j \partial x_k} \\ -(D'_{ij} - \langle y_i (\frac{1}{\phi} \langle v_j^0 \rangle - v_j^0) \rangle) \frac{\partial c^0}{\partial x_j} - D_{ij} \frac{\partial \bar{c}^1}{\partial x_j} \\ -c^0 \langle y_i \frac{\partial v_j^0}{\partial x_j} \rangle + c^0 \langle v_i^1 \rangle + \bar{c}^1 \langle v_i^0 \rangle. \end{array} \right. \quad (\text{D.5})$$

To be physically meaningful, the macroscopic fluid velocity must also be defined by a surface average. In order to determine $\langle v_i^1 \rangle_{\Sigma_{p_i}}$, let consider the identity

$$\frac{\partial}{\partial y_j} (y_i v_j^1) = y_i \frac{\partial v_j^1}{\partial y_j} + v_j^1. \quad (\text{D.6})$$

Integrating over Ω_p , we get

$$\langle v_i^1 \rangle_{\Sigma_{p_i}} = \langle y_i \frac{\partial v_j^1}{\partial y_j} \rangle + \langle v_i^1 \rangle. \quad (\text{D.7})$$

Now, since by Eq. (4.2) at $\mathcal{O}(\varepsilon^0)$

$$\frac{\partial v_j^1}{\partial y_j} = -\frac{\partial v_j^0}{\partial x_j}, \quad (\text{D.8})$$

we deduce that

$$\langle v_i^1 \rangle_{\Sigma_{p_i}} = -\langle y_i \frac{\partial v_j^0}{\partial x_j} \rangle + \langle v_i^1 \rangle. \quad (\text{D.9})$$

Substituting Eq. (D.9) into Eq. (D.5) and bearing in mind Eq. (6.23), we finally get Eq. (6.35) with Eqs. (6.36)-(6.37).

D.2 Derivation of $\langle q_i^2 \rangle_{\Sigma_{p_i}}$

Let consider Eq. (6.17) with $q_i = q_i^2$ and integrate over Ω_p :

$$\langle q_i^2 \rangle_{\Sigma_{p_i}} = \langle y_i \frac{\partial q_j^2}{\partial y_j} \rangle + \langle q_i^2 \rangle. \quad (\text{D.10})$$

From Eq. (6.10), we get

$$\frac{\partial q_j^2}{\partial y_j} = -\frac{\partial q_j^1}{\partial x_j} - \frac{\partial c^1}{\partial t}. \quad (\text{D.11})$$

Using the definition of \vec{q}^1 (Eq. (6.6)), we deduce:

$$\left\{ \begin{array}{l} \frac{\partial q_j^1}{\partial x_j} = -D_0 \gamma_{jkl}^1 \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} - (D_0 \frac{\partial \pi_k}{\partial y_j} - v_j^0 \chi_k) \frac{\partial^2 c^0}{\partial x_j \partial x_k} \\ -D_0 \gamma_{jk}^0 \frac{\partial^2 \bar{c}^1}{\partial x_j \partial x_k} + c^0 \frac{\partial v_j^1}{\partial x_j} + v_j^1 \frac{\partial c^0}{\partial x_j} + \bar{c}^1 \frac{\partial v_j^0}{\partial x_j} + v_j^0 \frac{\partial \bar{c}^1}{\partial x_j}, \end{array} \right. \quad (\text{D.12})$$

and by Eq. (5.46), we get

$$\frac{\partial \bar{c}^1}{\partial t} = \frac{1}{\phi} D'_{jk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} + \frac{1}{\phi} D_{jk} \frac{\partial^2 \bar{c}^1}{\partial x_j \partial x_k} - \frac{1}{\phi} \langle v_j^1 \rangle \frac{\partial c^0}{\partial x_j} - \frac{1}{\phi} \langle v_j^0 \rangle \frac{\partial \bar{c}^1}{\partial x_j}. \quad (\text{D.13})$$

Using Eqs. (D.11)-(D.13), we deduce

$$\left\{ \begin{array}{l} \langle y_i \frac{\partial q_j^2}{\partial y_j} \rangle = \langle D_0 y_i \gamma_{jkl}^1 \rangle \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} \\ + \langle D_0 y_i \frac{\partial \pi_k}{\partial y_j} - y_i v_j^0 \chi_k - \frac{1}{\phi} y_i D'_{jk} \rangle \frac{\partial^2 c^0}{\partial x_j \partial x_k} \\ + \langle D_0 y_i \gamma_{jk}^0 - \frac{1}{\phi} y_i D_{jk} \rangle \frac{\partial^2 \bar{c}^1}{\partial x_j \partial x_k} \\ - \langle y_i (v_j^1 - \frac{1}{\phi} \langle v_j^1 \rangle) \rangle \frac{\partial c^0}{\partial x_j} \\ - \langle y_i (v_j^0 - \frac{1}{\phi} \langle v_j^0 \rangle) \rangle \frac{\partial \bar{c}^1}{\partial x_j} \\ - c^0 \langle y_i \frac{\partial v_j^1}{\partial x_j} \rangle - \bar{c}^1 \langle y_i \frac{\partial v_j^0}{\partial x_j} \rangle. \end{array} \right. \quad (\text{D.14})$$

Using Eq. (6.17) successively for $q_i = v_i^1$ and $q_i = v_i^2$, and integrating both resulting equations over Ω_p , we can easily show that

$$-\bar{c}^1 \langle y_i \frac{\partial v_j^0}{\partial x_j} \rangle = \bar{c}^1 (\langle v_i^1 \rangle_{\Sigma_{p_i}} - \langle v_i^1 \rangle), \quad (\text{D.15})$$

$$-c^0 \langle y_i \frac{\partial v_j^1}{\partial x_j} \rangle = c^0 (\langle v_i^2 \rangle_{\Sigma_{p_i}} - \langle v_i^2 \rangle). \quad (\text{D.16})$$

By Eqs. (D.10) and (D.14), and using both above equations, together with the expression of $\langle q_i^2 \rangle$, Eq. (6.16), yields

$$\left\{ \begin{array}{l} \langle q_i^2 \rangle_{\Sigma_{p_i}} = -(F_{ijkl} - F_{ijkl}^{\Sigma}) \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} \\ -(E'_{ijk} - E'_{ijk}^{\Sigma}) \frac{\partial^2 c^0}{\partial x_j \partial x_k} \\ -(E_{ijk} - E_{ijk}^{\Sigma}) \frac{\partial^2 \bar{c}^1}{\partial x_j \partial x_k} \\ -(D''_{ij} - D''_{ij}^{\Sigma}) \frac{\partial c^0}{\partial x_j} \\ -(D'_{ij} - D'_{ij}^{\Sigma}) \frac{\partial \bar{c}^1}{\partial x_j} \\ -D_{ij} \frac{\partial \bar{c}^2}{\partial x_j} \\ +c^0 \langle v_i^2 \rangle_{\Sigma_{p_i}} + \bar{c}^1 \langle v_i^1 \rangle_{\Sigma_{p_i}} + \bar{c}^2 \langle v_i^0 \rangle_{\Sigma_{p_i}}, \end{array} \right. \quad (D.17)$$

in which

$$\left\{ \begin{array}{l} F_{ijkl}^{\Sigma} = \langle D_0 y_i \gamma_{jkl}^1 \rangle, \quad (D.18) \\ E'_{ijk} = \langle D_0 y_i \frac{\partial \pi_k}{\partial y_j} - y_i v_j^0 \chi_k - \frac{1}{\phi} y_i D'_{jk} \rangle, \quad (D.19) \\ D''_{ij} = \langle y_i (\frac{1}{\phi} \langle v_j^1 \rangle - v_j^1) \rangle. \quad (D.20) \end{array} \right.$$

From Eqs. (5.68) and (D.10), we get the following writing for the second corrector of the macroscopic mass-balance equation

$$\phi \frac{\partial \bar{c}^2}{\partial t} + \frac{\partial}{\partial x_i} \langle q_i^2 \rangle_{\Sigma_{p_i}} = \frac{\partial}{\partial x_i} (\langle y_i \frac{\partial q_j^2}{\partial y_j} \rangle) \quad (D.21)$$

Then, using the expression of $\langle y_i \frac{\partial q_j^2}{\partial y_j} \rangle$, Eq. (D.14), it becomes

$$\left\{ \begin{array}{l} \phi \frac{\partial \bar{c}^2}{\partial t} + \frac{\partial}{\partial x_i} \langle q_i^2 \rangle_{\Sigma_{p_i}} = \\ \frac{\partial}{\partial x_i} [F_{ijkl}^{\Sigma} \frac{\partial^3 c^0}{\partial x_j \partial x_k \partial x_l} + E'_{ijk} \frac{\partial^2 c^0}{\partial x_j \partial x_k} + E_{ijk}^{\Sigma} \frac{\partial^2 \bar{c}^1}{\partial x_j \partial x_k}] \\ + \frac{\partial}{\partial x_i} [D''_{ij} \frac{\partial c^0}{\partial x_j} + D'_{ij} \frac{\partial \bar{c}^1}{\partial x_j}] \\ - \frac{\partial}{\partial x_i} [c^0 (\langle v_i^2 \rangle - \langle v_i^2 \rangle_{\Sigma_{p_i}}) + c^1 (\langle v_i^1 \rangle - \langle v_i^1 \rangle_{\Sigma_{p_i}})]. \end{array} \right. \quad (D.22)$$

To obtain the expression of the third-order macroscopic description with respect to the macroscopic flux, let firstly add Eq. (6.12) to Eq. (6.39) multiplied by ε and to Eq.

(D.22) multiplied by ε^2 :

$$\left\{ \begin{array}{l} \phi \frac{\partial \langle c \rangle}{\partial t} + \frac{\partial}{\partial x_i} (\langle q_i \rangle_{\Sigma_{p_i}}) = \\ \frac{\partial}{\partial x_i} \left[\varepsilon^2 F_{ijkl}^{\Sigma} \frac{\partial^3 \langle c \rangle}{\partial x_j \partial x_k \partial x_l} + (\varepsilon E_{ijk}^{\Sigma} + \varepsilon^2 E'_{ijk}) \frac{\partial^2 \langle c \rangle}{\partial x_j \partial x_k} \right. \\ \left. + (\varepsilon D'_{ij}{}^{\Sigma} + \varepsilon^2 D''_{ij}{}^{\Sigma}) \frac{\partial \langle c \rangle}{\partial x_j} - \langle c \rangle (\langle v_i \rangle - \langle v_i \rangle_{\Sigma_{p_i}}) \right] \\ \left. + \mathcal{O}(\varepsilon^3) \left(\phi \frac{\partial \langle c \rangle}{\partial t} \right), \right. \end{array} \right. \quad (\text{D.23})$$

and then let add Eq. (6.12) to Eq. (6.35) multiplied ε and to Eq. (D.17) multiplied by ε^2

$$\left\{ \begin{array}{l} \langle q_i \rangle_{\Sigma_{p_i}} = -\varepsilon^2 (F_{ijkl} - F_{ijkl}^{\Sigma}) \frac{\partial^3 \langle c \rangle}{\partial x_j \partial x_k \partial x_l} \\ -[\varepsilon (E_{ijk} - E_{ijk}^{\Sigma}) + \varepsilon^2 (E'_{ijk} - E'_{ijk})] \frac{\partial^2 \langle c \rangle}{\partial x_j \partial x_k} \\ -[D_{ij} + \varepsilon (D'_{ij} - D'_{ij}) + \varepsilon^2 (D''_{ij} - D''_{ij})] \frac{\partial \langle c \rangle}{\partial x_j} \\ \left. + \langle c \rangle \langle v_i \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon^3 \langle q_i \rangle_{\Sigma_{p_i}}), \right. \end{array} \right. \quad (\text{D.24})$$

where

$$\left\{ \begin{array}{l} \langle q_i \rangle_{\Sigma_{p_i}} = \langle q_i^0 \rangle_{\Sigma_{p_i}} + \varepsilon \langle q_i^1 \rangle_{\Sigma_{p_i}} + \varepsilon^2 \langle q_i^2 \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon^3 \langle q_i \rangle_{\Sigma_{p_i}}) \quad (\text{D.25}) \\ \langle v_i \rangle_{\Sigma_{p_i}} = \langle v_i^0 \rangle_{\Sigma_{p_i}} + \varepsilon \langle v_i^1 \rangle_{\Sigma_{p_i}} + \varepsilon^2 \langle v_i^2 \rangle_{\Sigma_{p_i}} + \mathcal{O}(\varepsilon^3 \langle v_i \rangle_{\Sigma_{p_i}}). \quad (\text{D.26}) \end{array} \right.$$

References

- Ambard D., Swider P.: A predictive mechano-biological model of the bone-implant healing, *European Journal of Mechanics. A/ Solids*, **25**, 927–937, (2006).
- Andrianov I.V., Bolshakov V.I., Danishvskyy V.V. and Weichert D.: Higher order asymptotic homogenisation and wave propagation in periodic composite materials, *Proc. R. Soc. A*, 464, 1181–1201, (2008).
- Anvari M., Tabar M. R., Peinke, J., Lehnertz, K.: Disentangling the stochastic behavior of complex time series, *Scientific reports*, **6**, 35435, doi:10.1038/srep35435, (2016).
- Auriault J.-L.: Heterogeneous medium. Is an equivalent macroscopic description possible? *International Journal of Engineering Science*, **29** (7), 785-795 (1991).
- Auriault J.-L. and Adler P.: Taylor dispersion in porous media: Analysis by multiple scale expansions, *Advances in Water Resources*, **18**, (4), 217-226 (1995).

- Auriault J.-L., Geindreau C. and Boutin C.: Filtration law in porous media with poor separation of scales, *Transport in Porous Media*, 60, 89-108, (2005).
- Auriault J.-L., Lewandowska J.: On the validity of diffusion/dispersion tests in soils, *Engineering Transactions*, **45** (3-4), 395–417, (1997).
- Auriault J.-L., Moyne C. and Amaral Souto H. P.: On the Asymmetry of the Dispersion Tensor in Porous Media, *Transport in Porous Media*, 85 (3), 771-783 (2010).
- Bakhvalov N.S. and Eglit M.E.: Equations of higher order of accuracy describing the vibrations of thin plates, *J. Appl. Math. Mech.*, 69, 593–610, (2005).
- Bakhvalov N.S., Panasenko G.P. *Homogenization: Averaging processes in periodic media*, Kluwer, Dordrecht, Boston, London, (1989).
- Bear J: *Dynamics of Fluids in Porous media* Elsevier, New-York (1972)
- Bear J., Bachmat Y.: *Introduction to Modeling of Transport Phenomena in Porous Media*, Kluwer Academic Publishers, (1990).
- Becker S., Kuznetsov A. : *Transport in Biological Media*, Elsevier (2013).
- Bensoussan A., Lions J.-L. and Papanicolaou G.: *Asymptotic Analysis for Periodic Structures*, North-Holland Publishing Company, Amsterdam, (1978).
- Boutin C.: Microstructural influence on heat conduction, *Int. J. Heat Mass Transfer*, 38 (17), 3181-3195, (1995).
- Boutin C.: Microstructural effects in elastic composites, *Int. J. Solids Structures*, 33 (7), 102-1051, (1996).
- Boutin C. and Auriault J.-L.: Rayleigh scattering in elastic composite materials, *Int. J. Engng Sci.*, 31, 1669-1689, (1993).
- Buannic N. and Cartraud P.: Higher-order effective modelling of periodic heterogeneous beams - Part 2 : Derivation of the proper boundary conditions for the interior asymptotic solution, *Int. J. Solids Structures*, 38, 7163–7180, (2001).
- Chen W. and Fish J.: A dispersive model for wave propagation in periodic heterogeneous media based on homogenisation with multiple spatial and temporal scales, *J. Appl. Mech.*, 68, 153–161, (2001).
- Cherednichenko K. D. and Smyshlyaev V. P.: On full two-scale expansion of the solutions of nonlinear periodic rapidly oscillating problems and higher-order homogenised variational problems, *Arch. Ration. Mech. Anal.*, 174, 385–442, (2004).
- Costanzo F., Gray G.L. . and Andia P.C.: On the definitions of effective stress and deformation gradient for use in MD: Hill's macro-homogeneity and the virial theorem, *International Journal of Engineering Science*, **43**, 533-555, (2005).

- Dumontet, H.: Homogénéisation et effets de bords dans les matériaux composites. Thèse d'Etat, Université Paris 6, (1990).
- Fish J. and Chen W.: Higher-Order Homogenization of Initial/ Boundary-Value Problem, *Journal of Engineering Mechanics*, 127 (12), 1223-1230, (2001).
- Friedrich R., Peinke J., Sahimi M., Tabar M.R.R., Approaching complexity by stochastic methods: From biological systems to turbulence, *Physics Reports*, **506** (5), Pages 87-162, (2011).
- Gambin B. and Kroner E.: High order terms in the homogenised stress-strain relation of periodic elastic media, *Phys. Stat. Sol.*, 6 (151), 513-519, (1989).
- Goyeau, B., Benihaddadene, T., Gobin, D. and Quintard, M.: Averaged momentum equation for flow through a nonhomogeneous porous structure, *Transport in Porous Media*, **28**, 19–50 (1997).
- Goyeau B., Benihaddadene T., Gobin D., Quintard M.: Numerical calculation of the permeability in a dendritic mushy zone, *Metallical and Materials Transactions B*, **30B**, 613-622, (1999).
- Hassanzadeh M. and Gray W.: General conservation equations for multi-phase systems: 1. Averaging procedure, *Advances in Water Resources*, **2**, 131-144.
- Hill R.: On Constitutive Macro-Variables for Heterogeneous Solids at Finite Strain, *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, **326**, 131-147, (1972).
- van Kampen N.G.: *Stochastic processes in physics and chemistry*, North-Holland, Amsterdam, (1981).
- Kanazawa K.: *Statistical Mechanics for Athermal Fluctuation* Springer Theses, Springer, Singapore (2017).
- Lim G., Kim S., Scalas E., Kim K., Chang, K.-H.: Analysis of price fluctuations in futures exchange markets, *Physica A*, **387**, 2823–2830 (2008).
- Lemaire T. and Naili S.: Multiscale Approach to Understand the Multiphysics Phenomena in Bone Adaptation, *In: Gefen A. (eds) Multiscale Computer Modeling in Biomechanics and Biomedical Engineering*, Studies in Mechanobiology, Tissue Engineering and Biomaterials, , vol 14. Springer, Berlin, Heidelberg (2013).
- Mauri R.: Dispersion, convection, and reaction in porous media, *Phys. Fluids*, A3, 743-756, (1991).
- Mei C.C. and Vernescu B.: *Homogenization methods for multiscale mechanics*, World Scientific Publishing, New-Jersey, (2010)
- Moyne C., Murad M.: A Two-Scale Model for Coupled Electro-Chemo-Mechanical Phenomena and Onsager's Reciprocity Relations in Expansive Clays: I Homogenization Analysis, *Transport in Porous Media*, **62**, 333-380 (2006).

- Pawula R.F.: Approximation of the linear Boltzmann equation by the Fokker-Planck equation, *Phys. Rev.*, 162, 186-188, (1967).
- Petelczyc M., Żebrowski J.J., Baranowski R.: Kramers-Moyal coefficients in the analysis and modeling of heart rate variability, *Phys. Rev. E*, **80**, 031127, (2009).
- Petelczyc M., Żebrowski J.J., Orłowska-Baranowska E.: A fixed mass method for the Kramers-Moyal expansion - Application to time series with outliers, *Chaos*, **25**, 033115 (2015).
- Popescu, D.M., Lipan O.: A Kramers-Moyal Approach to the Analysis of Third-order noise with applications in option valuation, *PLoS ONE*, **10**, e0116752.
- Prusseit J., Lehnertz K.: Stochastic Qualifiers of Epileptic Brain Dynamics, *Phys. Rev. Lett.*, **98**, 138103, (2007).
- Risken H.: *The Fokker-Planck Equation*, Springer, Berlin, (1989).
- Royer P.: Low scale separation induces modification of apparent solute transport regime in porous media, *Mechanics Research Communications*, 87, 29–34, (2018).
- Sanchez-Palencia, E.: *Non-Homogeneous Media and Vibration Theory*, Lecture Notes in Physics 127, Springer-Verlag, B
- Smyshlyaev V.P. and Cherednichenko K.D: On rigorous derivation of strain gradient effects in the overall behaviour of periodic heterogeneous media, *Journal of the Mechanics and Physics of Solids*, 48, 1325-1357, (2000).
- Swider P., Accadbled F., Laffosse J.M., Sales de Gauzy J.: Influence of fluid-flow direction on effective permeability of the vertebral end plate: an analytical model, *Computer Methods in Biomechanics and Biomedical Engineering*, **15** (2), 151-156.
- Tutkun M., Mydlarski L.: Markovian properties of passive scalar increments in grid-generated turbulence, *New Journal of Physics*, **6**, 49, (2004).