7 Theoretical Analysis of Transport in Porous Media

Multi-Equation and Hybrid Models for a Generic Transport Problem with Nonlinear Source Terms

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CONTENTS

7.1 INTRODUCTION

Many challenges we face today in porous media sciences relate to a crucial need to better describe transport phenomena in heterogeneous multiscale systems. A typical multiscale problem is illustrated in Figure 7.1a, where the pore-scale properties, such as the indicator field describing the phase geometry, vary *rapidly* with the spatial coordinates relative to the length scale of the macroscopic domain. This can be interpreted as

$$\ell \ll L. \tag{7.1}$$

This inequality (7.1) implies a significant numerical and physical complexity. The numerical complexity arises from the necessity to compute coupled processes occurring over a broad spectrum of spatial and temporal scales. The physical complexity follows from the scale dependence of the partial differential equations that are used to describe transport phenomena. For example, Stokes equations at the pore-scale transition to Darcy's law at the macroscale. Another example is solute advection and diffusion at the pore-scale, which yield dispersion effects at a coarser scale. During solute biodegradation in soils, a stochastic reaction rate at the molecular level may be described via a Monod reaction rate at the cellular scale (due to metabolic limitations), which may become a Monod reaction rate at the biofilm scale (but with different parameters encompassing diffusion limitations), which in turn may be described by a first-order reaction rate at the Darcy scale (e.g., due to low solute concentration). This cascade of reaction rates illustrates the complexity of the problem and is schematized in Figure 7.2.

A common approach to tackling these theoretical and numerical issues is to determine a scale of interest and adopt a macroscopic or effective viewpoint in which high-frequency fluctuations have been filtered out (see Figure 7.1b). Early examples of such ideas include Maxwell's work on the conductivity of dilute suspensions [1] and Einstein's analysis of the viscosity of a dilute suspension of neutrally buoyant hard spheres [2]. One of the first fundamental analyses related to porous media was devised in the 1950s by Taylor and Aris in [3,4]. It was concerned with solute transport in a tube (Poiseuille flow) and deriving an asymptotic equation that would describe the transport of the average cross-section concentration. Taylor and Aris showed that this average satisfies a 1D advection–dispersion equation and that the dispersion coefficient is proportional to the square of the

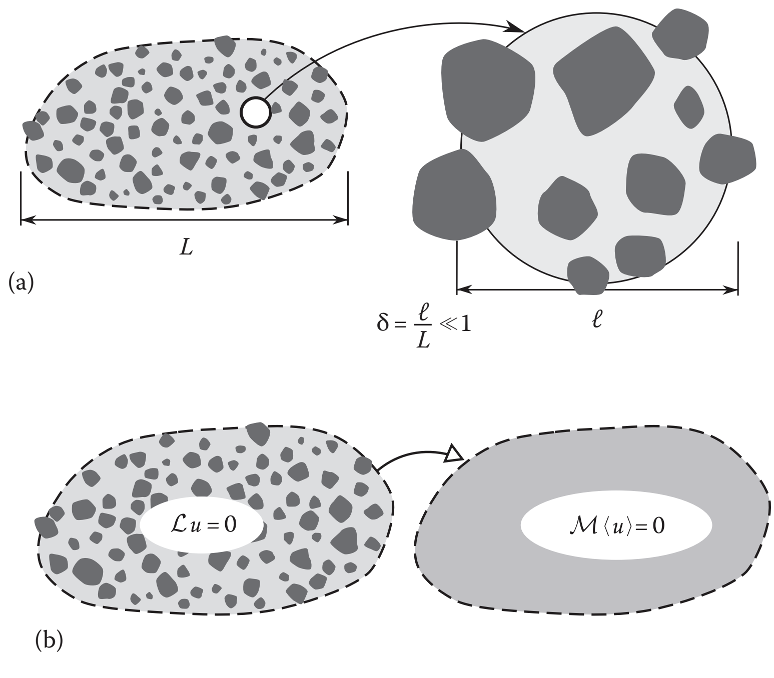


FIGURE 7.1 Schematic illustration of (a) a hierarchy of scales in a porous medium; and (b) the homogenization procedure where the micro-scale differential operator, $\mathcal{L}$, applying to u, is transformed into a macro-scale operator, $\mathcal{M}$, applying to the average value $\langle u \rangle$.

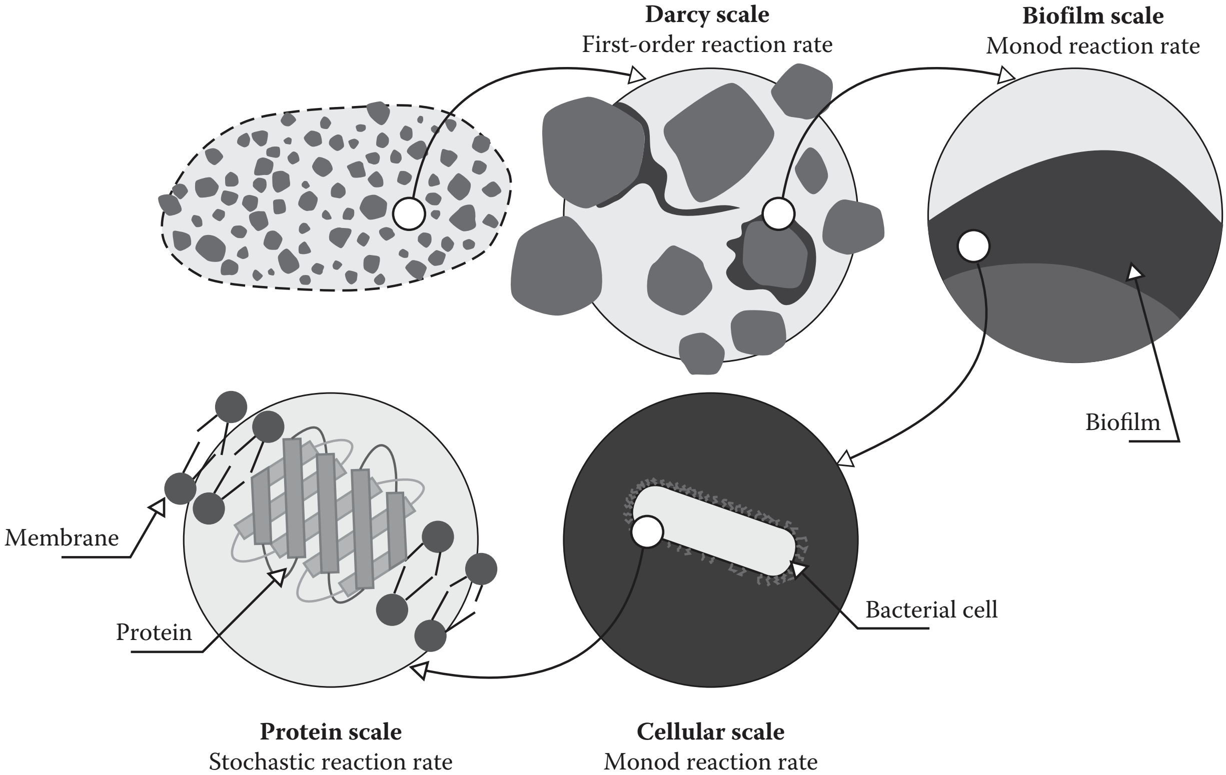


FIGURE 7.2 Multiscale system with microbial biodegradation illustrating the scaledependence of the reaction rate.

Péclet number. This result is valid only in the long-time limit, the relevant timescale being the time for a molecule of solute to travel across the tube by molecular diffusion. Therefore, this analysis is particularly useful when the diameter of the tube is much smaller than the total length. More generally, effective viewpoints require a notion of separation of scales, such as the inequality (7.1) (see [5] or [6] for a broader historical perspective).

Nowadays, effective theories and upscaling techniques have a wide spectrum of applications in Earth, biological, and engineered systems, for example, for describing flow in aquifers [7], petroleum reservoirs [8], composite materials [9], biological tissues [10], networks of large-scale bodies such as buildings [11], reservoirs with large faults [12], reactive transport in the subsurface [13], transport in the brain microvascular network [14], optimal design [15], or shape optimization [16]. In many of these applications, problems involving two or more phases, sources, and sinks are ubiquitous.

In the remainder of this work, we will focus on a prototypical transport problem, as described in Section 7.2, and develop a variety of macroscale representations. This contribution proposes a synthetic presentation of previous upscaling results scattered in different papers, with additional ingredients, in particular a second-order closure and the treatment of nonlinear homogeneous (bulk) and heterogeneous (surface) sources. As such, it is an extension of a previous handbook chapter [17] on the subject.

This chapter is organized as follows. In Section 7.2, we set up the microscale problem. In Section 7.3, we detail the method of volume averaging with closure that will be used for the homogenization of partial differential equations. We then present the macroscale models in Section 7.4. The mathematical developments that yield these macroscale models are derived in Section 7.5 for two-equation models, in Section 7.6 for the one-equation local equilibrium (LE) model, in Section 7.7 for one-equation nonequilibrium models, and in Section 7.8 for the hybrid models. In Section 7.9, we show how effective parameters can be calculated directly by using a 3D reconstruction of a bead packing obtained via x-ray computed microtomography. In Section 7.10, we give several example applications of our models, with a focus on two-equation models. Finally, in Section 7.11, we conclude and discuss example open problems in the field.

7.2 PORE-SCALE EQUATIONS

Here, we present the microscale equations that are used to describe momentum and scalar transport in saturated porous media with homogeneous and heterogeneous nonlinear sources and sinks. The porous medium consists of a solid porous structure, phase σ, fully saturated by a fluid, phase β (see Figure 7.3).

7.2.1 Momentum and Scalar Transport

In many situations, the relaxation of the flow problem is much faster than the relaxation of the transport problem. Therefore, we consider a steady mass and momentum conservation in the fluid phase that can be written as

$$\nabla \cdot \mathbf{v}_\beta = 0 \text{ in } \mathcal{V}_\beta, \tag{7.2a}$$

$$\mathbf{v}_\beta = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.2b}$$

$$\rho_\beta \mathbf{v}_\beta \cdot \nabla \mathbf{v}_\beta = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta \text{ in } \mathcal{V}_\beta, \tag{7.2c}$$

for a Newtonian flow, with constant density (i.e., not depending on pressure, temperature, and concentration).

We further consider the following transient scalar transport problem:

$$a_\beta \rho_\beta \left[\partial_t u_\beta + \nabla \cdot \left(\mathbf{v}_\beta u_\beta \right) \right] = \nabla \cdot \left(\mathsf{A}_\beta \cdot \nabla u_\beta \right) + R_\beta \left(u_\beta \right) \text{ in } \mathcal{V}_\beta, \tag{7.3a}$$

$$\text{BC1} \quad u_\beta - u_\sigma = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.3b}$$

$$\text{BC2} \quad -\mathbf{n}_{\beta\sigma} \cdot \left(\mathsf{A}_\beta \cdot \nabla u_\beta - \mathsf{A}_\sigma \cdot \nabla u_\sigma \right) = \Omega\left(u_\sigma \right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.3c}$$

$$\text{BC3} \quad \text{Domain boundary conditions}, \tag{7.3d}$$

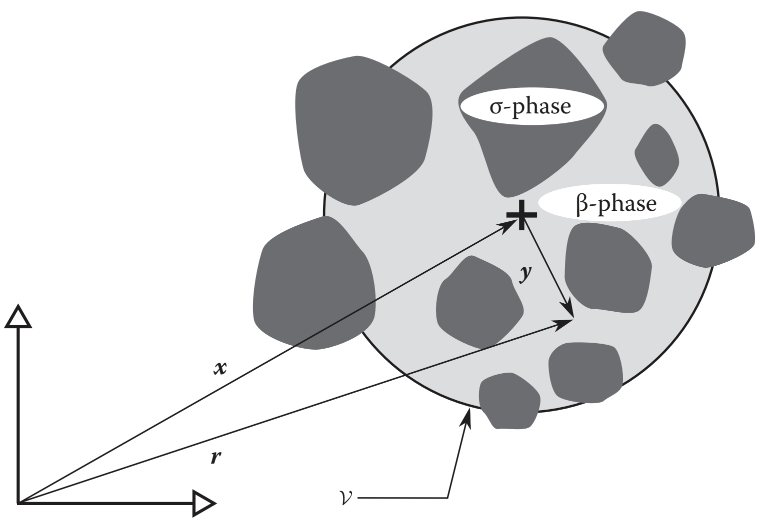


FIGURE 7.3 Averaging volume and the corresponding notations.

$$\text{IC}\quad u_\beta(t=0)=u_\sigma(t=0)=0, \tag{7.3e}$$

$$a_\sigma\rho_\sigma\partial_t u_\sigma=\nabla\cdot\left(\mathbf{A}_\sigma\cdot\nabla u_\sigma\right)+R_\sigma\left(u_\sigma\right)\ \text{in}\ \mathcal{V}_\sigma, \tag{7.3f}$$

where

ρ_α [kg · m^{-3}] is the constant mass density of phase α
$\mathbf{n}_{\beta\sigma}$ is the unit vector normal to $\mathcal{A}_{\beta\sigma}$ pointing from β to σ
BC3 is a set of unspecified domain boundary conditions

For upscaling, we usually assume that effective parameters and closure variables do not depend on these boundaries, so that BC3 can be left unspecified. We have also introduced homogeneous R_α and heterogeneous Ω sources/sinks.

This problem may describe heat transport in porous media (see, e.g., [18]) where $u \equiv \mathrm{T}$ [K] is the temperature, $\mathbf{A}\equiv k\mathbf{I}$ [W · m^{-1} · K^{-1}] the thermal conductivity, and $a \equiv c_p$ [J · K^{-1} · m^{-3}] the specific heat capacity (assumed to be constant in the following developments). Another example problem is the diffusion of a solute in multiphase or multiregion systems. Mass conservation yields a similar type of problem where $u\equiv\omega$ is the mass fraction, $\mathbf{A}\equiv\rho\mathbf{D}$ [kg · m^{-3} · m^{2} · s^{-1}] is the diffusion tensor times the mass density, and a_β, $a_\sigma = 1$. Homogeneous and heterogeneous sources, $R_\beta(u_\beta)$ and $\Omega(u_\sigma)$, may be the consequence of various processes, including chemical or biochemical reactions, radioactive decay, or microwave heating.

7.2.2 Nondimensionalization

Using the characteristic microscale length, ℓ, for spatial nondimensionalization, this system of equations reads

$$\nabla'\cdot\mathbf{v}'_\beta=0\ \text{in}\ \mathcal{V}_\beta, \tag{7.4a}$$

$$\mathbf{v}'_\beta=0\ \text{on}\ \mathcal{A}_{\beta\sigma}, \tag{7.4b}$$

$$\mathrm{Re}_\beta^\ell\mathbf{v}'_\beta\cdot\nabla'\mathbf{v}'_\beta=-\nabla p'_\beta+\nabla^2\mathbf{v}'_\beta\ \text{in}\ \mathcal{V}_\beta, \tag{7.4c}$$

for momentum and total mass conservation. The scalar transport problem reads

$$\partial_{t'}u'_\beta+\nabla'\cdot\left(\mathrm{Pe}_\beta^\ell\mathbf{v}'_\beta u'_\beta\right)=\nabla'\cdot\left(\mathbf{A}'_\beta\cdot\nabla u'_\beta\right)+R'_\beta\left(u'_\beta\right)\ \text{in}\ \mathcal{V}_\beta, \tag{7.5a}$$

$$\text{BC1}\quad u'_\beta-u'_\sigma=0\ \text{on}\ \mathcal{A}_{\beta\sigma}, \tag{7.5b}$$

$$\text{BC2}\quad -\mathbf{n}_{\beta\sigma}\cdot\left(\mathbf{A}'_\beta\cdot\nabla' u'_\beta-\Gamma_A\mathbf{A}'_\sigma\cdot\nabla' u'_\sigma\right)=\Omega'(u'_\sigma)\ \text{on}\ \mathcal{A}_{\beta\sigma} \tag{7.5c}$$

$$\text{BC3}\quad \text{Domain boundary conditions}, \tag{7.5d}$$

$$\text{IC}\quad u'_\beta(t'=0)=u'_\sigma(t'=0)=0, \tag{7.5e}$$

$$\Gamma_a\partial_{t'}u'_\sigma=\nabla'\cdot\left(\Gamma_A\mathbf{A}'_\sigma\cdot\nabla u'_\sigma\right)+R'_\sigma\left(u'_\sigma\right)\ \text{in}\ \mathcal{V}_\sigma, \tag{7.5f}$$

with

$$u'_\alpha = \frac{u_\alpha}{u_0}, \quad \mathbf{v}'_\beta = \frac{\mathbf{v}_\beta}{\left\|\langle \mathbf{v}_\beta \rangle^\beta\right\|}, \quad p'_\beta = \frac{\left(p_\beta - \rho_\beta \mathbf{g}\cdot\mathbf{r}\right)\ell}{\mu_\beta \left\|\langle \mathbf{v}_\beta \rangle^\beta\right\|}, \quad \mathsf{A}'_\alpha = \frac{\mathsf{A}_\alpha}{\left\|\mathsf{A}_\beta\right\|}, \quad t' = \frac{t}{\tau} \text{ with } \tau = \frac{\ell^2\left(a_\beta\rho_\beta\right)}{\left\|\mathsf{A}_\beta\right\|},$$

and

$$\mathrm{Pe}_\beta^\ell = \frac{\left\|\langle \mathbf{v}_\beta \rangle^\beta\right\| \ell\left(a_\beta\rho_\beta\right)}{\left\|\mathsf{A}_\beta\right\|}, \quad R'_\alpha(u'_\alpha) = \frac{R_\alpha(u_\alpha)\ell^2}{u_0\left\|\mathsf{A}_\beta\right\|}, \quad \Omega'(u'_\sigma) = \frac{\Omega(u_\sigma)\ell}{u_0\left\|\mathsf{A}_\beta\right\|}, \quad \Gamma_a = \frac{a_\sigma\rho_\sigma}{a_\beta\rho_\beta}, \quad \Gamma_A = \frac{\left\|\mathsf{A}_\sigma\right\|}{\left\|\mathsf{A}_\beta\right\|}.$$

We have used $\|\langle \mathbf{v}_\beta\rangle^\beta\|$, which is the norm of a spatially averaged value of the velocity (see Section 7.3 for a precise definition of the spatial averaging operators). For space, we have used the microscale length ℓ, that is, $\mathbf{x}' = \mathbf{x}/\ell$, so that we have the following relationship between the macro- and microscale Péclet numbers:

$$\mathrm{Pe}_\beta^L = \frac{\left\|\langle \mathbf{v}_\beta \rangle^\beta\right\| L\left(a_\beta\rho_\beta\right)}{\left\|\mathsf{A}_\beta\right\|} = \delta^{-1}\mathrm{Pe}_\beta^\ell$$

with $\delta = \dfrac{\ell}{L}$. Similarly, we have the microscale Reynolds number as

$$\mathrm{Re}_\beta^\ell = \frac{\rho_\beta \left\|\langle \mathbf{v}_\beta \rangle^\beta\right\| \ell}{\mu_\beta},$$

and the macroscale one as

$$\mathrm{Re}_\beta^L \equiv \frac{\rho_\beta \left\|\langle \mathbf{v}_\beta \rangle^\beta\right\| L}{\mu_\beta} = \delta^{-1}\mathrm{Re}_\beta^\ell.$$

To improve readability, we eliminate the $'$ notation for the dimensionless variables and consider that BC3 and IC are implicit in the remainder of this chapter.

7.2.3 Operator Notation

To facilitate presentation and highlight the structure of the mathematical problems, we further use an operator notation, that is, calligraphic symbols $\mathcal{L}$ for the bulk and $\mathcal{B}$ for the boundaries. This yields

$$\partial_t u_\beta = \mathcal{L}_\beta u_\beta + R_\beta\left(u_\beta\right) \text{ in } \mathcal{V}_\beta, \tag{7.6a}$$

$$\text{BC1} \quad u_\beta - u_\sigma = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.6b}$$

$$\text{BC2} \quad \mathcal{B}_\beta u_\beta - \mathcal{B}_\sigma u_\sigma = \Omega\left(u_\sigma\right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.6c}$$

$$\Gamma_a \partial_t u_\sigma = \mathcal{L}_\sigma u_\sigma + R_\sigma\left(u_\sigma\right) \text{ in } \mathcal{V}_\sigma, \tag{7.6d}$$

with

$$\mathcal{L}_\beta u_\beta = \nabla \cdot \left(\mathbf{A}_\beta \cdot \nabla u_\beta - \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta u_\beta \right), \quad \mathcal{L}_\sigma u_\sigma = \nabla \cdot \left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla u_\sigma \right), \tag{7.7}$$

$$\mathcal{B}_\beta u_\beta = -\mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla u_\beta \right), \quad \mathcal{B}_\sigma u_\sigma = -\mathbf{n}_{\beta\sigma} \cdot \left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla u_\sigma \right). \tag{7.8}$$

Now that we have defined the transport problem at the microscale, we present, in the next section, the volume averaging methodology that will be used to perform upscaling and obtain several macroscale descriptions for this microscale problem.

7.3 VOLUME AVERAGING METHODOLOGY

The analysis of multiscale systems has produced a variety of upscaling tools. These include *homogenization theory* (see [19–22]), *variants of volume averaging and mixture theories* (see [23–29]), the *Taylor–Aris–Brenner method of moments* (see [30–32]), and *stochastic approaches* (see [33–36]). Although the methodologies are different, the goal of all these approaches is to answer the same questions: Can we obtain a macroscale representation? If yes, what is its domain of validity? How do we define macroscale quantities? How do we treat boundary conditions?

In this work, we use the particular type of volume averaging that is presented in Whitaker's book [37], the idea of which is to obtain the macroscale equations by averaging the microscale equations in space and then using scaling approximations. Before detailing the algorithm, we must first define the averaging operators along with several fundamental theorems.

7.3.1 Definitions and Theorems

For any tensor ψ (including scalars, vectors, and dyadics), we define the volume average as (see [24,27,38–41])

$$\psi_m(\boldsymbol{x},t) \equiv \int_{\mathbb{R}^n} m(\xi)\psi(\boldsymbol{x}-\xi,t)\,dV_\xi \equiv m \star \psi, \tag{7.9}$$

where

$\star$ denotes the spatial convolution

$m : \mathbb{R}^n \to \mathbb{R}$ is a smoothing kernel that has compact support in $\mathbb{R}^n$ and is normalized so that $\int_{\mathbb{R}^n} m(\xi)\,dV_\xi \equiv 1$

In practice, we are often interested in problems for which the spatial dimension, n, is such that $n \le 3$ with a particular emphasis on $n = 3$ and sets measured as *volumes*. A standard choice for the kernel is

$$m(\xi) = \begin{cases} \dfrac{1}{V} & \text{if } \|\xi\| \le R \\ 0 & \text{if } \|\xi\| > R \end{cases}, \tag{7.10}$$

so that

$$\psi(\boldsymbol{x},t) \equiv \frac{1}{V}\int_{\boldsymbol{r}\in\mathcal{V}(\boldsymbol{x})} \psi(\boldsymbol{r},t)\,dV_r, \tag{7.11}$$

where

$\mathcal{V}(\boldsymbol{x}) \equiv \mathcal{B}_r(\boldsymbol{x})$ is the closed ball with radius R centered at point $\boldsymbol{x}$ (see Figure 7.3)

V its volume $\left(V \equiv \int_{\mathcal{V}(\boldsymbol{x})} dV\right)$

In multiphase systems, we also often define the phase and intrinsic averages. For phase α (the set $\mathcal{V}_\alpha$ within the averaging volume $\mathcal{V}$, see Figure 7.3 where $\alpha = \sigma$ or β), these correspond to the following:

$$\text{Phase average:}\quad \langle\psi_\alpha\rangle = \frac{1}{V}\int_{\mathcal{V}_\alpha}\psi_\alpha dV, \tag{7.12}$$

$$\text{Intrinsic average:}\quad \langle\psi_\alpha\rangle^\alpha = \frac{1}{V_\alpha}\int_{\mathcal{V}_\alpha}\psi_\alpha dV, \tag{7.13}$$

where $V_\alpha \equiv \int_{\mathcal{V}_\alpha} dV$. With these notations, we have the simple relationship

$$\langle\psi_\alpha\rangle = \varepsilon_\alpha \langle\psi_\alpha\rangle^\alpha, \tag{7.14}$$

where $\varepsilon_\alpha = V_\alpha/V$ is the volume fraction of phase α.

As mentioned earlier, the method relies on averaging of partial differential equations. Therefore, it is often useful to interchange the spatial integration and the differential operators, an operation that follows a specific set of rules. For sufficiently smooth tensor fields ψ_α (see discussion in [42]) defined in phase α, we have (proofs are available in, among others [25,39,40,43–45])

$$\langle\nabla\cdot\psi_\alpha\rangle = \nabla\cdot\langle\psi_\alpha\rangle + \frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \boldsymbol{n}_\alpha\cdot\psi_\alpha dA, \tag{7.15}$$

$$\langle\nabla\psi_\alpha\rangle = \nabla\langle\psi_\alpha\rangle + \frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \boldsymbol{n}_\alpha\psi_\alpha dA, \tag{7.16}$$

$$\langle\partial_t\psi_\alpha\rangle = \partial_t\langle\psi_\alpha\rangle - \frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} (\boldsymbol{n}_\alpha\cdot\boldsymbol{w}_\alpha)\psi_\alpha dA. \tag{7.17}$$

where

$\mathcal{A}_{\beta\sigma}$ represents the interphase boundary

$\boldsymbol{n}_\alpha$ denotes the outward unit normal vector to the boundary of phase α

$\boldsymbol{w}_\alpha$ is the velocity of the corresponding boundary

In the remainder of this work, we assume that boundaries are immobile so that

$$\left\langle \partial_t \psi_\alpha \right\rangle = \partial_t \left\langle \psi_\alpha \right\rangle. \tag{7.18}$$

We further define decompositions of the microscale fields in terms of an average value, $\langle \psi_\alpha \rangle^\alpha$, and a perturbation, $\tilde{\psi}_\alpha$, as

$$\psi_\alpha = \left\langle \psi_\alpha \right\rangle^\alpha + \tilde{\psi}_\alpha. \tag{7.19}$$

We will also use a weighted or mixture intrinsic average over both phases

$$\left\langle \psi \right\rangle^{\beta\sigma} = \frac{\varepsilon_\beta}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \left\langle \psi_\beta \right\rangle^\beta + \frac{\varepsilon_\sigma \Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \left\langle \psi_\sigma \right\rangle^\sigma, \tag{7.20}$$

with the corresponding perturbation decomposition

$$\psi_\alpha = \left\langle \psi \right\rangle^{\beta\sigma} + \hat{\psi}_\alpha. \tag{7.21}$$

7.3.2 Upscaling Algorithm

The detailed algorithm for the volume averaging with closure methodology is detailed in Figure 7.4 for a linear problem at the microscale and can be summarized as follows. The first steps involve averaging the microscale initial boundary value problem (IBVP), using the perturbative decomposition,

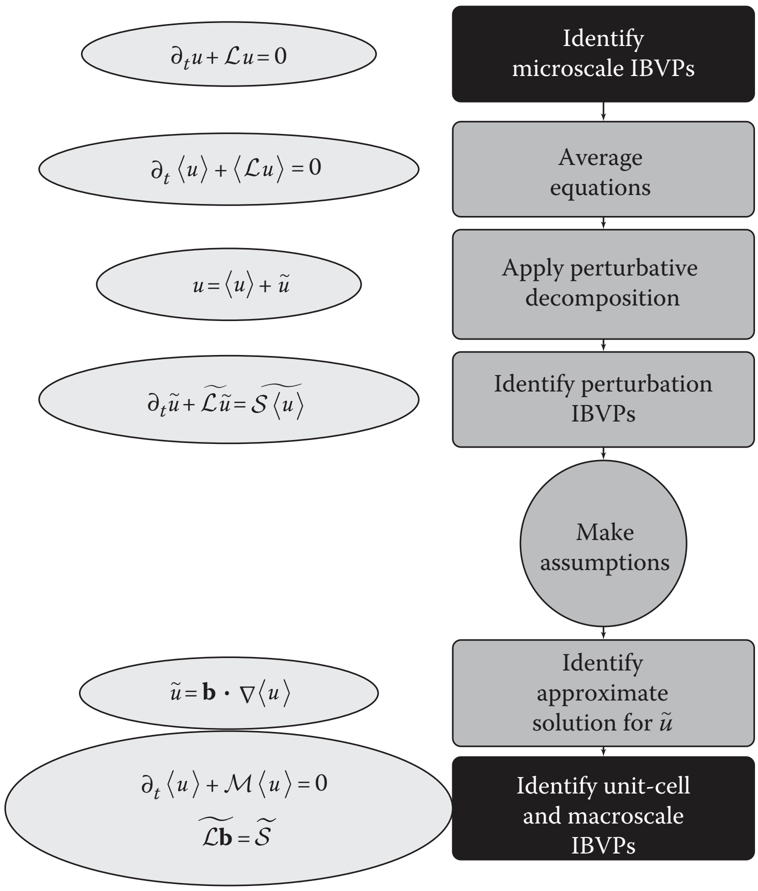


FIGURE 7.4 Volume averaging algorithm for a linear operator $\mathcal{L}$ at the micro-scale, with $\mathcal{M}$ the corresponding macro-scale operator and $\mathcal{S}$ the sources.

and obtaining the perturbation IBVP. Then we make several assumptions in order to obtain an approximate solution to the perturbation IBVP. This approximate solution is further introduced in the unclosed form of the macroscale equations to obtain a homogenized problem.

Although varying from problem to problem, approximations often involve a separation of scales, a notion that states that variables exhibit two dominant (one slow, one fast) spatial frequencies. This approximation is connected to the notion of representative volume element (RVE), which relies on the quasi-stationarity of the medium's geometry (for hierarchical systems, see [7,46–48] and further discussions in [42,49]). We also often use the hypothesis of time quasi-stationarity, which is based on the fact that processes at the scale of the RVE relax quickly compared to macroscopic timescales, and assume that the porous medium of interest can be approximated by a locally periodic structure. The effects of this latter approximation are often difficult to evaluate, especially for images of non-periodic media (e.g., subsurface) and for large values of the Péclet number. We further discuss the limitations of periodic unit cells in Section 7.9.

7.3.3 Resolution Algorithm

The solution procedure depends on the type of macroscale model that has been derived. In the local case, effective parameters can be expressed as functions of closure variables that are calculated separately using auxiliary problems. Many academic works have focused on 2D with analytical (e.g., stratified media) or numerical approaches (see [17,50]). Advances in imaging techniques, such as x-ray microtomography, combined with the computing power of today's workstation make it possible to solve closure problems in realistic 3D unit cells. Even commercially available softwares (see, e.g., Avizo Fire® [51] or GeoDict® [52]) offer tools for both image processing and calculations of effective properties such as diffusivities or permeabilities. We also refer to the special issue [53] for a broader perspective on digital rock physics, benchmarking of codes, and applications in the geosciences.

If the problem is nonlocal (see [54–58]), however, the numerical solution is generally much more tedious to obtain. For example, in the special case of time nonlocality, which generally takes the form of integrodifferential equations with temporal convolutions, the solution at a given time may strongly depend upon solutions at earlier times, therefore complicating numerical schemes and resolutions. For spatial nonlocality, discretization of integrodifferential descriptions, such as fractional derivatives or spatial convolutions, yields dense linear systems that are more difficult to inverse than sparse matrices produced by purely local models. Other types of nonlocal spatial representations are hybrid models for which microscale and averaged equations are solved simultaneously. For instance, the solution in part of the domain is computed at the microscale, while only an averaged behavior is considered in the rest of the domain (see Sections 7.4 and 7.8 for further discussion on hybrid models).

The volume averaging methodology presented here can be used to obtain macroscale equations for a number of transport problems. Depending on the set of approximation that is used, we can obtain different macroscale representations. These are presented in the next section for the microscale problem in Section 7.2.

7.4 MACROSCALE AND HYBRID MODELS

In this section, we summarize and discuss the macroscale models without presenting the mathematical developments. We focus on scalar transport and assume that the velocity field is known pointwise and satisfies $\nabla \cdot \langle \mathbf{v}_\beta \rangle = 0$ and a no-slip boundary condition at the fluid–solid interface. We present three classes of macroscale models, each corresponding to different types of upscaling assumptions, that can be used to describe scalar transport in porous media: two-equation, one-equation, and hybrid models. Two-equation models rely on a phase/domain decomposition approach, where each equation describes the behavior of the intrinsic average of a phase and both are coupled via exchange terms. One-equation representations describe an average value over both phases, using either LE or time-asymptotic assumptions. Hybrid models couple a description of one phase at the macroscale with the description of the other phase at the microscale model. All these models can be further declined in several categories, corresponding to different upscaling assumptions. We will discuss these variants with an emphasis on fully transient and quasi-stationary models and their domains of validity. We further emphasize that results are presented with a *second-order closure* for the linear part of the operator and that we show how to deal with *nonlinear sources/sinks*. For simplicity, we consider here a homogeneous porous medium and a nonconservative form of the equations. We will discuss in the end of this section possible extensions to conservative forms and varying effective parameters.

7.4.1 Two-Equation Models

Two-equation models have been introduced in various different forms by different communities. In the geosciences, for instance, these are often termed mobile/mobile, mobile/immobile, dual-continua, dual-porosity, or two-region models (see, e.g., [59–61]). In volume averaging, we use the terminology *two-equation* that refers to the mathematical structure of the problem, rather than the scale of application or the variable of interest. Such models have been studied in various works using Whitaker's methodology (see [62–69]), variants of the volume averaging technique [70–72], and formal multiscale asymptotics (see [50,73]). The different types of two-equation models are as follows.

7.4.1.1 Two-Equation Transient

The fully transient two-equation model (see, e.g., [66]) reads

$$\underbrace{\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \Gamma_a \end{bmatrix} \partial_t \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix}}_{\text{Rate of change}} + \underbrace{\partial_t \begin{bmatrix} \mathbf{V}^\star_{\beta\beta} & \mathbf{V}^\star_{\beta\sigma} \\ \mathbf{V}^\star_{\sigma\beta} & \mathbf{V}^\star_{\sigma\sigma} \end{bmatrix} \cdot \star \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}}_{\text{Advection}}$$

$$= \underbrace{\partial_t \begin{bmatrix} \mathbf{A}^\star_{\beta\beta} & \mathbf{A}^\star_{\beta\sigma} \\ \mathbf{A}^\star_{\sigma\beta} & \mathbf{A}^\star_{\sigma\sigma} \end{bmatrix} : \star \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}}_{\text{Dispersion}} + \underbrace{\partial_t \begin{bmatrix} -h^\star & +h^\star \\ +h^\star & -h^\star \end{bmatrix} \star \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix}}_{\text{First-order exchange}}$$

$$+ \underbrace{\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \end{bmatrix} \begin{bmatrix} R_\beta\left(\langle u_\beta \rangle^\beta\right) \\ R_\sigma\left(\langle u_\sigma \rangle^\sigma\right) \end{bmatrix}}_{\text{Bulk source/sink}} - \underbrace{\partial_t \begin{bmatrix} a_v \xi^\star & 0 \\ 0 & a_v\left(H(t) - \xi^\star\right) \end{bmatrix} \star \begin{bmatrix} \Omega\left(\langle u_\sigma \rangle^\sigma\right) \\ \Omega\left(\langle u_\sigma \rangle^\sigma\right) \end{bmatrix}}_{\text{Surface source/sink}} \tag{7.22}$$

where $\star$ denotes the time convolution, $f \star g = \int_0^t f(\tau) g(t-\tau) d\tau$, and the algebra is written in terms of block matrices. For instance, we have

$$\partial_t \begin{bmatrix} \mathbf{V}^\star_{\beta\beta} & \mathbf{V}^\star_{\beta\sigma} \\ \mathbf{V}^\star_{\sigma\beta} & \mathbf{V}^\star_{\sigma\sigma} \end{bmatrix} \cdot \star \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} = \begin{bmatrix} \partial_t \mathbf{V}^\star_{\beta\beta} \cdot \star \nabla \langle u_\beta \rangle^\beta + \partial_t \mathbf{V}^\star_{\beta\sigma} \cdot \star \nabla \langle u_\sigma \rangle^\sigma \\ \partial_t \mathbf{V}^\star_{\sigma\beta} \cdot \star \nabla \langle u_\beta \rangle^\beta + \partial_t \mathbf{V}^\star_{\sigma\sigma} \cdot \star \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix},$$

with $\partial_t \mathbf{V}^\star_{\beta\beta} \cdot \star \nabla \langle u_\beta \rangle^\beta = \partial_t V^\star_{\beta\beta,i} \star \partial_i \langle u \rangle$.

Equation 7.22 exhibits the following:

- Advective terms that represent both the physical velocity and the coupling between the two phases.
- Diffusive terms.
- A first-order exchange term of the form $\partial_t h^\star \star \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma\right)$.
- Bulk sources/sinks $R_\alpha\left(\langle u_\alpha \rangle^\alpha\right)$.
- Surface sources/sinks $\Omega\left(\langle u_\sigma \rangle^\sigma\right)$ with a coefficient ξ that distributes the surface effects between each phase. This distribution coefficient was already introduced in [17] and used to develop a local nonequilibrium (LNE) model taking into account radiation effects through a generalized radiation transfer equation in [74].

For all operator types, the convolution products account for the relaxation times of the effective parameters, therefore capturing a broad range of characteristic times. Such convolutions are particularly useful to describe the short-time regime (see [75–78]). This is easily shown for a sinusoidal excitation in a simple stratified system (see [79]) where the nonlocal model recovers the exact solution for all excitation frequencies. In practice, if the topology of the microscale problem is unknown and if the relaxation of effective parameters cannot be calculated over a representative unit cell, the kernels may also be approximated using empirical functions (see [80,81]).

7.4.1.2 Two-Equation Quasi-Stationary

A simpler version of the two-equation model is quasi-stationary (see, e.g., [76]) and reads

$$
\begin{aligned}
&\underbrace{\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \Gamma_a \end{bmatrix} \partial_t \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix}}_{\text{Rate of change}} + \underbrace{\begin{bmatrix} \mathbf{V}_{\beta\beta} & \mathbf{V}_{\beta\sigma} \\ \mathbf{V}_{\sigma\beta} & \mathbf{V}_{\sigma\sigma} \end{bmatrix} \cdot \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}}_{\text{Advection}} \\
= &\underbrace{\begin{bmatrix} \mathsf{A}_{\beta\beta} & \mathsf{A}_{\beta\sigma} \\ \mathsf{A}_{\sigma\beta} & \mathsf{A}_{\sigma\sigma} \end{bmatrix} : \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}}_{\text{Dispersion}} + \underbrace{\begin{bmatrix} -h & +h \\ +h & -h \end{bmatrix} \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix}}_{\text{First-order exchange}} \\
&+ \underbrace{\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \end{bmatrix} \begin{bmatrix} R_\beta\left(\langle u_\beta \rangle^\beta\right) \\ R_\sigma\left(\langle u_\sigma \rangle^\sigma\right) \end{bmatrix}}_{\text{Bulk source/sink}} - \underbrace{\begin{bmatrix} a_v \xi & 0 \\ 0 & a_v(1-\xi) \end{bmatrix} \begin{bmatrix} \Omega\left(\langle u_\sigma \rangle^\sigma\right) \\ \Omega\left(\langle u_\sigma \rangle^\sigma\right) \end{bmatrix}}_{\text{Surface source/sink}}
\end{aligned}
\tag{7.23}
$$

This model differs from the previous one in that the temporal convolution products have disappeared. This approximation is valid when the times for the relaxation of the effective parameters $\mathbf{V}^\star$, $\mathsf{A}^\star$, $h^\star$, and $\xi^\star$ are much smaller than the characteristic times corresponding to the average variables $\nabla\langle u \rangle$, $\nabla\nabla\langle u \rangle$, $\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma$ and $\Omega\left(\langle u_\sigma \rangle^\sigma\right)$ (see [79]).

7.4.1.3 Two-Equation Quasi-Stationary with Fluxes

The two-equation model is often written by grouping terms of similar mathematical types, for example, advective and diffusive parts of the operators. Two-equation models may also be written in a way that emphasizes the physical, rather than mathematical, nature of the different terms. For the quasi-stationary version, this reads

$$\varepsilon_\beta\left[\underbrace{\partial_t\langle u_\beta\rangle^\beta}_{\text{Rate of change}}+\mathrm{Pe}_\beta^\ell\nabla\cdot\left(\underbrace{\langle\mathbf{v}_\beta\rangle^\beta\langle u_\beta\rangle^\beta}_{\text{Convection}}+\underbrace{\theta_\beta}_{\text{Velocity fluctuation effects}}\right)\right]$$

$$=\nabla\cdot\left[\varepsilon_\beta\mathbf{A}_\beta\cdot\left(\underbrace{\nabla\langle u_\beta\rangle^\beta}_{\text{Diffusion}}+\underbrace{\zeta_\beta}_{\text{Surface effects}}\right)\right]-\underbrace{\mathsf{J}_{\beta\sigma}}_{\text{Interfacial flux}}+\underbrace{\varepsilon_\beta R_\beta\left(\langle u_\beta\rangle^\beta\right)}_{\text{Bulk reaction rate}}, \tag{7.24}$$

and

$$\varepsilon_\sigma\Gamma_a\underbrace{\partial_t\langle u_\sigma\rangle^\sigma}_{\text{Rate of change}}=\nabla\cdot\left[\varepsilon_\sigma\Gamma_A\mathbf{A}_\sigma\cdot\left(\underbrace{\nabla\langle u_\sigma\rangle^\sigma}_{\text{Diffusion}}+\underbrace{\zeta_\sigma}_{\text{Surface effects}}\right)\right]-\underbrace{\mathsf{J}_{\sigma\beta}}_{\text{Interfacial flux}}+\underbrace{\varepsilon_\sigma R_\sigma\left(\langle u_\sigma\rangle^\sigma\right)}_{\text{Bulk reaction rate}}. \tag{7.25}$$

For instance, the term $h(\langle u_\beta\rangle^\beta-\langle u_\sigma\rangle^\sigma)$ is often wrongly interpreted as the interfacial flux in the mathematical version of the two-equation model, whereas it is only part of the flux:

$$\mathsf{J}_{\beta\sigma}=\underbrace{h\left(\langle u_\beta\rangle^\beta-\langle u_\sigma\rangle^\sigma\right)}_{\text{First-order exchange}}+\underbrace{a_v\xi\Omega\left(\langle u_\sigma\rangle^\sigma\right)}_{\text{Flux component from the surface source}}$$

$$\underbrace{+\mathcal{O}\left(\begin{bmatrix}\nabla\langle u_\beta\rangle^\beta\\ \nabla\langle u_\sigma\rangle^\sigma\end{bmatrix}\right)+\mathcal{O}\left(\begin{bmatrix}\nabla\nabla\langle u_\beta\rangle^\beta\\ \nabla\nabla\langle u_\sigma\rangle^\sigma\end{bmatrix}\right)}_{\text{Higher-order corrections}}. \tag{7.26}$$

This shows that the flux is affected by the source/sink term on the interface, $a_v\xi\Omega(\langle u_\sigma\rangle^\sigma)$, and higher-order corrections in $\left[\nabla\langle u_\beta\rangle^\beta\quad\nabla\langle u_\sigma\rangle^\sigma\right]^T$ and $\left[\nabla\nabla\langle u_\beta\rangle^\beta\quad\nabla\nabla\langle u_\sigma\rangle^\sigma\right]^T$.

We further emphasize that the surface terms translate tortuosity effects, both for the advective and diffusive operators:

$$\zeta_\beta\simeq\underbrace{\langle\nabla\mathbf{a}_\beta\rangle^\beta}_{\text{Advective tortuosity}}\left(\langle u_\beta\rangle^\beta-\langle u_\sigma\rangle^\sigma\right)$$

$$+\underbrace{\left\langle\nabla\left[\mathbf{b}_{\beta\beta}\quad\mathbf{b}_{\beta\sigma}\right]\right\rangle^\beta}_{\text{Diffusive tortuosity}}\cdot\begin{bmatrix}\nabla\langle u_\beta\rangle^\beta\\ \nabla\langle u_\sigma\rangle^\sigma\end{bmatrix}. \tag{7.27}$$

Similarly, velocity fluctuations lead to enhanced dispersion effects and corrections of the advective terms:

$$\theta_\beta\equiv\langle\tilde{\mathbf{v}}_\beta\tilde{u}_\beta\rangle^\beta\simeq\underbrace{\langle\tilde{\mathbf{v}}_\beta\mathbf{a}_\beta\rangle^\beta}_{\text{Velocity correction}}\left(\langle u_\beta\rangle^\beta-\langle u_\sigma\rangle^\sigma\right)$$

$$+\underbrace{\left\langle\tilde{\mathbf{v}}_\beta\left[\mathbf{b}_{\beta\beta}\quad\mathbf{b}_{\beta\sigma}\right]\right\rangle^\beta}_{\text{Hydrodynamic dispersion}}\cdot\begin{bmatrix}\nabla\langle u_\beta\rangle^\beta\\ \nabla\langle u_\sigma\rangle^\sigma\end{bmatrix}. \tag{7.28}$$

7.4.1.4 Two-Equation Variant

The relaxation times for $\mathbf{V}^\star$, $\mathbf{A}^\star$, $h^\star$, and $\xi^\star$ are different. For example, $\mathbf{V}^\star$ and $\mathbf{A}^\star$ may relax much faster than $\xi^\star$ and $h^\star$ (e.g., for fractured media, see [76,82,83] Chapter 4), in which case we obtain a macroscale model of the form (see, e.g., [84])

$$\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \Gamma_a \end{bmatrix} \partial_t \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix} + \begin{bmatrix} \mathbf{V}_{\beta\beta} & \mathbf{V}_{\beta\sigma} \\ \mathbf{V}_{\sigma\beta} & \mathbf{V}_{\sigma\sigma} \end{bmatrix} \cdot \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}$$
$$= \begin{bmatrix} \mathbf{A}_{\beta\beta} & \mathbf{A}_{\beta\sigma} \\ \mathbf{A}_{\sigma\beta} & \mathbf{A}_{\sigma\sigma} \end{bmatrix} : \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} + \partial_t \begin{bmatrix} -h^\star & +h^\star \\ +h^\star & -h^\star \end{bmatrix} \star \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix}$$
$$+ \begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \end{bmatrix} \begin{bmatrix} R_\beta \left(\langle u_\beta \rangle^\beta \right) \\ R_\sigma \left(\langle u_\sigma \rangle^\sigma \right) \end{bmatrix} - \partial_t \begin{bmatrix} a_v \xi^\star & 0 \\ 0 & a_v \left(H(t) - \xi^\star \right) \end{bmatrix} \star \begin{bmatrix} \Omega\left(\langle u_\sigma \rangle^\sigma \right) \\ \Omega\left(\langle u_\sigma \rangle^\sigma \right) \end{bmatrix} \tag{7.29}$$

The fully transient model can therefore be adapted to the timescales of interest using any combination of convolution products that is suited to the timescales of the physical problem.

7.4.1.5 Telegrapher's Equation

Other nonequilibrium models have been proposed in the literature. For instance, it has been shown in [85,86] that the two-equation model is equivalent under certain conditions to a dual-phase-lagging heat conduction model. Similarly, other types of equations may potentially reproduce some of the features of LNE situations, for instance, equations with fractional derivatives that have already been used to describe dispersion in porous media [87].

7.4.1.6 Link with Multirate Approaches

The two-equation quasi-stationary model with a linear exchange term, Equation 7.23, features only one characteristic time for describing the fluid–solid relaxation. This limitation can be overcome using temporal convolution products, as is done in Equation 7.22, although these can be impractical for numerical implementations. Alternatively, simplified models have been designed to incorporate more characteristic times in the macroscale equations, such as the multirate mass transfer (MRMT) models (see, e.g., [80,88]). These models can be derived by an N-phase decomposition of the fields, defined either by geometrical considerations (for instance, grains with large and small diameters) or through a more sophisticated mathematical approach, for example, using the properties of the eigenvalue spectrum for the diffusion process in the solid phase. This leads to N-equation models (similarly to what is discussed for MRMT in [88]), which may capture more accurately the temporal behavior without the inconvenience of convolution products. They can also be presented by considering the variant of the two-equation model Equation 7.29 that retains only the convolution associated with the linear exchange term (see further discussions based on volume averaging in [84]).

7.4.2 One-Equation Models

One-equation models describe the behavior of a mixture average over the different phases. They do not capture timescales associated with exchange phenomena so that they require a form of relaxation between the phases. For multiphase systems, these can be primarily obtained using the LE or time-asymptotic LNE approximations. The LE assumption states that (see [17])

$$\langle u_\beta \rangle^\beta \cong \langle u_\sigma \rangle^\sigma \cong \langle u \rangle^{\beta\sigma}. \tag{7.30}$$

Combined with the quasi-stationarity assumption, this yields a model of the form

$$\underbrace{\left(\varepsilon_\beta + \Gamma_a \varepsilon_\sigma\right)\partial_t \left\langle u\right\rangle^{\beta\sigma}}_{\text{Rate of change}} + \underbrace{\varepsilon_\beta \mathrm{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta\right\rangle^\beta \cdot \nabla \left\langle u\right\rangle^{\beta\sigma}}_{\text{Advection}}$$
$$= \underbrace{\mathbf{A}^{\mathrm{LE}} : \nabla\nabla \left\langle u\right\rangle^{\beta\sigma}}_{\text{Dispersion}} + \underbrace{\varepsilon_\beta R_\beta\left(\left\langle u\right\rangle^{\beta\sigma}\right) + \varepsilon_\sigma R_\sigma\left(\left\langle u\right\rangle^{\beta\sigma}\right)}_{\text{Bulk source/sink}} - \underbrace{a_v \Omega\left(\left\langle u\right\rangle^{\beta\sigma}\right)}_{\text{Surface source/sink}}. \tag{7.31}$$

On the contrary, the LNE transient one-equation model does not make the assumption, Equation 7.30, but rather considers a long-time relaxation and reads

$$\left(\varepsilon_\beta + \Gamma_a \varepsilon_\sigma\right)\partial_t \left\langle u\right\rangle^{\beta\sigma} + \varepsilon_\beta \mathrm{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta\right\rangle^\beta \cdot \nabla \left\langle u\right\rangle^{\beta\sigma}$$
$$= \mathbf{A}^{\mathrm{LNE}} : \nabla\nabla \left\langle u\right\rangle^{\beta\sigma} + \varepsilon_\beta R_\beta\left(\left\langle u\right\rangle^{\beta\sigma}\right) + \varepsilon_\sigma R_\sigma\left(\left\langle u\right\rangle^{\beta\sigma}\right) - a_v \Omega\left(\left\langle u\right\rangle^{\beta\sigma}\right). \tag{7.32}$$

The LNE model can be derived at least in two different ways, either as the asymptotic behavior of the two-equation model or via a special perturbation decomposition. The asymptotic method was studied in detail in [63,89,90]. The more direct one-step derivation can be obtained by averaging over the two phases simultaneously and using a nonconventional perturbation decomposition (see [79,91,92]). We further remark that we have the relationship

$$\mathbf{A}^{\mathrm{LNE}} = \mathbf{A}^{\mathrm{LE}} + \text{correction}, \tag{7.33}$$

with $\|\mathbf{A}^{\mathrm{LNE}}\| \geq \|\mathbf{A}^{\mathrm{LE}}\|$. This stems from the fact that the nonequilibrium effects induce additional dispersion effects that the LE model fails to capture. Examples and comparisons of models with direct numerical simulations at the microscale can be found in [93,94]. We also have the following relationship between the LE dispersion tensor and the two-equation effective parameters:

$$\mathbf{A}^{\mathrm{LE}} = \mathbf{A}_{\beta\beta} + \mathbf{A}_{\beta\sigma} + \mathbf{A}_{\sigma\beta} + \mathbf{A}_{\sigma\sigma}. \tag{7.34}$$

7.4.3 Hybrid Models

Hybrid models combine the resolution of coupled micro- and macroscale models as a compromise between computational cost and accuracy. Here, we focus on the simple model derived in Section 7.8, which is based on the assumption that the diffusion in the solid phase is much smaller than in the fluid phase, that is,

$$\Gamma_A \ll 1. \tag{7.35}$$

We obtain the following macroscale model for phase β:

$$\varepsilon_\beta \left[\underbrace{\partial_t \left\langle u_\beta\right\rangle^\beta}_{\text{Rate of change}} + \underbrace{\nabla\cdot\left(\mathrm{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta\right\rangle^\beta \left\langle u_\beta\right\rangle^\beta\right)}_{\text{Advection}}\right] = \underbrace{\nabla\cdot\left(\mathbf{A}^{\mathrm{HYB}}\cdot\nabla\left\langle u_\beta\right\rangle^\beta\right)}_{\text{Dispersion}} - \underbrace{\mathbf{J}_{\beta\sigma}}_{\text{Interfacial flux}} + \underbrace{R^{\mathrm{HYB}}}_{\text{Bulk source/sink}}, \tag{7.36}$$

$$\text{BC} \quad \text{Macro scale domain boundary}, \tag{7.37}$$

$$\text{IC} \quad \langle u_\beta \rangle^\beta (t = 0) = 0, \tag{7.38}$$

where $\mathsf{J}_{\beta\sigma}$ is the interfacial flux, and

$$\Gamma_a \partial_t u_\sigma = \mathcal{L}_\sigma u_\sigma + R_\sigma(u_\sigma) \text{ in } \mathcal{V}_\sigma, \tag{7.39}$$

$$\text{BC1} \quad u_\sigma = \langle u_\beta \rangle^\beta \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.40}$$

$$\text{BC2} \quad \text{Macro scale domain boundary}, \tag{7.41}$$

$$\text{IC} \quad u_\sigma(t = 0) = 0, \tag{7.42}$$

at the microscale.

Coupling of the micro- and macroscale fields occurs via both $\mathsf{J}_{\beta\sigma}$ and BC1, hence the word hybrid (or mixed). Solving the hybrid model requires (1) solving the closure problem to estimate the dispersion tensor in Equation 7.36 and then (2) solving the coupled hybrid problem expressed by Equations 7.36 through 7.40.

There exist various ways to deal with hybrid problems, corresponding to different computational costs and levels of accuracy. Figure 7.5 represents a schematic view of these strategies in the case of a 1D macroscale problem. The most direct approach consists in transforming the 3D pore-scale problem, Figure 7.5a, in a 1D averaged equation for the β-phase, plus a series of 3D pore-scale problems for the σ-phase, Figure 7.5b. We can reduce the computational cost via additional assumptions regarding the solid phase. For example, if phase σ consists of monodisperse grains, the problem for one grain can be used to calculate $\mathsf{J}_{\beta\sigma}$ in Equation 7.36, Figure 7.5c. To further facilitate solution, we can reduce the number of hybrid grains and extrapolate values of $\mathsf{J}_{\beta\sigma}$, Figure 7.5d, at the macroscale. Several other simplifications may further improve the efficiency of hybrid models, for example, by solving the problem over a few representative grains in the polydisperse case or by using analytical/semianalytical solutions at the microscale.

We have also presented an example variant formulation in Figure 7.5e, where the domain is decomposed in two regions. This allows us to solve the original pore-scale problem in a smaller portion where average representations may fail to describe scalar transport. Such an approach may be useful to describe sharp fronts [95], or to deal with specific macroscale boundary conditions and microscale singularities (see, e.g., [96]).

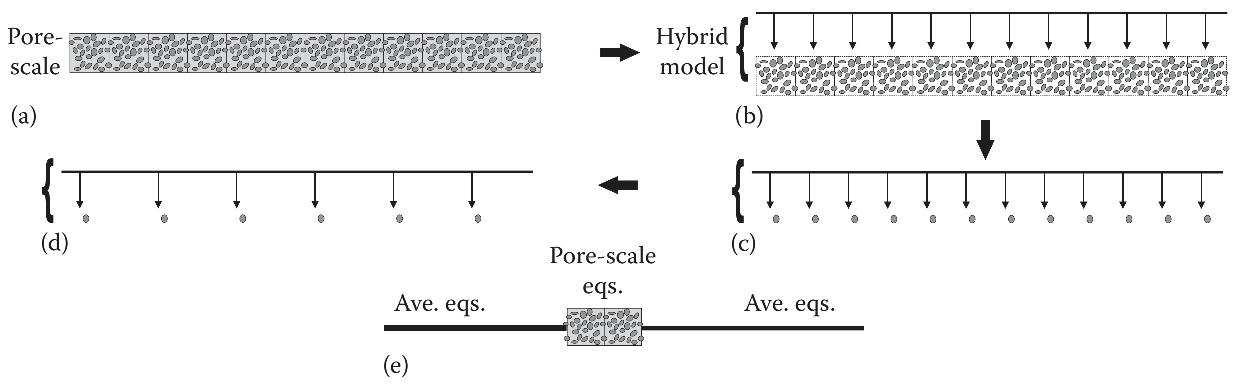


FIGURE 7.5 Schematic illustration of hybrid models.

7.4.4 Domains of Validity

7.4.4.1 LE versus LNE

LE models are based on the assumption that microscale gradients are relatively small, so that both phases can be treated in exactly the same way and $\langle u_\beta \rangle^\beta \simeq \langle u_\sigma \rangle^\sigma$ (see discussion and additional references in [17]). When this is not the case, for instance, if there exists a strong gradient at the interface between phases, the situation is termed LNE. LE situations are described via the one-equation LE model, and LNE situations via the one-equation LNE, two-equation, or hybrid models.

Nonequilibrium effects are often the consequence of properties contrast between phases and boundary conditions. For the case presented in Section 7.2, very large or small ratios of diffusivities may induce nonequilibrium effects. This is the case for heat wave propagation with a smaller diffusivity in the solid phase, a case for which the temperature profile exhibits a well-known tailing effect. The relaxation processes involve a range of different timescales/eigenvalues that are captured more or less accurately by the different macroscale models.

For each macroscale representation, we can usually identify regions of parameter space that describe the validity of the LE, LNE, or other hypotheses. In general, the LE approximation will be verified if $\Gamma_a = \mathcal{O}(1)$, $\Gamma_A = \mathcal{O}(1)$, $\mathrm{Pe}_\beta^\ell < 1$, and the characteristic times for sources/sinks are larger than transport times (see [17,97] for a more detailed description of domains of validity). An example of a more complicated diagram of validity involving a larger set of dimensionless parameters can be found in [98] or in [79,99] for temporal regimes.

These simple estimates of the various time and length scales that are interpreted as order of magnitude estimates of dimensionless parameters may be sufficient in many practical instances to decide whether a nonequilibrium analysis is needed or not. However, this is not always possible to decide on the basis of an order of magnitude analysis as attempted in [100]. The matter is in general more complex and depends on, among others, the geometry and topology of the unit cell [97]; the boundary conditions and the type of problem [101–103]; the processes involved, for instance, natural convection [104]; phase change [105,106]; and the coupling with reactive transport [107,108].

7.4.4.2 Hybrid Model

The hybrid model described earlier has been used in many applications including flows in fractured porous media (see a review in [82], original articles [109–111] for a derivation using homogenization theory). The advantage of such a hybrid model is that the whole spectrum of eigenvalues/characteristic times for the diffusion problem in the phase σ is captured, without the use of tedious convolution products. Another important advantage is that it can be used for highly nonlinear problems, such as combustion or pyrolysis fronts in the solid phase [112]. Hybrid models are also often utilized to derive expressions for the exchange coefficient via the introduction of approximate analytical solutions: parabolic profiles, such as in [113], or piecewise linear profiles [114] (see also [76] for a discussion on various proposals). On the other hand, hybrid models have strong limitations, including their significant computational cost. For the approach presented earlier, we have also assumed that $\Gamma_A \ll 1$ and $\tilde{u}_\beta \ll \left\langle u_\beta \right\rangle^\beta$. If these constraints are not satisfied, the hybrid model will not provide an accurate representation compared with two-equation models as discussed in [115].

7.4.4.3 Conservative Forms and Variations of Effective Parameters

In this chapter, we primarily consider a homogeneous porous medium with constant effective parameters and nonconservative versions of the macroscale models. If effective parameters vary in space, the macroscale models can be written in a conservative way without too much difficulty. However, this means that we must specify how these variations occur and, possibly, compute numerous unit-cell problems, therefore increasing computational cost. In some cases, we can use probability density functions to describe the variation of effective parameters (see [116]).

7.5 DERIVATION OF THE TWO-EQUATION MODELS

We have presented in the previous section a perspective on the various models. In this section, we provide details about the mathematical development of these models, in particular the way approximate solutions of the coupled micro- and macroscale equations are obtained (the so-called *closure*).

7.5.1 Averaging

Applying the spatial averaging operators to Equations 7.6a through d with an immobile porous structure yields

$$\varepsilon_\beta \partial_t \langle u_\beta \rangle^\beta = \langle \mathcal{L}_\beta u_\beta \rangle + \langle R_\beta(u_\beta) \rangle, \tag{7.43}$$

$$\varepsilon_\sigma \Gamma_a \partial_t \langle u_\sigma \rangle^\sigma = \langle \mathcal{L}_\sigma u_\sigma \rangle + \langle R_\sigma(u_\sigma) \rangle. \tag{7.44}$$

We further use the perturbation decompositions $u_\beta = \langle u_\beta \rangle^\beta + \tilde{u}_\beta$ and $u_\sigma = \langle u_\sigma \rangle^\sigma + \tilde{u}_\sigma$, along with the linearity of the spatial operators $\mathcal{L}_\beta$ and $\mathcal{L}_\sigma$, to obtain

$$\varepsilon_\beta \partial_t \langle u_\beta \rangle^\beta = \left\langle \mathcal{L}_\beta \langle u_\beta \rangle^\beta \right\rangle + \langle \mathcal{L}_\beta \tilde{u}_\beta \rangle + \langle R_\beta(u_\beta) \rangle, \tag{7.45}$$

$$\varepsilon_\sigma \Gamma_a \partial_t \langle u_\sigma \rangle^\sigma = \left\langle \mathcal{L}_\sigma \langle u_\sigma \rangle^\sigma \right\rangle + \langle \mathcal{L}_\sigma \tilde{u}_\sigma \rangle + \langle R_\sigma(u_\sigma) \rangle. \tag{7.46}$$

These equations use operator notations that are rather abstract but have the advantage of being compact and emphasizing the mathematical structure of the problem. In the literature, a more physical interpretation has often been used based on the averaging theorems and scaling constraints. To facilitate physical interpretation, we present here these developments, although subsequent analysis will be mainly based on Equations 7.45 and 7.46. The first term on the right-hand side (RHS) of Equation 7.45 reads

$$\langle \mathcal{L}_\beta u_\beta \rangle = \left\langle \nabla \cdot \left(\mathbf{A}_\beta \cdot \nabla u_\beta - \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta u_\beta \right) \right\rangle. \tag{7.47}$$

Applying the averaging theorems to the divergence operator and the no-slip boundary condition leads to

$$\begin{aligned} \langle \mathcal{L}_\beta u_\beta \rangle = \nabla \cdot \langle \mathbf{A}_\beta \cdot \nabla u_\beta \rangle - \nabla \cdot \langle \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta u_\beta \rangle \\ + \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla u_\beta \right) dA, \end{aligned} \tag{7.48}$$

where the last term on the RHS is the average surface flux. We can further apply the averaging theorems to the gradient operator in the first term on the RHS of Equation 7.48, so that we have

$$\nabla \cdot \langle \mathbf{A}_\beta \cdot \nabla u_\beta \rangle = \nabla \cdot \left[\mathbf{A}_\beta \cdot \left(\nabla \langle u_\beta \rangle + \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} u_\beta dA \right) \right]. \tag{7.49}$$

This equation involves the phase-average $\langle u_\beta \rangle$ that we can transform into the intrinsic-average $\langle u_\beta \rangle^\beta$ using $\langle u_\beta \rangle = \varepsilon_\beta \langle u_\beta \rangle^\beta$ so that

$$\nabla \left\langle u_\beta \right\rangle = \left\langle u_\beta \right\rangle^\beta \nabla \varepsilon_\beta + \varepsilon_\beta \nabla \left\langle u_\beta \right\rangle^\beta . \tag{7.50}$$

Similarly, we obtain $\langle u_\beta \rangle^\beta$ in the interfacial term $\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} u_\beta dA$ using the average plus perturbation decomposition $u_\beta = \left\langle u_\beta \right\rangle^\beta + \tilde{u}_\beta$,

$$\begin{aligned}
\frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} u_\beta \, dA &= \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{u}_\beta dA + \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \left\langle u_\beta \right\rangle^\beta dA, \\
&\simeq \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{u}_\beta dA + \left(\frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} dA \right) \left\langle u_\beta \right\rangle^\beta \\
&\simeq \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{u}_\beta dA - \left\langle u_\beta \right\rangle^\beta \nabla \varepsilon_\beta .
\end{aligned} \tag{7.51}$$

We have used the symbol $\simeq$ to emphasize the approximation that $\langle u_\beta \rangle^\beta$ can be extracted from the surface integral (all the aforementioned simplifications have been discussed at length for the cases of ordered and disordered media in [39,40,117–119]). We also have that $\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} dA = -\nabla \varepsilon_\beta$, from a simple application of the averaging theorems to the β-phase indicator function, γ_β (unity in the β-phase and zero elsewhere)

$$\begin{aligned}
\left\langle \nabla \gamma_\beta \right\rangle &= \nabla \left\langle \gamma_\beta \right\rangle + \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} dA \\
&= \nabla \varepsilon_\beta + \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} dA = 0
\end{aligned} \tag{7.52}$$

Therefore, we can eliminate terms $\langle u_\beta \rangle^\beta \nabla \varepsilon_\beta$ when adding Equations 7.51 and 7.50 into Equation 7.49 to obtain

$$\nabla \cdot \left\langle \mathbf{A}_\beta \cdot \nabla u_\beta \right\rangle \simeq \nabla \cdot \left[\varepsilon_\beta \mathbf{A}_\beta \cdot \left(\nabla \left\langle u_\beta \right\rangle^\beta + \frac{1}{V_\beta} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{u}_\beta dA \right) \right] . \tag{7.53}$$

We have also extracted $\mathbf{A}_\beta$ from the integrals using the assumption that the porous medium is homogeneous. The second term on the RHS of Equation 7.48 can be treated as follows:

$$\nabla \cdot \left\langle \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta u_\beta \right\rangle \simeq \nabla \cdot \left(\mathrm{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta u_\beta \right\rangle \right), \tag{7.54}$$

with

$$\left\langle \mathbf{v}_\beta u_\beta \right\rangle \simeq \varepsilon_\beta \left\langle \mathbf{v}_\beta \right\rangle^\beta \left\langle u_\beta \right\rangle^\beta + \left\langle \tilde{\mathbf{v}}_\beta \tilde{u}_\beta \right\rangle, \tag{7.55}$$

that can be proven using $\langle \tilde{\mathbf{v}}_\beta \rangle \simeq 0$ and $\langle \tilde{u}_\beta \rangle \simeq 0$ (see [17,37]). Therefore, Equation 7.48 may be approximated by

$$\begin{aligned}\langle \mathcal{L}_\beta u_\beta \rangle \simeq \nabla \cdot \left[\varepsilon_\beta \mathbf{A}_\beta \cdot \left(\nabla \langle u_\beta \rangle^\beta + \frac{1}{V_\beta} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{u}_\beta dA \right) \right] \\ + \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla u_\beta \right) dA \\ - \nabla \cdot \left(\mathrm{Pe}_\beta^\ell \langle \tilde{\mathbf{v}}_\beta \tilde{u}_\beta \rangle \right) - \nabla \cdot \left(\varepsilon_\beta \mathrm{Pe}_\beta^\ell \langle \mathbf{v}_\beta \rangle^\beta \langle u_\beta \rangle^\beta \right).\end{aligned} \tag{7.56}$$

Using this result, we can rewrite the average equation over the phase β as

$$\begin{aligned}\varepsilon_\beta \left[\underbrace{\partial_t \langle u_\beta \rangle^\beta}_{\text{Rate of change}} + \underbrace{\nabla \cdot \left(\mathrm{Pe}_\beta^\ell \langle \mathbf{v}_\beta \rangle^\beta \langle u_\beta \rangle^\beta \right)}_{\text{Convection}} + \underbrace{\nabla \cdot \left(\mathrm{Pe}_\beta^\ell \langle \tilde{\mathbf{v}}_\beta \tilde{u}_\beta \rangle^\beta \right)}_{\text{Velocity fluctuation effects}} \right] \\ = \nabla \cdot \left[\varepsilon_\beta \mathbf{A}_\beta \cdot \left(\underbrace{\nabla \langle u_\beta \rangle^\beta}_{\text{Diffusion}} + \underbrace{\frac{1}{V_\beta} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{u}_\beta dA}_{\text{Surface effects}} \right) \right] \\ + \underbrace{\frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla u_\beta \right) dA}_{\text{Interfacial flux}} + \underbrace{\langle R_\beta (u_\beta) \rangle}_{\text{Average reaction rate}} .\end{aligned} \tag{7.57}$$

For the solid phase, similar manipulations of the average and differential operators yield an identical expression, minus the convection and velocity fluctuation terms:

$$\begin{aligned}\varepsilon_\sigma \Gamma_a \underbrace{\partial_t \langle u_\sigma \rangle^\sigma}_{\text{Rate of change}} = \nabla \cdot \left[\varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma \cdot \left(\underbrace{\nabla \langle u_\sigma \rangle^\sigma}_{\text{Diffusion}} + \underbrace{\frac{1}{V_\sigma} \int_{\mathcal{A}_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \tilde{u}_\sigma dA}_{\text{Surface effects}} \right) \right] \\ + \underbrace{\frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\sigma\beta} \cdot \left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla u_\sigma \right) dA}_{\text{Interfacial flux}} + \underbrace{\langle R_\sigma (u_\sigma) \rangle}_{\text{Average reaction rate}} .\end{aligned} \tag{7.58}$$

We remark that these equations use approximations, in particular the fact that average quantities are quasi-linear within the REV. This is a form of spatial localization that allows us to extract such variables from the differential operators and integrals. These equations provide insight into the physics of the problem, as we can clearly identify, for example, fluxes and surface effects. Mathematically, however, it is convenient to use Equations 7.45 and 7.46 to derive the perturbation problem.

7.5.2 Perturbation

We now focus on the equations that describe the behavior of the perturbations. Recall that these perturbations are defined as $\tilde{u}_\beta = u_\beta - \langle u_\beta \rangle^\beta$ and $\tilde{u}_\sigma = u_\sigma - \langle u_\sigma \rangle^\sigma$. Therefore, the perturbation equations are obtained by performing the following operations: (Equation 7.6a minus ε_β^{-1} times Equation 7.45) and (Equation 7.6d minus ε_σ^{-1} times Equation 7.46). This results in the following two problems:

$$\partial_t \tilde{u}_\beta - \widetilde{\mathcal{L}_\beta \tilde{u}_\beta} - \widetilde{R_\beta (u_\beta)} = \widetilde{\mathcal{L}_\beta \langle u_\beta \rangle^\beta} \text{ in } \mathcal{V}_\beta, \tag{7.59}$$

$$\Gamma_a \partial_t \tilde{u}_\sigma - \widetilde{\mathcal{L}_\sigma \tilde{u}_\sigma} - \widetilde{R_\sigma(u_\sigma)} = \widetilde{\mathcal{L}_\sigma \langle u_\sigma \rangle^\sigma} \text{ in } \mathcal{V}_\sigma, \tag{7.60}$$

where we have organized the equations with the microscale differential operators on the left-hand side (LHS) and the macroscale source terms on the RHS. We have also used the following notation for the perturbation differential operators:

$$\widetilde{\mathcal{L}_\beta \phi_\beta} = \mathcal{L}_\beta \phi_\beta - \langle \mathcal{L}_\beta \phi_\beta \rangle^\beta = \nabla \cdot \left(\mathbf{A}_\beta \cdot \nabla \phi_\beta - \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta \phi_\beta \right) - \left\langle \nabla \cdot \left(\mathbf{A}_\beta \cdot \nabla \phi_\beta - \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta \phi_\beta \right) \right\rangle^\beta, \tag{7.61}$$

in the phase β and

$$\widetilde{\mathcal{L}_\sigma \phi_\sigma} = \mathcal{L}_\sigma \phi_\sigma - \langle \mathcal{L}_\sigma \phi_\sigma \rangle^\sigma = \nabla \cdot \left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla \phi_\sigma \right) - \left\langle \nabla \cdot \left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla \phi_\sigma \right) \right\rangle^\sigma, \tag{7.62}$$

in the phase σ. Similarly, the reaction rate perturbation functions are defined by

$$\widetilde{R_\beta(\phi_\beta)} = R_\beta(\phi_\beta) - \langle R_\beta(\phi_\beta) \rangle^\beta, \tag{7.63}$$

$$\widetilde{R_\sigma(\phi_\sigma)} = R_\sigma(\phi_\sigma) - \langle R_\sigma(\phi_\sigma) \rangle^\sigma. \tag{7.64}$$

The corresponding boundary conditions are obtained by introducing the average plus perturbation decomposition in Equations 7.6b and c:

$$\tilde{u}_\beta - \tilde{u}_\sigma = -\left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.65}$$

$$\mathcal{B}_\beta \tilde{u}_\beta - \mathcal{B}_\beta \tilde{u}_\sigma = -\left(\mathcal{B}_\beta \langle u_\beta \rangle^\beta - \mathcal{B}_\sigma \langle u_\sigma \rangle^\sigma \right) + \Omega(u_\sigma) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.66}$$

with

$$-\left(\mathcal{B}_\beta \langle u_\beta \rangle^\beta - \mathcal{B}_\sigma \langle u_\sigma \rangle^\sigma \right) = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla \langle u_\beta \rangle^\beta - \Gamma_A \mathbf{A}_\sigma \cdot \nabla \langle u_\sigma \rangle^\sigma \right). \tag{7.67}$$

7.5.3 Approximations

So far, except during the digression that resulted in Equations 7.57 and 7.58, we have not made scaling approximations. Further progress, however, requires such approximations that we present in this section.

7.5.3.1 Spatial Frequency Approximation

Effective medium theories usually require a notion of separation of length scales. In our approach, this can be expressed as spatial localization constraints imposed upon averaged fields. Roughly speaking, we assume that average quantities are quasi-linear within the REV since they vary over the macroscopic length scale, L. This simplification allows us to extract average quantities from microscale differential operators and integrals. For instance, consider that

$$\left\langle \nabla\cdot\left(\Gamma_A \mathbf{A}_\sigma\cdot\nabla\langle u_\sigma\rangle^\sigma\right)\right\rangle^\sigma = \nabla\cdot\left[\Gamma_A \mathbf{A}_\sigma\cdot\left(\nabla\langle u_\sigma\rangle^\sigma + \frac{1}{V_\sigma}\int_{\mathcal{A}_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\langle u_\sigma\rangle^\sigma\, dA\right)\right] + \frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\sigma\beta}\cdot\left(\Gamma_A \mathbf{A}_\sigma\cdot\nabla\langle u_\sigma\rangle^\sigma\right) dA. \tag{7.68}$$

We assume that $\langle u_\sigma\rangle^\sigma$ and $\nabla\langle u_\sigma\rangle^\sigma$ vary slowly in space so that we have

$$\frac{1}{V_\sigma}\int_{\mathcal{A}_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\langle u_\sigma\rangle^\sigma\, dA \simeq \left(\frac{1}{V_\sigma}\int_{\mathcal{A}_{\sigma\beta}} \mathbf{n}_{\sigma\beta}\, dA\right)\langle u_\sigma\rangle^\sigma \simeq 0, \tag{7.69}$$

for a homogeneous porous medium (constant porosity). Similarly,

$$\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\sigma\beta}\cdot\left(\Gamma_A \mathbf{A}_\sigma\cdot\nabla\langle u_\sigma\rangle^\sigma\right) dA \simeq \left(\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\sigma\beta}\cdot\Gamma_A \mathbf{A}_\sigma\, dA\right)\cdot\nabla\langle u_\sigma\rangle^\sigma \simeq 0. \tag{7.70}$$

Therefore, we obtain

$$\widetilde{\mathcal{L}_\sigma\langle u_\sigma\rangle^\sigma} = \nabla\cdot\left(\Gamma_A \mathbf{A}_\sigma\cdot\nabla\langle u_\sigma\rangle^\sigma\right) - \left\langle \nabla\cdot\left(\Gamma_A \mathbf{A}_\sigma\cdot\nabla\langle u_\sigma\rangle^\sigma\right)\right\rangle^\sigma \simeq 0. \tag{7.71}$$

For the phase β, we have

$$\widetilde{\mathcal{L}_\beta\langle u_\beta\rangle^\beta} \simeq -\mathrm{Pe}_\beta^\ell \tilde{\mathbf{v}}_\beta\cdot\nabla\langle u_\beta\rangle^\beta \equiv \widetilde{\mathcal{L}_\beta}\langle u_\beta\rangle^\beta. \tag{7.72}$$

These approximations can be further justified by considering Taylor expansions of the form

$$\langle u_\sigma\rangle^\sigma|_{\mathbf{x}+\mathbf{y}} = \langle u_\sigma\rangle^\sigma|_{\mathbf{x}} + \delta\mathbf{y}\cdot\nabla_L\langle u_\sigma\rangle^\sigma|_{\mathbf{x}} + \delta^2\mathbf{y}\mathbf{y}:\nabla_L\nabla_L\langle u_\sigma\rangle^\sigma|_{\mathbf{x}} + \mathcal{O}\left(\delta^3\right), \tag{7.73}$$

where

x is the center of the averaging volume
y is the vector pointing inside the averaging volume
∇_L is rescaled with the macroscale length L so that $\left\|\nabla_L\langle u_\sigma\rangle^\sigma\right\| = \mathcal{O}(1)$ and $\delta = \frac{\ell}{L}$

In volume averaging, we often neglect terms involving **y** using $\delta \ll 1$ (see [39,40,117–119]).

7.5.3.2 Amplitude Approximation

In addition to these upscaling assumptions, we need to linearize the system to obtain a closure and an approximate form of the perturbations. We assume that perturbations are small enough so that

$$R_i\left(u_i\right) \simeq R_i\left(\left\langle u_i\right\rangle^i\right) \quad \text{and} \quad \Omega\left(u_A\right) \simeq \Omega\left(\left\langle u_\sigma\right\rangle^\sigma\right). \tag{7.74}$$

Such approximations are nonstandard, as volume averaging usually requires only *spatial* frequency approximations for linear operators. This is, however, a frequent approximation for nonlinear operators featuring changes in density, viscosity, diffusivities, and others (see example in [120] for the case of multicomponent mixtures). We emphasize that this approximation is very limiting and may break down relatively easily for large microscale gradients. This also implies that the closure problems are systematically independent from the reaction rates, an assumption that is known to hold when the Damköhler number is smaller than ≈ 10 (see [93]).

7.5.3.3 Simplified Form

We can now use approximations discussed earlier to obtain an approximate form of Equations 7.59 and 7.60 along with the boundary conditions (Equations 7.65 and 7.66). This yields

$$\partial_t \tilde{u}_\beta - \widetilde{\mathcal{L}_\beta \tilde{u}_\beta} = -\mathrm{Pe}_\beta^\ell \tilde{\mathbf{v}}_\beta \cdot \nabla \left\langle u_\beta \right\rangle^\beta \text{ in } \mathcal{V}_\beta, \tag{7.75}$$

$$\Gamma_a \partial_t \tilde{u}_\sigma - \widetilde{\mathcal{L}_\sigma \tilde{u}_\sigma} = 0 \text{ in } \mathcal{V}_\sigma, \tag{7.76}$$

with the set of boundary conditions

$$\tilde{u}_\beta - \tilde{u}_\sigma = -\left(\left\langle u_\beta \right\rangle^\beta - \left\langle u_\sigma \right\rangle^\sigma\right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.77}$$

$$\mathcal{B}_\beta \tilde{u}_\beta - \mathcal{B}_\beta \tilde{u}_\sigma = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla \left\langle u_\beta \right\rangle^\beta - \Gamma_A \mathbf{A}_\sigma \cdot \nabla \left\langle u_\sigma \right\rangle^\sigma\right) + \Omega\left(\left\langle u_\sigma \right\rangle^\sigma\right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.78}$$

where sources appear on the RHS. At this point in the developments, we have obtained a linear IBVP for the perturbation. This problem still involves $\langle u_\sigma \rangle^\sigma$ and $\langle u_\beta \rangle^\beta$ so that the micro- and macroscale problems are still coupled.

7.5.4 Closure

Fortunately, there is only a weak coupling between the micro- and macroscale problems, and we can use the linearity of the spatial operators to decompose the perturbations into several components corresponding to each of the macroscopic source terms: $\langle u_\sigma \rangle^\sigma - \langle u_\beta \rangle^\beta$, $\nabla \langle u_\beta \rangle^\beta$, $\nabla \langle u_\sigma \rangle^\sigma$, and $\Omega(\langle u_\sigma \rangle^\sigma)$.

7.5.4.1 Two-Equation Transient Closure

A generic form of the solution reads

$$\begin{bmatrix} \tilde{u}_\beta \\ \tilde{u}_\sigma \end{bmatrix} = \partial_t \begin{bmatrix} \mathsf{a}_\beta^\star \\ \mathsf{a}_\sigma^\star \end{bmatrix} \star \left(\left\langle u_\beta \right\rangle^\beta - \left\langle u_\sigma \right\rangle^\sigma\right) + \partial_t \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star & \mathbf{b}_{\beta\sigma}^\star \\ \mathbf{b}_{\sigma\beta}^\star & \mathbf{b}_{\sigma\sigma}^\star \end{bmatrix} \cdot \star \begin{bmatrix} \nabla \left\langle u_\beta \right\rangle^\beta \\ \nabla \left\langle u_\sigma \right\rangle^\sigma \end{bmatrix}$$
$$+ \partial_t \begin{bmatrix} \mathbf{W}_{\beta\beta}^\star & \mathbf{W}_{\beta\sigma}^\star \\ \mathbf{W}_{\sigma\beta}^\star & \mathbf{W}_{\sigma\sigma}^\star \end{bmatrix} : \star \begin{bmatrix} \nabla\nabla \left\langle u_\beta \right\rangle^\beta \\ \nabla\nabla \left\langle u_\sigma \right\rangle^\sigma \end{bmatrix} + \partial_t \begin{bmatrix} \mathsf{c}_\beta^\star \\ \mathsf{c}_\sigma^\star \end{bmatrix} \star \Omega\left(\left\langle u_\sigma \right\rangle^\sigma\right), \tag{7.79}$$

where $\star$ denotes a time convolution and

$$\begin{bmatrix} \mathsf{a}_\beta^\star \\ \mathsf{a}_\sigma^\star \end{bmatrix}, \quad \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star & \mathbf{b}_{\beta\sigma}^\star \\ \mathbf{b}_{\sigma\beta}^\star & \mathbf{b}_{\sigma\sigma}^\star \end{bmatrix}, \quad \begin{bmatrix} \mathbf{W}_{\beta\beta}^\star & \mathbf{W}_{\beta\sigma}^\star \\ \mathbf{W}_{\sigma\beta}^\star & \mathbf{W}_{\sigma\sigma}^\star \end{bmatrix}, \quad \text{and} \quad \begin{bmatrix} \mathsf{c}_\beta^\star \\ \mathsf{c}_\sigma^\star \end{bmatrix}$$

are mapping variables. $\mathsf{a}_\alpha^\star$ and $\mathsf{c}_\alpha^\star$ are scalars, $\mathbf{b}_{\alpha\gamma}^\star$ are vectors, and $\mathbf{W}_{\alpha\gamma}^\star$ are dyadics. We have also used the convenient block notations

$$\begin{bmatrix} \mathbf{b}_{\beta\beta}^\star & \mathbf{b}_{\beta\sigma}^\star \\ \mathbf{b}_{\sigma\beta}^\star & \mathbf{b}_{\sigma\sigma}^\star \end{bmatrix} \cdot\star \begin{bmatrix} \nabla\langle u_\beta\rangle^\beta \\ \nabla\langle u_\sigma\rangle^\sigma \end{bmatrix} = \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \cdot\star\nabla\langle u_\beta\rangle^\beta + \mathbf{b}_{\beta\sigma}^\star\cdot\star\nabla\langle u_\sigma\rangle^\sigma \\ \mathbf{b}_{\sigma\beta}^\star \cdot\star\nabla\langle u_\beta\rangle^\beta + \mathbf{b}_{\sigma\sigma}^\star\cdot\star\nabla\langle u_\sigma\rangle^\sigma \end{bmatrix}, \tag{7.80}$$

and

$$\begin{bmatrix} \mathbf{W}_{\beta\beta}^\star & \mathbf{W}_{\beta\sigma}^\star \\ \mathbf{W}_{\sigma\beta}^\star & \mathbf{W}_{\sigma\sigma}^\star \end{bmatrix} :\star \begin{bmatrix} \nabla\nabla\langle u_\beta\rangle^\beta \\ \nabla\nabla\langle u_\sigma\rangle^\sigma \end{bmatrix} = \begin{bmatrix} \mathbf{W}_{\beta\beta}^\star :\star\nabla\nabla\langle u_\beta\rangle^\beta + \mathbf{W}_{\beta\sigma}^\star :\star\nabla\nabla\langle u_\sigma\rangle^\sigma \\ \mathbf{W}_{\sigma\beta}^\star :\star\nabla\nabla\langle u_\beta\rangle^\beta + \mathbf{W}_{\sigma\sigma}^\star :\star\nabla\nabla\langle u_\sigma\rangle^\sigma \end{bmatrix}, \tag{7.81}$$

with

$$\mathbf{b}^\star\cdot\star\nabla\langle u\rangle = \mathsf{b}_i^\star \star \partial_i\langle u\rangle = \int_0^t \mathsf{b}_i^\star(\tau)\,\partial_i\langle u\rangle(t-\tau)\,d\tau \quad \text{and} \quad \mathbf{W}^\star :\star\nabla\nabla\langle u\rangle = \mathsf{W}_{ij}^\star \star \partial_{ji}\langle u\rangle.$$

This is not obvious yet why we have chosen this specific decomposition Equation 7.79. It will become straightforward later on that this allows us to uncouple the micro- and macroscale problems.

7.5.4.2 Two-Equation Quasi-Stationary Closure

A simplification of this transient problem consists in considering that the timescales for the relaxation of the mapping variables are much faster than the variations of the corresponding macroscale quantities, $\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma$, $\left[\nabla\langle u_\beta\rangle^\beta\ \nabla\langle u_\sigma\rangle^\sigma\right]^T$, $\left[\nabla\nabla\langle u_\beta\rangle^\beta\ \nabla\nabla\langle u_\sigma\rangle^\sigma\right]^T$, and $\Omega(\langle u_\sigma\rangle^\sigma)$. When this holds, we can ignore the transient behavior of the mapping variables and use the following form:

$$\begin{bmatrix} \tilde{u}_\beta \\ \tilde{u}_\sigma \end{bmatrix} = \begin{bmatrix} \mathsf{a}_\beta \\ \mathsf{a}_\sigma \end{bmatrix}\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right) + \begin{bmatrix} \mathbf{b}_{\beta\beta} & \mathbf{b}_{\beta\sigma} \\ \mathbf{b}_{\sigma\beta} & \mathbf{b}_{\sigma\sigma} \end{bmatrix}\cdot\begin{bmatrix} \nabla\langle u_\beta\rangle^\beta \\ \nabla\langle u_\sigma\rangle^\sigma \end{bmatrix}$$
$$+ \begin{bmatrix} \mathbf{W}_{\beta\beta} & \mathbf{W}_{\beta\sigma} \\ \mathbf{W}_{\sigma\beta} & \mathbf{W}_{\sigma\sigma} \end{bmatrix} : \begin{bmatrix} \nabla\nabla\langle u_\beta\rangle^\beta \\ \nabla\nabla\langle u_\sigma\rangle^\sigma \end{bmatrix} + \begin{bmatrix} \mathsf{c}_\beta \\ \mathsf{c}_\sigma \end{bmatrix}\Omega\left(\langle u_\sigma\rangle^\sigma\right). \tag{7.82}$$

Roughly speaking, in the limit where a function f relaxes infinitely fast toward a constant C with $f(t=0)=0$, we have $\partial_t f\star\langle u\rangle \simeq C\partial_t H\star\langle u\rangle = C\delta\star\langle u\rangle = C\langle u\rangle$, where H is the unit-step function and δ is a Dirac distribution.

7.5.4.3 Transient Closure Problems

The IBVPs corresponding to the mapping variables, which are often termed closure problems, can be obtained by introducing Equations 7.82 and 7.79 into Equations 7.75 through 7.78. To facilitate solution with the time convolutions, we can work in Laplace space where $\mathcal{T}f(t) = \underline{f}(p)$ denotes the Laplace transform and p is the Laplace variable (although it is not mandatory to do so, see, e.g., [78]). Applying this transform to Equation 7.79 with zero initial conditions yields

$$\begin{bmatrix} \underline{\tilde{u}}_\beta \\ \underline{\tilde{u}}_\sigma \end{bmatrix} = p\begin{bmatrix} \underline{\mathbf{a}}^\star_\beta \\ \underline{\mathbf{a}}^\star_\sigma \end{bmatrix}\left(\langle \underline{u}_\beta\rangle^\beta - \langle \underline{u}_\sigma\rangle^\sigma\right) + p\begin{bmatrix} \underline{\mathbf{b}}^\star_{\beta\beta} & \underline{\mathbf{b}}^\star_{\beta\sigma} \\ \underline{\mathbf{b}}^\star_{\sigma\beta} & \underline{\mathbf{b}}^\star_{\sigma\sigma} \end{bmatrix}\cdot\begin{bmatrix} \nabla\langle \underline{u}_\beta\rangle^\beta \\ \nabla\langle \underline{u}_\sigma\rangle^\sigma \end{bmatrix}$$
$$+p\begin{bmatrix} \underline{\mathbf{W}}^\star_{\beta\beta} & \underline{\mathbf{W}}^\star_{\beta\sigma} \\ \underline{\mathbf{W}}^\star_{\sigma\beta} & \underline{\mathbf{W}}^\star_{\sigma\sigma} \end{bmatrix} : \begin{bmatrix} \nabla\nabla\langle \underline{u}_\beta\rangle^\beta \\ \nabla\nabla\langle \underline{u}_\sigma\rangle^\sigma \end{bmatrix} + p\begin{bmatrix} \underline{\mathbf{c}}^\star_\beta \\ \underline{\mathbf{c}}^\star_\sigma \end{bmatrix}\underline{\Omega}\left(\langle u_\sigma\rangle^\sigma\right) \tag{7.83}$$

Similarly, Equations 7.75 through 7.78 become

$$p\underline{\tilde{u}}_\beta - \widetilde{\mathcal{L}_\beta\underline{\tilde{u}}_\beta} = -\mathrm{Pe}^\ell_\beta\tilde{\mathbf{v}}_\beta\cdot\nabla\langle \underline{u}_\beta\rangle^\beta \text{ in } \mathcal{V}_\beta, \tag{7.84}$$

$$\Gamma_a p\underline{\tilde{u}}_\sigma - \widetilde{\mathcal{L}_\sigma\underline{\tilde{u}}_\sigma} = 0 \text{ in } \mathcal{V}_\sigma, \tag{7.85}$$

along with the set of boundary conditions

$$\underline{\tilde{u}}_\beta - \underline{\tilde{u}}_\sigma = -\left(\langle \underline{u}_\beta\rangle^\beta - \langle \underline{u}_\sigma\rangle^\sigma\right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.86}$$

$$\mathcal{B}_\beta\underline{\tilde{u}}_\beta - \mathcal{B}_\beta\underline{\tilde{u}}_\sigma = \mathbf{n}_{\beta\sigma}\cdot\left(\mathbf{A}_\beta\cdot\nabla\langle \underline{u}_\beta\rangle^\beta - \Gamma_A\mathbf{A}_\sigma\cdot\nabla\langle \underline{u}_\sigma\rangle^\sigma\right) + \underline{\Omega}\left(\langle u_\sigma\rangle^\sigma\right) \text{ on } \mathcal{A}_{\beta\sigma}. \tag{7.87}$$

We are looking for solutions that hold for any value of $\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma$, $\nabla\langle u_\beta\rangle^\beta\ldots$ This means that we can separate problems involving the different macroscopic source terms by identifying terms corresponding to the different source terms. In Laplace space, this leads to

$$p\underline{\mathbf{a}}^\star_\beta - \widetilde{\mathcal{L}_\beta\underline{\mathbf{a}}^\star_\beta} = 0 \text{ in } \mathcal{V}_\beta, \tag{7.88a}$$

$$\text{BC1} \quad \underline{\mathbf{a}}^\star_\beta - \underline{\mathbf{a}}^\star_\sigma = -\frac{1}{p} \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.88b}$$

$$\text{BC2} \quad \mathcal{B}_\beta\underline{\mathbf{a}}^\star_\beta - \mathcal{B}_\sigma\underline{\mathbf{a}}^\star_\sigma = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.88c}$$

$$\Gamma_a p\underline{\mathbf{a}}^\star_\sigma - \widetilde{\mathcal{L}_\sigma\underline{\mathbf{a}}^\star_\sigma} = 0 \text{ in } \mathcal{V}_\sigma. \tag{7.88d}$$

Applying the inverse Laplace transform $\mathcal{T}^{-1}$ to these expressions yields the following:

7.5.4.3.1 Problem 2eq-Transient-I

$$\partial_t\mathbf{a}^\star_\beta - \widetilde{\mathcal{L}_\beta\mathbf{a}^\star_\beta} = 0 \text{ in } \mathcal{V}_\beta, \tag{7.89a}$$

$$\text{BC1} \quad \mathbf{a}^\star_\beta - \mathbf{a}^\star_\sigma = -H(t) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.89b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathsf{a}_\beta^\star - \mathcal{B}_\sigma \mathsf{a}_\sigma^\star = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.89c}$$

$$\text{Periodicity 1} \quad \mathsf{a}_\alpha^\star\left(\mathbf{x}+\mathbf{l}_i\right) = \mathsf{a}_\alpha^\star\left(\mathbf{x}\right) \text{with } \alpha = \beta, \sigma, \tag{7.89d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathsf{a}_\alpha^\star\left(\mathbf{x}+\mathbf{l}_i\right) = \mathcal{J}_\alpha \mathsf{a}_\alpha^\star\left(\mathbf{x}\right) \text{with } \alpha = \beta, \sigma, \tag{7.89e}$$

$$\text{Average} \quad \left\langle \mathsf{a}_\alpha^\star \right\rangle = 0 \text{ with } \alpha = \beta, \sigma, \tag{7.89f}$$

$$\Gamma_a \partial_t \mathsf{a}_\sigma^\star - \widetilde{\mathcal{L}_\sigma \mathsf{a}_\sigma^\star} = 0 \text{ in } \mathcal{V}_\sigma, \tag{7.89g}$$

where we have used the flux notation

$$\mathcal{J}_\beta \phi_\beta = -\mathbf{A}_\beta \cdot \nabla \phi_\beta + \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta \phi_\beta, \tag{7.90}$$

$$\mathcal{J}_\sigma \phi_\sigma = -\Gamma_A \mathbf{A}_\sigma \cdot \nabla \phi_\sigma. \tag{7.91}$$

We have also completed the problem with periodicity conditions ($\mathbf{l}_i$ are the periodicity vectors, with $i = 1, 2, 3$ for $\mathbf{x} \in \mathbb{R}^3$) and have introduced the average conditions $\left\langle \mathsf{a}_\alpha^\star \right\rangle = 0$, which are derived from $\left\langle \tilde{u}_\alpha \right\rangle \simeq 0$. Indeed, recall that $u_\alpha = \left\langle u_\alpha \right\rangle^\alpha + \tilde{u}_\alpha$, so that averaging yields $\left\langle u_\alpha \right\rangle^\alpha = \left\langle \left\langle u_\alpha \right\rangle^\alpha \right\rangle^\alpha + \left\langle \tilde{u}_\alpha \right\rangle^\alpha$. The localization (frequency assumption) leads to $\left\langle \left\langle u_\alpha \right\rangle^\alpha \right\rangle^\alpha \simeq \left\langle u_\alpha \right\rangle^\alpha$, so that $\left\langle \tilde{u}_\alpha \right\rangle \simeq 0$. On introducing Equation 7.79 in $\left\langle \tilde{u}_\alpha \right\rangle \simeq 0$ and identifying terms that are $\mathcal{O}\left(\left\langle u_\beta \right\rangle^\beta - \left\langle u_\sigma \right\rangle^\sigma\right)$, we obtain $\left\langle \mathsf{a}_\alpha^\star \right\rangle = 0$.

An identical procedure for the other source terms leads to the following sequence of closure problems:

7.5.4.3.2 Problem 2eq-Transient-II

$$\partial_t \mathbf{b}_{\beta\beta}^\star - \widetilde{\mathcal{L}_\beta \mathbf{b}_{\beta\beta}^\star} + \widetilde{\mathcal{J}_\beta \mathsf{a}_\beta^\star} = \mathbf{A}_\beta \cdot \widetilde{\nabla \mathsf{a}_\beta^\star} - \mathrm{Pe}_\beta^\ell \tilde{\mathbf{v}}_\beta H\left(t\right) \text{ in } \mathcal{V}_\beta, \tag{7.92a}$$

$$\text{BC1} \quad \mathbf{b}_{\beta\beta}^\star - \mathbf{b}_{\sigma\beta}^\star = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.92b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{b}_{\beta\beta}^\star - \mathcal{B}_\sigma \mathbf{b}_{\sigma\beta}^\star = \mathbf{n}_{\beta\sigma} \cdot \left[\mathbf{A}_\beta\left(H\left(t\right) + \mathsf{a}_\beta^\star\right) - \Gamma_A \mathbf{A}_\sigma \mathsf{a}_\sigma^\star\right] \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.92c}$$

$$\text{Periodicity 1} \quad \mathbf{b}_{\alpha\beta}^\star\left(\mathbf{x}+\mathbf{l}_i\right) = \mathbf{b}_{\alpha\beta}^\star\left(\mathbf{x}\right) \text{with } \alpha = \beta, \sigma, \tag{7.92d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{b}_{\alpha\beta}^\star\left(\mathbf{x}+\mathbf{l}_i\right) = \mathcal{J}_\alpha \mathbf{b}_{\alpha\beta}^\star\left(\mathbf{x}\right) \text{ with } \alpha = \beta, \sigma, \tag{7.92e}$$

$$\text{Average} \quad \left\langle \mathbf{b}_{\alpha\beta}^\star \right\rangle = 0 \text{ with } \alpha = \beta, \sigma, \tag{7.92f}$$

$$\Gamma_a \partial_t \mathbf{b}_{\sigma\beta}^\star - \widetilde{\mathcal{L}_\sigma \mathbf{b}_{\sigma\beta}^\star} + \widetilde{\mathcal{J}_\sigma \mathsf{a}_\sigma^\star} = \Gamma_A \mathbf{A}_\sigma \cdot \widetilde{\nabla \mathsf{a}_\sigma^\star} \text{ in } \mathcal{V}_\sigma. \tag{7.92g}$$

7.5.4.3.3 Problem 2eq-Transient-III

$$\partial_t \mathbf{b}^\star_{\beta\sigma} - \widetilde{\mathcal{L}_\beta \mathbf{b}^\star_{\beta\sigma}} - \widetilde{\mathcal{J}_\beta \mathsf{a}^\star_\beta} = -\mathbf{A}_\beta \cdot \widetilde{\nabla \mathsf{a}^\star_\beta} \text{ in } \mathcal{V}_\beta, \tag{7.93a}$$

$$\text{BC1} \quad \mathbf{b}^\star_{\beta\sigma} - \mathbf{b}^\star_{\sigma\sigma} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.93b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{b}^\star_{\beta\sigma} - \mathcal{B}_\sigma \mathbf{b}^\star_{\sigma\sigma} = \mathbf{n}_{\beta\sigma} \cdot \left[-\mathbf{A}_\beta \mathsf{a}^\star_\beta + \Gamma_A \mathbf{A}_\sigma \left(-H(t) + \mathsf{a}^\star_\sigma \right) \right] \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.93c}$$

$$\text{Periodicity 1} \quad \mathbf{b}^\star_{\alpha\sigma}(\mathbf{x} + \mathbf{l}_i) = \mathbf{b}^\star_{\alpha\sigma}(\mathbf{x}) \text{ with } \alpha = \beta, \sigma, \tag{7.93d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{b}^\star_{\alpha\sigma}(\mathbf{x} + \mathbf{l}_i) = \mathcal{J}_\alpha \mathbf{b}^\star_{\alpha\sigma}(\mathbf{x}) \text{ with } \alpha = \beta, \sigma, \tag{7.93e}$$

$$\text{Average} \quad \langle \mathbf{b}^\star_{\alpha\sigma} \rangle = 0 \text{ with } \alpha = \beta, \sigma, \tag{7.93f}$$

$$\Gamma_a \partial_t \mathbf{b}^\star_{\sigma\sigma} - \widetilde{\mathcal{L}_\sigma \mathbf{b}^\star_{\sigma\sigma}} - \widetilde{\mathcal{J}_\sigma \mathsf{a}^\star_\sigma} = -\Gamma_A \mathbf{A}_\sigma \cdot \widetilde{\nabla \mathsf{a}^\star_\sigma} \text{ in } \mathcal{V}_\sigma. \tag{7.93g}$$

7.5.4.3.4 Problem 2eq-Transient-IV

$$\partial_t \mathbf{W}^\star_{\beta\beta} - \widetilde{\mathcal{L}_\beta \mathbf{W}^\star_{\beta\beta}} + \widetilde{\mathcal{J}_\beta \mathbf{b}^\star_{\beta\beta}} = \mathbf{A}_\beta \cdot \widetilde{\nabla \mathbf{b}^\star_{\beta\beta}} + \mathbf{A}_\beta \mathsf{a}^\star_\beta \text{ in } \mathcal{V}_\beta, \tag{7.94a}$$

$$\text{BC1} \quad \mathbf{W}^\star_{\beta\beta} - \mathbf{W}^\star_{\sigma\beta} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.94b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{W}^\star_{\beta\beta} - \mathcal{B}_\sigma \mathbf{W}^\star_{\sigma\beta} = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \mathbf{b}^\star_{\beta\beta} - \Gamma_A \mathbf{A}_\sigma \mathbf{b}^\star_{\sigma\beta} \right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.94c}$$

$$\text{Periodicity 1} \quad \mathbf{W}^\star_{\alpha\beta}(\mathbf{x} + \mathbf{l}_i) = \mathbf{W}^\star_{\alpha\beta}(\mathbf{x}) \text{ with } \alpha = \beta, \sigma, \tag{7.94d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{W}^\star_{\alpha\beta}(\mathbf{x} + \mathbf{l}_i) = \mathcal{J}_\alpha \mathbf{W}^\star_{\alpha\beta}(\mathbf{x}) \text{ with } \alpha = \beta, \sigma, \tag{7.94e}$$

$$\text{Average} \quad \langle \mathbf{W}^\star_{\alpha\beta} \rangle = 0 \text{ with } \alpha = \beta, \sigma, \tag{7.94f}$$

$$\Gamma_a \partial_t \mathbf{W}^\star_{\sigma\beta} - \widetilde{\mathcal{L}_\sigma \mathbf{W}^\star_{\sigma\beta}} + \widetilde{\mathcal{J}_\sigma \mathbf{b}^\star_{\sigma\beta}} = \Gamma_A \mathbf{A}_\sigma \cdot \widetilde{\nabla \mathbf{b}^\star_{\sigma\beta}} + \Gamma_A \mathbf{A}_\sigma \mathsf{a}^\star_\sigma \text{ in } \mathcal{V}_\sigma. \tag{7.94g}$$

7.5.4.3.5 Problem 2eq-Transient-V

$$\partial_t \mathbf{W}^\star_{\beta\sigma} - \widetilde{\mathcal{L}_\beta \mathbf{W}^\star_{\beta\sigma}} + \widetilde{\mathcal{J}_\beta \mathbf{b}^\star_{\beta\sigma}} = \mathbf{A}_\beta \cdot \widetilde{\nabla \mathbf{b}^\star_{\beta\sigma}} - \mathbf{A}_\beta \mathsf{a}^\star_\beta \text{ in } \mathcal{V}_\beta, \tag{7.95a}$$

$$\text{BC1} \quad \mathbf{W}^\star_{\beta\sigma} - \mathbf{W}^\star_{\sigma\sigma} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.95b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{W}^\star_{\beta\sigma} - \mathcal{B}_\sigma \mathbf{W}^\star_{\sigma\sigma} = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \mathbf{b}^\star_{\beta\sigma} - \Gamma_A \mathbf{A}_\sigma \mathbf{b}^\star_{\sigma\sigma} \right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.95c}$$

$$\text{Periodicity 1} \quad \mathbf{W}^{\star}_{\alpha\sigma}(\mathbf{x}+\mathbf{l}_i) = \mathbf{W}^{\star}_{\alpha\sigma}(\mathbf{x}) \text{ with } \alpha = \beta,\sigma, \tag{7.95d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{W}^{\star}_{\alpha\sigma}(\mathbf{x}+\mathbf{l}_i) = \mathcal{J}_\alpha \mathbf{W}^{\star}_{\alpha\sigma}(\mathbf{x}) \text{ with } \alpha = \beta,\sigma, \tag{7.95e}$$

$$\text{Average} \quad \left\langle \mathbf{W}^{\star}_{\alpha\sigma} \right\rangle = 0 \text{ with } \alpha = \beta,\sigma, \tag{7.95f}$$

$$\Gamma_a \partial_t \mathbf{W}^{\star}_{\sigma\sigma} - \widetilde{\mathcal{L}_\sigma \mathbf{W}^{\star}_{\sigma\sigma}} + \widetilde{\mathcal{J}_\sigma \mathbf{b}^{\star}_{\sigma\sigma}} = \Gamma_A \mathbf{A}_\sigma \cdot \widetilde{\nabla \mathbf{b}^{\star}_{\sigma\sigma}} - \Gamma_A \mathbf{A}_\sigma \mathbf{a}^{\star}_\sigma \text{ in } \mathcal{V}_\sigma. \tag{7.95g}$$

7.5.4.3.6 Problem 2eq-Transient-VI

$$\partial_t \mathbf{c}^{\star}_\beta - \widetilde{\mathcal{L}_\beta \mathbf{c}^{\star}_\beta} = 0 \text{ in } \mathcal{V}_\beta, \tag{7.96a}$$

$$\text{BC1} \quad \mathbf{c}^{\star}_\beta - \mathbf{c}^{\star}_\sigma = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.96b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{c}^{\star}_\beta - \mathcal{B}_\sigma \mathbf{c}^{\star}_\sigma = H(t) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.96c}$$

$$\text{Periodicity 1} \quad \mathbf{c}^{\star}_\alpha(\mathbf{x}+\mathbf{l}_i) = \mathbf{c}^{\star}_\alpha(\mathbf{x}) \text{ with } \alpha = \beta,\sigma, \tag{7.96d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{c}^{\star}_\alpha(\mathbf{x}+\mathbf{l}_i) = \mathcal{J}_\alpha \mathbf{c}^{\star}_\alpha(\mathbf{x}) \text{ with } \alpha = \beta,\sigma, \tag{7.96e}$$

$$\text{Average} \quad \left\langle \mathbf{c}^{\star}_\alpha \right\rangle = 0 \text{ with } \alpha = \beta,\sigma, \tag{7.96f}$$

$$\Gamma_a \partial_t \mathbf{c}^{\star}_\sigma - \widetilde{\mathcal{L}_\sigma \mathbf{c}^{\star}_\sigma} = 0 \text{ in } \mathcal{V}_\sigma. \tag{7.96g}$$

In most cases, these problems are coupled via flux terms. They appear when developing the derivatives of products. For example,

$$\begin{aligned}\mathcal{L}_\sigma\left[\mathbf{a}_\sigma\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right)\right] &= \nabla\cdot\left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{a}_\sigma\right)\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right)\\ &\quad + 2\left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{a}_\sigma\right)\cdot\nabla\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right)\\ &\quad + \Gamma_A \mathbf{A}_\sigma \mathbf{a}_\sigma : \nabla\nabla\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right),\end{aligned} \tag{7.97}$$

therefore implying a coupling between $\mathbf{a}$ and $\mathbf{b}$ for $\mathcal{O}\left(\nabla\langle u_\alpha\rangle^\alpha\right)$ and between $\mathbf{a}$ and $\mathbf{W}$ for $\mathcal{O}\left(\nabla\nabla\langle u_\alpha\rangle^\alpha\right)$.

7.5.4.4 Stationary Closure Problems

The corresponding stationary closure problems for $\mathbf{a}$, $\mathbf{b}$, $\mathbf{W}$, and $\mathbf{c}$ are obtained by removing the time derivatives and replacing $H(t)$ by 1 in the transient problems earlier. The notations are similar, except that we remove the upper ⋆ symbol from the variables.

7.5.5 Macroscale Models

Recall the average equations

$$\varepsilon_\beta \partial_t \langle u_\beta \rangle^\beta - \left\langle \mathcal{L}_\beta \langle u_\beta \rangle^\beta \right\rangle - \varepsilon_\beta R_\beta \left(\langle u_\beta \rangle^\beta \right) = \langle \mathcal{L}_\beta \tilde{u}_\beta \rangle, \tag{7.98}$$

$$\Gamma_a \varepsilon_\sigma \partial_t \langle u_\sigma \rangle^\sigma - \left\langle \mathcal{L}_\sigma \langle u_\sigma \rangle^\sigma \right\rangle - \varepsilon_\sigma R_\sigma \left(\langle u_\sigma \rangle^\sigma \right) = \langle \mathcal{L}_\sigma \tilde{u}_\sigma \rangle, \tag{7.99}$$

that are obtained by introducing the linearization of the reaction rate and the localization assumptions in Equations 7.45 and 7.46. We further explicitly detail the terms $\left\langle \mathcal{L}_\beta \langle u_\beta \rangle^\beta \right\rangle$ and $\left\langle \mathcal{L}_\sigma \langle u_\sigma \rangle^\sigma \right\rangle$ as

$$\begin{aligned} \left\langle \mathcal{L}_\beta \langle u_\beta \rangle^\beta \right\rangle &= \left\langle \nabla \cdot \left(\mathbf{A}_\beta \cdot \nabla \langle u_\beta \rangle^\beta - \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta \langle u_\beta \rangle^\beta \right) \right\rangle \\ &\simeq \nabla \cdot \left(\varepsilon_\beta \mathbf{A}_\beta \cdot \nabla \langle u_\beta \rangle^\beta - \mathrm{Pe}_\beta^\ell \langle \mathbf{v}_\beta \rangle \langle u_\beta \rangle^\beta \right) \equiv \langle \mathcal{L}_\beta \rangle \langle u_\beta \rangle^\beta, \end{aligned} \tag{7.100}$$

$$\begin{aligned} \left\langle \mathcal{L}_\sigma \langle u_\sigma \rangle^\sigma \right\rangle &= \left\langle \nabla \cdot \left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla \langle u_\sigma \rangle^\sigma \right) \right\rangle \\ &\simeq \nabla \cdot \left(\varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma \cdot \nabla \langle u_\sigma \rangle^\sigma \right) \equiv \langle \mathcal{L}_\sigma \rangle \langle u_\sigma \rangle^\sigma, \end{aligned} \tag{7.101}$$

so that

$$\varepsilon_\beta \partial_t \langle u_\beta \rangle^\beta - \langle \mathcal{L}_\beta \rangle \langle u_\beta \rangle^\beta - \varepsilon_\beta R_\beta \left(\langle u_\beta \rangle^\beta \right) = \langle \mathcal{L}_\beta \tilde{u}_\beta \rangle, \tag{7.102}$$

$$\Gamma_a \varepsilon_\sigma \partial_t \langle u_\sigma \rangle^\sigma - \langle \mathcal{L}_\sigma \rangle \langle u_\sigma \rangle^\sigma - \varepsilon_\sigma R_\sigma \left(\langle u_\sigma \rangle^\sigma \right) = \langle \mathcal{L}_\sigma \tilde{u}_\sigma \rangle. \tag{7.103}$$

These equations are not in a closed form, since they involve the perturbations via the terms $\langle \mathcal{L}_\beta \tilde{u}_\beta \rangle$ and $\langle \mathcal{L}_\sigma \tilde{u}_\sigma \rangle$. The next step of the volume averaging process is to introduce the approximate analytical forms of the perturbations (Equations 7.79 and 7.82 in Equations 7.102 and 7.103).

7.5.5.1 Two-Equation Fully Transient

For the transient closure, we obtain

$$\begin{aligned} \langle \mathcal{L}_\beta \tilde{u}_\beta \rangle = &\left\langle \mathcal{L}_\beta \partial_t \mathbf{a}_\beta^\star \star \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right) \right\rangle \\ &+ \left\langle \mathcal{L}_\beta \partial_t \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \\ \mathbf{b}_{\beta\sigma}^\star \end{bmatrix} \cdot \star \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} \right\rangle \\ &+ \left\langle \mathcal{L}_\beta \partial_t \begin{bmatrix} \mathbf{W}_{\beta\beta}^\star \\ \mathbf{W}_{\sigma\beta}^\star \end{bmatrix} : \star \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} \right\rangle \\ &+ \left\langle \mathcal{L}_\beta \partial_t \mathbf{c}_\beta^\star \star \Omega \left(\langle u_\sigma \rangle^\sigma \right) \right\rangle, \end{aligned} \tag{7.104}$$

using Equation 7.79. We now treat each term on the RHS of Equation 7.104 separately. For the first term, we obtain

$$\left\langle \mathcal{L}_\beta \partial_t \mathbf{a}_\beta^\star \star \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right) \right\rangle \simeq \partial_t \left\langle \mathcal{L}_\beta \mathbf{a}_\beta^\star \right\rangle \star \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right)$$
$$- \partial_t \left\langle \mathcal{J}_\beta \mathbf{a}_\beta^\star \right\rangle \cdot \star \nabla \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right)$$
$$+ \partial_t \left\langle \mathbf{A}_\beta \cdot \nabla \mathbf{a}_\beta^\star \right\rangle \cdot \star \nabla \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right), \tag{7.105}$$

where terms in $\nabla\nabla$ have disappeared since $\left\langle \mathbf{a}_\alpha^\star \right\rangle = 0$. The second term on the RHS of Equation 7.104 yields

$$\left\langle \mathcal{L}_\beta \partial_t \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \\ \mathbf{b}_{\beta\sigma}^\star \end{bmatrix} \cdot \star \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} \right\rangle \simeq \partial_t \left\langle \mathcal{L}_\beta \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \\ \mathbf{b}_{\beta\sigma}^\star \end{bmatrix} \right\rangle \cdot \star \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}$$
$$- \partial_t \left\langle \mathcal{J}_\beta \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \\ \mathbf{b}_{\beta\sigma}^\star \end{bmatrix} \right\rangle : \star \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}$$
$$+ \partial_t \left\langle \mathbf{A}_\beta \cdot \nabla \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \\ \mathbf{b}_{\beta\sigma}^\star \end{bmatrix} \right\rangle : \star \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}. \tag{7.106}$$

The third term on the RHS of Equation 7.104 can be written as

$$\left\langle \mathcal{L}_\beta \partial_t \begin{bmatrix} \mathbf{W}_{\beta\beta}^\star \\ \mathbf{W}_{\sigma\beta}^\star \end{bmatrix} : \star \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} \right\rangle \simeq \partial_t \left\langle \mathcal{L}_\beta \begin{bmatrix} \mathbf{W}_{\beta\beta}^\star \\ \mathbf{W}_{\sigma\beta}^\star \end{bmatrix} \right\rangle : \star \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} \tag{7.107}$$

Finally, the last term on the RHS of Equation 7.104 reads

$$\left\langle \mathcal{L}_\beta \partial_t \mathbf{c}_\beta^\star \star \Omega \left(\langle u_\sigma \rangle^\sigma \right) \right\rangle \simeq \partial_t \left\langle \mathcal{L}_\beta \mathbf{c}_\beta^\star \right\rangle \star \Omega \left(\langle u_\sigma \rangle^\sigma \right). \tag{7.108}$$

We can combine these equations to obtain an approximate form of Equation 7.104:

$$\left\langle \mathcal{L}_\beta \tilde{u}_\beta \right\rangle \simeq \partial_t \left\langle \mathcal{L}_\beta \mathbf{a}_\beta^\star \right\rangle \star \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right) + \partial_t \left\langle \mathcal{L}_\beta \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \\ \mathbf{b}_{\beta\sigma}^\star \end{bmatrix} \right\rangle \cdot \star \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}$$
$$+ \left\langle -\mathcal{J}_\beta \mathbf{a}_\beta^\star + \mathbf{A}_\beta \cdot \nabla \mathbf{a}_\beta^\star \right\rangle \cdot \star \nabla \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right)$$
$$+ \partial_t \left\langle \mathcal{L}_\beta \begin{bmatrix} \mathbf{W}_{\beta\beta}^\star \\ \mathbf{W}_{\sigma\beta}^\star \end{bmatrix} - \mathcal{J}_\beta \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \\ \mathbf{b}_{\beta\sigma}^\star \end{bmatrix} + \mathbf{A}_\beta \cdot \nabla \begin{bmatrix} \mathbf{b}_{\beta\beta}^\star \\ \mathbf{b}_{\beta\sigma}^\star \end{bmatrix} \right\rangle : \star \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}$$
$$+ \partial_t \left\langle \mathcal{L}_\beta \mathbf{c}_\beta^\star \right\rangle \star \Omega \left(\langle u_\sigma \rangle^\sigma \right). \tag{7.109}$$

The closed macroscale model for the phase β can be written as

$$\varepsilon_\beta \partial_t \langle u_\beta \rangle^\beta - \langle \mathcal{L}_\beta \rangle \langle u_\beta \rangle^\beta - \varepsilon_\beta R_\beta \left(\langle u_\beta \rangle^\beta \right) = -\nabla \cdot \left(\partial_t \mathbf{d}^\star_{\beta\beta} \star \langle u_\beta \rangle^\beta \right) - \nabla \cdot \left(\partial_t \mathbf{d}^\star_{\beta\sigma} \star \langle u_\sigma \rangle^\sigma \right)$$
$$+ \nabla \cdot \left(\partial_t \mathbf{B}^\star_{\beta\beta} \cdot\star \nabla \langle u_\beta \rangle^\beta \right) + \nabla \cdot \left(\partial_t \mathbf{B}^\star_{\beta\sigma} \cdot\star \nabla \langle u_\sigma \rangle^\sigma \right)$$
$$+ \partial_t h^\star_\beta \star \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right) + a_v \partial_t \xi^\star_\beta \star \Omega \left(\langle u_\sigma \rangle^\sigma \right), \quad (7.110)$$

where $a_v = A_{\sigma\beta}/V$ is the specific surface.

The effective velocity-like terms, $\mathbf{d}_{\beta\beta}$ and $\mathbf{d}_{\beta\sigma}$, are

$$\mathbf{d}^\star_{\beta\beta} = -\left\langle \mathcal{L}_\beta \mathbf{b}^\star_{\beta\beta} - \mathcal{J}_\beta \mathsf{a}^\star_\beta + \mathbf{A}_\beta \cdot \nabla \mathsf{a}^\star_\beta \right\rangle, \quad (7.111)$$

$$\mathbf{d}^\star_{\beta\sigma} = -\left\langle \mathcal{L}_\beta \mathbf{b}^\star_{\beta\sigma} + \mathcal{J}_\beta \mathsf{a}^\star_\beta - \mathbf{A}_\beta \cdot \nabla \mathsf{a}^\star_\beta \right\rangle. \quad (7.112)$$

Similarly, dispersion-like effective parameters, $\mathbf{B}_{\beta\beta}$ and $\mathbf{B}_{\beta\sigma}$, may be written as

$$\mathbf{B}^\star_{\beta\beta} = \left\langle \mathcal{L}_\beta \mathbf{W}^\star_{\beta\beta} - \mathcal{J}_\beta \mathbf{b}^\star_{\beta\beta} + \mathbf{A}_\beta \cdot \nabla \mathbf{b}^\star_{\beta\beta} \right\rangle, \quad (7.113)$$

$$\mathbf{B}^\star_{\beta\sigma} = \left\langle \mathcal{L}_\beta \mathbf{W}^\star_{\beta\sigma} - \mathcal{J}_\beta \mathbf{b}^\star_{\beta\sigma} + \mathbf{A}_\beta \cdot \nabla \mathbf{b}^\star_{\beta\sigma} \right\rangle. \quad (7.114)$$

The first-order exchange and distribution coefficients read

$$h^\star_\beta = \left\langle \mathcal{L}_\beta \mathsf{a}^\star_\beta \right\rangle \quad \text{and} \quad \xi^\star_\beta = a_v^{-1} \left\langle \mathcal{L}_\beta \mathsf{c}^\star_\beta \right\rangle. \quad (7.115)$$

For the other phase, we obtain an equivalent expression

$$\varepsilon_\sigma \Gamma_a \partial_t \langle u_\sigma \rangle^\sigma - \langle \mathcal{L}_\sigma \rangle \langle u_\sigma \rangle^\sigma - \varepsilon_\sigma R_\sigma \left(\langle u_\sigma \rangle^\sigma \right) = -\nabla \cdot \left(\partial_t \mathbf{d}^\star_{\sigma\beta} \star \langle u_\beta \rangle^\beta \right) - \nabla \cdot \left(\partial_t \mathbf{d}^\star_{\sigma\sigma} \star \langle u_\sigma \rangle^\sigma \right)$$
$$+ \nabla \cdot \left(\partial_t \mathbf{B}^\star_{\sigma\beta} \cdot\star \nabla \langle u_\beta \rangle^\beta \right) + \nabla \cdot \left(\partial_t \mathbf{B}^\star_{\sigma\sigma} \cdot\star \nabla \langle u_\sigma \rangle^\sigma \right)$$
$$+ \partial_t h^\star_\sigma \star \left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma \right) + a_v \partial_t \xi^\star_\sigma \star \Omega \left(\langle u_\sigma \rangle^\sigma \right), \quad (7.116)$$

with velocity-like terms

$$\mathbf{d}^\star_{\sigma\beta} = -\left\langle \mathcal{L}_\sigma \mathbf{b}^\star_{\sigma\beta} - \mathcal{J}_\sigma \mathsf{a}^\star_\sigma + \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathsf{a}^\star_\sigma \right\rangle, \quad (7.117)$$

$$\mathbf{d}^\star_{\sigma\sigma} = -\left\langle \mathcal{L}_\sigma \mathbf{b}^\star_{\sigma\sigma} + \mathcal{J}_\sigma \mathsf{a}^\star_\sigma - \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathsf{a}^\star_\sigma \right\rangle, \quad (7.118)$$

and dispersion-like terms

$$\mathbf{B}^\star_{\sigma\beta} = \left\langle \mathcal{L}_\sigma \mathbf{W}^\star_{\sigma\beta} - \mathcal{J}_\sigma \mathbf{b}^\star_{\sigma\beta} + \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{b}^\star_{\sigma\beta} \right\rangle, \tag{7.119}$$

$$\mathbf{B}^\star_{\sigma\sigma} = \left\langle \mathcal{L}_\sigma \mathbf{W}^\star_{\sigma\sigma} - \mathcal{J}_\sigma \mathbf{b}^\star_{\sigma\sigma} + \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{b}^\star_{\sigma\sigma} \right\rangle. \tag{7.120}$$

The first-order exchange and distribution coefficients read

$$h^\star_\sigma = \left\langle \mathcal{L}_\sigma \mathsf{a}^\star_\sigma \right\rangle \quad \text{and} \quad \xi^\star_\sigma = a_v^{-1} \left\langle \mathcal{L}_\sigma \mathsf{c}^\star_\sigma \right\rangle. \tag{7.121}$$

The macroscale expressions can be slightly simplified by remarking that these effective parameters are not independent. In particular, we have that

$$-h^\star_\beta = h^\star_\sigma \equiv h^\star, \tag{7.122}$$

$$-\xi^\star_\beta = H(t) + \xi^\star_\sigma \equiv \xi^\star. \tag{7.123}$$

These relations can be easily proven via flux considerations. For example,

$$h^\star_\beta = \left\langle \mathcal{L}_\beta \mathsf{a}^\star_\beta \right\rangle \simeq \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla \mathsf{a}^\star_\beta \right) dA, \tag{7.124}$$

$$h^\star_\sigma = \left\langle \mathcal{L}_\sigma \mathsf{a}^\star_\sigma \right\rangle \simeq \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\sigma\beta} \cdot \left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathsf{a}^\star_\sigma \right) dA, \tag{7.125}$$

with

$$\mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla \mathsf{a}^\star_\beta - \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathsf{a}^\star_\sigma \right) = 0, \tag{7.126}$$

on the boundary, so that $-h^\star_\beta = h^\star_\sigma$. For $\xi^\star$, we must consider a jump in the flux value that yields $-\xi^\star_\beta = H(t) + \xi^\star_\sigma \equiv \xi^\star$.

We can therefore rewrite the system of equations as

$$\begin{aligned}
\varepsilon_\beta \partial_t \left\langle u_\beta \right\rangle^\beta - \left\langle \mathcal{L}_\beta \right\rangle \left\langle u_\beta \right\rangle^\beta - \varepsilon_\beta R_\beta \left(\left\langle u_\beta \right\rangle^\beta \right) = &-\nabla \cdot \left(\partial_t \mathbf{d}^\star_{\beta\beta} \star \left\langle u_\beta \right\rangle^\beta \right) - \nabla \cdot \left(\partial_t \mathbf{d}^\star_{\beta\sigma} \star \left\langle u_\sigma \right\rangle^\sigma \right) \\
&+ \nabla \cdot \left(\partial_t \mathbf{B}^\star_{\beta\beta} \cdot \star \nabla \left\langle u_\beta \right\rangle^\beta \right) + \nabla \cdot \left(\partial_t \mathbf{B}^\star_{\beta\sigma} \cdot \star \nabla \left\langle u_\sigma \right\rangle^\sigma \right) \\
&- \partial_t h^\star \star \left(\left\langle u_\beta \right\rangle^\beta - \left\langle u_\sigma \right\rangle^\sigma \right) - a_v \partial_t \xi^\star \star \Omega \left(\left\langle u_\sigma \right\rangle^\sigma \right),
\end{aligned} \tag{7.127}$$

$$\begin{aligned}
\varepsilon_\sigma \Gamma_a \partial_t \left\langle u_\sigma \right\rangle^\sigma - \left\langle \mathcal{L}_\sigma \right\rangle \left\langle u_\sigma \right\rangle^\sigma - \varepsilon_\sigma R_\sigma \left(\left\langle u_\sigma \right\rangle^\sigma \right) + a_v \Omega \left(\left\langle u_\sigma \right\rangle^\sigma \right) = &-\nabla \cdot \left(\partial_t \mathbf{d}^\star_{\sigma\beta} \star \left\langle u_\beta \right\rangle^\beta \right) - \nabla \cdot \left(\partial_t \mathbf{d}^\star_{\sigma\sigma} \star \left\langle u_\sigma \right\rangle^\sigma \right) \\
&+ \nabla \cdot \left(\partial_t \mathbf{B}^\star_{\sigma\beta} \cdot \star \nabla \left\langle u_\beta \right\rangle^\beta \right) + \nabla \cdot \left(\partial_t \mathbf{B}^\star_{\sigma\sigma} \cdot \star \nabla \left\langle u_\sigma \right\rangle^\sigma \right) \\
&+ \partial_t h^\star \star \left(\left\langle u_\beta \right\rangle^\beta - \left\langle u_\sigma \right\rangle^\sigma \right) + a_v \partial_t \xi^\star \star \Omega \left(\left\langle u_\sigma \right\rangle^\sigma \right).
\end{aligned} \tag{7.128}$$

Note that we have grouped terms involving the time convolution on the RHS of the fully transient model. We can write these equations in a more compact nonconservative way as

$$\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \Gamma_a \end{bmatrix} \partial_t \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix} + \partial_t \begin{bmatrix} \mathbf{V}^\star_{\beta\beta} & \mathbf{V}^\star_{\beta\sigma} \\ \mathbf{V}^\star_{\sigma\beta} & \mathbf{V}^\star_{\sigma\sigma} \end{bmatrix} \cdot\star \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}$$
$$= \partial_t \begin{bmatrix} \mathbf{A}^\star_{\beta\beta} & \mathbf{A}^\star_{\beta\sigma} \\ \mathbf{A}^\star_{\sigma\beta} & \mathbf{A}^\star_{\sigma\sigma} \end{bmatrix} :\star \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} + \partial_t \begin{bmatrix} -h^\star & +h^\star \\ +h^\star & -h^\star \end{bmatrix} \star \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix}$$
$$+ \begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \end{bmatrix} \begin{bmatrix} R_\beta\left(\langle u_\beta \rangle^\beta\right) \\ R_\sigma\left(\langle u_\sigma \rangle^\sigma\right) \end{bmatrix} - \partial_t \begin{bmatrix} a_v \xi^\star & 0 \\ 0 & a_v\left(H(t) - \xi^\star\right) \end{bmatrix} \star \begin{bmatrix} \Omega\left(\langle u_\sigma \rangle^\sigma\right) \\ \Omega\left(\langle u_\sigma \rangle^\sigma\right) \end{bmatrix} \quad (7.129)$$

with

$$\begin{bmatrix} \mathbf{V}^\star_{\beta\beta} & \mathbf{V}^\star_{\beta\sigma} \\ \mathbf{V}^\star_{\sigma\beta} & \mathbf{V}^\star_{\sigma\sigma} \end{bmatrix} = \begin{bmatrix} \mathrm{Pe}^\ell_\beta \langle \mathbf{v}_\beta \rangle H(t) + \mathbf{d}^\star_{\beta\beta} & \mathbf{d}^\star_{\beta\sigma} \\ \mathbf{d}^\star_{\sigma\beta} & \mathbf{d}^\star_{\sigma\sigma} \end{bmatrix}, \quad (7.130)$$

$$\begin{bmatrix} \mathbf{A}^\star_{\beta\beta} & \mathbf{A}^\star_{\beta\sigma} \\ \mathbf{A}^\star_{\sigma\beta} & \mathbf{A}^\star_{\sigma\sigma} \end{bmatrix} = \begin{bmatrix} \varepsilon_\beta \mathbf{A}_\beta H(t) + \mathbf{B}^\star_{\beta\beta} & \mathbf{B}^\star_{\beta\sigma} \\ \mathbf{B}^\star_{\sigma\beta} & \varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma H(t) + \mathbf{B}^\star_{\sigma\sigma} \end{bmatrix}. \quad (7.131)$$

7.5.5.2 Two-Equation Quasi-Stationary

For the quasi-stationary version of the two-equation model, we can write

$$\varepsilon_\beta \left[\partial_t \langle u_\beta \rangle^\beta + \nabla\cdot\left(\mathrm{Pe}^\ell_\beta \langle \mathbf{v}_\beta \rangle^\beta \langle u_\beta \rangle^\beta\right)\right] + \nabla\cdot\left(\mathbf{d}_{\beta\beta} \langle u_\beta \rangle^\beta\right) + \nabla\cdot\left(\mathbf{d}_{\beta\sigma} \langle u_\sigma \rangle^\sigma\right)$$
$$= \nabla\cdot\left[\left(\varepsilon_\beta \mathbf{A}_\beta + \mathbf{B}_{\beta\beta}\right)\cdot\nabla\langle u_\beta \rangle^\beta\right] + \nabla\cdot\left(\mathbf{B}_{\beta\sigma}\cdot\nabla\langle u_\sigma \rangle^\sigma\right)$$
$$- h\left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma\right) + \varepsilon_\beta R_\beta\left(\langle u_\beta \rangle^\beta\right) - a_v \xi \Omega\left(\langle u_\sigma \rangle^\sigma\right), \quad (7.132)$$

$$\varepsilon_\sigma \Gamma_a \partial_t \langle u_\sigma \rangle^\sigma + \nabla\cdot\left(\mathbf{d}_{\sigma\beta} \langle u_\beta \rangle^\beta\right) + \nabla\cdot\left(\mathbf{d}_{\sigma\sigma} \langle u_\sigma \rangle^\sigma\right)$$
$$= \nabla\cdot\left(\mathbf{B}_{\sigma\beta}\cdot\nabla\langle u_\beta \rangle^\beta\right) + \nabla\cdot\left[\left(\varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma + \mathbf{B}_{\sigma\sigma}\right)\cdot\nabla\langle u_\sigma \rangle^\sigma\right]$$
$$+ h\left(\langle u_\beta \rangle^\beta - \langle u_\sigma \rangle^\sigma\right) + \varepsilon_\sigma R_\sigma\left(\langle u_\sigma \rangle^\sigma\right) - a_v (1-\xi) \Omega\left(\langle u_\sigma \rangle^\sigma\right). \quad (7.133)$$

Effective velocities are

$$\mathbf{d}_{\beta\beta} = -\left\langle \mathcal{L}_\beta \mathbf{b}_{\beta\beta} - \mathcal{J}_\beta \mathsf{a}_\beta + \mathbf{A}_\beta \cdot \nabla \mathsf{a}_\beta \right\rangle, \quad \mathbf{d}_{\beta\sigma} = -\left\langle \mathcal{L}_\beta \mathbf{b}_{\beta\sigma} + \mathcal{J}_\beta \mathsf{a}_\beta - \mathbf{A}_\beta \cdot \nabla \mathsf{a}_\beta \right\rangle, \quad (7.134)$$

$$\mathbf{d}_{\sigma\beta} = -\left\langle \mathcal{L}_\sigma \mathbf{b}_{\sigma\beta} - \mathcal{J}_\sigma \mathsf{a}_\sigma + \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathsf{a}_\sigma \right\rangle, \quad \mathbf{d}_{\sigma\sigma} = -\left\langle \mathcal{L}_\sigma \mathbf{b}_{\sigma\sigma} + \mathcal{J}_\sigma \mathsf{a}_\sigma - \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathsf{a}_\sigma \right\rangle, \quad (7.135)$$

and dispersion-like terms are

$$\mathbf{B}_{\beta\beta} = \left\langle \mathcal{L}_\beta \mathbf{W}_{\beta\beta} - \mathcal{J}_\beta \mathbf{b}_{\beta\beta} + \mathbf{A}_\beta \cdot \nabla \mathbf{b}_{\beta\beta} \right\rangle, \quad \mathbf{B}_{\beta\sigma} = \left\langle \mathcal{L}_\beta \mathbf{W}_{\beta\sigma} - \mathcal{J}_\beta \mathbf{b}_{\beta\sigma} + \mathbf{A}_\beta \cdot \nabla \mathbf{b}_{\beta\sigma} \right\rangle, \quad (7.136)$$

$$\mathbf{B}_{\sigma\beta} = \left\langle \mathcal{L}_\sigma \mathbf{W}_{\sigma\beta} - \mathcal{J}_\sigma \mathbf{b}_{\sigma\beta} + \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{b}_{\sigma\beta} \right\rangle, \quad \mathbf{B}_{\sigma\sigma} = \left\langle \mathcal{L}_\sigma \mathbf{W}_{\sigma\sigma} - \mathcal{J}_\sigma \mathbf{b}_{\sigma\sigma} + \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{b}_{\sigma\sigma} \right\rangle. \tag{7.137}$$

The first-order exchange and distribution coefficients read

$$h = -\left\langle \mathcal{L}_\beta \mathbf{a}_\beta \right\rangle \quad \text{and} \quad \xi = -a_v^{-1} \left\langle \mathcal{L}_\beta \mathbf{c}_\beta \right\rangle. \tag{7.138}$$

A more compact nonconservative version of these equations reads

$$\begin{aligned} &\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \Gamma_a \end{bmatrix} \partial_t \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix} + \begin{bmatrix} \mathbf{V}_{\beta\beta} & \mathbf{V}_{\beta\sigma} \\ \mathbf{V}_{\sigma\beta} & \mathbf{V}_{\sigma\sigma} \end{bmatrix} \cdot \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} \\ = &\begin{bmatrix} \mathbf{A}_{\beta\beta} & \mathbf{A}_{\beta\sigma} \\ \mathbf{A}_{\sigma\beta} & \mathbf{A}_{\sigma\sigma} \end{bmatrix} : \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} + \begin{bmatrix} -h & +h \\ +h & -h \end{bmatrix} \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix} \\ &+ \begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \end{bmatrix} \begin{bmatrix} R_\beta \left(\langle u_\beta \rangle^\beta \right) \\ R_\sigma \left(\langle u_\sigma \rangle^\sigma \right) \end{bmatrix} - \begin{bmatrix} a_v \xi & 0 \\ 0 & a_v (1-\xi) \end{bmatrix} \begin{bmatrix} \Omega \left(\langle u_\sigma \rangle^\sigma \right) \\ \Omega \left(\langle u_\sigma \rangle^\sigma \right) \end{bmatrix} \end{aligned} \tag{7.139}$$

with

$$\begin{bmatrix} \mathbf{V}_{\beta\beta} & \mathbf{V}_{\beta\sigma} \\ \mathbf{V}_{\sigma\beta} & \mathbf{V}_{\sigma\sigma} \end{bmatrix} = \begin{bmatrix} \mathrm{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta \right\rangle + \mathbf{d}_{\beta\beta} & \mathbf{d}_{\beta\sigma} \\ \mathbf{d}_{\sigma\beta} & \mathbf{d}_{\sigma\sigma} \end{bmatrix}, \tag{7.140}$$

and

$$\begin{bmatrix} \mathbf{A}_{\beta\beta} & \mathbf{A}_{\beta\sigma} \\ \mathbf{A}_{\sigma\beta} & \mathbf{A}_{\sigma\sigma} \end{bmatrix} = \begin{bmatrix} \varepsilon_\beta \mathbf{A}_\beta + \mathbf{B}_{\beta\beta} & \mathbf{B}_{\beta\sigma} \\ \mathbf{B}_{\sigma\beta} & \varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma + \mathbf{B}_{\sigma\sigma} \end{bmatrix}. \tag{7.141}$$

7.5.5.3 Two-Equation Quasi-Stationary with Fluxes

In the previous equations, we have grouped together terms that are of similar mathematical types. For instance, this was done for terms involving convolutions, or advective and diffusive parts of the spatial operators. Two-equation models can also be interpreted in a more physical way where the macroscale equations for each phase are decomposed in advection–dispersion equations with multiphase corrections and an interfacial flux that contains different types of mathematical operators. To obtain this formulation for the steady closure, we use Equations 7.57 and 7.58, which can be written, using the spatial amplitude and frequency approximations, as

$$\begin{aligned} &\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \Gamma_a \end{bmatrix} \partial_t \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix} + \begin{bmatrix} \mathbf{V}_{\beta\beta} & \mathbf{V}_{\beta\sigma} \\ \mathbf{V}_{\sigma\beta} & \mathbf{V}_{\sigma\sigma} \end{bmatrix} \cdot \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} \\ = &\begin{bmatrix} \mathbf{A}_{\beta\beta} & \mathbf{A}_{\beta\sigma} \\ \mathbf{A}_{\sigma\beta} & \mathbf{A}_{\sigma\sigma} \end{bmatrix} : \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} + \begin{bmatrix} -h & +h \\ +h & -h \end{bmatrix} \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix} \\ &+ \begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \end{bmatrix} \begin{bmatrix} R_\beta \left(\langle u_\beta \rangle^\beta \right) \\ R_\sigma \left(\langle u_\sigma \rangle^\sigma \right) \end{bmatrix} - \begin{bmatrix} a_v \xi & 0 \\ 0 & a_v (1-\xi) \end{bmatrix} \begin{bmatrix} \Omega \left(\langle u_\sigma \rangle^\sigma \right) \\ \Omega \left(\langle u_\sigma \rangle^\sigma \right) \end{bmatrix} \end{aligned} \tag{7.142}$$

and

$$\underbrace{\varepsilon_\sigma\Gamma_a\,\partial_t\langle u_\sigma\rangle^\sigma}_{\text{Rate of change}} = \nabla\cdot\left[\varepsilon_\sigma\Gamma_A\mathbf{A}_\sigma\cdot\left(\underbrace{\nabla\langle u_\sigma\rangle^\sigma}_{\text{Diffusion}} + \underbrace{\frac{1}{V_\sigma}\int_{\mathcal{A}_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\tilde{u}_\sigma dA}_{\text{Surface effects}}\right)\right]$$

$$+\underbrace{\frac{1}{V}\int_{\mathcal{A}_{\sigma\beta}}\mathbf{n}_{\sigma\beta}\cdot\left(\Gamma_A\mathbf{A}_\sigma\cdot\nabla\tilde{u}_\sigma\right)dA}_{\text{Interfacial flux}} + \underbrace{\varepsilon_\sigma R_\sigma\left(\langle u_\sigma\rangle^\sigma\right)}_{\text{Average reaction rate}}. \tag{7.143}$$

We first focus on the interfacial flux in Equation 7.142, which reads

$$\mathsf{J}_{\beta\sigma} \equiv -\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\left(\mathbf{A}_\beta\cdot\nabla\tilde{u}_\beta\right)dA. \tag{7.144}$$

We also have

$$\mathsf{J}_{\beta\sigma} \equiv \frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}}\mathbf{n}_{\sigma\beta}\cdot\left(\Gamma_A\mathbf{A}_\sigma\cdot\nabla\tilde{u}_\sigma\right)dA + a_v\Omega\left(\langle u_\sigma\rangle^\sigma\right), \tag{7.145}$$

using the reactive boundary condition with $a_v = \dfrac{A_{\beta\sigma}}{V}$ and therefore

$$\mathsf{J}_{\beta\sigma} = -\mathsf{J}_{\sigma\beta} + a_v\Omega\left(\langle u_\sigma\rangle^\sigma\right). \tag{7.146}$$

We can use the steady closure

$$\tilde{u}_\beta = \mathsf{a}_\beta\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right) + \begin{bmatrix}\mathbf{b}_{\beta\beta} & \mathbf{b}_{\beta\sigma}\end{bmatrix}\cdot\begin{bmatrix}\nabla\langle u_\beta\rangle^\beta \\ \nabla\langle u_\sigma\rangle^\sigma\end{bmatrix}$$

$$+\begin{bmatrix}\mathbf{W}_{\beta\beta} & \mathbf{W}_{\beta\sigma}\end{bmatrix}:\begin{bmatrix}\nabla\nabla\langle u_\beta\rangle^\beta \\ \nabla\nabla\langle u_\sigma\rangle^\sigma\end{bmatrix} + \mathsf{c}_\beta\Omega\left(\langle u_\sigma\rangle^\sigma\right), \tag{7.147}$$

to obtain

$$
\begin{aligned}
\mathbf{J}_{\beta\sigma} = &-\left[\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(\mathbf{A}_\beta\cdot\nabla \mathbf{a}_\beta\right)dA\right]\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right)\\
&-\left[\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left[\mathbf{A}_\beta\cdot\left(\nabla\mathbf{b}_{\beta\beta} + \mathbf{a}_\beta\mathbf{I}\right)\right]dA\right]\cdot\nabla\langle u_\beta\rangle^\beta\\
&-\left[\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left[\mathbf{A}_\beta\cdot\left(\nabla\mathbf{b}_{\beta\sigma} - \mathbf{a}_\beta\mathbf{I}\right)\right]dA\right]\cdot\nabla\langle u_\sigma\rangle^\sigma\\
&-\left[\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left[\mathbf{A}_\beta\cdot\left(\nabla\mathbf{W}_{\beta\beta} + \mathbf{b}_{\beta\beta}\mathbf{I}\right)\right]dA\right]:\nabla\nabla\langle u_\beta\rangle^\beta\\
&-\left[\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left[\mathbf{A}_\beta\cdot\left(\nabla\mathbf{W}_{\beta\sigma} + \mathbf{b}_{\beta\sigma}\mathbf{I}\right)\right]dA\right]:\nabla\nabla\langle u_\sigma\rangle^\sigma\\
&-\left[\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(\mathbf{A}_\beta\cdot\nabla \mathbf{c}_\beta\right)dA\right]\Omega\left(\langle u_\sigma\rangle^\sigma\right),
\end{aligned}
\tag{7.148}
$$

which for a homogeneous porous medium can be put as

$$
\begin{aligned}
\mathbf{J}_{\beta\sigma} = &\, h\underbrace{\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right)}_{\text{First-order exchange}} + \underbrace{a_v\xi\Omega\left(\langle u_\sigma\rangle^\sigma\right)}_{\text{Flux component from the surface source}}\\
&-\left\langle\nabla\cdot\left(\mathbf{A}_\beta\cdot\nabla\mathbf{b}_{\beta\beta}\right) + \mathbf{A}_\beta\cdot\nabla\mathbf{a}_\beta\right\rangle\cdot\nabla\langle u_\beta\rangle^\beta\\
&-\left\langle\nabla\cdot\left(\mathbf{A}_\beta\cdot\nabla\mathbf{b}_{\beta\sigma}\right) - \mathbf{A}_\beta\cdot\nabla\mathbf{a}_\beta\right\rangle\cdot\nabla\langle u_\sigma\rangle^\sigma\\
&-\left\langle\nabla\cdot\left(\mathbf{A}_\beta\cdot\nabla\mathbf{W}_{\beta\beta}\right) + \mathbf{A}_\beta\cdot\nabla\mathbf{b}_{\beta\beta}\right\rangle\cdot\nabla\nabla\langle u_\beta\rangle^\beta\\
&-\left\langle\nabla\cdot\left(\mathbf{A}_\beta\cdot\nabla\mathbf{W}_{\beta\sigma}\right) + \mathbf{A}_\beta\cdot\nabla\mathbf{b}_{\beta\sigma}\right\rangle\cdot\nabla\nabla\langle u_\sigma\rangle^\sigma.
\end{aligned}
\tag{7.149}
$$

We also have the relationship

$$
\mathbf{J}_{\sigma\beta} = -\mathbf{J}_{\beta\sigma} + a_v\Omega\left(\langle u_\sigma\rangle^\sigma\right). \tag{7.150}
$$

The surface effect term reads

$$\zeta_\beta \equiv \frac{1}{V_\beta}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{u}_\beta dA \simeq \frac{1}{V_\beta}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\mathsf{a}_\beta dA\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right)$$
$$+\frac{1}{V_\beta}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\left[\mathbf{b}_{\beta\beta} \quad \mathbf{b}_{\beta\sigma}\right] dA \cdot \begin{bmatrix}\nabla\langle u_\beta\rangle^\beta \\ \nabla\langle u_\sigma\rangle^\sigma\end{bmatrix}$$
$$+\frac{1}{V_\beta}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\mathsf{c}_\beta dA\,\Omega\left(\langle u_\sigma\rangle^\sigma\right), \tag{7.151}$$

that we approximate as

$$\zeta_\beta \simeq \underbrace{\langle\nabla\mathsf{a}_\beta\rangle^\beta}_{\text{Advective tortuosity}}\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right) + \underbrace{\langle\nabla\left[\mathbf{b}_{\beta\beta} \quad \mathbf{b}_{\beta\sigma}\right]\rangle^\beta}_{\text{Diffusive tortuosity}}\cdot\begin{bmatrix}\nabla\langle u_\beta\rangle^\beta \\ \nabla\langle u_\sigma\rangle^\sigma\end{bmatrix} + \underbrace{\langle\nabla\mathsf{c}_\beta\rangle^\beta}_{\text{Reactive tortuosity}}\Omega\left(\langle u_\sigma\rangle^\sigma\right). \tag{7.152}$$

Similarly, we have

$$\zeta_\sigma \simeq \underbrace{\langle\nabla\mathsf{a}_\sigma\rangle^\sigma}_{\text{Advective tortuosity}}\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right) + \underbrace{\langle\nabla\left[\mathbf{b}_{\sigma\beta} \quad \mathbf{b}_{\sigma\sigma}\right]\rangle^\sigma}_{\text{Diffusive tortuosity}}\cdot\begin{bmatrix}\nabla\langle u_\beta\rangle^\beta \\ \nabla\langle u_\sigma\rangle^\sigma\end{bmatrix} + \underbrace{\langle\nabla\mathsf{c}_\sigma\rangle^\sigma}_{\text{Reactive tortuosity}}\Omega\left(\langle u_\sigma\rangle^\sigma\right). \tag{7.153}$$

Further, the velocity fluctuation effects may be written as

$$\theta_\beta \equiv \langle\tilde{\mathbf{v}}_\beta\tilde{u}_\beta\rangle^\beta \simeq \underbrace{\langle\tilde{\mathbf{v}}_\beta\mathsf{a}_\beta\rangle^\beta}_{\text{Flux velocity correction}}\left(\langle u_\beta\rangle^\beta - \langle u_\sigma\rangle^\sigma\right) + \underbrace{\langle\tilde{\mathbf{v}}_\beta\left[\mathbf{b}_{\beta\beta} \quad \mathbf{b}_{\beta\sigma}\right]\rangle^\beta}_{\text{Hydrodynamic dispersion}}\cdot\begin{bmatrix}\nabla\langle u_\beta\rangle^\beta \\ \nabla\langle u_\sigma\rangle^\sigma\end{bmatrix}$$
$$+ \underbrace{\langle\tilde{\mathbf{v}}_\beta\mathsf{c}_\beta\rangle^\beta}_{\text{Flux reactive correction}}\Omega\left(\langle u_\sigma\rangle^\sigma\right). \tag{7.154}$$

We neglect terms involving $\Omega(\langle u_\sigma\rangle^\sigma)$ assuming that $\nabla\Omega(\langle u_\sigma\rangle^\sigma)$ are small when considering $\nabla\cdot\boldsymbol{\zeta}$ and $\nabla\cdot\theta$ and keeping in mind that the most restrictive assumption is $\Omega(u_\sigma) \simeq \Omega\,(\langle u_\sigma\rangle^\sigma)$. Therefore, we obtain the following macroscale equations:

$$\varepsilon_\beta\left[\underbrace{\partial_t\langle u_\beta\rangle^\beta}_{\text{Rate of change}} + \mathrm{Pe}_\beta^\ell\nabla\cdot\left(\underbrace{\langle\mathbf{v}_\beta\rangle^\beta\langle u_\beta\rangle^\beta}_{\text{Convection}} + \underbrace{\theta_\beta}_{\text{Velocity fluctuation effects}}\right)\right]$$
$$= \nabla\cdot\left[\varepsilon_\beta\mathbf{A}_\beta\cdot\left(\underbrace{\nabla\langle u_\beta\rangle^\beta}_{\text{Diffusion}} + \underbrace{\zeta_\beta}_{\text{Surface effects}}\right)\right] + \underbrace{\varepsilon_\beta R_\beta\left(\langle u_\beta\rangle^\beta\right)}_{\text{Average reaction rate}} - \underbrace{\mathsf{J}_{\beta\sigma}}_{\text{Interfacial flux}}. \tag{7.155}$$

and

$$\varepsilon_\sigma \Gamma_a \underbrace{\partial_t \left\langle u_\sigma \right\rangle^\sigma}_{\text{Rate of change}} = \nabla \cdot \left[\varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma \cdot \left(\underbrace{\nabla \left\langle u_\sigma \right\rangle^\sigma}_{\text{Diffusion}} + \underbrace{\zeta_\sigma}_{\text{Surface effects}} \right) \right] - \underbrace{\mathbf{J}_{\sigma\beta}}_{\text{Interfacial flux}} + \underbrace{\varepsilon_\sigma R_\sigma \left(\left\langle u_\sigma \right\rangle^\sigma \right)}_{\text{Average reaction rate}}. \tag{7.156}$$

We remark that higher-order exchange terms are often overlooked in the literature, as well as the additional advective terms. There is no clear answer as to the relative effect of these terms, although several examples have shown that they may significantly affect the macroscale fields [67,121], at least for simple unit cells.

7.5.5.4 Two-Equation Variants

The hypothesis regarding the timescales for the relaxation of the mapping variables can be made independently for each effective parameter. Physically, this stems from the fact that there may be significant differences between characteristic times for relaxation of these mapping variables. In particular, it has been shown that the exchange parameters $h^\star$ and $\xi^\star$ [76] may exhibit a longer relaxation than other effective parameters. Therefore, it may be interesting to consider the following variant of the two-equation transient model:

$$\begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \Gamma_a \end{bmatrix} \partial_t \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix} + \begin{bmatrix} \mathbf{V}_{\beta\beta} & \mathbf{V}_{\beta\sigma} \\ \mathbf{V}_{\sigma\beta} & \mathbf{V}_{\sigma\sigma} \end{bmatrix} \cdot \begin{bmatrix} \nabla \langle u_\beta \rangle^\beta \\ \nabla \langle u_\sigma \rangle^\sigma \end{bmatrix}$$

$$= \begin{bmatrix} \mathbf{A}_{\beta\beta} & \mathbf{A}_{\beta\sigma} \\ \mathbf{A}_{\sigma\beta} & \mathbf{A}_{\sigma\sigma} \end{bmatrix} : \begin{bmatrix} \nabla\nabla \langle u_\beta \rangle^\beta \\ \nabla\nabla \langle u_\sigma \rangle^\sigma \end{bmatrix} + \partial_t \begin{bmatrix} -h^\star & +h^\star \\ +h^\star & -h^\star \end{bmatrix} \star \begin{bmatrix} \langle u_\beta \rangle^\beta \\ \langle u_\sigma \rangle^\sigma \end{bmatrix}$$

$$+ \begin{bmatrix} \varepsilon_\beta & 0 \\ 0 & \varepsilon_\sigma \end{bmatrix} \begin{bmatrix} R_\beta \left(\langle u_\beta \rangle^\beta \right) \\ R_\sigma \left(\langle u_\sigma \rangle^\sigma \right) \end{bmatrix} - \partial_t \begin{bmatrix} a_v \xi^\star & 0 \\ 0 & a_v \left(H(t) - \xi^\star \right) \end{bmatrix} \star \begin{bmatrix} \Omega\left(\langle u_\sigma \rangle^\sigma \right) \\ \Omega\left(\langle u_\sigma \rangle^\sigma \right) \end{bmatrix} \tag{7.157}$$

7.6 DERIVATION OF THE ONE-EQUATION LE MODEL

7.6.1 Approximations

The LE model is based on the idea that gradients at the microscale are sufficiently small, so that we can use the following approximation (see [17,37]):

$$\left\langle u_\beta \right\rangle^\beta \simeq \left\langle u_\sigma \right\rangle^\sigma \simeq \left\langle u \right\rangle^{\beta\sigma}. \tag{7.158}$$

We use this approximation for any value of the spatial variable $\mathbf{x}$ and any time t, so that we also have

$$\nabla \left\langle u_\beta \right\rangle^\beta \simeq \nabla \left\langle u_\sigma \right\rangle^\sigma \simeq \nabla \left\langle u \right\rangle^{\beta\sigma}, \tag{7.159}$$

$$\nabla\nabla \left\langle u_\beta \right\rangle^\beta \simeq \nabla\nabla \left\langle u_\sigma \right\rangle^\sigma \simeq \nabla\nabla \left\langle u \right\rangle^{\beta\sigma}, \tag{7.160}$$

$$\partial_t \left\langle u_\beta \right\rangle^\beta \simeq \partial_t \left\langle u_\sigma \right\rangle^\sigma \simeq \partial_t \left\langle u \right\rangle^{\beta\sigma}. \tag{7.161}$$

7.6.2 Closure

7.6.2.1 LE Quasi-Stationary Closure

With these approximations, we can now simplify the more general closure proposed in Section 7.5. LE is already a restrictive constraint, and it is often not compatible with a fully transient closure. We therefore focus on the following stationary form of the perturbations that is derived directly from Equation 7.82:

$$\begin{bmatrix} \tilde{u}_\beta \\ \tilde{u}_\sigma \end{bmatrix} = \begin{bmatrix} \mathbf{b}_\beta^{\mathrm{LE}} \\ \mathbf{b}_\sigma^{\mathrm{LE}} \end{bmatrix} \cdot \nabla \langle u \rangle^{\beta\sigma} + \begin{bmatrix} \mathbf{W}_\beta^{\mathrm{LE}} \\ \mathbf{W}_\sigma^{\mathrm{LE}} \end{bmatrix} : \nabla\nabla \langle u \rangle^{\beta\sigma} + \begin{bmatrix} \mathbf{c}_\beta^{\mathrm{LE}} \\ \mathbf{c}_\sigma^{\mathrm{LE}} \end{bmatrix} \Omega\left(\langle u \rangle^{\beta\sigma} \right), \tag{7.162}$$

with the relationships $\mathbf{b}_\beta^{\mathrm{LE}} = \mathbf{b}_{\beta\beta} + \mathbf{b}_{\beta\sigma}$, $\mathbf{b}_\sigma^{\mathrm{LE}} = \mathbf{b}_{\sigma\beta} + \mathbf{b}_{\sigma\sigma}$, $\mathbf{W}_\beta^{\mathrm{LE}} = \mathbf{W}_{\beta\beta} + \mathbf{W}_{\beta\sigma}$, and $\mathbf{W}_\sigma^{\mathrm{LE}} = \mathbf{W}_{\sigma\beta} + \mathbf{W}_{\sigma\sigma}$.

7.6.2.2 Closure Problems

The corresponding closure problems are as follows (see also [17]):

7.6.2.2.1 *Problem LE-Stationary-I*

$$-\widetilde{\mathcal{L}_\beta \mathbf{b}_\beta^{\mathrm{LE}}} = -\tilde{\mathbf{v}}_\beta \text{ in } \mathcal{V}_\beta, \tag{7.163a}$$

$$\text{BC1} \quad \mathbf{b}_\beta^{\mathrm{LE}} - \mathbf{b}_\sigma^{\mathrm{LE}} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.163b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{b}_\beta^{\mathrm{LE}} - \mathcal{B}_\sigma \mathbf{b}_\sigma^{\mathrm{LE}} = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta - \Gamma_A \mathbf{A}_\sigma \right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.163c}$$

$$\text{Periodicity 1} \quad \mathbf{b}_\alpha^{\mathrm{LE}}\left(\mathbf{x} + \mathbf{l}_i\right) = \mathbf{b}_\alpha^{\mathrm{LE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta, \sigma, \tag{7.163d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{b}_\alpha^{\mathrm{LE}}\left(\mathbf{x} + \mathbf{l}_i\right) = \mathcal{J}_\alpha \mathbf{b}_\alpha^{\mathrm{LE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta, \sigma, \tag{7.163e}$$

$$\text{Average} \quad \left\langle \mathbf{b}_\alpha^{\mathrm{LE}} \right\rangle = 0 \text{ with } \alpha = \beta, \sigma, \tag{7.163f}$$

$$-\widetilde{\mathcal{L}_\sigma \mathbf{b}_\sigma^{\mathrm{LE}}} = 0 \text{ in } \mathcal{V}_\sigma. \tag{7.163g}$$

7.6.2.2.2 *Problem LE-Stationary-II*

$$-\widetilde{\mathcal{L}_\beta \mathbf{W}_\beta^{\mathrm{LE}}} + \widetilde{\mathcal{J}_\beta \mathbf{b}_\beta^{\mathrm{LE}}} = \mathbf{A}_\beta \cdot \widetilde{\nabla \mathbf{b}_\beta^{\mathrm{LE}}} \text{ in } \mathcal{V}_\beta, \tag{7.164a}$$

$$\text{BC1} \quad \mathbf{W}_\beta^{\mathrm{LE}} - \mathbf{W}_\sigma^{\mathrm{LE}} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.164b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{W}_\beta^{\mathrm{LE}} - \mathcal{B}_\sigma \mathbf{W}_\sigma^{\mathrm{LE}} = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \mathbf{b}_\beta^{\mathrm{LE}} - \Gamma_A \mathbf{A}_\sigma \mathbf{b}_\sigma^{\mathrm{LE}} \right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.164c}$$

$$\text{Periodicity 1} \quad \mathbf{W}_\alpha^{\mathrm{LE}}\left(\mathbf{x} + \mathbf{l}_i\right) = \mathbf{W}_\alpha^{\mathrm{LE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta, \sigma, \tag{7.164d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{W}_\alpha^{\mathrm{LE}}\left(\mathbf{x} + \mathbf{l}_i\right) = \mathcal{J}_\alpha \mathbf{W}_\alpha^{\mathrm{LE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta, \sigma, \tag{7.164e}$$

$$\text{Average} \quad \left\langle \mathbf{W}_\alpha^{\mathrm{LE}} \right\rangle = 0 \text{ with } \alpha = \beta, \sigma, \tag{7.164f}$$

$$-\widetilde{\mathcal{L}_\sigma \mathbf{W}_\sigma^{\mathrm{LE}}} + \widetilde{\mathcal{J}_\sigma \mathbf{b}_\sigma^{\mathrm{LE}}} = \Gamma_A \mathbf{A}_\sigma \cdot \widetilde{\nabla \mathbf{b}_\sigma^{\mathrm{LE}}} \text{ in } \mathcal{V}_\sigma. \tag{7.164g}$$

7.6.2.2.3 Problem LE-Stationary-III

$$-\widetilde{\mathcal{L}_\beta \mathsf{c}_\beta^{\mathrm{LE}}} = 0 \text{ in } \mathcal{V}_\beta, \tag{7.165a}$$

$$\text{BC1} \quad \mathsf{c}_\beta^{\mathrm{LE}} - \mathsf{c}_\sigma^{\mathrm{LE}} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.165b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathsf{c}_\beta^{\mathrm{LE}} - \mathcal{B}_\sigma \mathsf{c}_\sigma^{\mathrm{LE}} = 1 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.165c}$$

$$\text{Periodicity 1} \quad \mathsf{c}_\alpha^{\mathrm{LE}}\left(\mathbf{x}+\mathbf{l}_i\right) = \mathsf{c}_\alpha^{\mathrm{LE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta,\sigma, \tag{7.165d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathsf{c}_\alpha^{\mathrm{LE}}\left(\mathbf{x}+\mathbf{l}_i\right) = \mathcal{J}_\alpha \mathsf{c}_\alpha^{\mathrm{LE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta,\sigma, \tag{7.165e}$$

$$\text{Average} \quad \left\langle \mathsf{c}_\alpha^{\mathrm{LE}} \right\rangle = 0 \text{ with } \alpha = \beta,\sigma, \tag{7.165f}$$

$$-\widetilde{\mathcal{L}_\sigma \mathsf{c}_\sigma^{\mathrm{LE}}} = 0 \text{ in } \mathcal{V}_\sigma. \tag{7.165g}$$

7.6.3 Macroscale Model

The macroscale model is obtained by summing up Equations 7.132 and 7.133, an operation that leads to

$$\left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\partial_t \langle u \rangle^{\beta\sigma} + \nabla \cdot \left(\varepsilon_\beta \mathrm{Pe}_\beta^\ell \langle \mathbf{v}_\beta \rangle^\beta \langle u \rangle^{\beta\sigma}\right) = \nabla \cdot \left(\mathbf{A}^{\mathrm{LE}} \cdot \nabla \langle u \rangle^{\beta\sigma}\right) + R^{\mathrm{LE}}, \tag{7.166}$$

where we have used the notations

$$\mathbf{A}^{\mathrm{LE}} = \varepsilon_\beta \mathbf{A}_\beta + \mathbf{B}_{\beta\beta} + \mathbf{B}_{\beta\sigma} + \varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma + \mathbf{B}_{\sigma\beta} + \mathbf{B}_{\sigma\sigma}, \tag{7.167}$$

which can also be written as

$$\mathbf{A}^{\mathrm{LE}} = \mathbf{A}_{\beta\beta} + \mathbf{A}_{\beta\sigma} + \mathbf{A}_{\sigma\beta} + \mathbf{A}_{\sigma\sigma}, \tag{7.168}$$

for the effective dispersion tensor, and

$$R^{\mathrm{LE}} = \varepsilon_\beta R_\beta\left(\langle u \rangle^{\beta\sigma}\right) + \varepsilon_\sigma R_\sigma\left(\langle u \rangle^{\beta\sigma}\right) - a_v \Omega\left(\langle u \rangle^{\beta\sigma}\right) \tag{7.169}$$

for the effective reaction rate, which includes both homogeneous and heterogeneous sources. It is also interesting to note that velocity-like terms have disappeared since we have the relationship

$$\mathbf{d}_{\beta\beta} + \mathbf{d}_{\beta\sigma} + \mathbf{d}_{\sigma\beta} + \mathbf{d}_{\sigma\sigma} = 0 \tag{7.170}$$

that can be easily proven by remarking that terms involving the mapping variable a cancel out and that the remaining terms are opposite average fluxes (see Equations 7.124 through 7.126 for similar developments). We also have

$$\begin{aligned}\mathbf{B}_{\beta\beta} + \mathbf{B}_{\beta\sigma} + \mathbf{B}_{\sigma\beta} + \mathbf{B}_{\sigma\sigma} = {} & \left\langle \mathcal{L}_\beta \mathbf{W}_\beta - \mathcal{J}_\beta \mathbf{b}_\beta + \mathbf{A}_\beta \cdot \nabla \mathbf{b}_\beta \right\rangle \\ & + \left\langle \mathcal{L}_\sigma \mathbf{W}_\sigma - \mathcal{J}_\sigma \mathbf{b}_\sigma + \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{b}_\sigma \right\rangle,\end{aligned} \tag{7.171}$$

which can be simplified in

$$\mathbf{B}_{\beta\beta} + \mathbf{B}_{\beta\sigma} + \mathbf{B}_{\sigma\beta} + \mathbf{B}_{\sigma\sigma} = \left\langle \mathbf{A}_\beta \cdot \nabla \mathbf{b}_\beta \right\rangle + \left\langle \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{b}_\sigma \right\rangle - \left\langle \mathbf{v}_\beta \mathbf{b}_\beta \right\rangle, \tag{7.172}$$

where the second-order terms in $\mathbf{W}$ disappear from the macroscale equation because

$$\left\langle \mathcal{L}_\beta \mathbf{W}_\beta - \mathcal{J}_\beta \mathbf{b}_\beta \right\rangle + \left\langle \mathcal{L}_\sigma \mathbf{W}_\sigma - \mathcal{J}_\sigma \mathbf{b}_\sigma \right\rangle = 0,$$

and we have

$$\mathbf{A}^{\mathrm{LE}} = \underbrace{\varepsilon_\beta \mathbf{A}_\beta + \varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma}_{\text{Weighted arithmetic mean}} + \underbrace{\left\langle \mathbf{A}_\beta \cdot \nabla \mathbf{b}_\beta \right\rangle + \left\langle \Gamma_A \mathbf{A}_\sigma \cdot \nabla \mathbf{b}_\sigma \right\rangle}_{\text{Tortuosity}} - \underbrace{\left\langle \mathbf{v}_\beta \mathbf{b}_\beta \right\rangle}_{\text{Hydrodynamic dispersion}}. \tag{7.173}$$

7.7 DERIVATION OF THE ONE-EQUATION NONEQUILIBRIUM MODELS

There are primarily two ways to develop the one-equation nonequilibrium model. One is based on direct averaging and using a special perturbation decomposition. This is the method that we will present in this chapter. The other approach is based on an asymptotic analysis of the two-equation models in terms of spatial moments. This equivalence has been discussed in [94].

7.7.1 Averaging

We define an average over both phases as

$$\langle u \rangle^{\beta\sigma} = \frac{\varepsilon_\beta}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \langle u_\beta \rangle^\beta + \frac{\varepsilon_\sigma \Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \langle u_\sigma \rangle^\sigma, \tag{7.174}$$

and the corresponding perturbation decompositions are

$$u_\beta = \langle u \rangle^{\beta\sigma} + \hat{u}_\beta, \quad u_\sigma = \langle u \rangle^{\beta\sigma} + \hat{u}_\sigma. \tag{7.175}$$

The one-equation macroscale equation is obtained from the phase-average equations derived in Section 7.5 as

$$\varepsilon_\beta \partial_t \langle u_\beta \rangle^\beta = \langle \mathcal{L}_\beta u_\beta \rangle + \langle R_\beta(u_\beta) \rangle, \tag{7.176}$$

$$\varepsilon_\sigma \Gamma_a \partial_t \langle u_\sigma \rangle^\sigma = \langle \mathcal{L}_\sigma u_\sigma \rangle + \langle R_\sigma(u_\sigma) \rangle, \tag{7.177}$$

and summing them yields

$$(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a) \partial_t \langle u \rangle^{\beta\sigma} = \langle \mathcal{L}_\beta u_\beta \rangle + \langle \mathcal{L}_\sigma u_\sigma \rangle + \langle R_\beta(u_\beta) \rangle + \langle R_\sigma(u_\sigma) \rangle. \tag{7.178}$$

We can then apply the average plus perturbation decompositions, so that we have

$$\begin{aligned}(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a) \partial_t \langle u \rangle^{\beta\sigma} &= \left\langle \mathcal{L}_\beta \langle u \rangle^{\beta\sigma} \right\rangle + \left\langle \mathcal{L}_\sigma \langle u \rangle^{\beta\sigma} \right\rangle \\ &\quad + \langle \mathcal{L}_\beta \hat{u}_\beta \rangle + \langle \mathcal{L}_\sigma \hat{u}_\sigma \rangle + \langle R_\beta(u_\beta) \rangle + \langle R_\sigma(u_\sigma) \rangle.\end{aligned} \tag{7.179}$$

7.7.2 Perturbation

We consider the microscale operators that are given by Equations 7.6a and 7.6d and use the perturbation decomposition to obtain

$$\partial_t \langle u \rangle^{\beta\sigma} + \partial_t \hat{u}_\beta = \mathcal{L}_\beta \langle u \rangle^{\beta\sigma} + \mathcal{L}_\beta \hat{u}_\beta + R_\beta(u_\beta) \text{ in } \mathcal{V}_\beta, \tag{7.180a}$$

$$\Gamma_a \partial_t \langle u \rangle^{\beta\sigma} + \Gamma_a \partial_t \hat{u}_\sigma = \mathcal{L}_\sigma \langle u \rangle^{\beta\sigma} + \mathcal{L}_\sigma \hat{u}_\sigma + R_\sigma(u_\sigma) \text{ in } \mathcal{V}_\sigma. \tag{7.180b}$$

The perturbation equations for phase β can be obtained by the operation (($\varepsilon_\beta + \varepsilon_\sigma \Gamma_a$) times Equations 7.180a minus Equation 7.179), which yields

$$\begin{aligned}(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a)\partial_t \hat{u}_\beta &= (\varepsilon_\beta + \varepsilon_\sigma\Gamma_a)\mathcal{L}_\beta \langle u \rangle^{\beta\sigma} - \left\langle \mathcal{L}_\beta \langle u \rangle^{\beta\sigma} \right\rangle - \left\langle \mathcal{L}_\sigma \langle u \rangle^{\beta\sigma} \right\rangle \\ &\quad + (\varepsilon_\beta + \varepsilon_\sigma\Gamma_a)\mathcal{L}_\beta \hat{u}_\beta - \langle \mathcal{L}_\beta \hat{u}_\beta \rangle - \langle \mathcal{L}_\sigma \hat{u}_\beta \rangle \\ &\quad + (\varepsilon_\beta + \varepsilon_\sigma\Gamma_a) R_\beta(u_\beta) - \langle R_\beta(u_\beta) \rangle - \langle R_\sigma(u_\sigma) \rangle. \end{aligned} \tag{7.181}$$

A similar operation can be performed for the other phase (($\varepsilon_\beta + \varepsilon_\sigma \Gamma_a$) times Equations 7.180b minus Γ_a times Equation 7.179 minus) and leads to

$$\begin{aligned}(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a)\Gamma_a\partial_t \hat{u}_\sigma &= (\varepsilon_\beta + \varepsilon_\sigma\Gamma_a)\mathcal{L}_\sigma \langle u \rangle^{\beta\sigma} - \Gamma_a\left\langle \mathcal{L}_\beta \langle u \rangle^{\beta\sigma} \right\rangle - \Gamma_a\left\langle \mathcal{L}_\sigma \langle u \rangle^{\beta\sigma} \right\rangle \\ &\quad + (\varepsilon_\beta + \varepsilon_\sigma\Gamma_a)\mathcal{L}_\sigma \hat{u}_\sigma - \Gamma_a\langle \mathcal{L}_\beta \hat{u}_\beta \rangle - \Gamma_a\langle \mathcal{L}_\sigma \hat{u}_\beta \rangle \\ &\quad + (\varepsilon_\beta + \varepsilon_\sigma\Gamma_a) R_\sigma(u_\sigma) - \Gamma_a\langle R_\beta(u_\beta) \rangle - \Gamma_a\langle R_\sigma(u_\sigma) \rangle. \end{aligned} \tag{7.182}$$

We further have the set of boundary conditions as

$$\hat{u}_\beta - \hat{u}_\sigma = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.183}$$

$$\mathcal{B}_\beta \hat{u}_\beta - \mathcal{B}_\beta \hat{u}_\sigma = \mathbf{n}_{\beta\sigma} \cdot (\mathbf{A}_\beta - \Gamma_A \mathbf{A}_\sigma) \cdot \nabla \langle u \rangle^{\beta\sigma} + \Omega(u_\sigma) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.184}$$

that is simply obtained by using the average plus perturbation decomposition.

7.7.3 Approximations

7.7.3.1 Spatial Frequency Approximation

Similar to approximations detailed in Section 7.5.3, we will assume that we can neglect terms involving the intra-REV spatial variable, **y**, so the first term on the RHS of Equation 7.181 is

$$\begin{aligned}\left\langle \mathcal{L}_\beta \langle u \rangle^{\beta\sigma} \right\rangle &= \left\langle \nabla \cdot \left(\mathbf{A}_\beta \cdot \nabla \langle u \rangle^{\beta\sigma} - \mathrm{Pe}_\beta^\ell \mathbf{v}_\beta \langle u \rangle^{\beta\sigma} \right) \right\rangle \\ &\simeq \langle \mathcal{L}_\beta \rangle \langle u \rangle^{\beta\sigma}, \end{aligned} \tag{7.185}$$

and the first term on the RHS of Equation 7.182 is

$$\left\langle \mathcal{L}_\sigma \langle u \rangle^{\beta\sigma} \right\rangle \simeq \langle \mathcal{L}_\sigma \rangle \langle u \rangle^{\beta\sigma}. \tag{7.186}$$

7.7.3.2 Amplitude Approximation

We further linearize our system using the zero-order Taylor expansions

$$R_i\left(u_i\right) \simeq R_i\left(\left\langle u\right\rangle^{\beta\sigma}\right), \tag{7.187}$$

$$\Omega\left(u_A\right) \simeq \Omega\left(\left\langle u\right\rangle^{\beta\sigma}\right). \tag{7.188}$$

We emphasize that such approximations are nonstandard, as the analysis of linear systems only requires approximation on the frequencies of the signals (see discussion in Section 7.5.3).

7.7.3.3 Approximate Form

Applying all these approximations to Equation 7.181 leads to

$$\begin{aligned}
&\left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\partial_t\hat{u}_\beta - \left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\mathcal{L}_\beta\hat{u}_\beta + \left(\left\langle\mathcal{L}_\beta\hat{u}_\beta\right\rangle + \left\langle\mathcal{L}_\sigma\hat{u}_\sigma\right\rangle\right)\\
&\quad= \left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\mathcal{L}_\beta\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\beta\left\langle\mathcal{L}_\beta\right\rangle^{\beta}\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\sigma\left\langle\mathcal{L}_\sigma\right\rangle^{\sigma}\left\langle u\right\rangle^{\beta\sigma}\\
&\qquad+ \left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)R_\beta\left(\left\langle u\right\rangle^{\beta\sigma}\right) - \varepsilon_\beta R_\beta\left(\left\langle u\right\rangle^{\beta\sigma}\right) - \varepsilon_\sigma R_\sigma\left(\left\langle u\right\rangle^{\beta\sigma}\right).
\end{aligned} \tag{7.189}$$

For Equation 7.182, we have

$$\begin{aligned}
&\left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\Gamma_a\partial_t\hat{u}_\sigma - \left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\mathcal{L}_\sigma\hat{u}_\sigma + \Gamma_a\left(\left\langle\mathcal{L}_\beta\hat{u}_\beta\right\rangle + \left\langle\mathcal{L}_\sigma\hat{u}_\beta\right\rangle\right)\\
&\quad= \left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\mathcal{L}_\sigma\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\beta\Gamma_a\left\langle\mathcal{L}_\beta\right\rangle^{\beta}\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\sigma\Gamma_a\left\langle\mathcal{L}_\sigma\right\rangle^{\sigma}\left\langle u\right\rangle^{\beta\sigma}\\
&\qquad+ \left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)R_\sigma\left(u_\sigma\right) - \varepsilon_\beta\Gamma_a R_\beta\left(\left\langle u\right\rangle^{\beta\sigma}\right) - \varepsilon_\sigma\Gamma_a R_\sigma\left(\left\langle u\right\rangle^{\beta\sigma}\right).
\end{aligned} \tag{7.190}$$

The first line on the RHS of Equation 7.189 can be decomposed to make source terms explicit

$$\begin{aligned}
&\left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\mathcal{L}_\beta\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\beta\left\langle\mathcal{L}_\beta\right\rangle^{\beta}\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\sigma\left\langle\mathcal{L}_\sigma\right\rangle^{\sigma}\left\langle u\right\rangle^{\beta\sigma}\\
&\quad= \left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\widetilde{\mathcal{L}}_\beta\left\langle u\right\rangle^{\beta\sigma} + \varepsilon_\sigma\Gamma_a\left\langle\mathcal{L}_\beta\right\rangle^{\beta}\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\sigma\left\langle\mathcal{L}_\sigma\right\rangle^{\sigma}\left\langle u\right\rangle^{\beta\sigma}.
\end{aligned} \tag{7.191}$$

We have that

$$\begin{aligned}
&\left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\widetilde{\mathcal{L}}_\beta\left\langle u\right\rangle^{\beta\sigma} + \varepsilon_\sigma\Gamma_a\left\langle\mathcal{L}_\beta\right\rangle^{\beta}\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\sigma\left\langle\mathcal{L}_\sigma\right\rangle^{\sigma}\left\langle u\right\rangle^{\beta\sigma}\\
&\quad= -\left[\left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\mathrm{Pe}_\beta^\ell\tilde{\mathbf{v}}_\beta + \varepsilon_\sigma\Gamma_a\mathrm{Pe}_\beta^\ell\left\langle\mathbf{v}_\beta\right\rangle^{\beta}\right]\cdot\nabla\left\langle u\right\rangle^{\beta\sigma} + \varepsilon_\sigma\left(\Gamma_a\mathbf{A}_\beta - \Gamma_A\mathbf{A}_\sigma\right):\nabla\nabla\left\langle u\right\rangle^{\beta\sigma},
\end{aligned} \tag{7.192}$$

with $\widetilde{\mathcal{L}}_\beta\left\langle u\right\rangle^{\beta\sigma} \equiv -\mathrm{Pe}_\beta^\ell\tilde{\mathbf{v}}_\beta\cdot\nabla\left\langle u\right\rangle^{\beta\sigma}$. Similarly for the first line on the RHS of Equation 7.190, we have

$$\begin{aligned}
&\left(\varepsilon_\beta + \varepsilon_\sigma\Gamma_a\right)\mathcal{L}_\sigma\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\beta\Gamma_a\left\langle\mathcal{L}_\beta\right\rangle^{\beta}\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\sigma\Gamma_a\left\langle\mathcal{L}_\sigma\right\rangle^{\sigma}\left\langle u\right\rangle^{\beta\sigma}\\
&\quad= \varepsilon_\beta\Gamma_a\mathrm{Pe}_\beta^\ell\left\langle\mathbf{v}_\beta\right\rangle^{\beta}\cdot\nabla\left\langle u\right\rangle^{\beta\sigma} - \varepsilon_\beta\left(\Gamma_a\mathbf{A}_\beta - \Gamma_A\mathbf{A}_\sigma\right):\nabla\nabla\left\langle u\right\rangle^{\beta\sigma}.
\end{aligned} \tag{7.193}$$

Equation 7.189 can therefore be written as

$$\left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\partial_t \hat{u}_\beta - \left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\mathcal{L}_\beta \hat{u}_\beta + \left\langle \mathcal{L}_\beta \hat{u}_\beta \right\rangle + \left\langle \mathcal{L}_\sigma \hat{u}_\sigma \right\rangle$$

$$= -\left[\left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\mathrm{Pe}_\beta^\ell \tilde{\mathbf{v}}_\beta + \varepsilon_\sigma \Gamma_a \mathrm{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta \right\rangle^\beta\right] \cdot \nabla \left\langle u \right\rangle^{\beta\sigma}$$

$$+ \varepsilon_\sigma \left(\Gamma_a \mathbf{A}_\beta - \Gamma_A \mathbf{A}_\sigma\right) : \nabla\nabla \left\langle u \right\rangle^{\beta\sigma} + \varepsilon_\sigma \left[\Gamma_a R_\beta\left(\left\langle u \right\rangle^{\beta\sigma}\right) - R_\sigma\left(\left\langle u \right\rangle^{\beta\sigma}\right)\right], \tag{7.194}$$

and Equation 7.190 as

$$\left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\Gamma_a \partial_t \hat{u}_\sigma - \left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\mathcal{L}_\sigma \hat{u}_\sigma + \Gamma_a\left(\left\langle \mathcal{L}_\beta \hat{u}_\beta \right\rangle + \left\langle \mathcal{L}_\sigma \hat{u}_\sigma \right\rangle\right)$$

$$= \varepsilon_\beta \Gamma_a \mathrm{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta \right\rangle^\beta \cdot \nabla \left\langle u \right\rangle^{\beta\sigma} - \varepsilon_\beta \left(\Gamma_a \mathbf{A}_\beta - \Gamma_A \mathbf{A}_\sigma\right) : \nabla\nabla \left\langle u \right\rangle^{\beta\sigma}$$

$$- \varepsilon_\beta \left[\Gamma_a R_\beta\left(\left\langle u \right\rangle^{\beta\sigma}\right) - R_\sigma\left(\left\langle u \right\rangle^{\beta\sigma}\right)\right], \tag{7.195}$$

with the set of boundary conditions

$$\hat{u}_\beta - \hat{u}_\sigma = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.196}$$

$$\mathcal{B}_\beta \hat{u}_\beta - \mathcal{B}_\beta \hat{u}_\sigma = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta - \Gamma_A \mathbf{A}_\sigma\right) \cdot \nabla \left\langle u \right\rangle^{\beta\sigma} + \Omega\left(\left\langle u \right\rangle^{\beta\sigma}\right) \text{on } \mathcal{A}_{\beta\sigma}. \tag{7.197}$$

7.7.4 Closure

In general, the transient closure is incompatible with the time-asymptotic limit so that we only consider the stationary closure:

$$\begin{bmatrix} \tilde{u}_\beta \\ \tilde{u}_\sigma \end{bmatrix} = \begin{bmatrix} \mathbf{b}_\beta^{\mathrm{LNE}} \\ \mathbf{b}_\sigma^{\mathrm{LNE}} \end{bmatrix} \cdot \nabla \left\langle u \right\rangle^{\beta\sigma} + \begin{bmatrix} \mathbf{W}_\beta^{\mathrm{LNE}} \\ \mathbf{W}_\sigma^{\mathrm{LNE}} \end{bmatrix} : \nabla\nabla \left\langle u \right\rangle^{\beta\sigma}$$

$$+ \begin{bmatrix} \mathbf{c}_\beta^{\mathrm{LNE}} \\ \mathbf{c}_\sigma^{\mathrm{LNE}} \end{bmatrix} \Omega\left(\left\langle u \right\rangle^{\beta\sigma}\right) + \begin{bmatrix} \mathbf{r}_\beta^{\mathrm{LNE}} \\ \mathbf{r}_\sigma^{\mathrm{LNE}} \end{bmatrix} \left[\Gamma_a R_\beta\left(\left\langle u \right\rangle^{\beta\sigma}\right) - R_\sigma\left(\left\langle u \right\rangle^{\beta\sigma}\right)\right]. \tag{7.198}$$

7.7.4.1 Closure Problems

We can now introduce Equation 7.198 in Equations 7.194 through 7.197 and identify the mapping variables corresponding to each source term. This leads to the following four problems.

7.7.4.1.1 Problem LNE-Stationary-I

$$-\mathcal{L}_\beta \mathbf{b}_\beta^{\mathrm{LNE}} + \frac{1}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a}\left(\left\langle \mathcal{L}_\beta \mathbf{b}_\beta^{\mathrm{LNE}} \right\rangle + \left\langle \mathcal{L}_\sigma \mathbf{b}_\beta^{\mathrm{LNE}} \right\rangle\right)$$

$$= -\mathrm{Pe}_\beta^\ell \tilde{\mathbf{v}}_\beta - \frac{\varepsilon_\sigma \Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \mathrm{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta \right\rangle^\beta \text{ in } \mathcal{V}_\beta, \tag{7.199a}$$

$$\text{BC1} \quad \mathbf{b}_\beta^{\text{LNE}} - \mathbf{b}_\sigma^{\text{LNE}} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.199b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{b}_\beta^{\text{LNE}} - \mathcal{B}_\sigma \mathbf{b}_\sigma^{\text{LNE}} = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta - \Gamma_A \mathbf{A}_\sigma \right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.199c}$$

$$\text{Periodicity 1} \quad \mathbf{b}_\alpha^{\text{LNE}} \left(\mathbf{x} + \mathbf{l}_i \right) = \mathbf{b}_\alpha^{\text{LNE}} \left(\mathbf{x} \right) \text{ with } \alpha = \beta, \sigma, \tag{7.199d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{b}_\alpha^{\text{LNE}} \left(\mathbf{x} + \mathbf{l}_i \right) = \mathcal{J}_\alpha \mathbf{b}_\alpha^{\text{LNE}} \left(\mathbf{x} \right) \text{ with } \alpha = \beta, \sigma, \tag{7.199e}$$

$$\text{Average} \quad \varepsilon_\beta \left\langle \mathbf{b}_\beta^{\text{LNE}} \right\rangle^\beta + \varepsilon_\sigma \left\langle \mathbf{b}_\sigma^{\text{LNE}} \right\rangle^\sigma = 0, \tag{7.199f}$$

$$-\mathcal{L}_\sigma \mathbf{b}_\sigma^{\text{LNE}} + \frac{\Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \left(\left\langle \mathcal{L}_\beta \mathbf{b}_\sigma^{\text{LNE}} \right\rangle + \left\langle \mathcal{L}_\sigma \mathbf{b}_\sigma^{\text{LNE}} \right\rangle \right) = \frac{\varepsilon_\beta \Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \text{Pe}_\beta^\ell \left\langle \mathbf{v}_\beta \right\rangle^\beta \text{ in } \mathcal{V}_\sigma. \tag{7.199g}$$

7.7.4.1.2 Problem LNE-Stationary-II

$$\begin{aligned} -\mathcal{L}_\beta \mathbf{W}_\beta^{\text{LNE}} &+ \frac{1}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \left(\left\langle \mathcal{L}_\beta \mathbf{W}_\beta^{\text{LNE}} \right\rangle + \left\langle \mathcal{L}_\sigma \mathbf{W}_\beta^{\text{LNE}} \right\rangle \right) \\ &= -\mathcal{J}_\beta \mathbf{b}_\beta^{\text{LNE}} + \frac{1}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \left(\left\langle \mathcal{J}_\beta \mathbf{b}_\beta^{\text{LNE}} \right\rangle + \left\langle \mathcal{J}_\sigma \mathbf{b}_\sigma^{\text{LNE}} \right\rangle \right) + \varepsilon_\sigma \left(\Gamma_a \mathbf{A}_\beta - \Gamma_A \mathbf{A}_\sigma \right), \end{aligned} \tag{7.200a}$$

$$\text{BC1} \quad \mathbf{W}_\beta^{\text{LNE}} - \mathbf{W}_\sigma^{\text{LNE}} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.200b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathbf{W}_\beta^{\text{LNE}} - \mathcal{B}_\sigma \mathbf{W}_\sigma^{\text{LNE}} = \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \mathbf{b}_\beta^{\text{LNE}} - \Gamma_A \mathbf{A}_\sigma \mathbf{b}_\sigma^{\text{LNE}} \right) \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.200c}$$

$$\text{Periodicity 1} \quad \mathbf{W}_\alpha^{\text{LNE}} \left(\mathbf{x} + \mathbf{l}_i \right) = \mathbf{W}_\alpha^{\text{LNE}} \left(\mathbf{x} \right) \text{ with } \alpha = \beta, \sigma, \tag{7.200d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathbf{W}_\alpha^{\text{LNE}} \left(\mathbf{x} + \mathbf{l}_i \right) = \mathcal{J}_\alpha \mathbf{W}_\alpha^{\text{LNE}} \left(\mathbf{x} \right) \text{ with } \alpha = \beta, \sigma, \tag{7.200e}$$

$$\text{Average} \quad \varepsilon_\beta \left\langle \mathbf{W}_\beta^{\text{LNE}} \right\rangle^\beta + \varepsilon_\sigma \left\langle \mathbf{W}_\sigma^{\text{LNE}} \right\rangle^\sigma = 0, \tag{7.200f}$$

$$\begin{aligned} -\mathcal{L}_\sigma \mathbf{W}_\sigma^{\text{LNE}} &+ \frac{\Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \left(\left\langle \mathcal{L}_\beta \mathbf{W}_\beta^{\text{LNE}} \right\rangle + \left\langle \mathcal{L}_\sigma \mathbf{W}_\beta^{\text{LNE}} \right\rangle \right) \\ &= -\mathcal{J}_\sigma \mathbf{b}_\sigma^{\text{LNE}} + \frac{\Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \left(\left\langle \mathcal{J}_\beta \mathbf{b}_\beta^{\text{LNE}} \right\rangle + \left\langle \mathcal{J}_\sigma \mathbf{b}_\sigma^{\text{LNE}} \right\rangle \right) - \varepsilon_\beta \left(\Gamma_a \mathbf{A}_\beta - \Gamma_A \mathbf{A}_\sigma \right). \end{aligned} \tag{7.200g}$$

7.7.4.1.3 Problem LNE-Stationary-III

$$-\mathcal{L}_\beta \mathbf{c}_\beta^{\text{LNE}} + \frac{1}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a} \left(\left\langle \mathcal{L}_\beta \mathbf{c}_\beta^{\text{LNE}} \right\rangle + \left\langle \mathcal{L}_\sigma \mathbf{c}_\beta^{\text{LNE}} \right\rangle \right) = 0 \text{ in } \mathcal{V}_\beta, \tag{7.201a}$$

$$\text{BC1} \quad \mathsf{c}_\beta^{\text{LNE}} - \mathsf{c}_\sigma^{\text{LNE}} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.201b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathsf{c}_\beta^{\text{LNE}} - \mathcal{B}_\sigma \mathsf{c}_\sigma^{\text{LNE}} = 1 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.201c}$$

$$\text{Periodicity 1} \quad \mathsf{c}_\alpha^{\text{LNE}}\left(\mathbf{x} + \mathbf{l}_i\right) = \mathsf{c}_\alpha^{\text{LNE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta,\sigma, \tag{7.201d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathsf{c}_\alpha^{\text{LNE}}\left(\mathbf{x} + \mathbf{l}_i\right) = \mathcal{J}_\alpha \mathsf{c}_\alpha^{\text{LNE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta,\sigma, \tag{7.201e}$$

$$\text{Average} \quad \varepsilon_\beta \left\langle \mathsf{c}_\beta^{\text{LNE}} \right\rangle^\beta + \varepsilon_\sigma \left\langle \mathsf{c}_\sigma^{\text{LNE}} \right\rangle^\sigma = 0, \tag{7.201f}$$

$$-\mathcal{L}_\sigma \mathsf{c}_\sigma^{\text{LNE}} + \frac{\Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a}\left(\left\langle \mathcal{L}_\beta \mathsf{c}_\beta^{\text{LNE}} \right\rangle + \left\langle \mathcal{L}_\sigma \mathsf{c}_\sigma^{\text{LNE}} \right\rangle\right) = 0 \text{ in } \mathcal{V}_\sigma. \tag{7.201g}$$

7.7.4.1.4 Problem LNE-Stationary-IV

$$-\mathcal{L}_\beta \mathsf{r}_\beta^{\text{LNE}} + \frac{1}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a}\left(\left\langle \mathcal{L}_\beta \mathsf{r}_\beta^{\text{LNE}} \right\rangle + \left\langle \mathcal{L}_\sigma \mathsf{r}_\sigma^{\text{LNE}} \right\rangle\right) = \varepsilon_\sigma \text{ in } \mathcal{V}_\beta, \tag{7.202a}$$

$$\text{BC1} \quad \mathsf{r}_\beta^{\text{LNE}} - \mathsf{r}_\sigma^{\text{LNE}} = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.202b}$$

$$\text{BC2} \quad \mathcal{B}_\beta \mathsf{r}_\beta^{\text{LNE}} - \mathcal{B}_\sigma \mathsf{r}_\sigma^{\text{LNE}} = 1 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.202c}$$

$$\text{Periodicity 1} \quad \mathsf{r}_\alpha^{\text{LNE}}\left(\mathbf{x} + \mathbf{l}_i\right) = \mathsf{r}_\alpha^{\text{LNE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta,\sigma, \tag{7.202d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathsf{r}_\alpha^{\text{LNE}}\left(\mathbf{x} + \mathbf{l}_i\right) = \mathcal{J}_\alpha \mathsf{r}_\alpha^{\text{LNE}}\left(\mathbf{x}\right) \text{ with } \alpha = \beta,\sigma, \tag{7.202e}$$

$$\text{Average} \quad \varepsilon_\beta \left\langle \mathsf{r}_\beta^{\text{LNE}} \right\rangle^\beta + \varepsilon_\sigma \left\langle \mathsf{r}_\sigma^{\text{LNE}} \right\rangle^\sigma = 0, \tag{7.202f}$$

$$-\mathcal{L}_\sigma \mathsf{r}_\sigma^{\text{LNE}} + \frac{\Gamma_a}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_a}\left(\left\langle \mathcal{L}_\beta \mathsf{r}_\beta^{\text{LNE}} \right\rangle + \left\langle \mathcal{L}_\sigma \mathsf{r}_\sigma^{\text{LNE}} \right\rangle\right) = -\varepsilon_\beta \text{ in } \mathcal{V}_\sigma. \tag{7.202g}$$

7.7.5 Macroscale Model

Applying the frequency and amplitude approximations to Equation 7.179 leads to

$$\begin{aligned}\left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\partial_t \langle u \rangle^{\beta\sigma} &= \langle \mathcal{L}_\beta \rangle \langle u \rangle^{\beta\sigma} + \langle \mathcal{L}_\sigma \rangle \langle u \rangle^{\beta\sigma} + \langle \mathcal{L}_\beta \hat{u}_\beta \rangle + \langle \mathcal{L}_\sigma \hat{u}_\sigma \rangle \\ &\quad + R_\beta\left(\langle u \rangle^{\beta\sigma}\right) + R_\sigma\left(\langle u \rangle^{\beta\sigma}\right).\end{aligned} \tag{7.203}$$

Using Equation 7.198 in Equation 7.203, we have

$$\begin{aligned}
&\left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\partial_t \langle u\rangle^{\beta\sigma} + \nabla\cdot\left(\mathrm{Pe}_\beta^\ell \langle \mathbf{v}_\beta\rangle \langle u\rangle^{\beta\sigma}\right)\\
&-\nabla\cdot\left[\left(\varepsilon_\beta \mathbf{A}_\beta + \varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma + \mathbf{B}^{\mathrm{LNE}}\right)\cdot\nabla\langle u\rangle^{\beta\sigma}\right]\\
&= \varepsilon_\beta R_\beta\left(\langle u\rangle^{\beta\sigma}\right) + \varepsilon_\sigma R_\sigma\left(\langle u\rangle^{\beta\sigma}\right)\\
&+ M^{\mathrm{LNE}}\left(\Gamma_a R_\beta\left(\langle u\rangle^{\beta\sigma}\right) - R_\sigma\left(\langle u\rangle^{\beta\sigma}\right)\right) + N^{\mathrm{LNE}}\Omega\left(\langle u\rangle^{\beta\sigma}\right),
\end{aligned} \tag{7.204}$$

with

$$\begin{aligned}
\mathbf{B}^{\mathrm{LNE}} &= \left\langle \mathcal{L}_\beta \mathbf{W}_\beta^{\mathrm{LNE}} - \mathcal{J}_\beta \mathbf{b}_\beta^{\mathrm{LNE}} + \mathbf{A}_\beta\cdot\nabla\mathbf{b}_\beta^{\mathrm{LNE}}\right\rangle\\
&+ \left\langle \mathcal{L}_\sigma \mathbf{W}_\sigma^{\mathrm{LNE}} - \mathcal{J}_\sigma \mathbf{b}_\sigma^{\mathrm{LNE}} + \Gamma_A \mathbf{A}_\sigma\cdot\nabla\mathbf{b}_\sigma^{\mathrm{LNE}}\right\rangle.
\end{aligned} \tag{7.205}$$

Cancelling opposite fluxes leads to

$$\mathbf{B}^{\mathrm{LNE}} = \left\langle \mathbf{A}_\beta\cdot\nabla\mathbf{b}_\beta^{\mathrm{LNE}}\right\rangle + \left\langle \Gamma_A \mathbf{A}_\sigma\cdot\nabla\mathbf{b}_\sigma^{\mathrm{LNE}}\right\rangle - \left\langle \mathbf{v}_\beta \mathbf{b}_\beta^{\mathrm{LNE}}\right\rangle. \tag{7.206}$$

We also remark that a similar operation yields

$$M^{\mathrm{LNE}} = \left\langle \mathcal{L}_\beta \mathsf{r}_\beta^{\mathrm{LNE}}\right\rangle + \left\langle \mathcal{L}_\sigma \mathsf{r}_\sigma^{\mathrm{LNE}}\right\rangle = 0, \tag{7.207}$$

$$N^{\mathrm{LNE}} = \left\langle \mathcal{L}_\beta \mathsf{c}_\beta^{\mathrm{LNE}}\right\rangle + \left\langle \mathcal{L}_\sigma \mathsf{c}_\sigma^{\mathrm{LNE}}\right\rangle = -a_v. \tag{7.208}$$

Therefore, we obtain the following transient nonequilibrium model:

$$\left(\varepsilon_\beta + \varepsilon_\sigma \Gamma_a\right)\partial_t \langle u\rangle^{\beta\sigma} + \nabla\cdot\left(\mathrm{Pe}_\beta^\ell \langle \mathbf{v}_\beta\rangle \langle u\rangle^{\beta\sigma}\right) = \nabla\cdot\left(\mathbf{A}^{\mathrm{LNE}}\cdot\nabla\langle u\rangle^{\beta\sigma}\right) + R^{\mathrm{LNE}}, \tag{7.209}$$

with

$$\mathbf{A}^{\mathrm{LNE}} = \varepsilon_\beta \mathbf{A}_\beta + \varepsilon_\sigma \Gamma_A \mathbf{A}_\sigma + \left\langle \mathbf{A}_\beta\cdot\nabla\mathbf{b}_\beta^{\mathrm{LNE}}\right\rangle + \left\langle \Gamma_A \mathbf{A}_\sigma\cdot\nabla\mathbf{b}_\sigma^{\mathrm{LNE}}\right\rangle - \left\langle \mathbf{v}_\beta \mathbf{b}_\beta^{\mathrm{LNE}}\right\rangle, \tag{7.210}$$

and the effective reaction rate is

$$R^{\mathrm{LNE}} = \varepsilon_\beta R_\beta\left(\langle u\rangle^{\beta\sigma}\right) + \varepsilon_\sigma R_\sigma\left(\langle u\rangle^{\beta\sigma}\right) - a_v\Omega\left(\langle u\rangle^{\beta\sigma}\right). \tag{7.211}$$

We remark here that the source terms appear simply in the macroscale model as volume or surface averages.

7.8 DERIVATION OF THE HYBRID MODELS

Hybrid models (also referred to as mixed models) combine macro- and microscale descriptions of a porous medium. There are many different possible hybrid descriptions of a single problem, and here, we will just give a simple example of one such model in the case where the ratio of diffusivities verifies

$$\Gamma_A \ll 1, \tag{7.212}$$

which corresponds to a much larger diffusion coefficient in the fluid phase. Our goal is to obtain a macroscale equation for the phase β coupled with a microscale equation for the solid phase σ.

7.8.1 Averaging

Since our goal is to obtain a macroscopic description only for the phase β, we average as in Section 7.5.1 for phase β and simply obtain

$$\varepsilon_\beta \partial_t \langle u_\beta \rangle^\beta = \left\langle \mathcal{L}_\beta \langle u_\beta \rangle^\beta \right\rangle + \left\langle \mathcal{L}_\beta \tilde{u}_\beta \right\rangle + \left\langle R_\beta \left(u_\beta \right) \right\rangle. \tag{7.213}$$

7.8.2 Perturbations

The perturbation equation is obtained by subtracting ε_β^{-1} times Equation 7.213 from Equation 7.6a, an operation that yields

$$\partial_t \tilde{u}_\beta - \widetilde{\mathcal{L}_\beta \tilde{u}_\beta} - \widetilde{R_\beta \left(u_\beta \right)} = \widetilde{\mathcal{L}_\beta \langle u_\beta \rangle^\beta} \text{in } \mathcal{V}_\beta. \tag{7.214}$$

The corresponding boundary conditions result from the introduction of the average plus perturbation decompositions in Equations 7.6b and c:

$$\tilde{u}_\beta - u_\sigma = -\langle u_\beta \rangle^\beta \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.215}$$

$$\mathcal{B}_\beta \tilde{u}_\beta - \mathcal{B}_\beta u_\sigma = -\mathcal{B}_\beta \langle u_\beta \rangle^\beta + \Omega\left(u_\beta \right) \text{ on } \mathcal{A}_{\beta\sigma}. \tag{7.216}$$

Unfortunately, this problem is not well suited to a hybrid formulation since the boundary conditions strongly couple the micro- and macroscale problem. To circumvent this issue, we use the following approximations.

7.8.3 Approximations

7.8.3.1 Spatial Frequency Approximation

Similar to what was done previously, we use a frequency approximation so that

$$\widetilde{\mathcal{L}_\beta \langle u_\beta \rangle^\beta} \simeq -\mathrm{Pe}_\beta^\ell \tilde{\mathbf{v}}_\beta \cdot \nabla \langle u_\beta \rangle^\beta \equiv \widetilde{\mathcal{L}}_\beta \langle u_\beta \rangle^\beta. \tag{7.217}$$

7.8.3.2 Amplitude Approximation

The nonlinear reaction rates are approximated, using $\tilde{u}_\beta \ll \langle u_\beta \rangle^\beta$, so that

$$\Omega\left(u_\beta \right) \simeq \Omega\left(\langle u_\beta \rangle^\beta \right), \quad R_\beta \left(u_\beta \right) \simeq R_\beta \left(\langle u_\beta \rangle^\beta \right). \tag{7.218}$$

7.8.3.3 Hybrid Approximations

First, the flux boundary condition can be written as

$$\mathcal{B}_\beta \tilde{u}_\beta = -\mathcal{B}_\beta \left\langle u_\beta \right\rangle^\beta \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.219}$$

in the limit where $\Gamma_A \to 0$ and the interfacial source/sink does not influence the dispersion tensor (this is usually correct for Damkhöler numbers smaller than ≈ 10; see [93]). We will assume that these conditions hold only in the perturbation problem for the phase β, that is, that the BC does not modify the standard form of the dispersion coefficients, although it plays a role in the exchanged flux between the two phases. We will further simplify the system by considering the amplitude approximation $\tilde{u}_\beta \ll \left\langle u_\beta \right\rangle^\beta$, on the boundary $\mathcal{A}_{\beta\sigma}$. This yields

$$u_\sigma = \left\langle u_\beta \right\rangle^\beta \text{ on } \mathcal{A}_{\beta\sigma}. \tag{7.220}$$

We remark that this boundary condition is of a mixed type since it involves a macroscale value on the RHS and a microscale value on the LHS. Further, it is unclear how much the approximation $\tilde{u}_\beta \ll \left\langle u_\beta \right\rangle^\beta$ affects the results for the reactive case.

7.8.3.4 Quasi-Stationarity

We assume that the timescale for the relaxation of the phase β is much faster than in phase σ, which is consistent with the limit $\Gamma_A \to 0$, so that Equation 7.214 becomes

$$-\widetilde{\mathcal{L}_\beta \tilde{u}_\beta} - \widetilde{R_\beta\left(u_\beta\right)} = \widetilde{\mathcal{L}_\beta \left\langle u_\beta \right\rangle^\beta} \text{ in } \mathcal{V}_\beta. \tag{7.221}$$

7.8.3.5 Approximate Form

With the amplitude approximation, we have $\widetilde{R_\beta\left(u_\beta\right)} \simeq 0$. Therefore, we can write the perturbation problem as

$$-\widetilde{\mathcal{L}_\beta \tilde{u}_\beta} = -\mathrm{Pe}_\beta^\ell \tilde{\mathbf{v}}_\beta \cdot \nabla \left\langle u_\beta \right\rangle^\beta \text{ in } \mathcal{V}_\beta, \tag{7.222a}$$

$$\text{BC1} \quad \mathcal{B}_\beta \tilde{u}_\beta = -\mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla \left\langle u_\beta \right\rangle^\beta \right) \text{ on } \mathcal{A}_{\beta\sigma}. \tag{7.222b}$$

7.8.4 Closure

We look for a solution of the type

$$\tilde{u}_\beta = \mathbf{b}_\beta^{\mathrm{HYB}} \cdot \nabla \left\langle u_\beta \right\rangle^\beta \tag{7.223}$$

and obtain the following closure problems:

$$-\widetilde{\mathcal{L}_\beta \mathbf{b}_\beta^{\mathrm{HYB}}} = -\mathrm{Pe}_\beta^\ell \tilde{\mathbf{v}}_\beta \text{ in } \mathcal{V}_\beta, \tag{7.224a}$$

$$\mathcal{B}_\beta \mathbf{b}_\beta^{\mathrm{HYB}} = \mathbf{n}_{\beta\sigma} \cdot \mathbf{A}_\beta \text{ at } \mathcal{A}_{\beta\sigma}, \tag{7.224b}$$

$$\text{Periodicity} \quad \mathbf{b}_\beta^{\text{HYB}}(\mathbf{x}+\mathbf{l}_i) = \mathbf{b}_\beta^{\text{HYB}}(\mathbf{x}), \tag{7.224c}$$

$$\text{Average} \quad \left\langle \mathbf{b}_\beta^{\text{HYB}} \right\rangle = 0. \tag{7.224d}$$

7.8.5 Hybrid Model

We can reformulate the macroscale equation in a way similar to Equation 7.57, that is,

$$\varepsilon_\beta \left[\underbrace{\partial_t \langle u_\beta \rangle^\beta}_{\text{Rate of change}} + \underbrace{\nabla \cdot \left(\text{Pe}_\beta^\ell \langle \mathbf{v}_\beta \rangle^\beta \langle u_\beta \rangle^\beta \right)}_{\text{Convection}} + \underbrace{\nabla \cdot \left(\text{Pe}_\beta^\ell \langle \tilde{\mathbf{v}}_\beta \tilde{u}_\beta \rangle^\beta \right)}_{\text{Velocity fluctuation effects}} \right]$$
$$= \underbrace{\nabla \cdot \left[\varepsilon_\beta \Gamma_A \mathbf{A}_\beta \cdot \left(\nabla \langle u_\beta \rangle^\beta + \underbrace{\frac{1}{V_\beta} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{u}_\beta dA}_{\text{Surface effects}} \right) \right]}_{\text{Diffusion}}$$
$$+ \underbrace{\frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot (\Gamma_A \mathbf{A}_\beta \cdot \nabla u_\beta)\, dA}_{\text{Interfacial flux}} + \underbrace{\varepsilon_\beta R_\beta \left(\langle u_\beta \rangle^\beta \right)}_{\text{Average reaction rate}}. \tag{7.225}$$

While we have neglected the interfacial flux for estimating the dispersion tensor in the phase β, we do not neglect this flux in the averaged balance equations, as it is important to ensure conservation of properties (e.g., mass or energy). Neglecting it in the closure problems just means that we assume that it does not influence significantly the closure variables, not that we neglect it altogether.

The macroscale equation may be written as

$$\varepsilon_\beta \left[\partial_t \langle u_\beta \rangle^\beta + \nabla \cdot \left(\text{Pe}_\beta^\ell \langle \mathbf{v}_\beta \rangle^\beta \langle u_\beta \rangle^\beta \right) \right] = \nabla \cdot \left(\mathbf{A}^{\text{HYB}} \cdot \nabla \langle u_\beta \rangle^\beta \right) - \mathsf{J}_{\beta\sigma} + R^{\text{HYB}}, \tag{7.226}$$

with

$$\mathbf{A}^{\text{HYB}} = \varepsilon_\beta \mathbf{A}_\beta + \underbrace{\frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{b}_\beta dA}_{\text{Tortuosity}} - \underbrace{\text{Pe}_\beta^\ell \left\langle \tilde{\mathbf{v}}_\beta \mathbf{b}_\beta \right\rangle}_{\text{Dispersion}}, \tag{7.227}$$

$$R^{\text{HYB}} = -a_v \Omega \left(\langle u_\beta \rangle^\beta \right) + \varepsilon_\beta R_\beta \left(\langle u_\beta \rangle^\beta \right), \tag{7.228}$$

$$\mathsf{J}_{\beta\sigma} = -\frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(\mathbf{A}_\beta \cdot \nabla u_\beta \right) dA = \frac{1}{V} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \left(\Gamma_A \mathbf{A}_\sigma \cdot \nabla u_\sigma \right) dA. \tag{7.229}$$

Solving the macroscale equation, Equation 7.226, requires the knowledge of $\mathsf{J}_{\beta\sigma}$, which may be calculated by solving the following coupled pore-scale equations:

$$\Gamma_a \partial_t u_\sigma = \mathcal{L}_\sigma u_\sigma + R_\sigma (u_\sigma) \text{ in } \mathcal{V}_\sigma, \tag{7.230}$$

$$\text{BC1} \quad u_\sigma = \langle u_\beta \rangle^\beta \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.231}$$

$$\text{IC} \quad u_\sigma(t = 0) = 0. \tag{7.232}$$

7.9 COMPUTATION OF EFFECTIVE PARAMETERS IN REALISTIC MEDIA

The computation of effective properties by solving closure problems started in the 1980s with relatively simple unit cells [122–124], to become a standard practice for complex 3D images in several commercial softwares. This chapter [17] presents several results for thermal dispersion coefficients, heat exchange coefficient, and distribution coefficient for 1D, 2D, and 3D simple unit cells. Given the renewed interest on the distribution coefficient [50,74] and the sparsity of published results, we will focus on this effective property in this section and provide results for 3D images of porous media.

7.9.1 Distribution Coefficient ξ

The calculation of the distribution coefficient ξ requires to solve the closure problem 2eq-stationary-VI. This problem is integrodifferential and requires a specific change of variables; see [17,65,125]. Preliminary results for ξ were given in [17] for stratified systems and simple unit cells (Chang's unit cell, simple cubic arrays of spheres, in-line and staggered arrays of cylinders). Recent results in [74] for equilateral triangle arrays of cylinders are consistent with early results in [17] and showed that ξ is a fundamental parameter in nonequilibrium models with heat sources at the fluid–solid interface. Here, we study the behavior of ξ for more realistic porous structures obtained via x-ray microtomography.

The porous medium that we study consists of glass beads packed into a plastic column. The 3D structure was obtained via x-ray computed microtomography (Phoenix nanotom®). The segmentation of gray-scale images was performed in Avizo®, using basic filtering and thresholding methods. A cubic region of interest was then selected in the center of the bead packing, which is presented in Figure 7.6a. Another simpler structure (Figure 7.6b,c), a cubic-centered array of spheres, was also used in the simulations for two different purposes:

1. To validate the finite volume (FV) numerical method with a Cartesian mesh. To this end, we compare results for a_v and ξ obtained using an FV approach on a Cartesian grid, with results obtained using the finite element (FE) method with an unstructured mesh.
2. To illustrate the effect of the geometries on values of the effective parameters.

7.9.2 Closure Problems and Numerical Methods

For the theoretical part of this chapter, we focused on a generic transport problem. Here, we illustrate the application to a heat transfer in a porous medium with $a = c_p$ and $u = T$. The steady-state version of problem 2eq-transient-VI Equation 7.96 can be written in dimensionalized form for a heat transfer problem as

$$\rho_\beta c_{p\beta} \mathbf{v}_\beta \cdot \nabla \mathsf{c}_\beta = k_\beta \nabla^2 \mathsf{c}_\beta - a_v \varepsilon_\beta^{-1} \xi_\beta \text{ in } \mathcal{V}_\beta, \tag{7.233a}$$

$$\text{BC1} \quad \mathsf{c}_\beta - \mathsf{c}_\sigma = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.233b}$$

$$\text{BC2} \quad -\mathbf{n}_{\beta\sigma} \cdot \left(k_\beta \nabla \mathsf{c}_\beta - k_\sigma \nabla \mathsf{c}_\sigma\right) = 1 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.233c}$$

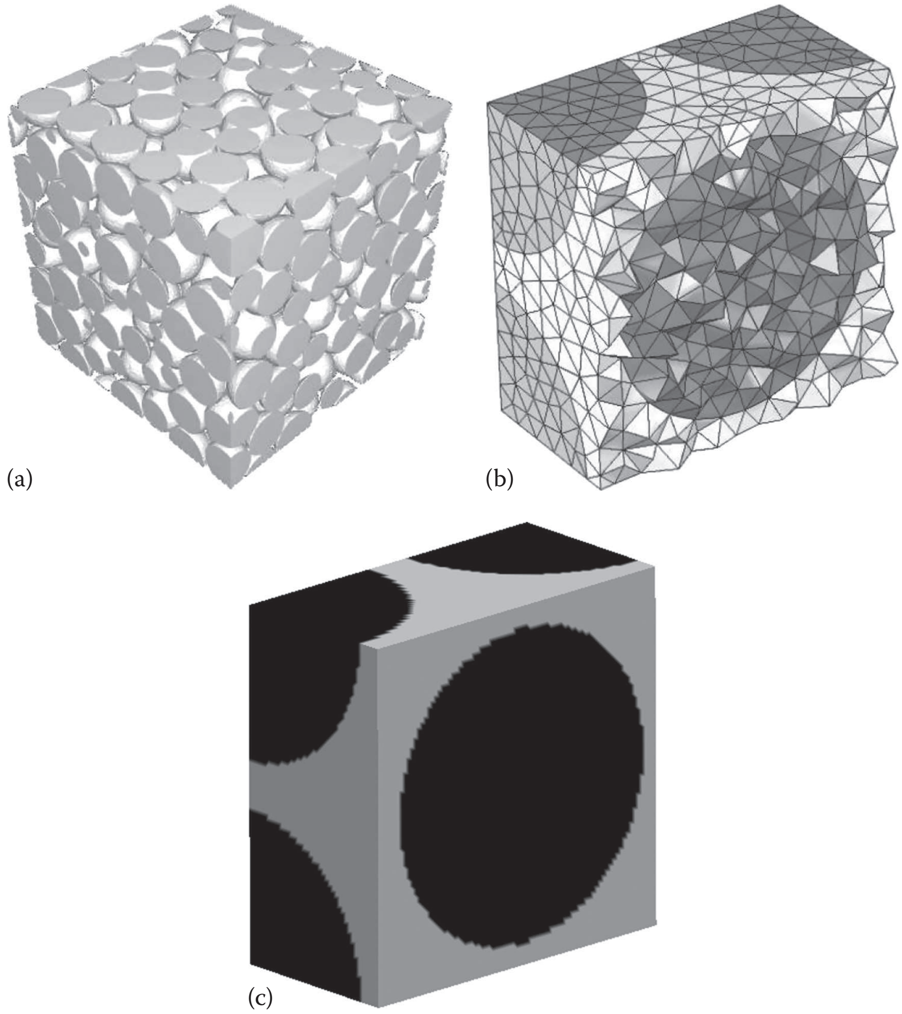


FIGURE 7.6 Geometries and meshes used for numerical calculations for (a) a 3D reconstruction of a bead packing obtained using x-ray microtomography, (b) an unstructured mesh used for the FE method, and (c) a Cartesian grid used for the FV method.

$$\text{Periodicity 1} \quad \mathsf{c}_\alpha\left(\mathbf{x}+\mathbf{l}_i\right)=\mathsf{c}_\beta\left(\mathbf{x}\right) \text{ with } \alpha=\beta,\sigma, \tag{7.233d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha\mathsf{c}_\alpha\left(\mathbf{x}+\mathbf{l}_i\right)=\mathcal{J}_\alpha\mathsf{c}_\alpha\left(\mathbf{x}\right) \text{ with } \alpha=\beta,\sigma, \tag{7.233e}$$

$$\text{Average} \quad \left\langle \mathsf{c}_\alpha \right\rangle = 0 \text{ with } \alpha=\beta,\sigma, \tag{7.233f}$$

$$0 = k_\sigma \nabla^2 \mathsf{c}_\sigma - a_v \varepsilon_\sigma^{-1} \xi_\sigma \text{ in } \mathcal{V}_\sigma, \tag{7.233g}$$

where the parameters ξ_β and ξ_σ are defined explicitly by

$$\xi_\beta = \frac{1}{A_{\beta\sigma}} \int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot k_\beta \nabla \mathsf{c}_\beta dA = a_v^{-1} \left\langle \nabla \cdot \left(k_\beta \nabla \mathsf{c}_\beta \right) \right\rangle, \tag{7.234}$$

$$\xi_\sigma = \frac{1}{A_{\sigma\beta}} \int_{\mathcal{A}_{\sigma\beta}} \mathbf{n}_{\sigma\beta} \cdot k_\sigma \nabla \mathsf{c}_\sigma dA = a_v^{-1} \left\langle \nabla \cdot \left(k_\sigma \nabla \mathsf{c}_\sigma \right) \right\rangle = -1 - \xi_\beta. \tag{7.235}$$

As in the theoretical part, we write the *distribution coefficient* as $\xi = -\xi_\beta$.

A practical way to solve this problem, based on the fact that ξ is constant over a unit cell, is to follow the procedure outlined in [65] and use the following change of variables:

$$\mathsf{c}_\beta = \mathsf{c}_\beta^0 + \xi \mathsf{c}_\beta^1, \quad \mathsf{c}_\sigma = \mathsf{c}_\sigma^0 + \xi \mathsf{c}_\sigma^1. \tag{7.236}$$

This leads to two independent closure problems that are given as

$$\rho_\beta c_{p\beta} \mathbf{v}_\beta \cdot \nabla \mathsf{c}_\beta^0 = k_\beta \nabla^2 \mathsf{c}_\beta^0 \text{ in } \mathcal{V}_\beta, \tag{7.237a}$$

$$\text{BC1} \quad \mathsf{c}_\beta^0 - \mathsf{c}_\sigma^0 = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.237b}$$

$$\text{BC2} \quad -\mathbf{n}_{\beta\sigma} \cdot \left(k_\beta \nabla \mathsf{c}_\beta^0 - k_\sigma \nabla \mathsf{c}_\sigma^0 \right) = 1 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.237c}$$

$$\text{Periodicity 1} \quad \mathsf{c}_\alpha^0 \left(\mathbf{x} + \mathbf{l}_i \right) = \mathsf{c}_\alpha^0 \left(\mathbf{x} \right) \text{ with } \alpha = \beta, \sigma, \tag{7.237d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathsf{c}_\alpha^0 \left(\mathbf{x} + \mathbf{l}_i \right) = \mathcal{J}_\alpha \mathsf{c}_\alpha^0 \left(\mathbf{x} \right) \text{ with } \alpha = \beta, \sigma, \tag{7.237e}$$

$$\text{Average} \quad \left\langle \mathsf{c}_\sigma^0 \right\rangle^\sigma = 0 \text{ with } \alpha = \beta, \sigma, \tag{7.237f}$$

$$0 = k_\sigma \nabla^2 \mathsf{c}_\sigma^0 + a_v \varepsilon_\sigma^{-1} \text{ in } \mathcal{V}_\sigma, \tag{7.237g}$$

and

$$\rho_\beta c_{p\beta} \mathbf{v}_\beta \cdot \nabla \mathsf{c}_\beta^1 = k_\beta \nabla^2 \mathsf{c}_\beta^1 - a_v \varepsilon_\beta^{-1} \text{ in } \mathcal{V}_\beta, \tag{7.238a}$$

$$\text{BC1} \quad \mathsf{c}_\beta^1 - \mathsf{c}_\sigma^1 = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.238b}$$

$$\text{BC2} \quad -\mathbf{n}_{\beta\sigma} \cdot \left(k_\beta \nabla \mathsf{c}_\beta^1 - k_\sigma \nabla \mathsf{c}_\sigma^1 \right) = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.238c}$$

$$\text{Periodicity 1} \quad \mathsf{c}_\alpha^1 \left(\mathbf{x} + \mathbf{l}_i \right) = \mathsf{c}_\alpha^1 \left(\mathbf{x} \right) \text{with } \alpha = \beta, \sigma, \tag{7.238d}$$

$$\text{Periodicity 2} \quad \mathcal{J}_\alpha \mathsf{c}_\alpha^1 \left(\mathbf{x} + \mathbf{l}_i \right) = \mathcal{J}_\alpha \mathsf{c}_\alpha^1 \left(\mathbf{x} \right) \text{ with } \alpha = \beta, \sigma, \tag{7.238e}$$

$$\text{Average} \quad \left\langle \mathsf{c}_\sigma^1 \right\rangle^\sigma = 0 \text{ with } \alpha = \beta, \sigma, \tag{7.238f}$$

$$0 = k_\sigma \nabla^2 \mathsf{c}_\sigma^1 + a_v \varepsilon_\sigma^{-1} \text{ in } \mathcal{V}_\sigma. \tag{7.238g}$$

The condition imposed on the phase average, $\langle \mathsf{c}_\beta \rangle = 0$, is not automatically satisfied by these two closure problems so that we have

$$\xi = -\frac{\langle \mathsf{c}_\beta^0 \rangle^\beta}{\langle \mathsf{c}_\beta^1 \rangle^\beta}. \tag{7.239}$$

We also remark that the two previous problems are well posed in the sense that they satisfy the solvability conditions/Fredholm alternative. In our case, looking at the adjoint problem is equivalent to averaging the closure problems in space (see, e.g., [42]). For instance, averaging the bulk equations in Problem 7.237 and using the periodicity conditions yields

$$\frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(k_\beta \nabla \mathsf{c}_\beta^0\right) dA = 0 \text{ in } \mathcal{V}_\beta, \quad \frac{1}{V}\int_{\mathcal{A}_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\cdot\left(k_\sigma \nabla \mathsf{c}_\sigma^0\right) dA = a_v \text{ in } \mathcal{V}_\sigma, \tag{7.240}$$

which is *consistent* with the boundary condition

$$\text{BC} - \mathbf{n}_{\beta\sigma}\cdot\left(k_\beta \nabla \mathsf{c}_\beta^0 - k_\sigma \nabla \mathsf{c}_\sigma^0\right) = 1 \text{ on } \mathcal{A}_{\beta\sigma}. \tag{7.241}$$

The two IBVPs 7.237 and 7.238 are local in space and can be solved via standard FV or FE methods. In this chapter, we use an FV method based on a voxel description of the material, which is the most direct way of using tomographic data. Equations are discretized on a Cartesian grid with the numerical scheme proposed in [125,126]. We remark that a Cartesian grid may not provide an accurate value of the specific area a_v, since the discretization of a surface by a piecewise constant function leads to an error that is independent of the mesh size. In order to evaluate the extent of this effect on the computation of ξ, we also compare results with those obtained via an FE method (COMSOL Multiphysics®) with unstructured grids in the case of the cubic-centered unit cell.

7.9.3 Challenges Associated with X-Ray Tomography Images

Beyond the difficulties associated with image filtering and segmentation, the calculation of effective parameters using x-ray images of porous media poses a number of challenges, including the choice of boundary conditions. In the theoretical developments presented in this work, we have used periodic boundary conditions. The geometry obtained via x-ray tomography, however, is usually not periodic. Although we can still use periodic conditions for the PDEs, this may yield erroneous results, for instance, if the operation produces a nonpercolating porous medium, as is illustrated in Figure 7.7a. A possible solution to this problem is to periodize the unit cell via geometrical transformations, for example, by translation and symmetry operations, as is illustrated in Figure 7.7b.

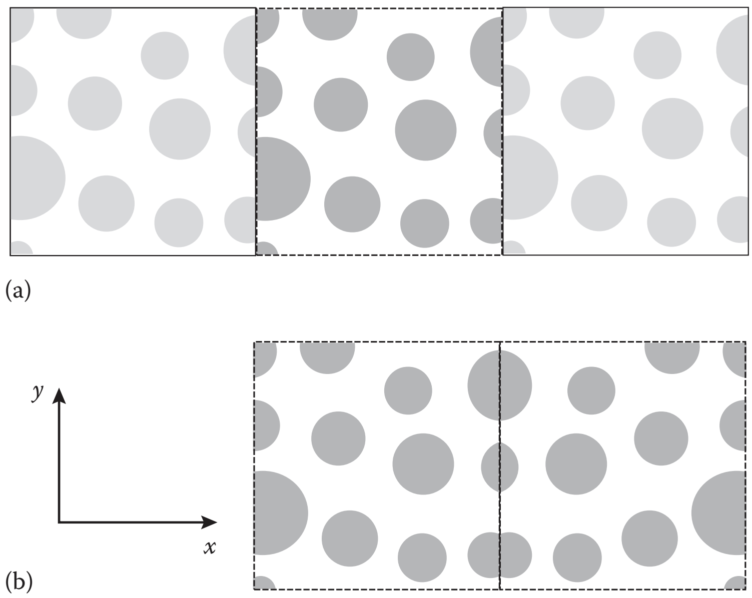


FIGURE 7.7 Schematics illustrating problems with boundary conditions. (a) Application of periodic boundary conditions to a nonperiodic geometry resulting in a nonpercolating porous medium. (b) Symmetry operation leading to a periodic unit-cell.

TABLE 7.1
Properties of the Set of Images and Comparison with Cubic-Centered Array

Image	1	2	3	CC
l_r	1.49	2.24	5.97	—
ε_β	0.309	0.339	0.357	0.319

This procedure is also not ideal since it modifies the original structure and may result in the loss of important features, such as anisotropy. These problems are even more crucial if advection effects are relatively large, as errors do not localize in the vicinities of the boundary. For h and ξ, in the diffusive regime, the impact of boundary conditions is usually small, so that we can use directly periodic boundary conditions.

Another important challenge associated with tomography techniques is the size of the images that can readily reach $1{,}000^3$ voxels and may go up to $10{,}000^3$, so that the computational cost associated with the numerical resolution of the closure problems with a similar spatial resolution can be enormous. If we restrict calculation to a region of interest, we must make sure that the size of the unit cell is much larger than the average spatial correlation length; otherwise values of the effective parameters may not be representative. In the case of the medium presented in Figure 7.6a, the correlation length corresponds to a few grain diameters, l_σ, and the size of the unit cell can be characterized using l_r, the ratio $l_r = l_{uc}/l_\sigma$, with l_{uc} as the size of the unit cell. Properties of the geometries are presented in Table 7.1.

7.9.4 Results for the Cubic-Centered Unit Cell

In [17], it was shown that ξ exhibits only a weak dependence upon the Péclet number, so that we focus here on the effects of the thermal conductivity ratio $\Gamma_k = k_\sigma/k_\beta$. Results are presented in Figure 7.8 for the FV and FE methods with various meshes.

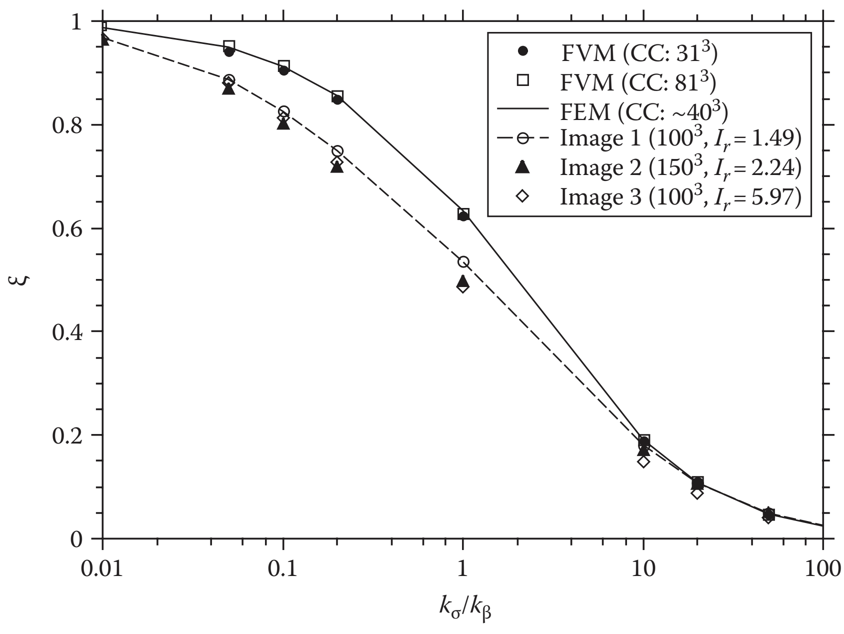


FIGURE 7.8 Distribution coefficient versus k_σ/k_β for the cubic-centered array of spheres (CC) and the tomographic data (images 1, 2, and 3). Images 1 and 2 are two subsets of the image presented in Figure 7.6a with a mesh size identical to the voxel size, while image 3 corresponds to the entire images in Figure 7.6a with a mesh size four times larger than the voxel size.

TABLE 7.2
Specific Area, a_v, for the Cubic-Centered Unit Cell

	FV (31^3)	FV (81^3)	FE ($\approx 40^3$)	Theoretical
a_v	5.955	5.978	4.045	4.081

First, we remark that the convergence with the mesh size is relatively fast, and even the coarser Cartesian grid (e.g., 31^3) provides good results. This shows that the Cartesian grid is suited to the resolution of such problems and that errors in the estimation of a_v (see Table 7.2) do not significantly impact results for ξ. Our interpretation of this result is that the integration procedure is consistent for all parameters, so that the errors cancel out during the evaluation of intensive variables. If one is interested in an accurate estimate of extensive variables, more sophisticated numerical schemes (see, e.g., [127]) can be used. These results also show that the FV approach can be used for the calculation of ξ over the geometry presented in Figure 7.6a.

7.9.5 Results for the X-Ray Tomography Unit Cell

Results of calculations over several subset of the original image, characterized by different values of l_r, are plotted in Figure 7.8. These show that the impact of l_r is relatively mild for this particular disordered structure, and we obtained reasonably good results for $l_r \geq 2$. The mesh size was equal to the tomograph voxel size for images 1 and 2, two subsets of the image presented in Figure 7.6a. Image 3 is the entire volume presented in Figure 7.6a, with a mesh size four times larger than the voxel size (i.e., 100^3 since the original image is 400^3). Although results are not presented here, we verified numerical convergence by performing additional calculations for image 3 with identical mesh and voxel sizes, that is, with a 400^3 grid. We observed a maximum relative error of about 1% between the 400^3 and 100^3 grids.

The goal of this section was to show that closure parameters can be solved over complex unit cells, so that we can determine effective parameters for realistic porous media. In the next section, we consider simpler unit cells, sometimes with analytical solutions, to characterize the behavior of the different models.

7.10 EXAMPLE PROBLEMS

In the theoretical part of this work, we have shown that there is a variety of macroscale models associated with a single microscale problem. Choosing among these models for a specific application is often based on an order of magnitude analysis of dimensionless parameters. However, this is often feasible only for simple conceptual cases, such as a 1D infinite medium, where the effects of boundary and initial conditions are abnormally weak. In this section, we provide several examples illustrating the importance of such conditions, with a particular focus on the two-equation quasi-stationary and one-equation LNE models.

7.10.1 Effect of Constant Source Terms in a Stratified Medium

The domain considered here is a periodic stratified geometry, as detailed in Figure 7.9, with $l_\beta + l_\sigma = 1$. We consider the following heat transfer problem:

$$\frac{\partial T'_\beta}{\partial t'} = \Delta' T'_\beta + R'_0 \text{ in } \mathcal{V}_\beta, \tag{7.242a}$$

$$\text{BC1} \quad T'_\beta - T'_\sigma = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.242b}$$

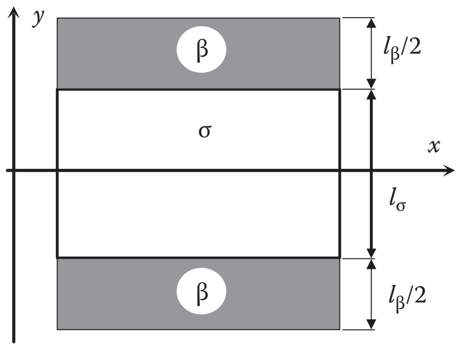


FIGURE 7.9 Unit cell for a stratified medium.

$$\text{BC2} \quad -\mathbf{n}_{\beta\sigma}\cdot\left(\nabla' T'_\beta - \Gamma_k \nabla' T'_\sigma\right) = -\Omega'_0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.242c}$$

$$\text{Periodicity} \quad T'_\beta\left(\frac{1}{2}\right) = T'_\beta\left(-\frac{1}{2}\right) \quad \text{and} \quad \frac{\partial T'_\beta}{\partial y'}\left(\frac{1}{2}\right) = \frac{\partial T'_\beta}{\partial y'}\left(-\frac{1}{2}\right), \tag{7.242d}$$

$$\text{IC} \quad T'_\beta\left(t=0\right) = T'_\sigma\left(t=0\right) = 0, \tag{7.242e}$$

$$\Gamma_{\rho c_p}\frac{\partial T'_\sigma}{\partial t'} = \nabla'\cdot\left(\Gamma_k \nabla' T'_\sigma\right) + R'_0 \text{ in } \mathcal{V}_\sigma, \tag{7.242f}$$

where we have used the ratio of the thermal diffusivities, $\Gamma_k = k_\sigma/k_\beta$, and $\Gamma_{\rho c_p} = \rho_\sigma c_{p\sigma}/\rho_\beta c_{p\beta}$. Here, Ω'_0 and R'_0 are constant bulk and surface sources, respectively. Note the minus sign in front of Ω'_0 in BC2 so that $\Omega'_0 > 0$ is a heat source.

We emphasize that this system of equations is underdetermined since boundary conditions on the LHS and RHS have not been imposed so far. Here, we consider (1) the case where the system is infinite in the x-direction, so that fields are uniform in the x-direction and averaging in the y-direction leads to a 0D macroscale problem, and (2) the case where we impose Dirichlet boundary conditions and average in the y-direction, so that the macroscale problem is 1D.

7.10.1.1 Effective Parameters

For this geometry, we can solve the closure problems analytically in order to obtain the following expressions for the exchange coefficient

$$h = \frac{12}{\varepsilon_\beta + \varepsilon_\sigma \Gamma_k} \tag{7.243}$$

and the distribution coefficient

$$\xi = \frac{\varepsilon_\sigma}{\varepsilon_\beta \Gamma_k + \varepsilon_\sigma}. \tag{7.244}$$

The evolution of ξ against the phase volume fraction and the thermal conductivity ratio is illustrated in Figure 7.10a. This figure shows the distribution of the boundary source depending on the relative conductivity of both phases and emphasizes that even for very large or very small ratios, this source affects both phases. The evolution of h against the phase volume fraction and the thermal conductivity ratio is illustrated in Figure 7.10b.

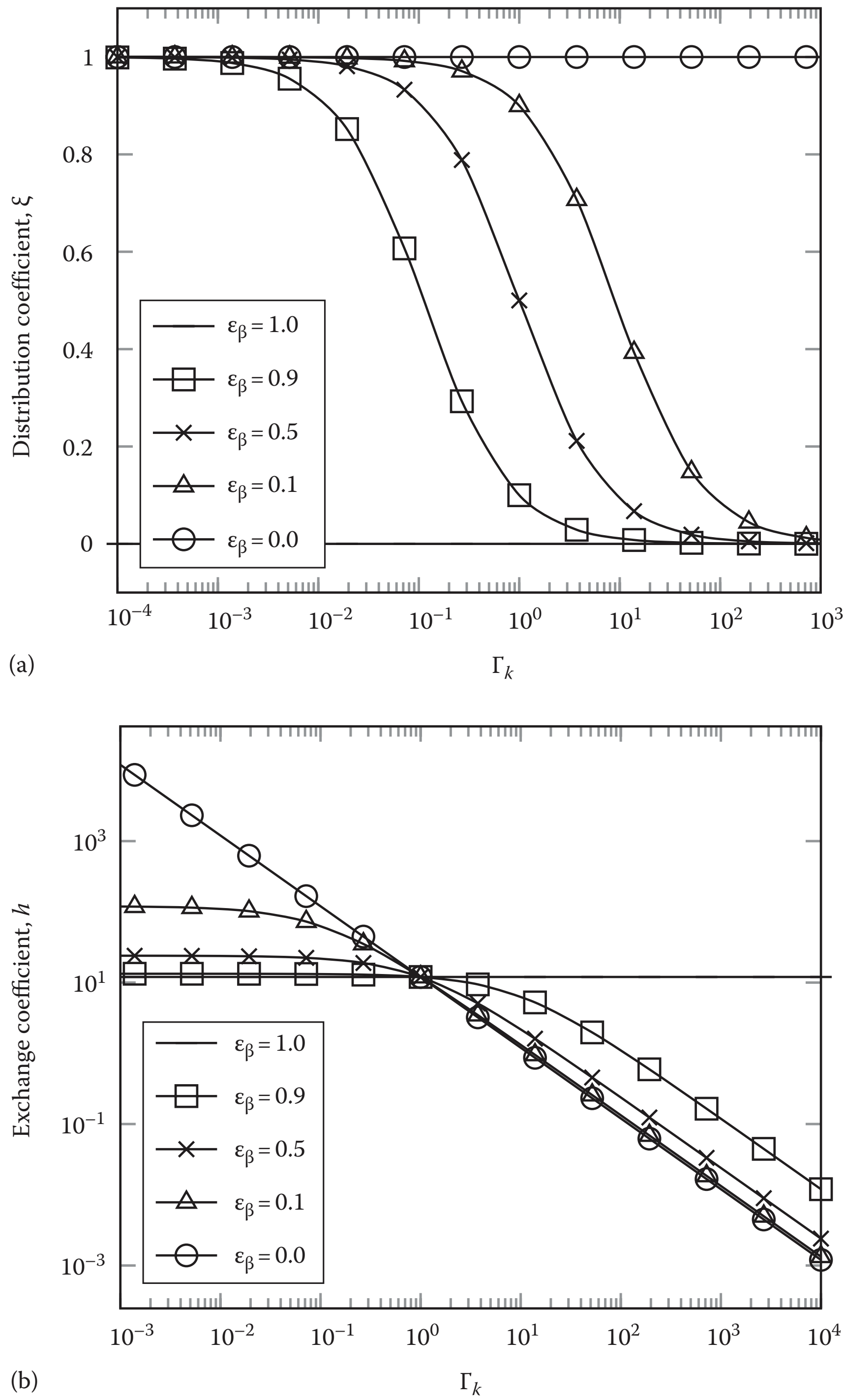


FIGURE 7.10 Evolution of (a) ξ and (b) h against the thermal conductivity ratio for various volume fractions.

7.10.1.2 Zero-Dimensional Case with Heterogeneous Sources, $R_0' = 0$

We consider here the case of an infinitely long stratified system. We focus on the two-equation quasi-stationary model at the macroscale and on the impact of heterogeneous sources ($R_0' = 0$). On averaging in the y-direction, the quasi-stationary two-equation model corresponding to this system only evolves in time so that we have

$$\varepsilon_\beta \frac{d\left\langle T_\beta' \right\rangle^\beta}{dt'} = -h\left(\left\langle T_\beta' \right\rangle^\beta - \left\langle T_\sigma' \right\rangle^\sigma\right) + a_v \xi \Omega_0', \tag{7.245}$$

$$\varepsilon_\sigma \Gamma_{\rho c_p} \frac{d\langle T'_\sigma\rangle^\sigma}{dt'} = h\left(\langle T'_\beta\rangle^\beta - \langle T'_\sigma\rangle^\sigma\right) + a_v(1-\xi)\Omega'_0, \tag{7.246}$$

with zero uniform temperatures at $t = 0$. The analytical solution of this problem is given as

$$\langle T'_\beta\rangle^\beta (t') = \frac{\varepsilon_\sigma \Gamma_{\rho c_p}}{\left(\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta\right)^2}\left[\varepsilon_\sigma \Gamma_{\rho c_p}\xi - \varepsilon_\beta(1-\xi)\right]\frac{a_v \Omega'_0}{h}\left(1 - e^{-\frac{h\left(\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta\right)}{\varepsilon_\beta \varepsilon_\sigma \Gamma_{\rho c_p}}t'}\right) + \frac{a_v \Omega'_0}{\left(\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta\right)} t', \tag{7.247}$$

$$\langle T'_\sigma\rangle^\sigma (t') = -\frac{\varepsilon_\beta}{\left(\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta\right)^2}\left[\varepsilon_\sigma \Gamma_{\rho c_p}\xi - \varepsilon_\beta(1-\xi)\right]\frac{a_v \Omega'_0}{h}\left(1 - e^{-\frac{h\left(\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta\right)}{\varepsilon_\beta \varepsilon_\sigma \Gamma_{\rho c_p}}t'}\right) + \frac{a_v \Omega'_0}{\left(\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta\right)} t'. \tag{7.248}$$

From a fundamental viewpoint, this problem is interesting because it mixes the effects of both the heat exchange and the distribution coefficients. The sign of $\langle T'_\beta\rangle^\beta - \langle T'_\sigma\rangle^\sigma$ will essentially depend on ξ, which distributes the heat between the two phases. We can study this effect by subtracting Equation 7.248 from Equation 7.247,

$$\langle T'_\beta\rangle^\beta - \langle T'_\sigma\rangle^\sigma = \frac{\left[\varepsilon_\sigma \Gamma_{\rho c_p}\xi - \varepsilon_\beta(1-\xi)\right]}{\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta}\frac{a_v \Omega'_0}{h}\left(1 - e^{-\frac{h\left(\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta\right)}{\varepsilon_\beta \varepsilon_\sigma \Gamma_{\rho c_p}}t'}\right), \tag{7.249}$$

and look at the limit as $t \to \infty$:

$$\lim_{t\to\infty}\left(\langle T'_\beta\rangle^\beta - \langle T'_\sigma\rangle^\sigma\right) = \frac{\left[\varepsilon_\sigma \Gamma_{\rho c_p}\xi - \varepsilon_\beta(1-\xi)\right]}{\varepsilon_\sigma \Gamma_{\rho c_p} + \varepsilon_\beta}\frac{a_v \Omega'_0}{h}. \tag{7.250}$$

This difference is proportional to the heat source and will decrease if the exchange between the phases is large. The influence of the distribution coefficient is more complex and influences the sign of this difference. Indeed, we have

$$\lim_{t\to\infty}\left(\langle T'_\beta\rangle^\beta - \langle T'_\sigma\rangle^\sigma\right) = 0 \Rightarrow \varepsilon_\sigma^2 \frac{\rho_\sigma c_{p\sigma}}{k_\sigma} = \varepsilon_\beta^2 \frac{\rho_\beta c_{p\beta}}{k_\beta}, \tag{7.251}$$

showing that the change in the sign of the temperature difference does not occur for equal diffusivities or equal conductivities but instead for equal Fourier numbers. We also see that the volume fraction (or relative thickness in the stratified case) of the phases plays an important role. In the nonstratified case, the sign change will also occur for $\varepsilon_\sigma \Gamma_{\rho c_p}\xi - \varepsilon_\beta(1-\xi) = 0$, but ξ must be obtained from the solution of the related closure problem.

To compare micro- and macroscale results, we now solve the problem given by Equations 7.242 numerically using an FE approach (COMSOL Multiphysics®). Results are presented in Figure 7.11. For the curves corresponding to $\Gamma_k = 20$ and $\Gamma_k = 0.05$, the important difference between the thermal conductivity of both phases produces a temperature field with the largest temperatures corresponding to the largest thermal conductivity. For $\Gamma_k = 1.2$, however, the conductivity of phase σ is only slightly larger than the conductivity of phase β so that the largest temperature corresponds to the thinnest stratum.

We compare these results with those obtained via the quasi-stationary two-equation model in Figure 7.12 where the averaged temperature fields were reconstructed discretely using quadrature

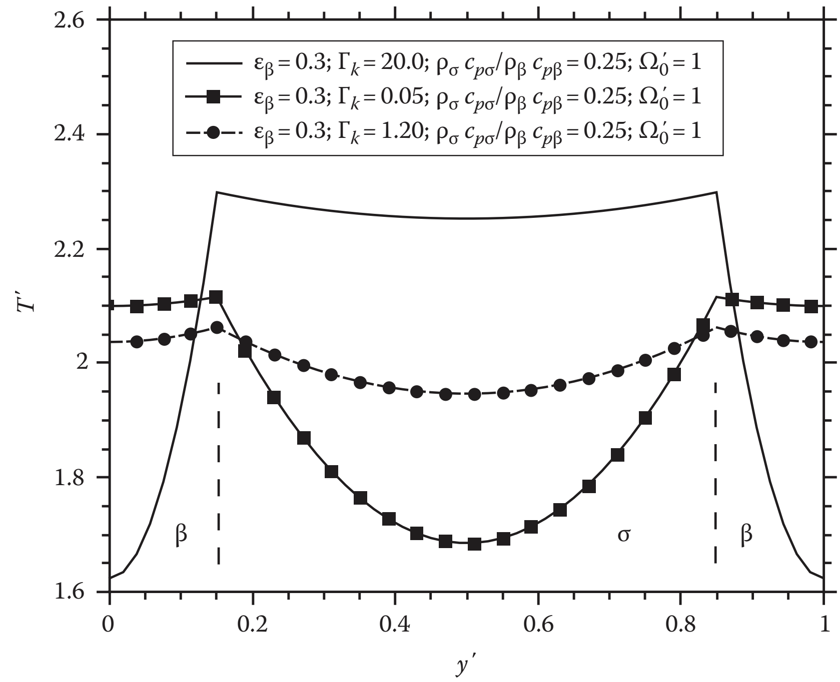


FIGURE 7.11 Pore-scale temperature field for different values of the pore-scale parameters as $t' \to \infty$.

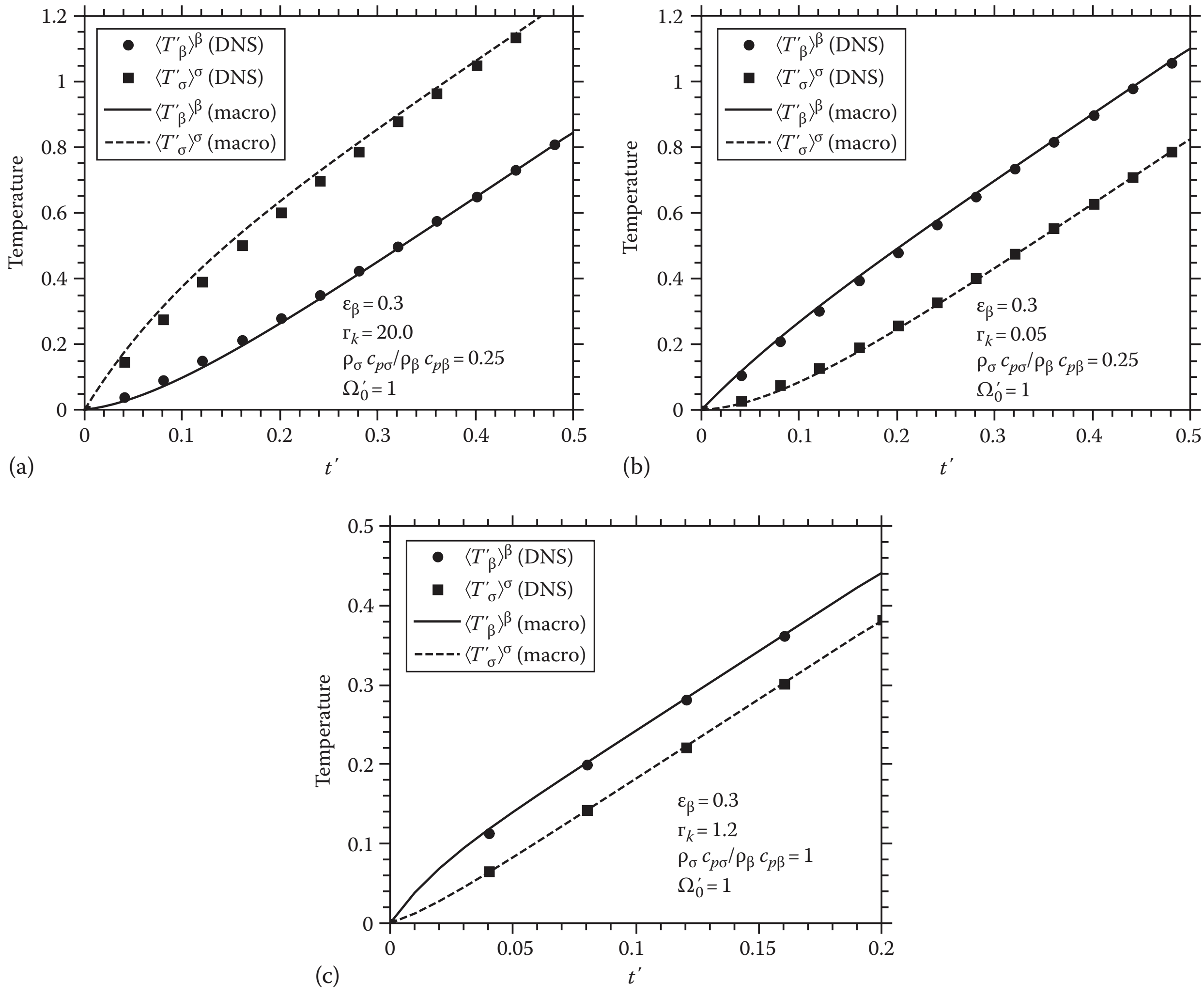


FIGURE 7.12 Evolution of $\langle T'_\beta \rangle^\beta$ and $\langle T'_\sigma \rangle^\sigma$ versus time for different parameters. (a) $\Gamma_k = 20$ and $(\rho c_p)_\sigma/(\rho c_p)_\beta = 0.25$; (b) $\Gamma_k = 0.05$ and $(\rho c_p)_\sigma/(\rho c_p)_\beta = 0.25$; and (c) $\Gamma_k = 1.2$ and $(\rho c_p)_\sigma/(\rho c_p)_\beta = 1$.

formulas. Typically, after a short transient evolution, the average temperature difference reaches a constant value. This evolution is perfectly captured by the two-equation quasi-stationary model, with only a small difference in the short-time limit where the steady closure fails to capture all characteristic times. The fact that the temperature difference is perfectly captured by the two-equation model means that both the exchange and the distribution coefficients are accurately calculated from the closure problems.

7.10.1.3 One-Dimensional Case with Homogeneous Sources, $\Omega_0' = 0$

Corrector results are reconstructions of the microscale fields from the average models, using the average temperature fields and the mapping variables. Here, our goal is to compare corrector results for the two-equation quasi-stationary and one-equation models with results of numerical simulations at the microscale. We consider the case of a homogeneous constant source of heat in both phases with a stratified system as presented in Figure 7.9. We study only the steady temperatures, so that analytical solutions are easily obtained for the average equations.

The stationary microscale problem becomes

$$0 = \Delta T_\beta' + R_0' \text{ in } \mathcal{V}_\beta, \tag{7.252a}$$

$$\text{BC1} \quad T_\beta' - T_\sigma' = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.252b}$$

$$\text{BC2} \quad \mathbf{n}_{\beta\sigma} \cdot \left(\nabla' T_\beta' - \Gamma_k \nabla' T_\sigma' \right) = 0 \text{ on } \mathcal{A}_{\beta\sigma}, \tag{7.252c}$$

$$\text{BC3} \quad \text{Periodicity} \tag{7.252d}$$

$$\text{IC} \quad T_\beta'\left(t = 0\right) = T_\sigma'\left(t = 0\right) = 0, \tag{7.252e}$$

$$0 = \Gamma_k \Delta' T_\sigma' + R_0' \text{ in } \mathcal{V}_\sigma, \tag{7.252f}$$

with $l_\beta = l_\sigma = 1/2$.

On averaging in the y-direction, the quasi-stationary two-equation model reads

$$0 = \varepsilon_\beta \frac{d^2 \left\langle T_\beta' \right\rangle^\beta}{dx'^2} - h\left(\left\langle T_\beta' \right\rangle^\beta - \left\langle T_\sigma' \right\rangle^\sigma \right) + \varepsilon_\beta R_0', \tag{7.253}$$

$$0 = \varepsilon_\sigma \Gamma_k \frac{d^2 \left\langle T_\sigma' \right\rangle^\sigma}{dx'^2} + h\left(\left\langle T_\beta' \right\rangle^\beta - \left\langle T_\sigma' \right\rangle^\sigma \right) + \varepsilon_\sigma R_0', \tag{7.254}$$

with zero uniform temperatures at $t = 0$ and boundaries $\left\langle T_\beta' \right\rangle^\beta = \left\langle T_\sigma' \right\rangle^\sigma = 0$ for $x = 0$ and $x = 5$. We remark that, for simplicity, we have used a standard first-order two-equation model here, not the

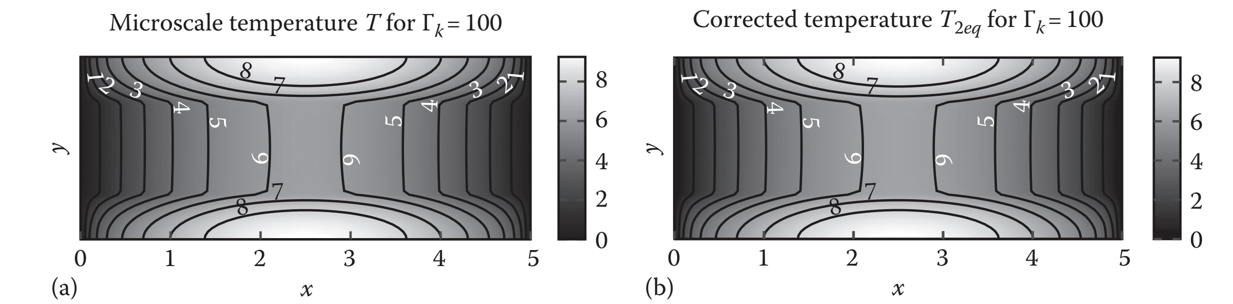


FIGURE 7.13 Results for (a) the microscale and (b) the corrector for the two-equation model.

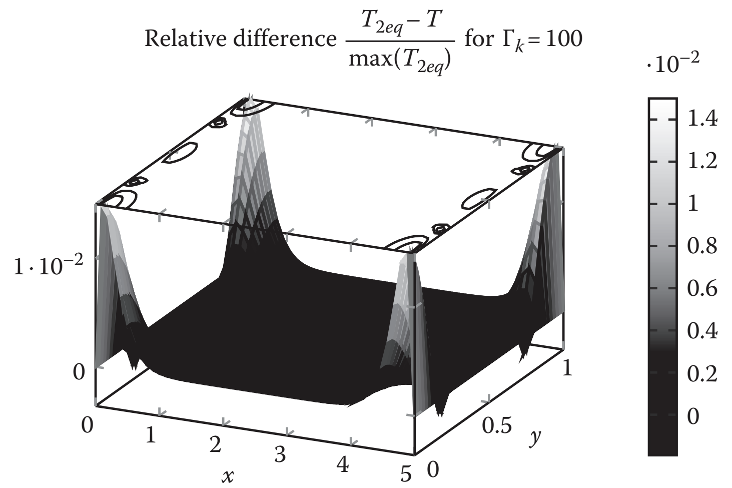


FIGURE 7.14 Relative difference between corrector-type and microscale results.

more general second-order closure used in this chapter. A microscale field was reconstructed by solving analytically the two-equation model and using

$$T_{\beta,2eq} = \langle T'_\beta \rangle^\beta (x) + \mathsf{a}_\beta (y) \left(\langle T'_\beta \rangle^\beta - \langle T'_\sigma \rangle^\sigma \right)(x), \tag{7.255}$$

$$T_{\sigma,2eq} = \langle T'_\sigma \rangle^\sigma (x) + \mathsf{a}_\sigma (y) \left(\langle T'_\beta \rangle^\beta - \langle T'_\sigma \rangle^\sigma \right)(x), \tag{7.256}$$

where a_β and a_σ are the closure variables (second-order polynomials in y here). Equations 7.252a through f were solved numerically using an FE approach. Comparison of the direct numerical solutions of the microscale result and the corrector results is plotted in Figure 7.13. A plot of the relative difference is given in Figure 7.14, showing that the error localizes close to the boundaries and the maximum is about one percent.

For comparison purposes, it is interesting to consider the cases of the one-equation quasi-stationary LE and LNE models, which in this case are equivalent. The corrector yields only a 1D field so that the one-equation model necessarily fails to recover the correct microscale solutions. This also suggests that even for a stationary problem, the two-equation models may provide a much better approximation (excellent here) of the solution than a one-equation model and therefore a more secure way of solving problems when a doubt exists about potential nonequilibrium effects.

7.10.2 Model Selection and Domains of Validity

In this section, we show that the choice of a specific macroscale model is a complex matter. A model may suddenly fail to describe accurately transport because of changes in the transport conditions,

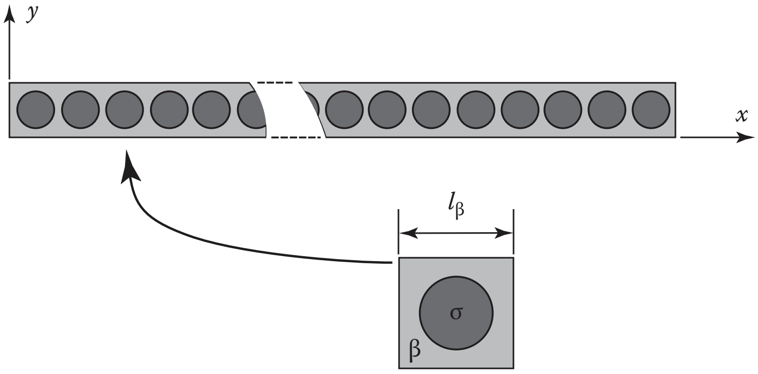


FIGURE 7.15 Array of cylinders.

for example, effect of heterogeneities, source terms, or proximity with a boundary condition. To illustrate this behavior, we further develop an example that was initially proposed in [128] for a 1D macroscale model. We perform pore-scale numerical simulations over an array of cylinders, as illustrated in Figure 7.15, consisting of n_{UC} unit cells of length l_β. We first solve Stokes equations, Equations 7.2a and 7.2c, to obtain the velocity field, v_β, and the corresponding intrinsic β-phase velocity, $U_\beta = \langle \mathrm{v}_\beta \rangle^\beta$. Then we use the velocity field to solve Equations 7.3a through 7.3f for heat transfer, that is, $u_\alpha = T_\alpha$ (for $\alpha = \beta, \sigma$), where T is the temperature and $a_\alpha = c_{p\alpha}$ is the specific heat capacity. The initial and boundary conditions read as follows:

- No sources or sinks.
- Impervious and adiabatic lateral walls.
- $T_\beta = T_\sigma = 1$ at $x = 0$ and $T_\beta = T_\sigma = 0$ at $x = n_{UC} l_\beta$. We will see later that this Dirichlet condition significantly affects heat transfer and the discussion.
- $T_\beta(\mathrm{x}, t) = T_\sigma(\mathrm{x}, t) = 0$ at $t = 0$.

Once we have obtained the microscale solution, we calculate the average temperature fields $\langle T_\beta \rangle^\beta$ and $\langle T_\sigma \rangle^\sigma$ and compare them with the numerical solutions of the three macroscale models: the two-equation quasi-stationary, one-equation LE, and one-equation LNE models. The two-equation model is

$$\varepsilon_\beta \rho_\beta c_{p\beta} \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} + \varepsilon_\beta \rho_\beta c_{p\beta} U_\beta \frac{\partial \langle T_\beta \rangle^\beta}{\partial x} = \frac{\partial}{\partial x}\left(K^*_{\beta\beta} \frac{\partial \langle T_\beta \rangle^\beta}{\partial x} + K^*_{\beta\sigma} \frac{\partial \langle T_\sigma \rangle^\sigma}{\partial x} \right)$$
$$- h\left(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma \right), \tag{7.257}$$

$$\varepsilon_\sigma \rho_\sigma c_{p\sigma} \frac{\partial \langle T_\beta \rangle^\beta}{\partial t} = \frac{\partial}{\partial x}\left(K^*_{\sigma\beta} \frac{\partial \langle T_\beta \rangle^\beta}{\partial x} + K^*_{\sigma\sigma} \frac{\partial \langle T_\sigma \rangle^\sigma}{\partial x} \right)$$
$$+ h\left(\langle T_\beta \rangle^\beta - \langle T_\sigma \rangle^\sigma \right), \tag{7.258}$$

with boundary conditions

$$\langle T_\beta \rangle^\beta = \langle T_\sigma \rangle^\sigma = 1 \quad \text{at } x = 0, \tag{7.259}$$

$$\langle T_\beta \rangle^\beta = \langle T_\sigma \rangle^\sigma = 0 \quad \text{at } x = n_{UC} l_\beta, \tag{7.260}$$

$$\langle T_\beta \rangle^\beta = \langle T_\sigma \rangle^\sigma = 0 \quad \text{at } t = 0. \tag{7.261}$$

The one-equation LE model reads

$$\left(\rho c_p\right)^* \frac{\partial T_{\mathrm{LE}}}{\partial t} + \varepsilon_\beta \rho_\beta c_{p\beta} U_\beta \frac{\partial T_{\mathrm{LE}}}{\partial x} = \frac{\partial}{\partial x}\left(K_{\mathrm{LE}}^* \frac{\partial T_{\mathrm{LE}}}{\partial x} \right), \tag{7.262}$$

where $(\rho c_p)^* = \varepsilon_\beta \rho_\beta c_{p\beta} + \varepsilon_\sigma \rho_\sigma c_{p\sigma}$, and the one-equation LNE model is

$$\left(\rho c_p\right)^* \frac{\partial T_{\mathrm{LNE}}}{\partial t} + \varepsilon_\beta \rho_\beta c_{p\beta} U_\beta \frac{\partial T_{\mathrm{LNE}}}{\partial x} = \frac{\partial}{\partial x}\left(K_{\mathrm{LNE}}^* \frac{\partial T_{\mathrm{LNE}}}{\partial x} \right), \tag{7.263}$$

where the mixture temperature, T_{LNE}, is given as

$$T_{LNE} = \frac{\varepsilon_\beta \rho_\beta c_{p\beta} \langle T_\beta \rangle^\beta + \varepsilon_\sigma \rho_\sigma c_{p\sigma} \langle T_\sigma \rangle^\sigma}{\varepsilon_\beta \rho_\beta c_{p\beta} + \varepsilon_\sigma \rho_\sigma c_{p\sigma}}, \tag{7.264}$$

and

$$K_{\mathrm{LNE}}^* = K_{\mathrm{LE}}^* + \frac{1}{h} \frac{\left(\varepsilon_\beta \rho_\beta c_{p\beta} \varepsilon_\sigma \rho_\sigma c_{p\sigma}\right)^2}{\left(\varepsilon_\beta \rho_\beta c_{p\beta} + \varepsilon_\sigma \rho_\sigma c_{p\sigma}\right)^2} U_\beta U_\beta. \tag{7.265}$$

The closure problems giving the effective parameters in these equations were solved following the numerical procedures in [65] with the following parameters:

$$n_{UC} = 480, \quad \frac{\rho_\sigma c_{p\sigma}}{\rho_\beta c_{p\beta}} = 1, \quad \varepsilon_\beta = 0.615, \quad \frac{k_\sigma}{k_\beta} = 0.01. \tag{7.266}$$

The resulting values are

$$\frac{K_{\beta\beta}^*}{k_\beta} \simeq 0.4455, \quad \frac{K_{\sigma\beta}^*}{k_\beta} = \frac{K_{\beta\sigma}^*}{k_\beta} \simeq 0.1757 \times 10^{-2}, \quad \frac{K_{\sigma\sigma}^*}{k_\beta} \simeq 0.3845 \times 10^{-2}, \quad \frac{h l_\beta^2}{k_\beta} \simeq 0.25, \tag{7.267}$$

for a Péclet number $\mathrm{Pe}_l \simeq 0.556$, defined as $\mathrm{Pe}_l = \frac{\rho_\beta c_{p\beta} U_\beta l_\beta}{k_\beta}$. We also found a value of K_{LNE}^* very close, as expected, to $K_{\beta\beta}^* + K_{\sigma\beta}^* + K_{\beta\sigma}^* + K_{\sigma\sigma}^*$, that is,

$$\frac{K_{\mathrm{LE}}^*}{k_\beta} = 0.453, \quad \frac{K_{\mathrm{LNE}}^*}{k_\beta} = 0522. \tag{7.268}$$

For Figure 7.16, we define the characteristic time t_{ad} as

$$t_{ad} = \frac{k_\beta t}{\rho_\beta c_{p\beta} l_\beta^2}, \tag{7.269}$$

and x is scaled by l_β. For the shortest time plotted in Figure 7.16a, we observe a progression of the thermal front only over a few unit cells. In principle, the close proximity of the boundary on the LHS and the corresponding boundary effects cannot be captured by homogenized models, although the two-equation model still captures essential features. For the second time, illustrated in Figure 7.16b, the temperature fields have had time to spread but still exhibit LNE effects. For the third time, illustrated in Figure 7.16c, the time-asymptotic regime has been reached. Finally, for the fourth time, illustrated in Figure 7.16c, the fields have reached steady state, which is strongly affected by the Dirichlet condition on the RHS boundary. We remark that the two-equation model provides accurate results for all times.

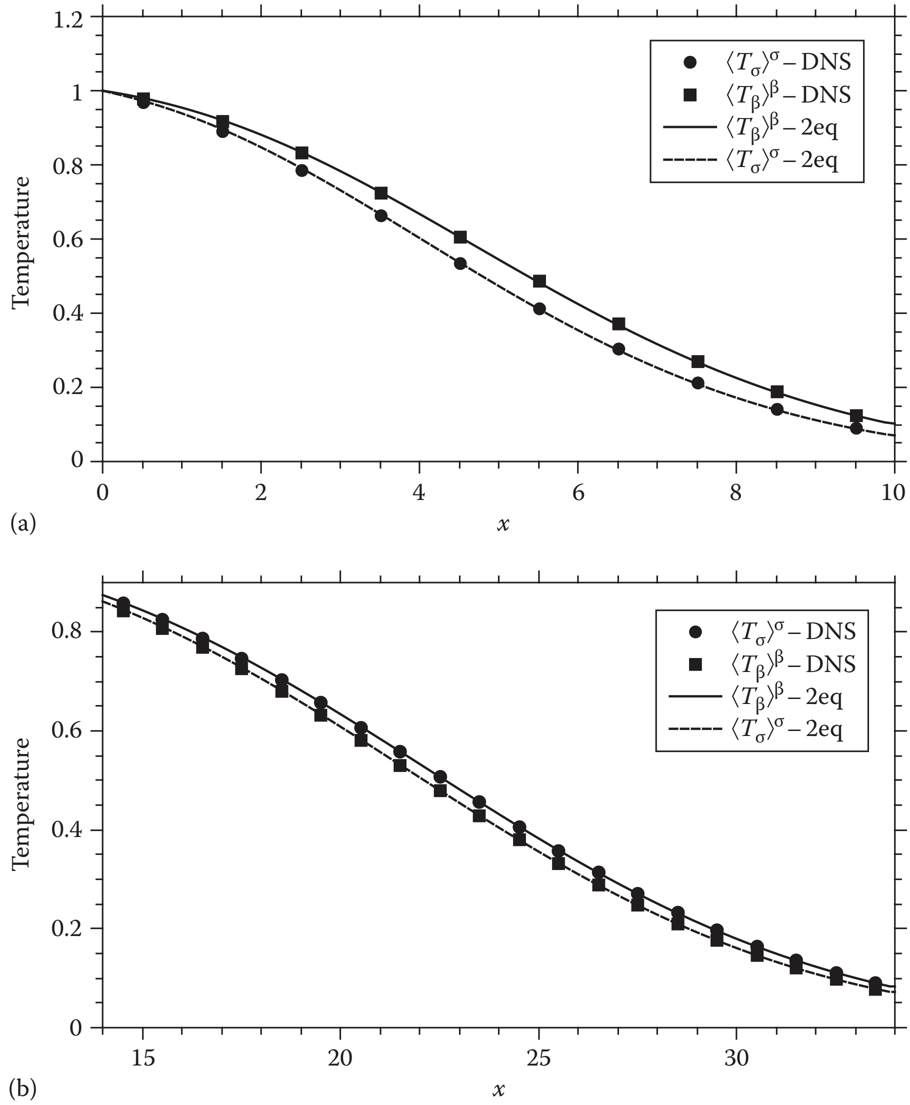
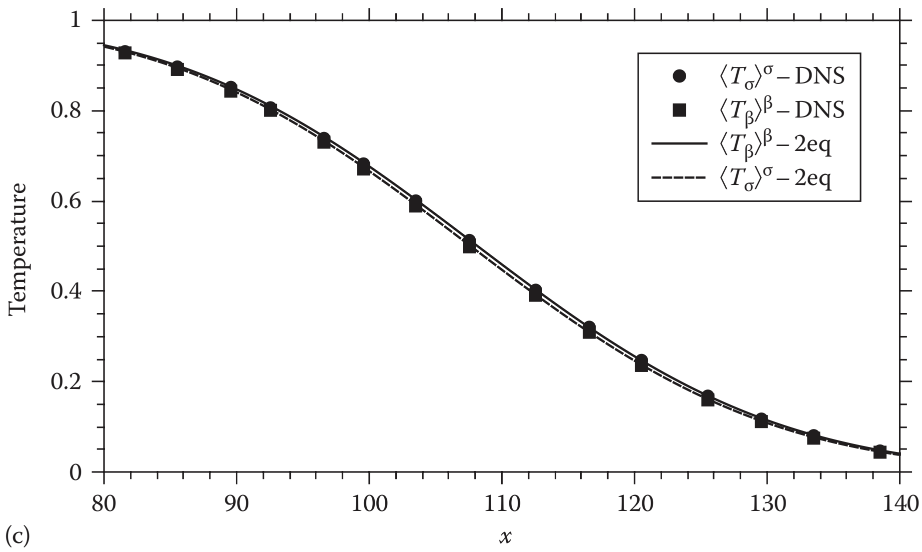
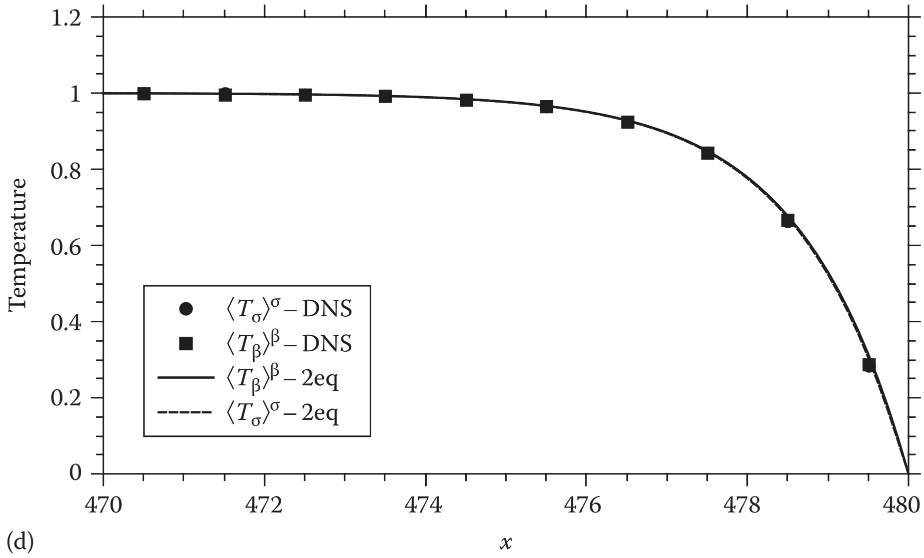


FIGURE 7.16 Comparison of the averaged phase temperatures for direct numerical simulation (symbols) and the two-equation quasi-stationary model (solid lines). Results are plotted against the dimensionless spatial variable, x, for different dimensionless times: (a) $t_{ad} = 5 \times 10^{-5}$, (b) $t_{ad} = 2.5 \times 10^{-4}$. (*Continued*)



(c)



(d)

FIGURE 7.16 (*Continued*) Comparison of the averaged phase temperatures for direct numerical simulation (symbols) and the two-equation quasi-stationary model (solid lines). Results are plotted against the dimensionless spatial variable, x, for different dimensionless times: (c) $t_{ad} = 1.25 \times 10^{-3}$, and (d) steady state $t_{ad} \to \infty$.

We now study results obtained using the one-equation representations and compare results with those obtained with the two-equation model, which is used as a reference (results for the mixture temperature difference between DNS and the two-equation model are small, on the order of numerical accuracy, as indicated by the results plotted in Figure 7.17). To quantify differences, we calculate the mixture temperature, $T^{\beta\sigma}$, defined as

$$T^{\beta\sigma} = \frac{\varepsilon_\beta \rho_\beta c_{p\beta} \left\langle T_\beta \right\rangle^\beta + \varepsilon_\sigma \rho_\sigma c_{p\sigma} \left\langle T_\sigma \right\rangle^\sigma}{\varepsilon_\beta \rho_\beta c_{p\beta} + \varepsilon_\sigma \rho_\sigma c_{p\sigma}}, \tag{7.270}$$

using results from the two-equation quasi-stationary model. We then consider the differences $T_{\text{LE}} - T_{2eq}^{\beta\sigma}$ and $T_{\text{LNE}} - T_{2eq}^{\beta\sigma}$ that are plotted in Figure 7.17. We remark that, at the early stages in Figure 7.17a and b, the temperature obtained via the one-equation models is significantly different from the mixture temperature obtained using the two-equation model. Between the two one-equation models, the one based on the LE assumption seems to provide slightly better results in

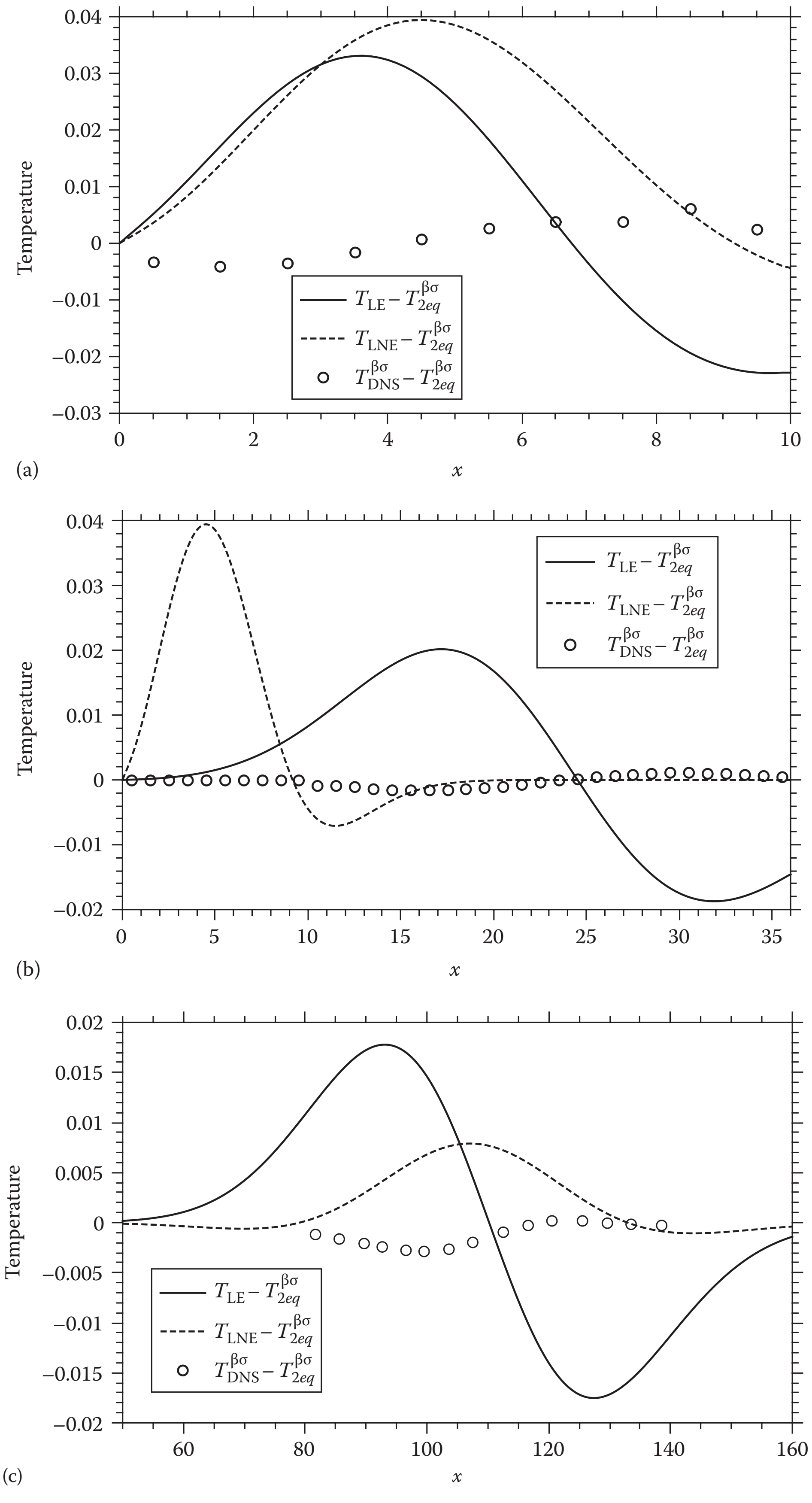


FIGURE 7.17 Differences between the mixture temperature $T_{2eq}^{\beta\sigma}$ calculated from the two-equation model and the results of the one-equation LE model, the LNE model, and the DNS. Results are plotted against the dimensionless spatial variable, x, for different dimensionless times: (a) $t_{ad} = 5 \times 10^{-5}$, (b) $t_{ad} = 2.5 \times 10^{-4}$, (c) $t_{ad} = 1.25 \times 10^{-3}$. *(Continued)*

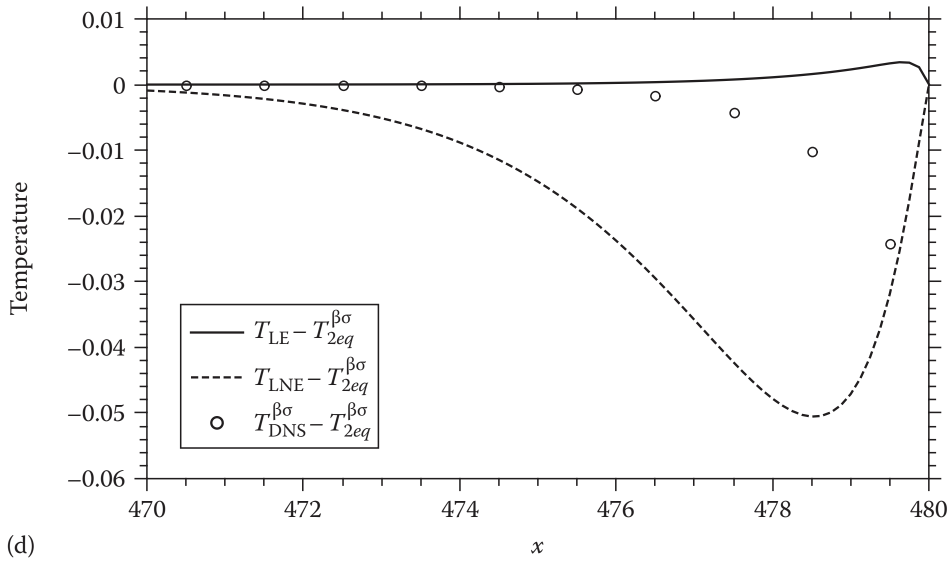


FIGURE 7.17 ***(Continued)*** Differences between the mixture temperature $T_{2eq}^{\beta\sigma}$ calculated from the two-equation model and the results of the one-equation LE model, the LNE model, and the DNS. Results are plotted against the dimensionless spatial variable, x, for different dimensionless times: (d) steady state $t_{ad} \to \infty$.

the early stages. As time increases, however, the asymptotic regime is reached and the one-equation LNE model provides a better estimation than the one-equation LE model (see Figure 7.17c). Finally, at *steady state*, the LE model provides surprisingly good results (see Figure 7.17d). On the other hand, the one-equation LNE model fails to capture accurately the temperature as it induces too much spreading. This stems from the fact that this particular *steady state* is strongly affected by the Dirichlet boundary condition, which imposes an LE-like situation. This situation is specific to the 1D configuration and the absence of heat sources/sinks (contrary to the problem treated in Section 7.10.2). We also emphasize that the two-equation model provides good results in all cases and conclude that, if a doubt exists as to the behavior of the system, the model of choice clearly is the two-equation representation.

7.11 DISCUSSION AND CONCLUSION

A single transport problem at the microscale usually leads to a multiplicity of macroscale models. Depending on the physical parameters of the problem, the boundary conditions, the tolerance, and the computational cost that are acceptable, we can use a variety of different macroscale models. In this work, we discussed models for scalar transport in porous media (see summary in Figure 7.18): one- and two-equation models both equilibrium and nonequilibrium, integrodifferential descriptions of time nonlocality, and hybrid approaches that couple partial differential equations acting at different scales. We presented the corresponding mathematical developments, discussed the domains of validity of the different models, and highlighted several fundamental features by comparing computations at the pore-scale with results of the homogenized models. As an example, we also showed how effective parameters can be calculated directly over a 3D image of a bead packing obtained using x-ray computed microtomography.

This contribution is, in many ways, an update of the previous handbook chapter by Quintard and Whitaker [17]. Quintard and Whitaker focused on two-equation quasi-stationary and one-equation LE models. Here, we have presented the one-equation LNE model; we have extended the models to the fully transient cases and to nonlinear bulk and surface sources/sinks; and we have discussed hybrid micro–macro strategies using a simple example. We have also derived the models using a second-order closure, a technical point that had never been performed before (although the idea was proposed in [129] to deal with the different problem of two-phase flow in heterogeneous porous media). We showed that this leads to additional terms in both the macro- and microscale equations.

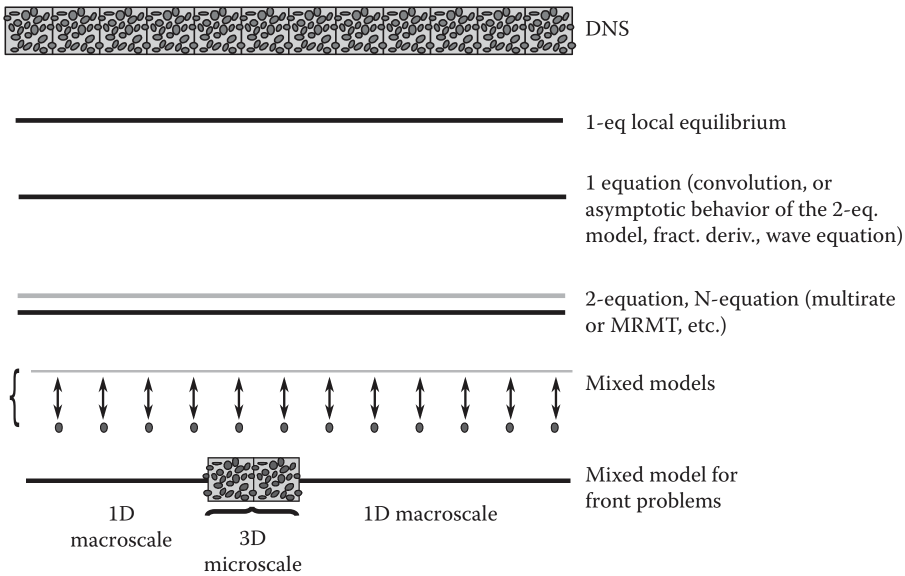


FIGURE 7.18 Schematic representation summarizing the different models reviewed in this chapter.

The different examples presented in Section 7.10 emphasize the difficulty to predict if one-equation models can be used accurately. The answer depends upon the topology of the problem, initial and boundary conditions, and the presence of sources/sinks. On the other hand, the two-equation model provides excellent results in most cases, even when in LNE conditions. Therefore, we recommend it as a model of choice if a doubt exists as to the behavior of the system. In particular, it may be used to examine domains of validity for various classes of problems, thus providing reference results for assessing the viability of one-equation models.

There are many other open problems in the field, in particular those involving strong nonlinear coupling between mass, momentum, and energy transfers. Bulk or surface heat sources in the energy equations may be uncoupled from heat transfer, for example, in the case of the cooling of nuclear reactor debris beds where the heat source is produced by radioactivity. They may also lead to strongly nonlinear coupled problems, as is the case for smoldering or combustion in porous media. Highly nonlinear reaction terms, such as Arrhenius equations, or the potential existence of sharp combustion fronts may require more complicated closures [107], direct numerical simulations, or hybrid models [95].

Similarly, weak coupling of thermodynamic quantities, that is, density, viscosity, thermal diffusion, or mass diffusion coefficients, can produce complex behaviors. From an averaging viewpoint, one way to treat such problems is to assume that perturbations are relatively small so that

$$\rho\left(T_\beta, p_\beta\right) \simeq \rho\left(\left\langle T_\beta\right\rangle^\beta, \left\langle p_\beta\right\rangle^\beta\right) + \tilde{T}_\beta \frac{\partial \rho}{\partial T} + \tilde{p}_\beta \frac{\partial \rho}{\partial p}, \tag{7.271}$$

or even

$$\rho\left(T_\beta, p_\beta\right) \simeq \rho\left(\left\langle T_\beta\right\rangle^\beta, \left\langle p_\beta\right\rangle^\beta\right). \tag{7.272}$$

An important consequence, however, is that the closure problems will still be coupled to these parameters and may therefore depend nonlinearly on $\langle c_\beta\rangle^\beta$ and $\langle T_\beta\rangle^\beta$.

One-sided coupling may be treated relatively easily. This is the case, for instance, when modeling thermodiffusion with only Soret effect (see [128]) where the thermal upscaling problem may be treated independently of the species transport problem. Most of the time, however, coupling is quite complicated and it is difficult to find a complete closure. This, of course, leaves the door opened to empirical or semiempirical models that are in fact used in many models in porous media physics. To illustrate such problems, consider transport in porous media with intense phase change, such as boiling occurring when cooling hot debris bed in nuclear reactor after a loss-of-coolant accident (LOCA). So far, closures have been proposed in which the momentum transport is treated independently. Practical models make use of generalized Darcy's laws or Forchheimer extensions [130–132]. These models remain largely heuristic and are not entirely supported by upscaling developments [133–136], which in fact are made without taking into account the specifics of the phase repartition when boiling occurs in the porous medium. The need for nonequilibrium heat transfer model for LOCA modeling has been recognized long ago [137,138]. The macroscale model can be written as a three-temperature model. A limited closure can be found for such a model assuming a quasi-static gas–liquid interface [106]. Calculations of the effective properties suggest a significant difference between the values for a wet solid surface, the so-called *slg* configuration, which occurs when boiling is not important, compared to an *slg* configuration with a vapor film near the solid surface. Moreover, pore-scale nucleate boiling does not fit with the idea of a quasi-static interface. Therefore, it is expected that both two-phase and energy models should be impacted by the phase change process taking place within the pores. Experimental evidence interpreted through a three-temperature model [139] suggests that there is indeed an impact of the two-phase configuration on the effective properties and that, at least for the heat exchange coefficients, Nukiyama curves [140] specific to porous media configurations should be introduced.

Further, several problems of paramount importance have not been addressed in this chapter, in particular numerical methods that are used to solve closure problems, evolving microscale structures, the development of experimental techniques for imaging porous media, and image processing, including thresholding and meshing difficulties associated with 3D imaging techniques. Absorption x-ray computed microtomography can be used to obtain the phase distribution and calculate effective parameters, as is illustrated for a bead packing in this work, but image processing and meshing of such structures poses a number of challenges (see, e.g., [141]).

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