Advances in Water Resources 51 (2013) 139–167

Contents lists available at SciVerse ScienceDirect

Advances in Water Resources

journal homepage: www.elsevier.com/locate/advwatres

Volume averaging: Local and nonlocal closures using a Green's function approach

Brian D. Wood [a,*], Francisco J. Valdés-Parada [b]

[a] School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, OR 97331, United States
[b] Area de Ingeniería en Recursos Energéticos, Universidad Autónoma Metropolitana-Iztapalapa, 09340 Mexico, DF, Mexico

ARTICLE INFO

Article history:
Available online 6 July 2012

Keywords:
Closure variable
Volume averaging
Green's function
Integro-differential equations
Nonlocal transport

ABSTRACT

Modeling transport phenomena in discretely hierarchical systems can be carried out using any number of upscaling techniques. In this paper, we revisit the method of volume averaging as a technique to pass from a microscopic level of description to a macroscopic one. Our focus is primarily on developing a more consistent and rigorous foundation for the relation between the microscale and averaged levels of description. We have put a particular focus on (1) carefully establishing statistical representations of the length scales used in volume averaging, (2) developing a time–space nonlocal closure scheme with as few assumptions and constraints as are possible, and (3) carefully identifying a sequence of simplifications (in terms of *scaling postulates*) that explain the conditions for which various upscaled models are valid. Although the approach is general for linear differential equations, we upscale the problem of linear convective diffusion as an example to help keep the discussion from becoming overly abstract.

In our efforts, we have also revisited the concept of a closure variable, and explain how closure variables can be based on an integral formulation in terms of Green's functions. In such a framework, a closure variable then represents the integration (in time and space) of the associated Green's functions that describe the influence of the average sources over the spatial deviations. The approach using Green's functions has utility not only in formalizing the method of volume averaging, but by clearly identifying how the method can be extended to transient and time or space nonlocal formulations.

In addition to formalizing the upscaling process using Green's functions, we also discuss the upscaling process itself in some detail to help foster improved understanding of how the process works. Discussion about the role of *scaling postulates* in the upscaling process is provided, and poised, whenever possible, in terms of measurable properties of (1) the parameter fields (including the indicator fields describing the medium geometry) associated with the transport phenomenon of interest, and (2) measurable properties of the independent variable itself. To highlight the relevance of this interpretation we study the benchmark problem of linear nonlocal diffusion in porous media.

1. Introduction

Transport phenomena modeling in hierarchical, multiscale systems requires the systematic passing of information from one scale to the others. Despite current advances in computational capabilities, it is still generally not feasible to model a complete macroscopic system (such as the discretely hierarchical system depicted in Fig. 1) by performing direct numerical simulations of microscale formulations. Furthermore, even if such a feat were possible, there is the question about how one would usefully apply such information. One method to address this problem is to directly derive models at an intermediate level of resolution between the microscale and the macroscale, using an averaging operator. The averaging operator itself may be viewed as the response of an instrument probing intensive field variables; this interpretation has been discussed by Baveye and Sposito [9] and by Cushman [24]. In this special issue of *Advances in Water Resources* two different (but related) perspectives on averaging are presented. One (known generally as the method of volume averaging with closure, or MVA) is represented by this paper; the second presents an overview of the thermodynamically constrained averaging theory (TCAT), which has been clearly presented in a separate paper by Gray et al. [34].

In this work, we consider the averaging of a linear convection–dispersion-reaction equation starting from the sub-pore scale of resolution. Developing an averaged model consists of applying an averaging operator to the relevant balances as they occur for the microscale level of resolution (Level I in Fig. 1). The averaging process allows one to develop a set of equations and boundary conditions at the macroscale level (Level III in Fig. 1). The result is a systematic reduction in the number of degrees of freedom involved in the microscale model by means of the process of upscaling (*cf.*

* Corresponding author.
E-mail address: brian.wood@oregonstate.edu (B.D. Wood).

0309-1708/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.advwatres.2012.06.008

Nomenclature

a	radius of the cylindrical-shaped obstacle in Chang's unit cell, m
$\mathbf{A}_\gamma$	a closure variable that maps $\nabla\nabla\langle\psi_\gamma\rangle^\gamma$ onto $\tilde{\psi}_\gamma$, m^2
$\mathcal{A}_{\gamma\kappa,M}$	surface domain of the fluid–solid interface within the entire macroscopic volume $\mathcal{V}_M$
$\mathcal{A}_{\gamma e,M}$	surface domain associated with the external boundary of the macroscopic volume $\mathcal{V}_M$ and intersecting the γ-phase
$\mathcal{A}_{\kappa e,M}$	surface domain associated with the external boundary of the macroscopic volume $\mathcal{V}_M$ and intersecting the κ-phase
$\mathcal{A}_{e,M}$	surface domain associated with the external boundary of the macroscopic volume $\mathcal{V}_M$ ($\mathcal{A}_{e,M} = \mathcal{A}_{\gamma e,M} \cup \mathcal{A}_{\kappa e,M}$)
$\mathcal{A}_{\gamma\kappa}(\mathbf{x})$	surface domain of the fluid–solid interface within the averaging region
$\mathcal{A}_{\gamma e}(\mathbf{x})$	domain of the entrance/exit boundaries on the surface of the averaging domain $\mathcal{V}(\mathbf{x})$
$A_{\gamma\kappa}(\mathbf{x})$	area of the γ–κ interface within the averaging domain $\mathcal{V}(\mathbf{x})$, m^2
$\mathbf{b}_\gamma$	closure variable that maps $\nabla\langle\psi_\gamma\rangle^\gamma$ onto $\tilde{\psi}_\gamma$, m
$c_{A\gamma}$	microscale concentration of species A in the γ-phase, mol/m^3
$\tilde{c}_{A\gamma}$	concentration deviations of species A, mol/m^3
$\langle c_{A\gamma}\rangle^\gamma$	intrinsic averaged concentration, mol/m^3
$\mathbb{C}_\gamma$	intrinsic averaged concentration, used in Section 7 to simplify notation, mol/m^3
$\mathcal{D}_\gamma$	molecular diffusion coefficient, m^2/s
$\mathbf{D}_\gamma$	diffusion tensor in the γ-phase, m^2/s
$\mathbf{D}_{0,eff}$	effective diffusivity tensor, m^2/s
$\mathbf{D}_{2,eff}$	second-order correction tensor, m^4/s
$\mathbf{e}_i$	unit vectors defining Cartesian coordinate system, $i = \zeta, \eta, \xi$
f	microscale volumetric source term
$\langle f\rangle^\gamma$	intrinsic average of f
$\mathcal{F}\{\cdot\}$	Fourier transform
$\mathcal{F}^{-1}\{\cdot\}$	inverse Fourier transform
g	microscale surface source term
$G(\mathbf{x}, t; \mathbf{y}, \tau)$	a Green's function
$\mathcal{G}$	source term in the closure problem, as defined by Eq. (5.3b)
I	initial distribution of ψ_γ
$\mathcal{I}$	initial distribution of $\tilde{\psi}_\gamma$, as defined by Eq. (5.3d)
$\mathbf{I}$	the identity tensor
k_1	homogeneous first-order reaction rate parameter in the γ-phase
k_s	heterogeneous first-order surface reaction rate parameter at the γ–κ interface
$\mathbf{K}_0, \mathbf{K}_1, K_2, K_3$	kernel functions
$\mathbf{l}_i$	unit cell lattice vectors, $i = x, y, z$, m
ℓ_γ	the characteristic length (integral scale) for the indicator function Φ_γ, m
ℓ_{p_γ}	integral scale for the parameter field $p_\gamma(\mathbf{x})$, where $p_\gamma(\mathbf{x})$ may be any of the parameter fields that appear in the microscale differential balance for ψ_γ
ℓ_{ch}	diameter of Chang's unit cell, m
ℓ_K	characteristic length associated with a kernel function, m
$\ell_{\tilde{\psi}_\gamma}$	characteristic length associated with the dependent variable deviation field, m
L	characteristic length associated with the macroscale, m
$L_{\mathbb{P}_\gamma}$	characteristic length (integral length scale) associated with the average of a parameter or source field $\mathbb{P}_\gamma$, m
$L_{\langle\psi_\gamma\rangle^\gamma}$	characteristic length (integral length scale) associated with $\langle\psi_\gamma\rangle^\gamma$, m
$\mathcal{L}\{\cdot\}$	linear second-order differential balance operator, m/s
$\mathcal{L}_0\{\cdot\}$	portion of $\mathcal{L}\{\cdot\}$ containing averaged parameter fields, m/s
$\tilde{\mathcal{L}}\{\cdot\}$	portion of $\mathcal{L}\{\cdot\}$ containing deviations of the parameter fields, m/s
M_p	p-th moment of distribution
$\mathbf{n}_{\gamma\kappa}$	unit normal vector directed from the γ-phase toward the κ-phase
N	nonlocal contribution associated with $\langle\psi_\gamma\rangle^\gamma$, and defined in Eq. (4.14b)
$\mathcal{N}$	nonlocal contribution associated with $\tilde{\psi}_\gamma$, and defined in Eq. (4.14c)
$\mathbf{O}$	order of magnitude symbol
p_γ	a generic parameter or source field for the microscale balance; p–γ may be a scalar, vector, or tensor field
$\mathbb{P}_\gamma$	intrinsic average of p_γ
$\tilde{p}_\gamma$	spatial deviations of p_γ
$\mathcal{P}$	a closure variable
$\mathcal{Q}$	contribution of the initial condition to the fields of $\tilde{\psi}_\gamma$, as defined by Eq. (5.3c)
r	the radial component of a cylindrical coordinate system, m
$\mathbf{r}$	position vector, m
r_0	radius of the averaging region, m
R_{K_2}	microscale correlation function associated to the kernel function K_2, m^{-2}
$R_{\langle\psi_\gamma\rangle^\gamma}$	macroscale correlation function associated to $\langle\psi_\gamma\rangle^\gamma$, m^{-2}
s_γ	closure variable that maps $\langle\psi_\gamma\rangle^\gamma$ onto $\tilde{\psi}_\gamma$
$\mathcal{S}$	source term in the closure problem, as defined by Eq. (5.3a)
$\mathbb{S}_\gamma$	second spatial moment (normalized) of a kernel function, m^2
t	time, s
t^*	characteristic time measure associated with the microscale, s
t^*_K	characteristic time measure associated with a kernel function in the closure problem, s
T^*	characteristic time (the integral time scale) associated with the macroscale, s
$T^*_{\langle\psi_\gamma\rangle^\gamma}$	characteristic time (the integral time scale) associated with the changes in $\langle\psi_\gamma\rangle^\gamma$, s
$\mathbf{v}_\gamma$	convective fluid velocity in the γ-phase, m/s
$\langle\mathbf{v}_\gamma\rangle^\gamma$	superficial average fluid velocity in the γ-phase, m/s
$\tilde{\mathbf{v}}_\gamma$	deviation for the fluid velocity in the γ-phase from the spatial average velocty, m/s
$\mathcal{V}_M$	domain of the entire macroscopic volume under consideration (Fig. 1)
$\mathcal{V}_{\gamma,M}$	domain of the fluid phase within the entire macroscopic volume $\mathcal{V}_M$
$\mathcal{V}_{\kappa,M}$	domain of the solid phase within the entire macroscopic volume $\mathcal{V}_M$
$\mathcal{V}(\mathbf{x})$	$= \mathcal{V}_\gamma(\mathbf{x}) \cup \mathcal{V}_\kappa(\mathbf{x})$, domain of an averaging volume
$\mathcal{V}_\gamma(\mathbf{x})$	domain occupied by the γ-phase within the averaging volume $\mathcal{V}(\mathbf{x})$
$\mathcal{V}_\kappa(\mathbf{x})$	domain occupied by the κ-phase within the averaging volume $\mathcal{V}(\mathbf{x})$
$V(\mathbf{x})$	volume of the averaging domain $\mathcal{V}(\mathbf{x})$, m^3
$V_\gamma(\mathbf{x})$	volume of the γ-phase contained within the averaging domain $\mathcal{V}(\mathbf{x})$, m^3
$\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$	position vectors, m

Greek symbols

α_1, α_2	measures of the magnitude of a Green's function as specified by Eqs. (5.12a) and (5.12b)
ε_γ	volume fraction (porosity) of the fluid phase
δ	Dirac's delta function

$\delta(\tau)$	time distribution function
$\delta_{\gamma\kappa}$	surface distribution function
Γ_γ	surface source term defined by Eq. (4.14a)
Φ_γ	γ-phase indicator function
φ_i	a maximum error estimate used to develop the definition of a representative volume
γ	kurtosis
κ_i	ith-cumulant, $i = 2, 4$
$\boldsymbol{\lambda}$	a directional vector with magnitude unity
ρ_{Φ_γ}	autocorrelation function for the microscale indicator function Φ_γ
ρ_{p_γ}	autocorrelation function for the parameter field $p(\mathbf{x})$, where $p(\mathbf{x})$ may be any of the parameter fields that appear in the microscale differential balance for ψ_γ
$\rho_{\mathbb{P}_\gamma}$	autocorrelation function for the parameter field $\mathbb{P}(\mathbf{x})$, where $\mathbb{P}_\gamma = \langle p_\gamma \rangle^\gamma$ is the volume average of any of the parameter fields p_γ that appear in the microscale differential balance for ψ_γ
$\sigma^2_{\Phi_\gamma}$	(spatial) variance of the indicator function Φ_γ
σ_{Φ_γ}	(spatial) standard deviation of the indicator function Φ_γ
$\sigma_{\mathbb{P}_\gamma}$	(spatial) standard deviation of a generic field property
θ	the angular component of a cylindrical coordinate system
ψ	intensive field property (*e.g.,* concentration) defined everywhere in a two-phase system
ψ_γ	intensive field property defined within in the γ-phase
ψ_κ	intensive field property defined within in the κ-phase
$\langle \psi_\gamma \rangle$	superficial spatial average of ψ_γ defined by Eq. (3.12)
$\langle \psi_\gamma \rangle^\gamma$	intrinsic spatial average of ψ_γ defined by Eq. (3.14)
$\tilde{\psi}_\gamma$	$= \psi_\kappa - \langle \psi_\gamma \rangle^\gamma$, spatial deviations of ψ_γ
(ζ, η, ξ)	components of a position vector, m

Subscripts

e	indicates the entrance/exit regions (*i.e.,* free fluid regions) of a boundary
s	indicates the quantity ψ associated with the fluid–solid interface
M	associated with the entire macroscale domain
γ	associated with the fluid phase
κ	associated with the fluid phase
$\gamma\kappa$	associated with the solid–fluid interface
ζ	ζ-component of a vector quantity
η	η-component of a vector quantity
ξ	ξ-component of a vector quantity

[10,63,41,1,73,76]). In other words, the derivation of models at the average scale can be achieved by *filtering* redundant information from the microscale. This is possible by adopting a set of *scaling postulates* (or *scaling laws* [76]), in the form of axiomatic statements imposing temporal and spatial constraints that bound the validity of the model. This approach leads to upscaled models containing effective medium coefficients that are the connection with the microscale.

Although volume averaging can be conduced in a broader context, for this work we focus on the more classical problem of a discretely hierarchical medium with two intrinsic length scales. In the context of averaging such a system, there are essentially *three* length scales of interest. Two of these scales are the intrinsic characteristic length scales associated with the medium (the microscale ℓ_γ, and the macroscale L); the third is associated with the characteristic size of the averaging volume (r_0). These scales will be given more formal definitions in the body of the paper; however, it is useful to introduce the fundamental physical concept of these scales here.

1. The *microscale* is the smallest resolved scale for the system. It is assumed that the microscale geometry is known, and that the relevant balance equations and boundary conditions can be proposed pointwise everywhere in the system (upon applying the concept of a representative region, the idea that the microscale is known everywhere can be relaxed). The characteristic length-scale associated with the microscale is often given the symbol ℓ_γ. The interpretation of length scales will be discussed in additional detail in Section 3.
2. The *support* scale is defined by the characteristic length associated with the *averaging operator* used to sample the microscale [9]. This support may, in principle, be compact (as is the case for conventional volume averaging, where the support is specified by a uniform distribution over a specific geometry) or non-compact (as in the case for a generalized weighting function), although noncompact support functions are best suited for unbounded domains. Additionally, the averaging operator may represent the response of a real instrument, or, it may represent an abstract mathematical operation (*e.g.,* a uniform weighting function could be adopted for finite difference methods). For the discussion here, we will consider only the compact uniform support function with characteristic length r_0. Most useful theories for upscaling *require* that the microscale length scale is much smaller than size of the averaging volume so that $r_0 \gg \ell_\gamma$.
3. The *macroscale* can be associated with some measure (usually an integral) of the properties of a particular parameter field of the system. In this work, the characteristic length associated

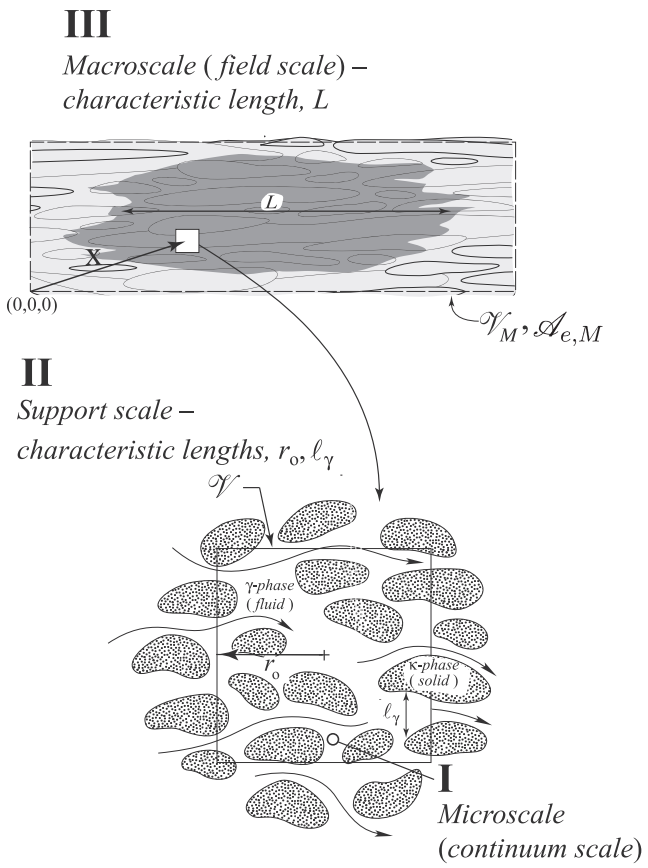

Fig. 1. Example of characteristic lengths for a porous medium.

with the macroscale is given the symbol L, and, like ℓ_γ, the interpretation of L will be in the context of an integral scale (this is described in detail in Section 3). One of our goals is to extend the volume averaging theory so that it is valid under the conditions that $r_0 \sim \mathbf{O}(L)$ (where $\mathbf{O}$ indicates the order of magnitude). This will be accomplished by developing a nonlocal form for the upscaled equations.

These definitions provide a reasonable starting point for systems that (1) are discretely hierarchical; (2) consist of only two intrinsic length-scales, ℓ_γ and L; and (3) are sampled by a compact and uniform instrument weighting function (imposing a third length scale imposed on the system by the characteristic size, r_0, of the averaging volume). This perspective will be adopted for the remainder of the paper.

In this work, we discuss the method of volume averaging for convection–diffusion-reaction type equations in the isothermal dilute-solution limit (so that the constitutive equation for the diffusive flux is given by Fick's law [69]) in a rigid porous medium. However, the approach is not dramatically changed for other types of balances that are linear in the dependent variable. Upscaling from the microscale to the macroscale can be broadly broken into two steps: (1) the *averaging* step itself, in which averaging (integral) operators are applied pointwise to the microscale balance equations, and (2) the development of *closure* schemes to predict various integrated functions of the microscale variables. The results from the closure process are expressed in terms of the so-called *closure variables*. The idea of closure in this context is very similar to, for example, the process of closure in the theory of turbulence. The essential idea is that, upon averaging, integrals involving the microscale dependent variable (concentration for our problem) arise in the upscaled balance equation. In order for the upscaled balance equation to be considered closed, one must find a scheme to re-express these integral quantities involving microscale dependent variable in terms of the *average* of the dependent variable. Closure is the essential problem facing all upscaling methods.

There are a number of closure methods that have been effectively adopted for upscaling in porous media. One example is the TCAT method referenced above; details on that method can be found in the paper by Gray et al. [34]. An excellent survey of closure methods (with an overview of closure schemes for TCAT, hybrid mixture theory, homogenization theory, moment methods, and MVA, among others) has been given by Cushman et al. [25]. One popular method used to close problems is to directly develop a differential balance equation for the unclosed terms. This is done in many perturbation-type upscaling schemes, and has been a reasonably successful method in many instances. Such differential balances are called *closure problems*; one example archetype familiar to many researchers is the differential balance for the Reynolds stress in the theory of turbulence.

In the MVA, there has been a convention of expressing the closure in terms of linear combinations of the source terms that arise in the ancillary closure problem. Although this has been a successful approach, a deeper interpretation of the meaning of the closure variables in the MVA has been lacking. The objective of this work is to explicitly address the physical interpretation of closure variables. We do this by exploring the connection between the microscale and the macroscale through the development of a generally space and time nonlocal model where the convolution kernels are specified by Green's functions. This puts volume averaging in a framework similar to that proposed by Shapiro and Brenner [65], where their Generalized Taylor Dispersion theory was cast in the context of Green's functions (in that work, however, the goal was only to develop time-asymptotic space localized balance equations). More importantly, it helps provide a more sound mathematical and physical basis for the closure schemes used in the MVA.

A second goal of this work is to extend the MVA approach to allow for the development of time and space nonlocal models. Nonlocal models have been developed successfully for porous media applications using a number of upscaling techniques. To date, however, no such method has been developed for the MVA approach (see, however, [76]) for problems where fluid–solid boundaries must be accounted for. Although it is not our purpose to provide an extensive review of the literature on nonlocal methods, a brief survey (with particular emphasis on porous media problems) of the literature follows.

Nonlocal methods for transport phenomena have a long history in physics in the context of statistical mechanics and field theory [79,80,48], but the first multi-variable nonlocal theory for a balance law appears to have been that of Chandrasekhar [14]. A summary of the history of nonlocal field theories can be found in the excellent reviews by Edelen [29] and Eringen [30, p. vii–xi]. In porous media, the first developments of nonlocal models were those of Beran [12] (for momentum transport) and Koch and Brady [39] (for solute transport). A number of different approaches have been since developed for applications to porous media, with some of the early primary references represented by the work of Cushman and Ginn [21,20], Neuman [51], Cushman and Hu [22], and Benson et al. [11]. Recent overviews on the development of nonlocal models in subsurface hydrology have been presented by Neuman and Federico [52], Neuman and Tartakovsky [50], Cushman et al. [23], Berkowitz et al. [13] and Zhang et al. [78]. Of particular note is the work of Tartakovsky and Neuman [68] and Souadnia et al. [66], who used a Green's function solution to the closure problem to generate their nonlocal representation of momentum transport. This is similar to the approach that we describe here. One significant difference between our work and those of [68,66] is that their development begins with a balance equation that was already upscaled from the pore scale; thus, their method is applied to a single, continuous phase in which there are random fluctuations. In contrast, the work that we describe in this report begins at the sub-pore scale, and averages up to develop the upscaled transport equation. This difference is significant in that we are forced to account for multiple phases (one fluid, one solid), and this requires special attention to the upscaling of spatial derivatives in the vicinity of the fluid–solid interface. This is readily handled in the method of volume averaging using spatial averaging theorems [19,33,36], and capability represents one of the significant strengths of volume averaging methods.

The paper is organized as follows. We first establish some fundamental definitions related to the microscale and the integral quantities in Sections 2 and 3, respectively. In Section 4 we examine the upscaling and closure process systematically, and make as few approximations as is possible. In Section 5 we study the closure problem in detail, and present solutions to the closure problem under very general conditions using Green's functions. We also explore in this section how various approximations influence the solution to the closure problem, and how these lead to (generally) nonlocal models. In Section 6, we present the full closed nonlocal upscaled balance law, and again examine how various approximations can yield a localized balance law taking the form of a conventional partial differential equation. One feature of this approach is that the general results from the averaging are time and space nonlocal integro-differential equations. When these equations meet more stringent restrictions, they can be localized. Our analysis shows that under these localized conditions, *a closure variable can be interpreted as the integration (in time and space) of the associated Green's functions that describe the influence of the average sources over the spatial deviations*. An attractive feature of this interpretation is that for transport processes that involve several sources, it is only necessary to solve one boundary-value problem in order to determine the associated Green's functions,

from which all the associated closure variables result. In this way, the kernel of the microstructure information is given by the Green's functions; while the convolution of the deviation sources with the kernel defines the closure variables. In Section 7 we provide an explicit example of nonlocal diffusion in a porous medium using the Green's function approach.

2. Microscale framework

In this section, we detail the process of upscaling via volume averaging. We pose a relatively general linear mass balance equation with boundary and initial conditions, and then describe the averaging and closure process for this model.

2.1. Field representation of discontinuous variables

We consider the differential balance equation for an intensive property, ψ (which could represent mass, momentum, or energy per unit volume), in a two-phase (fluid–solid) system, such as the porous medium sketched in Fig. 1. The macroscopic domain is identified as the region $\mathcal{V}_M$ externally bounded by $\mathcal{A}_{e,M}$ as illustrated in Fig. 1. For this system, the fluid phase saturates the porous matrix and is identified as the γ-phase (with associated domain, $\mathcal{V}_{\gamma,M}$), while the rigid solid is the κ-phase (with associated domain, $\mathcal{V}_{\kappa,M}$); the interface between the fluid and solid phases within $\mathcal{V}_M$ is represented by the subdomain $\mathcal{A}_{\gamma\kappa,M}$. In other words, we have

$$\mathcal{V}_M \equiv \mathcal{V}_{\gamma,M} \cup \mathcal{V}_{\kappa,M} \cup \mathcal{A}_{\gamma\kappa,M} \tag{2.1}$$

Similarly, the external boundary $\mathcal{A}_{e,M}$ can be divided into the portion that intersects the fluid phase ($\mathcal{A}_{\gamma e,M}$) and the portion that intersects the solid phase ($\mathcal{A}_{\kappa e,M}$).

$$\mathcal{A}_{e,M} \equiv \mathcal{A}_{\gamma e,M} \cup \mathcal{A}_{\kappa e,M} \tag{2.2}$$

For clarity, the boundaries and volumes involved are illustrated in Fig. 2.

The property ψ potentially exists in all of the phases present. For the purposes of this work, we assume that the property ψ is defined for all points within the system, regardless of the phase. For phases in which the property ψ is identically zero (*i.e.,* for this particular system, we make the approximation that the concentration of ψ is zero in the solid phase), indicator functions can be defined to help represent this condition. For example, if the κ-phase is a solid that is approximated as having an identically zero concentration for ψ, then we can define the indicator function

$$\Phi_\gamma(\mathbf{x}) = \begin{cases} 1, & \text{for } \mathbf{x} \text{ located in } \mathcal{V}_{\gamma,M} \\ 0, & \text{for } \mathbf{x} \text{ located in } \mathcal{V}_{\kappa,M} \end{cases}. \tag{2.3}$$

Now, we define the property ψ_γ, specified everywhere in the domain regardless of the phase, by

$$\psi_\gamma(\mathbf{x},t) \equiv \Phi_\gamma(\mathbf{x})\psi(\mathbf{x},t) \tag{2.4}$$

With this definition, ψ_γ is defined for every location $\mathbf{x}$ in the volume under consideration; however, for values of $\mathbf{x}$ that are not within the γ-phase, the value of ψ_γ is zero.

2.2. Microscale balance equations

For the developments that follow we assume that the balance equations for each phase are linear, as are the associated internal and external boundary conditions. For our purposes, let the transport of ψ_γ be expressed by

$$\frac{\partial \psi_\gamma}{\partial t} = \nabla\cdot(-\mathbf{v}_\gamma\psi_\gamma + \mathbf{D}_\gamma\cdot\nabla\psi_\gamma) - k_1\psi_\gamma + f(\mathbf{x},t), \quad \mathbf{x}\in\mathcal{V}_{\gamma,M} \tag{2.5a}$$

$$B.C.1 - \mathbf{n}_{\gamma\kappa}\cdot(\mathbf{D}_\gamma\cdot\nabla\psi_\gamma + \mathbf{v}_\gamma\psi_\gamma) = k_s\psi_\gamma + g(\mathbf{x},t), \quad \mathbf{x}\in\mathcal{A}_{\gamma\kappa,M} \tag{2.5b}$$

$$B.C.2 - \mathbf{n}_{\gamma e}\cdot(\mathbf{D}_\gamma\cdot\nabla\psi_\gamma + \mathbf{v}_\gamma\psi_\gamma) = q(\mathbf{x},t), \quad \mathbf{x}\in\mathcal{A}_{\gamma e,M} \tag{2.5c}$$

$$I.C.\psi_\gamma = I(\mathbf{x}), \quad \mathbf{x}\in\mathcal{V}_{\gamma,M} \tag{2.5d}$$

In these equations, $\mathbf{v}_\gamma$ is a vector parameter field (the fluid velocity in the case of dilute solute transport), $\mathbf{D}_\gamma$ is a tensor parameter field (the diffusion tensor in the case of dilute solute transport), k_1 is a first-order homogeneous reaction rate, f is an inhomogeneous source term within the volume $\mathcal{V}_{\gamma,M}$, k_s is a first-order surface reaction rate, g is an inhomogeneous surface source term on $\mathcal{A}_{\gamma\kappa,M}$, q is the magnitude of the flux of ψ_γ normal to the interface $\mathcal{A}_{\gamma e,M}$, and I is the initial distribution of ψ_γ within $\mathcal{V}_{\gamma,M}$. Note that we treat these parameters as fields (although they may be constant ones) which can, in general, exhibit fluctuations of their own. For example, the velocity field is itself governed by a momentum balance equation (*e.g.,* the Navier–Stokes equations) that applies within the fluid-filled pore space of the medium. Ultimately, however, it is various volume integrals of the parameter fields that we will need to determine an upscaled solution, and we will assume that these integrals are computable. The computation of integrals of the parameter fields is discussed in the section following.

Assuming that appropriate integrals of the parameter fields are computable, Eqs. (2.5a)–(2.5d) represent a fully-defined set of microscale balance equations that specify the space–time evolution of the property ψ_γ. Note that we are not considering non-equilibrium solid–fluid mass transfer (*e.g.,* via sorption). Although linear sorption reactions are easy to accommodate, they require additional balance equations, and part of our intention here is to provide an example that is simple and clear. The case outlined in

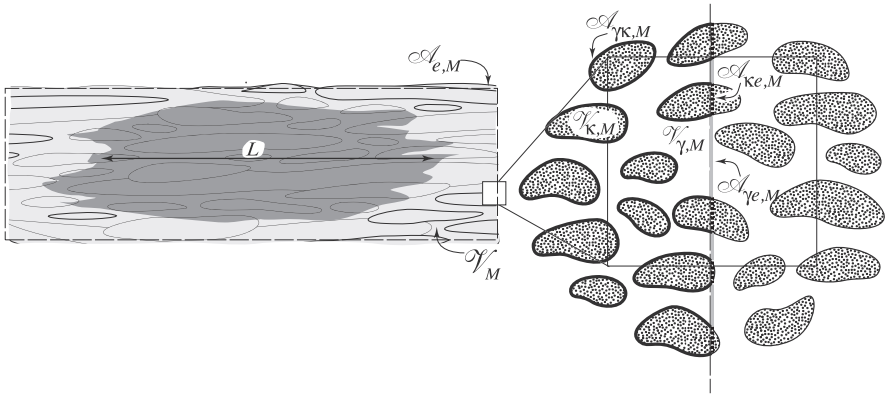

Fig. 2. Volume and surface definitions for the macroscopic region.

Eqs. (2.5a)–(2.5d) does, however, cover linear equilibrium sorption (*cf.* Whitaker [73, Section 1.1]). As mentioned above, we restrict ourselves to positive definite parabolic second-order differential equations, although this naturally includes the elliptic equation that arises from the steady-state case of Eqs. (2.5a)–(2.5d), and the special case where the coefficient of the second-order operator is identically zero yielding a first-order hyperbolic equation. Without any loss of generality, for the rest of the analysis ψ_γ is taken as a scalar field, although our results can be straightforwardly extended to vector or tensor fields.

At this point, one may wonder about the pertinence of solving the microscale problem in the whole macroscale domain. As mentioned in the introduction, in multiscale systems, the interest usually lies upon the *average fields* rather than the point fields. Therefore, one possible approach consists of averaging the solution of the microscale model given by Eqs. (2.5a)–(2.5d). We refer to this approach as performing direct numerical simulations (DNS). Although such solutions can be adopted (often with simplifications that reduce the complexity of the problem), the main drawback of this alternative is that the microscale solution is very complex (see, for example, Wood [76, Section 2.2]). Another approach is to first average the microscale balance laws, and then systematically apply a set of scaling postulates that allow simplification and ultimately an effective medium model. This alternative is explored below.

3. Integral quantities

3.1. Integral quantities of the media geometry

The process of spatially smoothing the governing microscale transport model consists of applying a weighted averaging operator to the microscale balance equations of interest. In general, the weighting functions may have compact or non compact support. For our averaging, we have adopted uniform weighting functions applied over a region of domain $\mathcal{V}(\mathbf{x})$. Thus, our weighting function is the uniform weighting function with value $1/V$, where V is given by the measure of $\mathcal{V}(\mathbf{x})$, or

$$V(\mathbf{x}) \equiv \int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})} dV(\mathbf{y}) \tag{3.1}$$

Analogously, the volume of the γ-phase within V is defined by

$$V_\gamma(\mathbf{x}) \equiv \int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})} \Phi_\gamma(\mathbf{x}+\mathbf{y})\, dV(\mathbf{y}) \tag{3.2}$$

Note that the terminology "$\mathbf{y}\in\mathcal{V}(\mathbf{x})$" is meant to indicate the set of all possible vectors $\mathbf{y}$ such that displacements from the centroid yield points that are within the averaging domain $\mathcal{V}(\mathbf{x})$. In this notation, $\mathbf{x}$ represents the centroid of the averaging volume, the vector $\mathbf{y}$ is a displacement relative to the location $\mathbf{x}$ (Fig. 3), and $\Phi_\gamma(\mathbf{x})$ is the indicator function defined previously. It should be stressed that the volume of the averaging domain, V, is a constant, whereas V_γ is in general a non-constant, continuous function of $\mathbf{x}$. In this context, we use $V(\mathbf{x})$ to indicate that for every $\mathbf{x}$ in the domain, there is a unique averaging domain $\mathcal{V}(\mathbf{x})$ with volume $V(\mathbf{x})$.

In several instances, it will be convenient to represent the surface area of the γ–κ interface as a volume integral. To facilitate that representation, we define the generalized function $\delta_{\gamma\kappa}$ by

$$A_{\gamma\kappa}(\mathbf{x}) \equiv \int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})} \delta_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\, dV(\mathbf{y}) \tag{3.3}$$

where $A_{\gamma\kappa}(\mathbf{x})$ is the area of the fluid–solid interface within the volume $\mathcal{V}(\mathbf{x})$.

It is useful to consider the spatial *statistics* of the microscale geometry of the system. Essentially, these are the statistics of the piecewise smooth function Φ_γ. We can think of the indicator function Φ_γ as being a representation of how the pore space is spatially distributed within an averaging volume. Thus, the spatial statistics of Φ_γ give us summary (integral) information about the distribution associated with Φ_γ. The first of these spatial statistics is the average, which is usually given the special nomenclature *porosity*, and is defined by (*cf.* Christakos [18, Section 2.3])

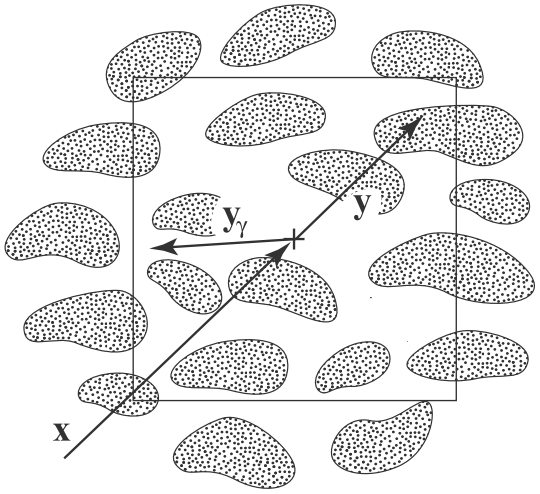

Fig. 3. The centroid of the averaging volume and displacements from this centroid.

$$\varepsilon_\gamma(\mathbf{x}) \equiv \frac{1}{V}\int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})} \Phi_\gamma(\mathbf{x}+\mathbf{y})\, dV(\mathbf{y}) \tag{3.4}$$

Hence the porosity is the superficial average value of Φ_γ, *i.e.*, $\varepsilon_\gamma = \langle\Phi_\gamma\rangle$. Note that, with Eq. (3.2), Eq. (3.4) gives the following relationship between volumes

$$V_\gamma(\mathbf{x}) = \varepsilon_\gamma(\mathbf{x})V(\mathbf{x}) \tag{3.5}$$

In this work, we will assume that the second-order spatial statistics of the fields involved exist and are finite. Then, the variance of Φ_γ is given by

$$\sigma^2_{\Phi_\gamma}(\mathbf{x}) = \frac{1}{V}\int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})} [\Phi_\gamma(\mathbf{x}+\mathbf{y}) - \varepsilon_\gamma(\mathbf{x}+\mathbf{y})]^2\, dV(\mathbf{y}) \tag{3.6}$$

and this quantity provides some information about how far away from a single homogenous phase the pore structure is. Note that ε_γ is itself a volume averaged quantity defined by Eq. (3.4). Eq. (3.6) can be re-expressed by

$$\sigma^2_{\Phi_\gamma}(\mathbf{x}) = \varepsilon_\gamma - 2\langle\varepsilon_\gamma\Phi_\gamma\rangle + \langle\varepsilon^2_\gamma\rangle \tag{3.7}$$

noting that $\langle\Phi^2_\gamma\rangle = \langle\Phi_\gamma\rangle = \varepsilon_\gamma$. For a system with a spatially constant porosity, the variance is given by $\sigma^2_{\Phi_\gamma}(\mathbf{x}) = \varepsilon_\gamma - \varepsilon^2_\gamma$, and is maximum for $\varepsilon_\gamma = 1/2$.

With the variance so defined, the autocorrelation function for the pore structure is defined, for any displacement vector $\mathbf{w}$, by (*cf.* Christakos [18, Section 2.3])

$$\rho_{\Phi_\gamma}(\mathbf{x},\mathbf{x}+\mathbf{w}) = \frac{1}{\sigma_{\Phi_\gamma}(\mathbf{x})\sigma_{\Phi_\gamma}(\mathbf{x}+\mathbf{w})}\times\frac{1}{V}\int_{\substack{\mathbf{y}\in\mathcal{V}(\mathbf{x})\\ \mathbf{w}\in\mathbb{R}^3}} [\Phi_\gamma(\mathbf{x}+\mathbf{y}) - \varepsilon_\gamma(\mathbf{x}+\mathbf{y})][\Phi_\gamma(\mathbf{x}+\mathbf{y}+\mathbf{w}) - \varepsilon_\gamma(\mathbf{x}+\mathbf{y}+\mathbf{w})]\, dV(\mathbf{y}) \tag{3.8}$$

Note that if the porosity is taken to be spatially constant, we have the simplification

$$\rho_{\Phi_\gamma}(\mathbf{x},\mathbf{x}+\mathbf{w}) = \frac{1}{\sigma_{\Phi_\gamma}(\mathbf{x})\sigma_{\Phi_\gamma}(\mathbf{x}+\mathbf{w})}\langle\Phi_\gamma(\mathbf{x}+\mathbf{y})\Phi_\gamma(\mathbf{x}+\mathbf{y}+\mathbf{w})\rangle - \frac{\varepsilon_\gamma}{1-\varepsilon_\gamma} \tag{3.9}$$

This yields an autocorrelation function that is, in general, a function of six spatial dimensions: the coordinates of the origin of the function evaluation ($\mathbf{x}$), and the displacement coordinates ($\mathbf{w}$). For a fixed, ($\mathbf{x}$), we can think of the function c_{Φ_γ} as being a decaying function with increasing distance from the origin, although the rate of decay might depend upon direction.

The autocorrelation function allows defining a unique set of length scales for the microscale geometry. First, introduce a unit directional vector, $\boldsymbol{\lambda}$, pointing in the direction of interest. Now, let

$$\mathbf{w} = w\boldsymbol{\lambda} \tag{3.10}$$

Then, the integral scale (*cf.* Christakos [18, Section 2.9]) associated with that direction is given by

$$\ell_\gamma(\mathbf{x};\boldsymbol{\lambda}) = \int_{w\in\mathbb{R}} \rho_{\Phi_\gamma}(\mathbf{x},\mathbf{x}+w\boldsymbol{\lambda})\,dw \tag{3.11}$$

In the statistical literature, ℓ_γ is often called the integral scale. Note that for an *isotropic* system, both the autocorrelation function dependence and the integral scale are independent of the direction vector, $\boldsymbol{\lambda}$. For the remainder of this work, we will assume that the $\rho_{\Phi_\gamma}(\mathbf{x},\mathbf{x}+\mathbf{w}) \to 0$ as $\|\mathbf{x}+\mathbf{w}\| \to \infty$, so that the integral scales of the underlying random fields are finite.

Because ε_γ is itself an average of a spatial random field (Φ_γ), in general it is not proper to think of it as being exactly constant. Instead, we can consider the concept of *quasi-stationarity*. There are significant simplifications to the definition of both the autocorrelation field, $c_{\Phi_\gamma}(\mathbf{x},\mathbf{x}+\mathbf{w})$, and the microscale length scale, ℓ_γ, when the geometry of the porous medium can be assumed to be quasi-stationary. This idea will be discussed in additional detail in Section 3.4.

3.2. Integral quantities of the dependent variable field

It is now possible to construct statistics of the dependent variable field, ψ_γ. To begin, the *superficial averaging operator* is defined by

$$\begin{aligned}\langle\psi_\gamma\rangle|_{(\mathbf{x},t)} &\equiv \frac{\int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})}\Phi_\gamma(\mathbf{x}+\mathbf{y})\psi(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y})}{\int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})}dV(\mathbf{y})}\\ &= \frac{1}{V}\int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})}\psi_\gamma(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y})\end{aligned} \tag{3.12}$$

In the conventional notation of volume averaging (*cf.* [73]), this definition is often simplified as

$$\langle\psi_\gamma\rangle = \frac{1}{V}\int_{\mathcal{V}_\gamma}\psi_\gamma\,dV. \tag{3.13}$$

To avoid confusion regarding functional dependence, we will adopt the explicit notation (Eq. (3.12)) for the remainder of the manuscript. The *intrinsic averaging operator* is defined by

$$\begin{aligned}\langle\psi_\gamma\rangle^\gamma|_{(\mathbf{x},t)} &= \frac{\int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})}\Phi_\gamma(\mathbf{x}+\mathbf{y})\psi(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y})}{\int_{\mathbf{y}\in\mathcal{V}(\mathbf{x})}\Phi_\gamma(\mathbf{x}+\mathbf{y})\,dV(\mathbf{y})}\\ &= \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\psi_\gamma(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y})\end{aligned} \tag{3.14}$$

Note that here, the domain $\mathcal{V}_\gamma$ is defined analogously to the definition given by Eq. (2.1); $\mathcal{V}_\gamma$ represents the fluid-filled portion of the averaging volume, $\mathcal{V}$.

3.3. Integral quantities of the parameter and source fields

The parameter fields ($\mathbf{v}_\gamma$, $\mathbf{D}_\gamma$, k_1, and k_s) and source fields (f, g, and q) can, in principle, each vary in space. Thus, they also have spatial statistics that can be computed in analogous ways as for the function Φ_γ. For notational convenience, denote any of these parameter fields by $p_\gamma(\mathbf{x})$, with average $\mathbb{P}_\gamma = \langle p_\gamma\rangle^\gamma$; note that, in general, the parameter or source field p_γ may be a scalar, vector or tensor field.

With this definition, any parameter field $p_\gamma(\mathbf{x})$ can be decomposed as follows

$$p_\gamma(\mathbf{x}) = \mathbb{P}_\gamma(\mathbf{x}) + \tilde{p}_\gamma(\mathbf{x}) \tag{3.15}$$

In analogy to the indicator function case, each of the parameter fields are assumed to have a finite variance and an autocorrelation function similar to that given by Eq. (3.8). Similarly, one can consider the characteristic length-scale for each such correlation function as specified in Eq. (3.11). As an example, suppose we were interested in the characteristic length scale associated with the ξ-component of the microscale velocity field (here, we use the notation $\mathbf{x} = (\zeta,\eta,\xi)$). Then, we would compute the correlation function, $\rho_{v_\xi}(\mathbf{x},\mathbf{x}+\mathbf{y})$ as specified above, and the characteristic length scale by

$$\ell_{v_\xi}(\mathbf{x};\boldsymbol{\lambda}) = \int_{w\in\mathbb{R}^+}\rho_{v_\xi}(\mathbf{x},\mathbf{x}+w\boldsymbol{\lambda})\,dw \tag{3.16}$$

Note that this is an integral of a microscale parameter field, and we expect the characteristic length to be not too different from ℓ_γ (which, itself, should be on the order of a pore length).

At times, it will be convenient to consider integral quantities of spatially averaged fields. As an example, one can compute the parameter field $\langle\mathbf{v}_\gamma\rangle^\gamma|_{\mathbf{x}}$ through an integral averaging of $\mathbf{v}_\gamma(\mathbf{x})$. In general, $\langle\mathbf{v}_\gamma\rangle^\gamma|_{\mathbf{x}}$ is not spatially stationary, and thus exhibits a dependence upon $\mathbf{x}$. Suppose we set $\langle\mathbf{v}_\gamma\rangle^\gamma|_{\mathbf{x}} = (\mathbb{V}_\zeta(\mathbf{x}), \mathbb{V}_\eta(\mathbf{x}), \mathbb{V}_\xi(\mathbf{x}))$. Then, $\mathbb{V}_\xi(\mathbf{x})$ is another parameter field; albeit, one in which the microscale fluctuations in $\mathbf{v}_\gamma$ have been filtered by the average. Because $\mathbb{V}_\xi(\mathbf{x})$ is a random variable, it has a correlation function defined in the same way as, for example, the indicator function $\Phi(\mathbf{x})$ (*i.e.*, Eq. (3.8)). With the correlation function so defined, an integral scale for $\mathbb{V}_\xi(\mathbf{x})$ can also be defined

$$L_{\mathbb{V}_\xi}(\mathbf{x};\boldsymbol{\lambda}) = \int_{w\in\mathbb{R}^+}\rho_{\mathbb{V}_\xi}(\mathbf{x},\mathbf{x}+w\boldsymbol{\lambda})\,dw \tag{3.17}$$

By convention, we use an upper-case Roman "L" to denote the integral scale associated with a macroscopic quantity. Note that we expect the characteristic length $L_{\mathbb{V}_\xi}$ to be, *at a minimum*, on the order of the characteristic size of the averaging volume (r_0), with no upper maximum necessarily defined (*e.g.,* this would occur, for example, were $\mathbb{V}_\xi$ to be constant).

These definitions developed for the ξ-component of the velocity field have clear analogues for any parameter or source field, p_γ. In general, we will use a notation of the form ℓ_{p_γ} to indicate the integral scale of a microscale field, and $L_{\mathbb{P}_\gamma}$ to indicate the integral scale of a macroscale (averaged) field.

3.4. Decompositions for the dependent variable

In the material that follows, it is convenient to define a decomposition the field $\psi_\gamma(\mathbf{x})$ into its spatial average field plus a field of deviations

$$\psi_\gamma(\mathbf{x},t) = \langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)} + \tilde{\psi}_\gamma(\mathbf{x},t) \tag{3.18}$$

It is useful to note that the quantity ψ_γ is defined for every point in the domain, regardless of the phase (Eqs. 2.3, 2.4). Hence, for any point $\mathbf{x}$ in the domain, one may uniquely define ψ_γ, $\langle\psi_\gamma\rangle^\gamma$, and $\tilde{\psi}_\gamma$. For the case defined here, we have explicitly indicated that the concentration of ψ in the κ-phase is identically zero. Thus, for all points $\mathbf{x}$ located in the κ-phase, we have $\tilde{\psi}_\gamma = -\langle\psi_\gamma\rangle^\gamma$. This is essentially an algebraic relationship, and, although formally correct, further consideration of deviations of ψ within the κ-phase will be unnecessary because of the condition that ψ itself is zero there.

3.5. Operator decomposition

The microscale balance given by Eq. (2.5a) is a linear partial differential equation. It is convenient here to rewrite this expression in the operator form

$$\frac{\partial \psi_\gamma}{\partial t} = \nabla \cdot \left[\mathcal{L}(\psi_\gamma)\right] - k_1 \psi_\gamma + f(\mathbf{x},t), \quad \mathbf{x} \in \mathcal{V}_{\gamma,M} \tag{3.19}$$

where

$$\mathcal{L}(\psi_\gamma) \equiv -\mathbf{v}_\gamma \psi_\gamma + \mathbf{D}_\gamma \cdot \nabla \psi_\gamma, \quad \mathbf{x} \in \mathcal{V}_{\gamma,M} \tag{3.20}$$

Because the operator $\mathcal{L}$ in Eq. (3.19) may have spatially variable parameter fields (*i.e.*, $\mathbf{v}_\gamma$ and $\mathbf{D}_\gamma$) associated with it, we propose the following decomposition for the operator

$$\mathcal{L}|_{\mathbf{x}} = \mathcal{L}_0|_{\mathbf{x}} + \tilde{\mathcal{L}}|_{\mathbf{x}} \tag{3.21}$$

where

$$\mathcal{L}_0\left(\psi_\gamma\right) = -\langle \mathbf{v}_\gamma \rangle^\gamma \psi_\gamma + \langle \mathbf{D}_\gamma \rangle^\gamma \cdot \nabla \psi_\gamma \tag{3.22a}$$

$$\tilde{\mathcal{L}}\left(\psi_\gamma\right) = -\tilde{\mathbf{v}}_\gamma \psi_\gamma + \tilde{\mathbf{D}}_\gamma \cdot \nabla \psi_\gamma \tag{3.22b}$$

In Eq. (3.21), the operator is conveniently broken up into its volume average component, $\mathcal{L}_0$, plus a deviation of the average from the microscale value, $\tilde{\mathcal{L}}$. Note, however, that $\mathcal{L}_0 \neq \langle \mathcal{L} \rangle^\gamma$. Also note that, in general, $\mathcal{L}_0$ is not a constant operator (because the spatial averages are not necessarily stationary); thus, $\mathcal{L}_0$, in the general case, continues to have a dependence upon $\mathbf{x}$. To make this explicit, suppose that $\mathbf{v}_\gamma$ and $\mathbf{D}_\gamma$ are spatially-varying parameter fields, and the reaction rate parameter k_1 is a constant. Then, the complete set of microscale balance equations can be stated as

$$\frac{\partial \psi_\gamma}{\partial t} - \nabla \cdot [\mathcal{L}_0(\psi_\gamma)] - \nabla \cdot [\tilde{\mathcal{L}}(\psi_\gamma)] + k_1 \psi_\gamma = f(\mathbf{x},t), \quad \mathbf{x} \in \mathcal{V}_{\gamma,M} \tag{3.23a}$$

$$B.C.1 \quad -\mathbf{n}_{\gamma\kappa} \cdot [\mathcal{L}_0(\psi_\gamma)] - \mathbf{n}_{\gamma\kappa} \cdot [\tilde{\mathcal{L}}(\psi_\gamma)] = k_s \psi_\gamma + g(\mathbf{x},t), \quad \mathbf{x} \in \mathcal{A}_{\gamma\kappa,M} \tag{3.23b}$$

$$B.C.2 \quad -\mathbf{n}_{\gamma e} \cdot [\mathcal{L}_0(\psi_\gamma)] - \mathbf{n}_{\gamma e} \cdot [\tilde{\mathcal{L}}(\psi_\gamma)] = q(\mathbf{x},t), \quad \mathbf{x} \in \mathcal{A}_{\gamma e,M} \tag{3.23c}$$

$$I.C. \quad \psi_\gamma = I(\mathbf{x}), \quad \mathbf{x} \in \mathcal{V}_{\gamma,M} \tag{3.23d}$$

4. Upscaling

The definitions presented in Section 3 allow us to examine the volume averaging of the microscale balance equations in a very efficient way. To begin the process of upscaling, the next step is to apply the superficial averaging operator (Eq. (3.14)) to the microscale governing equation (Eq. (3.23a)), in order to obtain

$$\frac{\partial \langle \psi_\gamma \rangle}{\partial t} - \langle \nabla \cdot \mathcal{L}_0(\psi_\gamma) \rangle - \langle \nabla \cdot \tilde{\mathcal{L}}(\psi_\gamma) \rangle + k_1 \langle \psi_\gamma \rangle = \langle f \rangle. \tag{4.1}$$

Here we have used the fact that, because the porous medium has been assumed to be rigid, Φ_γ (and, hence, V_γ) is not a function of time and it is acceptable to interchange spatial integration and temporal differentiation. We can make additional progress by application of the averaging theorem [36,73], which states, for any vector function, $\mathbf{a}_\gamma$

$$\langle \nabla \cdot \mathbf{a}_\gamma \rangle|_{(\mathbf{x},t)} = \nabla \cdot \langle \mathbf{a}_\gamma \rangle|_{(\mathbf{x},t)} + \frac{1}{V} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}(\mathbf{y}) \cdot \mathbf{a}_\gamma|_{(\mathbf{y},t)} \, dA(\mathbf{y}) \tag{4.2}$$

Using this form of the theorem in the balance equation yields

$$\frac{\partial \langle \psi_\gamma \rangle}{\partial t} - \nabla \cdot \langle \mathcal{L}_0(\psi_\gamma) \rangle - \nabla \cdot \langle \tilde{\mathcal{L}}(\psi_\gamma) \rangle - \frac{1}{V} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y}) \cdot \mathcal{L}_0[\psi_\gamma(\mathbf{x}+\mathbf{y},t)] \, dA(\mathbf{y}) - \frac{1}{V} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y}) \cdot \tilde{\mathcal{L}}[\psi_\gamma(\mathbf{x}+\mathbf{y},t)] \, dA(\mathbf{y}) + k_1 \langle \psi_\gamma \rangle = \langle f \rangle \tag{4.3}$$

The two integral terms can be combined, and, with the boundary condition given by Eq. (2.5b) the result is

$$\frac{\partial \langle \psi_\gamma \rangle}{\partial t} - \nabla \cdot \langle \mathcal{L}_0(\psi_\gamma) \rangle - \nabla \cdot \langle \tilde{\mathcal{L}}(\psi_\gamma) \rangle + \frac{1}{V} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} [k_s \psi_\gamma + g(\mathbf{x}+\mathbf{y},t)] \, dA(\mathbf{y}) + k_1 \langle \psi_\gamma \rangle = \langle f \rangle \tag{4.4}$$

In its present form, Eq. (4.4) is still expressed in terms of point fields. We introduce the spatial decomposition given previously by Eq. (3.18)

$$\psi_\gamma(\mathbf{x},t) = \langle \psi_\gamma \rangle^\gamma|_{(\mathbf{x},t)} + \tilde{\psi}_\gamma(\mathbf{x},t)$$

Note that here, ψ_γ, $\langle \psi_\gamma \rangle^\gamma$, and $\tilde{\psi}_\gamma$ are each well defined for every value of $\mathbf{x}$, regardless of the phase. Both ψ_γ and $\tilde{\psi}_\gamma$ contain discontinuities at the fluid–solid interface, $A_{\gamma\kappa}$, however, $\langle \psi_\gamma \rangle^\gamma$ is a macroscale quantity that varies smoothly and continuously with the spatial coordinate $\mathbf{x}$. Using the identity $\langle \psi_\gamma \rangle = \varepsilon_\gamma \langle \psi_\gamma \rangle^\gamma$, and the spatial decomposition in Eq. (4.1), the averaged balance equation takes the form

$$\begin{aligned} &\varepsilon_\gamma \frac{\partial \langle \psi_\gamma \rangle^\gamma}{\partial t} - \nabla \cdot \langle \mathcal{L}_0(\langle \psi_\gamma \rangle^\gamma) \rangle - \nabla \cdot \langle \tilde{\mathcal{L}}(\langle \psi_\gamma \rangle^\gamma) \rangle + \frac{k_s}{V} \\ &\quad \times \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \langle \psi_\gamma \rangle^\gamma \Big|_{(\mathbf{x}+\mathbf{y},t)} dA(\mathbf{y}) + \varepsilon_\gamma k_1 \langle \psi_\gamma \rangle^\gamma \\ &= \varepsilon_\gamma \langle f \rangle^\gamma + \nabla \cdot \langle \mathcal{L}_0(\tilde{\psi}_\gamma) \rangle + \nabla \cdot \langle \tilde{\mathcal{L}}(\tilde{\psi}_\gamma) \rangle - \frac{k_s}{V} \\ &\quad \times \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \tilde{\psi}_\gamma(\mathbf{x},t) \, dA(\mathbf{y}) - \frac{1}{V} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} g(\mathbf{x}+\mathbf{y},t) \, dA(\mathbf{y}) \end{aligned} \tag{4.5}$$

No assumptions or approximations about the structure of the underlying fields have been required to reach this point in the analysis. Accordingly, we have accomplished nothing more than a separation of the original fields and operators into their respective mean and deviation components. Although it is true that Eq. (4.5) provides a representation of the balance equation in terms of the average value of the dependent variable, it is also true that, without additional assumptions, this expression offers no advantages over the original, microscale equations (*i.e.*, Eq. (2.5)). In other words, without stating something concrete about the integrals of the parameter fields themselves (*cf.* Section 3.3), Eq. (4.5) does not eliminate any degrees of freedom associated with the original microscale equations. Without assumptions about the behavior of the averages of the parameter fields, no additional simplification can be made to Eq. (4.5), and the system remains fully nonlocal, with complete coupling between the microscale and macroscale fields for ψ_γ.

4.1. Quasi-stationarity

To make further progress on the averaging of the balance equation, we need to return to the explicit form of the operators. At this point, it is convenient to abandon the compact notation offered by the operators and express Eq. (4.5) in an expanded form. To this end, let us substitute the following identities

$$\mathcal{L}_0\left(\langle\psi_\gamma\rangle^\gamma\right) = -(\langle\mathbf{v}_\gamma\rangle^\gamma\langle\psi_\gamma\rangle^\gamma - \langle\mathbf{D}_\gamma\rangle^\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma) \tag{4.6a}$$

$$\mathcal{L}_0\left(\tilde{\psi}_\gamma\right) = -(\langle\mathbf{v}_\gamma\rangle^\gamma\tilde{\psi}_\gamma - \langle\mathbf{D}_\gamma\rangle^\gamma\cdot\nabla\tilde{\psi}_\gamma) \tag{4.6b}$$

$$\tilde{\mathcal{L}}\left(\langle\psi_\gamma\rangle^\gamma\right) = -(\tilde{\mathbf{v}}_\gamma\langle\psi_\gamma\rangle^\gamma - \tilde{\mathbf{D}}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma) \tag{4.6c}$$

$$\tilde{\mathcal{L}}\left(\tilde{\psi}_\gamma\right) = -(\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma - \tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma) \tag{4.6d}$$

into Eq. (4.5) to obtain

$$\begin{aligned}
&\varepsilon_\gamma\frac{\partial\langle\psi_\gamma\rangle^\gamma}{\partial t} + \nabla\cdot\left(\langle\langle\mathbf{v}_\gamma\rangle^\gamma\langle\psi_\gamma\rangle^\gamma\rangle - \langle\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma\rangle\right)\\
&+\nabla\cdot\left(\langle\tilde{\mathbf{v}}_\gamma\langle\psi_\gamma\rangle^\gamma\rangle - \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma\rangle\right)\\
&+\frac{k_s}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\langle\psi_\gamma\rangle^\gamma|_{(\mathbf{x}+\mathbf{y},t)}\,dA(\mathbf{y}) + \varepsilon_\gamma k_1\langle\psi_\gamma\rangle^\gamma\\
&=\varepsilon_\gamma\langle f\rangle^\gamma - \nabla\cdot\left(\langle\langle\mathbf{v}_\gamma\rangle^\gamma\tilde{\psi}_\gamma\rangle - \langle\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\nabla\tilde{\psi}_\gamma\rangle\right)\\
&-\nabla\cdot\left(\langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle - \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma\rangle\right) - \frac{k_s}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\\
&-\frac{1}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}g(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})
\end{aligned} \tag{4.7}$$

Wood [76] proposed that assumptions regarding the parameter fields should be posed in terms of *scaling laws*. The notion of scaling laws as axiomatic statements about the structure of the natural world date back to Galilei [31] and Peterson [57]. In our work, they are statements regarding the geometrical, statistical, or other integral quantities of the microscale parameter fields, that allow subsequent simplifications to be adopted. Scaling laws in this application are statements about the (spatial) integral quantities of fields; they are assumed to be true, must agree with existing experimental data or models for the system, but are generally not provable (although they are, in principle, falsifiable). Because the term *scaling law* is a term that has other meanings within mathematics and science, we will adopt the term *scaling postulate* for our particular applications below to help avoid confusion.

We stress the role of scaling postulates here because, although such axiomatic statements are widely adopted in the analysis of natural systems, they are often not identified explicitly (however, see the work of Battiato et al. [8], Battiato and Tartakovsky [7] for examples where the scaling postulates are explicitly identified). This makes it sometimes difficult to understand what has been done in an upscaling analysis, particularly when comparing different upscaling methods.

For notational convenience, assume that each component of the vector and tensor parameter fields are considered as scalar parameter fields p with i indexing each component (*e.g.,* if we had one velocity vector field and one diffusion tensor field, then there would yield a total of 12 parameter fields indexed by i). We adopt the following reasonably unconstraining scaling postulate.

Scaling Postulate 0 (Quasi-Stationarity for the parameter fields). Suppose that there are N random scalar parameter fields associated with the transport equation. Then, the parameter fields $p_\gamma(\mathbf{x})$ are *quasi-stationary* as measured by the volume average when the following constraint is met (Appendix A)

$$\frac{\sigma_{\mathbb{P}_\gamma}}{\mathbb{P}_\gamma}\frac{r_0}{L_{\mathbb{P}_\gamma}} \ll 1 \tag{4.8}$$

Here, $\mathbb{P}_\gamma = \langle p_\gamma\rangle^\gamma$, $\sigma_{\mathbb{P}_\gamma}$ is the standard deviation for the field $\langle p_\gamma\rangle^\gamma$, r_0 is the characteristic dimension of the averaging volume, and $L_{\mathbb{P}_\gamma}$ is the integral scale for the field $\langle p_\gamma\rangle^\gamma$; these terms are explicitly defined in Appendix A. Note that we consider the indicator function, Φ_γ, to be among the parameter fields, and this implies that the average of the indicator field, $\varepsilon_\gamma = \langle\Phi_\gamma\rangle$, can be treated as being quasi-stationary.

Support for this constraint is developed in Appendix A. Briefly, the constraint can be developed by conducting a Taylor series expansion of the average field property, and then averaging this expansion (*cf.* [73, Section 1.3.2]). When this constraint is met, there is a separation of the length scale of the average of the parameter fields ($L_{\mathbb{P}_\gamma}$) and the characteristic scale of the averaging volume (r_0) such that

$$r_0 \ll L_{\mathbb{P}_\gamma} \tag{4.9}$$

It is important to note, however, that this constraint applies only to the *parameter fields* associated with the differential operator $\mathcal{L}$; at this point *no such assumption is made regarding the dependent variable*, ψ_γ. This is important because, even though we have imposed a separation of length scales constraint on the structure of the parameter fields, the dependent variable ψ_γ can still exhibit time and space nonlocal behavior in such fields. Thus, our goal here is to develop a nonlocal theory that extends the range of validity of the upscaled model (*e.g.,* to "early" times or under conditions when the spatial changes in $\langle\psi_\gamma\rangle^\gamma$ are "large").

If we assume that this approximation is valid, then the upscaled balance equation takes the form

$$\begin{aligned}
&\varepsilon_\gamma\frac{\partial\langle\psi_\gamma\rangle^\gamma}{\partial t} + \nabla\cdot(\langle\mathbf{v}_\gamma\rangle^\gamma\langle\langle\psi_\gamma\rangle^\gamma\rangle - \langle\mathbf{D}_\gamma\rangle^\gamma\cdot\langle\nabla\langle\psi_\gamma\rangle^\gamma\rangle)\\
&+\nabla\cdot(\langle\tilde{\mathbf{v}}_\gamma\langle\psi_\gamma\rangle^\gamma\rangle - \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma\rangle)\\
&+\frac{k_s}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\langle\psi_\gamma\rangle^\gamma|_{(\mathbf{x}+\mathbf{y},t)}\,dA(\mathbf{y}) + \varepsilon_\gamma k_1\langle\psi_\gamma\rangle^\gamma\\
&=\varepsilon_\gamma\langle f\rangle^\gamma - \nabla\cdot(\langle\mathbf{v}_\gamma\rangle^\gamma\langle\tilde{\psi}_\gamma\rangle - \langle\mathbf{D}_\gamma\rangle^\gamma\cdot\langle\nabla\tilde{\psi}_\gamma\rangle)\\
&-\nabla\cdot(\langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle - \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma\rangle) - \frac{k_s}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\\
&-\frac{1}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}g(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})
\end{aligned} \tag{4.10}$$

A final set of simplifications are possible here without imposing any additional assumptions. First, we can use the spatial averaging theorem a second time to interchange the gradient and averaging operators in two of the terms in this equation. Secondly, we can take the average of both sides of Eq. (3.18) to show that

$$\langle\langle\psi_\gamma\rangle^\gamma\rangle^\gamma = \langle\psi_\gamma\rangle^\gamma - \langle\tilde{\psi}_\gamma\rangle^\gamma \tag{4.11}$$

This gives, after some algebra

$$\begin{aligned}
&\varepsilon_\gamma\frac{\partial\langle\psi_\gamma\rangle^\gamma}{\partial t} + \nabla\cdot(\varepsilon_\gamma\langle\mathbf{v}_\gamma\rangle^\gamma\langle\psi_\gamma\rangle^\gamma)\\
&-\nabla\cdot\left[\varepsilon_\gamma\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\left(\nabla\langle\psi_\gamma\rangle^\gamma + \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right)\right]\\
&+\nabla\cdot[\varepsilon_\gamma(\langle\tilde{\mathbf{v}}_\gamma\langle\psi_\gamma\rangle^\gamma\rangle^\gamma - \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma\rangle^\gamma)] + \frac{k_s}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\langle\psi_\gamma\rangle^\gamma|_{(\mathbf{x}+\mathbf{y},t)}\,dA(\mathbf{y})\\
&-\nabla\cdot\left(\varepsilon_\gamma\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}\langle\psi_\gamma\rangle^\gamma|_{(\mathbf{x}+\mathbf{y},t)}\,dA(\mathbf{y})\right) + \varepsilon_\gamma k_1\langle\psi_\gamma\rangle^\gamma\\
&=\varepsilon_\gamma\langle f\rangle^\gamma - \nabla\cdot[\varepsilon_\gamma(\langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma - \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma\rangle^\gamma)]\\
&-\frac{k_s}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y}) - \frac{1}{V}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}g(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})
\end{aligned} \tag{4.12}$$

We have used the relationship $V_\gamma = \varepsilon_\gamma V$ in developing this result. To write this expression in a more conventional-looking form, let us neglect the spatial variations of the porosity so that Eq. (4.12) can be rearranged as follows (*cf.* [2])

$$\underbrace{\frac{\partial\langle\psi_\gamma\rangle^\gamma}{\partial t}}_{\text{Accumulation}} = \underbrace{-\nabla\cdot(\langle\mathbf{v}_\gamma\rangle^\gamma\langle\psi_\gamma\rangle^\gamma)}_{\text{Convection}} + \underbrace{\nabla\cdot\left(\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma\right)}_{\text{Diffusion}} - \underbrace{k_1\langle\psi_\gamma\rangle^\gamma}_{\text{Reaction}} - \underbrace{\mathcal{N}(\mathbf{x},t;\tilde{\psi}_\gamma)}_{\text{Unclosed Terms}} + \underbrace{\langle f\rangle^\gamma}_{\substack{\text{Volumetric}\\ \text{Source Term}}} - \underbrace{\Gamma_\gamma(\mathbf{x},t)}_{\substack{\text{Surface}\\ \text{Source Term}}} + \underbrace{N(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma)}_{\substack{\text{Nonlocal}\\ \text{Term}}} \tag{4.13}$$

where, for simplicity in notation, we introduced

$$\Gamma_\gamma(\mathbf{x},t) = \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})} g(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y}) \tag{4.14a}$$

$$\begin{aligned} N(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma) = &-\nabla\cdot(\langle\tilde{\mathbf{v}}_\gamma\langle\psi_\gamma\rangle^\gamma\rangle^\gamma - \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma\rangle^\gamma)\\ &-\frac{k_s}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\langle\psi_\gamma\rangle^\gamma|_{(\mathbf{x}+\mathbf{y},t)}\,dA(\mathbf{y})\\ &+\nabla\cdot\left(\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}\langle\psi_\gamma\rangle^\gamma|_{(\mathbf{x}+\mathbf{y},t)}\,dA(\mathbf{y})\right) \end{aligned} \tag{4.14b}$$

$$\begin{aligned} \mathcal{N}(\mathbf{x},t;\tilde{\psi}_\gamma) = &\nabla\cdot\underbrace{\langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma}_{\substack{\text{Unclosed}\\ \text{Integral}\\ \text{Quantity, }\mathbf{M}_1}}\\ &-\nabla\cdot\underbrace{\left(\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right)}_{\substack{\text{Unclosed}\\ \text{Integral Quantity, }\mathbf{M}_2}}\\ &-\nabla\cdot\underbrace{\langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma\rangle^\gamma}_{\substack{\text{Unclosed}\\ \text{Integral}\\ \text{Quantity, }\mathbf{M}_3}} + \underbrace{k_s\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})}_{\substack{\text{Unclosed}\\ \text{Integral Quantity, }M_4}} \end{aligned} \tag{4.14c}$$

In Eq. (4.14c), there are exactly four terms that involve spatial integrations of either $\tilde{\psi}_\gamma$ or products of the deviation of a field variable with $\tilde{\psi}_\gamma$; in Section 5 we explain how these unclosed integral quantities can be treated via closure models. For later convenience, we will refer to these four integrals generically by the symbol M_i (where $i = 1,\ldots,4$, corresponding to each of the four terms identified). The term $N(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma)$ in Eq. (4.13) represents spatially nonlocal contributions involving the average $\langle\psi_\gamma\rangle^\gamma$; as such, substantial simplification is possible for cases where the variations of $\langle\psi_\gamma\rangle^\gamma$ can be neglected within the integration domains. If $\langle\psi_\gamma\rangle^\gamma$ were smooth enough such that it could be removed from under the integrals (this would be the case if the characteristic length $L_{\langle\psi_\gamma\rangle^\gamma}$ for the $\langle\psi_\gamma\rangle^\gamma$ field were large compared with r_0), then from Eq. (4.11) we have that $\langle\langle\psi_\gamma\rangle^\gamma\rangle^\gamma = \langle\psi_\gamma\rangle^\gamma$ and consequently $\langle\tilde{\psi}_\gamma\rangle^\gamma = 0$. If the same separation of length scales applies for the fields of $\langle\mathbf{v}_\gamma\rangle^\gamma$ and $\langle\mathbf{D}_\gamma\rangle^\gamma$, then $N(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma)$ would reduce to $N = k_s a_v\varepsilon_\gamma^{-1}\langle\psi_\gamma\rangle^\gamma$, where a_v is the interfacial surface area per unit volume (*i.e.*, $a_v = A_{\gamma\kappa}/V$). To this point, we have made no assumptions regarding the variability of $\langle\psi_\gamma\rangle^\gamma$, and thus we will keep the nonlocal term in the analysis.

In summary, although the analysis leading to Eq. (4.13) has been somewhat complex, the mathematical form of this expression is similar to the equation that applies at the microscale; this is a typical result for linear equations as we have here. The analysis leading to Eq. (4.13) has been constrained by a single scaling postulate to this juncture, and this requirement is that each of the *parameter fields* associated with the microscale transport equation have a spatially quasi-stationary mean and finite variance and correlation structure, as indicated by the inequality (4.8). Note that, to this point in the analysis, we have imposed no constraints upon the dependent variable field, ψ_γ.

Although formally upscaled, Eq. (4.13) remains unclosed because of the various integrals involving the unknown quantity $\tilde{\psi}_\gamma$. Our next step in the analysis is to express the deviation fields, $\tilde{\psi}_\gamma$, in terms of the source terms (including functions of the average concentration, $\langle\psi_\gamma\rangle^\gamma$), boundary terms, and the initial condition. This process is usually termed *closure*. The closure problem involves five steps:

(1) Derivation of the initial-boundary value problem for $\tilde{\psi}_\gamma$.
(2) Imposition of additional scaling postulates (if applicable) that allow simplifying the problem in step (1).
(3) Determination of the general *functional form* of the solution for $\tilde{\psi}_\gamma$ in terms of the initial conditions, boundary data, and sources via Green's functions.
(4) Solution of the closure problem (via analytical or numerical methods); this is explained in detail in Section 5).
(5) Integration of closure results for $\tilde{\psi}_\gamma$ to compute the integral quantities (effective parameters) that appear in the macroscale balance equation.

Note that it has become common to refer to the process of developing a convolution solution to a partial differential equation with initial and boundary data as determining the *Green's function solution*, although other terminologies are in use. For the remainder of this manuscript, we will use this terminology to indicate the process of finding such convolution solutions to linear differential operators.

5. Closure

5.1. Derivation of closure relations

According to the decomposition given by Eq. (3.18), the governing equation for $\tilde{\psi}_\gamma$ can be obtained by subtracting Eq. (4.13) from Eq. (2.5a). Although the deviations are defined everywhere in the domain $\mathcal{V}_M$, we do not need to solve for the deviation equation within the solid matrix because the integral quantities arising in Eq. (4.13) do not require them. For the boundary conditions, one must use the decomposition given by Eq. (3.18) to eliminate the function $\tilde{\psi}_\gamma$. Before proceeding, note

$$-\mathbf{v}_\gamma\psi_\gamma = -(\langle\mathbf{v}_\gamma\rangle^\gamma\langle\psi_\gamma\rangle^\gamma + \tilde{\mathbf{v}}_\gamma\langle\psi_\gamma\rangle^\gamma + \mathbf{v}_\gamma\tilde{\psi}_\gamma) \tag{5.1a}$$

$$\mathbf{D}_\gamma\cdot\nabla\psi_\gamma = \langle\mathbf{D}_\gamma\rangle^\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma + \tilde{\mathbf{D}}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma + \langle\mathbf{D}_\gamma\rangle^\gamma\cdot\nabla\tilde{\psi}_\gamma + \tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma \tag{5.1b}$$

Using Eqs. (5.1a) and (5.1b) in the microscale equation (Eq. (2.5a)), and then subtracting the averaged equation (Eq. (4.13)) gives the following balance equation for $\tilde{\psi}_\gamma$ (*cf.* [2])

$$\begin{aligned} \frac{\partial\tilde{\psi}_\gamma}{\partial t} = &-\nabla\cdot(\mathbf{v}_\gamma\tilde{\psi}_\gamma - \langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma)\\ &+\nabla\cdot\left[\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\left(\nabla\tilde{\psi}_\gamma - \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right)\right.\\ &\left.+(\tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma - \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma\rangle^\gamma)\right] - k_1\tilde{\psi}_\gamma\\ &+\frac{k_s}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y}) + \mathcal{S}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma,\nabla\nabla\langle\psi_\gamma\rangle^\gamma) \end{aligned} \tag{5.2a}$$

Using the decomposition given in Eq. (3.18) in the boundary and initial conditions of the microscale problem (*i.e.*, Eqs. (2.5b)–(2.5d)) leads to

$$B.C.1\ \ \mathbf{n}_{\gamma\kappa}\cdot(\mathbf{D}_\gamma\cdot\nabla\tilde{\psi}_\gamma)+k_s\tilde{\psi}_\gamma=\mathcal{G}(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma),\quad \mathbf{x}\in\mathcal{A}_{\gamma\kappa,M} \tag{5.2b}$$

$$B.C.2\ \ \mathbf{n}_{\gamma e}\cdot(\mathbf{D}_\gamma\cdot\nabla\tilde{\psi}_\gamma+\mathbf{v}_\gamma\tilde{\psi}_\gamma)=\mathcal{Q}(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma),\quad \mathbf{x}\in\mathcal{A}_{\gamma e,M} \tag{5.2c}$$

$$I.C.\ \ \tilde{\psi}_\gamma=\mathcal{I}(\mathbf{x}),\quad \mathbf{x}\in\mathcal{V}_{\gamma,M} \tag{5.2d}$$

For the first boundary condition, we have used the result that the convective flux normal to the fluid–solid interface is zero. For the sake of simplicity, we have also introduced the following definitions

$$\mathcal{S}(\mathbf{x},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma,\nabla\nabla\langle\psi_\gamma\rangle^\gamma)=f_\gamma-\langle f_\gamma\rangle^\gamma+\Gamma_\gamma(\mathbf{x},t)$$
$$-N(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma)+\nabla\cdot(\tilde{\mathbf{D}}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma)-\nabla\cdot(\tilde{\mathbf{v}}_\gamma\langle\psi_\gamma\rangle^\gamma) \tag{5.3a}$$

$$\mathcal{G}(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)=-g(\mathbf{x},t)-\mathbf{n}_{\gamma\kappa}\cdot(\mathbf{D}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma)-k_s\langle\psi_\gamma\rangle^\gamma \tag{5.3b}$$

$$\mathcal{Q}(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma)=-q(\mathbf{x},t)-\mathbf{n}_{\gamma e}\cdot(\mathbf{D}_\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma+\mathbf{v}_\gamma\langle\psi_\gamma\rangle^\gamma) \tag{5.3c}$$

$$\mathcal{I}(\mathbf{x})=I(\mathbf{x})-\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},0)} \tag{5.3d}$$

Although somewhat complicated looking, Eqs. (5.2a)–(5.2d) are nothing more than a linear balance equation for $\tilde{\psi}_\gamma$ with boundary and initial conditions. The presentation of the deviation equations is helped somewhat if we make one additional grouping of terms. With this idea, let us recall the function $\mathcal{N}(\mathbf{x},t;\tilde{\psi}_\gamma)$ given in Eq. (4.14c) in order to put together all the nonlocal terms involving the dependent variable $(\tilde{\psi}_\gamma)$ into a single integral contribution

$$\mathcal{N}(\mathbf{x},t;\tilde{\psi}_\gamma)=\nabla\cdot\left(\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}[\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)-\tilde{\mathbf{D}}_\gamma(\mathbf{x}+\mathbf{y})\right.$$
$$\cdot\nabla\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)-\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\mathbf{n}_{\gamma\kappa}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\delta_{\gamma\kappa}(\mathbf{x}+\mathbf{y})$$
$$\left.+k_s\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\delta_{\gamma\kappa}(\mathbf{x}+\mathbf{y})]\,dV(\mathbf{y})\right) \tag{5.4}$$

In this expression, $\delta_{\gamma\kappa}$ is the surface delta-function, defined in Eq. (3.3). In this way, we find the following balance, which has substantially more intuitive appeal

$$\frac{\partial\tilde{\psi}_\gamma}{\partial t}=\underbrace{\nabla\cdot\left(-\mathbf{v}_\gamma\tilde{\psi}_\gamma+\mathbf{D}_\gamma\cdot\nabla\tilde{\psi}_\gamma\right)}_{\mathcal{L}(\tilde{\psi}_\gamma)}-k_1\tilde{\psi}_\gamma$$
$$+\underbrace{\mathcal{S}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma,\nabla\nabla\langle\psi_\gamma\rangle^\gamma)}_{\text{Net Source}}+\underbrace{\mathcal{N}(\mathbf{x},t;\tilde{\psi}_\gamma)}_{\text{Nonlocal Term}} \tag{5.5a}$$

$$B.C.1\ \ \mathbf{n}_{\gamma\kappa}\cdot(\mathbf{D}_\gamma\cdot\nabla\tilde{\psi}_\gamma)+k_s\tilde{\psi}_\gamma=\underbrace{\mathcal{G}(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)}_{\text{Source}},\quad \mathbf{x}\in\mathcal{A}_{\gamma\kappa,M} \tag{5.5b}$$

$$B.C.2\ \ \mathbf{n}_{\gamma e}\cdot(\mathbf{D}_\gamma\cdot\nabla\tilde{\psi}_\gamma+\mathbf{v}_\gamma\tilde{\psi}_\gamma)=\underbrace{\mathcal{Q}(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)}_{\text{Source}},\quad \mathbf{x}\in\mathcal{A}_{\gamma e,M} \tag{5.5c}$$

$$I.C.\tilde{\psi}_\gamma=\underbrace{\mathcal{I}(\mathbf{x})}_{\text{Source}},\quad \mathbf{x}\in\mathcal{V}_{\gamma,M} \tag{5.5d}$$

Note that Eqs. (5.5a)–(5.5d) are in a form that is, except for the nonlocal terms, completely analogous to the microscale balance given by Eqs. (2.5a)–(2.5d). For linear problems, this is generally the case. The equations are integro-differential, and there are a number of source terms (*i.e.*, terms independent of $\tilde{\psi}_\gamma$). Nonlocal integro-differential equations of this form have been studied extensively [28,32]. For this particular problem, Garroni and Menaldi [32] provide formal proofs for closely-related integro-differential equations. Because of the linearity of the problem, the solution to the particular form given by Eqs. (5.5a)–(5.5d) can be constructed in terms of Green's functions.

5.2. Solutions to the closure problem and simplifications

5.2.1. General solution

In Appendix B, we propose a solution to the nonlocal closure problem given by Eqs. (5.5a)–(5.5d) in terms of convolutions of the source terms over the Green's function, $G(\mathbf{x},t;\mathbf{y},\tau)$, for the differential balance equation. This result is

$$\tilde{\psi}_\gamma(\mathbf{x},t)=\underbrace{\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}}G(\mathbf{x},t;\mathbf{y},\tau)\mathcal{S}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma,\nabla\nabla\langle\psi_\gamma\rangle^\gamma)\,dV(\mathbf{y})\,d\tau}_{\text{influence of the volume sources}}$$
$$+\underbrace{\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}}G(\mathbf{x},t;\mathbf{y},0)\mathcal{I}(\mathbf{y})\,dV(\mathbf{y})}_{\text{influence of the initial condition}}$$
$$+\underbrace{\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa,M}}G(\mathbf{x},t;\mathbf{y},\tau)\mathcal{G}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)\,dA(\mathbf{y})\,d\tau}_{\text{influence of the interfacial sources}=S_1(\mathbf{x},t)}$$
$$+\underbrace{\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{A}_{\gamma e,M}}G(\mathbf{x},t;\mathbf{y},\tau)\mathcal{Q}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)\,dA(\mathbf{y})\,d\tau}_{\text{influence of the entrance and exit sources}=S_2(\mathbf{x},t)} \tag{5.6}$$

5.2.2. Simplification 1: neglecting nonlocal contributions involving $\tilde{\psi}_\gamma$

For many situations, one can justify neglecting the nonlocal transport terms with respect to their local counterparts for the purpose of solving the closure problem (see Chapters 1–3 in [73]). We emphasize that the proposal is to neglect nonlocal contributions only for the purposes of solving the (microscale) closure problem. Although we do expect that nonlocal effects can be important within the macroscale balance equation (and many examples in the literature discussed in Section 1 support this), at the microscale we do not necessarily expect these nonlocal effects to be important. However, *a priori* it is not necessarily true that this is always the case, and some highly non-stationary fields may involve microscale nonlocal terms that are not negligible. For such cases, the solution detailed in Appendix B would be required. Nonetheless, there are many situations for which the structure of the deviation fields allows this simplification. We impose this simplification by stating a second scaling postulate.

Scaling Postulate 1 (Influence of Nonlocal Contributions to the Closure Problem). The structure of the $\tilde{\psi}_\gamma$ fields is such that the integrals in Eq. (5.4) (generating nonlocal terms in the closure problem) have a magnitude that is negligible compared with other terms in the balance for $\tilde{\psi}_\gamma$ (see Eq. (5.5a)). In other words,

$$\mathcal{N}(\tilde{\psi}_\gamma)\ll\mathcal{L}(\tilde{\psi}_\gamma) \tag{5.7}$$

Thus, these nonlocal terms may be safely dropped from the closure problem.

It is extremely difficult to develop a general restriction that indicates when such an approximation is true, although Whitaker [73] has provided a number of compelling arguments indicating that this approximation is frequently valid. The essential features of the argument rely on the fact that on the left-hand side of Eq. (5.7) we are integrating the deviation quantity, whereas on the right-hand side, it is differentiated. When there is a separation of length scales between the microscale, ℓ_{p_γ}, and the macroscale, $L_{\mathbb{P}_\gamma}$, then arguments can be drawn to justify this inequality. Because we have already assumed that $\ell_{p_\gamma}\ll r_0\sim\mathbf{O}(L_{\mathbb{P}_\gamma})$, we will adopt this scaling postulate without further consideration.

The simplified boundary value problem for closure takes the form

$$\frac{\partial \tilde{\psi}_\gamma}{\partial t} = \underbrace{\nabla \cdot \left(-\mathbf{v}_\gamma \tilde{\psi}_\gamma + \mathbf{D}_\gamma \cdot \nabla \tilde{\psi}_\gamma\right)}_{\mathcal{L}(\tilde{\psi}_\gamma)} - k_1 \tilde{\psi}_\gamma + \underbrace{\mathcal{S}(\mathbf{y}, \tau; \langle\psi_\gamma\rangle^\gamma, \nabla\langle\psi_\gamma\rangle^\gamma, \nabla\nabla\langle\psi_\gamma\rangle^\gamma)}_{\text{volume source}} \tag{5.8a}$$

$$B.C.1 \quad \mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_\gamma \cdot \nabla \tilde{\psi}_\gamma + \mathbf{v}_\gamma \tilde{\psi}_\gamma) = -k_s \tilde{\psi}_\gamma + \underbrace{\mathcal{G}(\mathbf{x}, t; \langle\psi_\gamma\rangle^\gamma, \langle\psi_\gamma\rangle^\gamma)}_{\text{source}}, \mathbf{x} \in \mathcal{A}_{\gamma\kappa,M} \tag{5.8b}$$

$$B.C.2 \quad \mathbf{n}_{\gamma e} \cdot (\mathbf{D}_\gamma \cdot \nabla \tilde{\psi}_\gamma + \mathbf{v}_\gamma \tilde{\psi}_\gamma) = \underbrace{\mathcal{Q}(\mathbf{x}, t; \langle\psi_\gamma\rangle^\gamma, \langle\psi_\gamma\rangle^\gamma)}_{\text{source}}, \mathbf{x} \in \mathcal{A}_{\gamma e,M} \tag{5.8c}$$

$$I.C. \quad \tilde{\psi}_\gamma = \underbrace{\mathcal{I}(\mathbf{x})}_{\text{source}}, \mathbf{x} \in \mathcal{V}_{\gamma,M} \tag{5.8d}$$

Given the linear nature of this problem, it is possible to find a unique solution in terms of the corresponding Green's function, $G(\mathbf{x}, \mathbf{y}, t-\tau)$. Because none of the parameters of the closure problem are functions of time (only the sources are), the Green's function is somewhat simplified in that it depends only upon the elapsed time, $(t-\tau)$ [58]. Because the nonlocal terms are not themselves sources, the form of the solution does not change-only the relevant Green's function is different. Thus, the solution in this case is identical in mathematical form to that given by Eq. (5.6), where the Green's function is determined by solving

$$\frac{\partial G}{\partial t} - \nabla \cdot \left(-\mathbf{v}_\gamma G + \mathbf{D}_\gamma \cdot \nabla G\right) + k_1 G = 0 \tag{5.9a}$$

$$B.C.1 \quad \mathbf{n}_{\gamma\kappa} \cdot (\mathbf{D}_\gamma \cdot \nabla G + \mathbf{v}_\gamma G) + k_s G = 0, \quad \mathbf{x} \in \mathcal{A}_{\gamma\kappa,M} \tag{5.9b}$$

$$B.C.2 \quad \mathbf{n}_{\gamma e} \cdot (\mathbf{D}_\gamma \cdot \nabla G + \mathbf{v}_\gamma G) = 0, \quad \mathbf{x} \in \mathcal{A}_{\gamma e,M} \tag{5.9c}$$

$$I.C. \quad G = \delta(\mathbf{x} - \mathbf{y}, t - \tau) \tag{5.9d}$$

5.2.3. Simplification 2: neglecting the influence of macroscopic boundaries

The most significant problem with the solution given by Eq. (5.6), is that the source term $\mathcal{Q}$ (Eq. (5.3c)) requires knowledge of the average, $\langle\psi_\gamma\rangle^\gamma$ at the entrances and exits of the macroscopic domain. Although this does not make a solution impossible (as evidenced by the fact that we have the formal solution already!), it does couple the solution of the closure problem to the particular values of the average field at the boundaries of the macroscopic solution domain. Our hope in applications is, frequently, to obtain a model for $\langle\psi_\gamma\rangle^\gamma$ in which the effective parameters are not dependent upon particular values of the dependent variable itself. Not only would this lead to nonlinear behavior in the model, but it also, in principle, requires full knowledge of the microscale structure of the system at the boundaries of the macroscopic domain $\mathcal{A}_{\gamma e,M}$ (Fig. 1). Under these conditions, it is not clear that such a model for $\langle\psi_\gamma\rangle^\gamma$ would be in any way more efficient than would be solving directly for the microscale variable ψ_γ.

In many systems where there is a disparity of characteristic lengths between the microscale and the macroscale, the fields of $\tilde{\psi}_\gamma$ only experience significant variations over distances on the order of ℓ_γ (Fig. 1). Thus we assume that the boundary conditions at the entrances and exits of the macroscopic region influence the fields of $\tilde{\psi}_\gamma$ only over a thin layer near the boundary of the macroscopic region. Recent studies (*cf.* Refs. [67,71,45,64]) have shown that the thickness of this layer to be on the order of $3\ell_\gamma$ to $10\ell_\gamma$ for several representative examples of processes in random media. In other words, on the basis of the length scale constraint $\ell_\gamma \ll L_{\mathbb{P}_\gamma}$, it is reasonable, for many cases, to assume that the boundary conditions at the entrances and exits of the *macroscopic region* have a limited range of influence on the deviation quantities. When this approximation is valid, one may be able to solve the closure problem in a subset of the entire macroscopic domain, and still obtain a solution that represents the essential physics of the problem. We have adopted the term *unit cell* to indicate such a subset of the microstructure of the system. An example of a unit cell is depicted in Fig. 4.

The problem at this juncture is that if we consider a subset of the entire domain, we must impose some boundary conditions at the surfaces of the domain, and these are typically not known *a priori*. Again, one potential alternative to handling this problem would be to couple the solution from the unit cell model to the solution for the macroscale problem. The difficulty with this approach is that one would need to solve the unit cell problem for every combination of boundary conditions that occurs at the macroscale. This would be a computationally expensive proposition, although such approaches have been suggested [72].

As an alternative, if the unit cell is significantly larger than ℓ_γ, then the discussion above suggests that, for many such systems, the external boundary conditions will have only a weak influence on the solution. Note further that the upscaled model ultimately depends upon integrals of the closure problem, and this process itself generally helps to weaken the dependence of the macroscale model over the microscale boundary conditions. For any particular system of interest, the appropriateness of this assumption will have to be validated heuristically. For those instances where this type of approximation appears to be valid, we propose the following scaling postulate.

Scaling Postulate 2 (Influence of Macroscale Boundary Conditions). Suppose that the Green's function, G, is characterized by an integral scale, ℓ_K, and that $\ell_K \sim \mathbf{O}(\ell_\gamma)$. Then, when ℓ_γ is sufficiently small relative to the large length scales $(\ell_\gamma \ll L_{\mathbb{P}_\gamma})$, the particular boundary conditions imposed at the entrances and exits of the domain have only a weak influence on the resulting solution for the deviation quantity $\tilde{\psi}_\gamma$. Under these conditions, the influence of the macroscopic boundaries may be neglected.

Imposing periodicity on the boundary conditions is one method that has been used in the MVA approach to specify what happens at the macroscopic boundaries $\mathcal{A}_{\gamma e,M}$. As an example, for a parallelepiped unit cell, periodicity can be imposed by requiring

$$\tilde{\psi}_\gamma(\mathbf{x} + \mathbf{L}_i, t) = \tilde{\psi}_\gamma(\mathbf{x}, t), \quad \mathbf{x} \in \mathcal{A}_{\gamma e,M}, \quad i = 1,2,3 \tag{5.10}$$

$$\nabla\tilde{\psi}_\gamma(\mathbf{x} + \mathbf{L}_i, t) = \nabla\tilde{\psi}_\gamma(\mathbf{x}, t) = 0, \quad \mathbf{x} \in \mathcal{A}_{\gamma e,M}, \quad i = 1,2,3, \tag{5.11}$$

where $\mathbf{L}_i$ is the set of three unique lattice vectors (each parallel to a side of the parallelpiped) defining the displacements needed to ensure periodicity on the macroscopic parallelpiped boundaries, $\mathcal{A}_{\gamma e,M}$. Note that for periodic boundary conditions, the last term in Eq. (5.6) is identically zero. This can be seen by integrating both sides of Eq. (5.8c) over $\mathcal{A}_{\gamma e,M}$. Because the normal $\mathbf{n}_{\gamma e}$ has opposite signs on

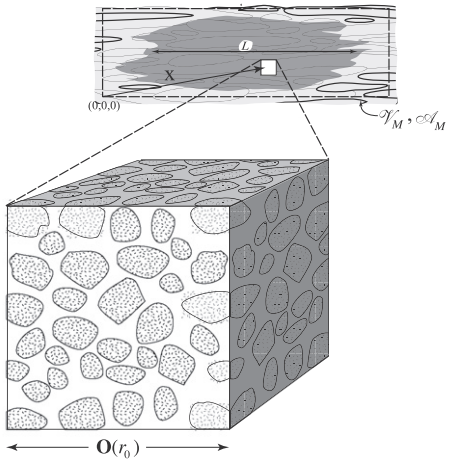

Fig. 4. Representative volume for the solution of the closure problem.

opposing faces, the integral of $\mathbf{n}_{\gamma e} \cdot (\mathbf{D}_\gamma \cdot \nabla\tilde{\psi}_\gamma + \mathbf{v}_\gamma\tilde{\psi}_\gamma)$ is identically zero.

In this sense, neglecting the influence of the macroscopic boundary conditions yields the same net effect as imposing periodicity in the macroscopic boundaries; in both cases, the final term in Eq. (5.6) is eliminated. It is possible to make some rough approximations to provide constraints indicating when this approximation is valid. In Section 5.2.5, we develop the notion of a length scale associated with a kernel. Putting that discussion off for now, assume that we can define a length scale ℓ_K that characterizes the Green's function. Then, we make some estimates of the area integrals appearing in Eq. (5.6)

$$S_1(\mathbf{x},t) = \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa,M}} G(\mathbf{x},\mathbf{y},t-\tau)\mathcal{G}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)\,dA(\mathbf{y})\,d\tau \sim \mathbf{O}(\alpha_1\|\mathcal{G}\|t^*) \tag{5.12a}$$

$$S_2(\mathbf{x},t) = \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{A}_{\gamma e,M}} G(\mathbf{x},\mathbf{y},t-\tau)\mathcal{Q}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)\,dA(\mathbf{y})\,d\tau \sim \mathbf{O}(\alpha_2\|\mathcal{Q}\|t^*) \tag{5.12b}$$

Here, t^* is the characteristic (integral) time associated with the Green's function G, and $\|\mathcal{G}\|$ and $\|\mathcal{Q}\|$ are appropriate measures (for example, the maximum) of the functions $\mathcal{G}$ and $\mathcal{Q}$. The parameters α_1 and α_2 measure the contribution of the Green's function to these integrals. Because of the structure of the $\mathcal{A}_{\gamma\kappa}$ interface, α_1 is always of about $\mathbf{O}(1)$ for the first integral, but in the second integral α_2 is only $\mathbf{O}(1)$ when $|\mathbf{x}-\mathbf{y}| \sim \mathbf{O}(\ell_\gamma)$. Assuming that $\|\mathcal{G}\| \sim \|\mathcal{Q}\|$, then scaling postulate 2 (above) requires that the third term on the right-hand side of Eq. (5.6) be substantially larger than the fourth term, *i.e.*,

$$(\alpha_1\|\mathcal{G}\|t^*) \gg (\alpha_2\|\mathcal{Q}\|t^*) \tag{5.13}$$

and this is generally true whenever $|\mathbf{x}-\mathbf{y}| \gg \ell_\gamma$. In other words, this restriction will be met in the interior of the macroscopic domain; in this sense, by interior we mean the portions of the domain that are a few integral scales (ℓ_γ) away from the macroscopic boundaries. The specific distance away from the boundaries will be dependent upon the particular nature of the problem (operators involved, microscale geometry, etc.) Note, however, that this is related to the problem of determining the appropriate macroscale boundary condition to be applied to the upscaled model [4,53,70]. So, although our macroscopic equations are technically not valid near the boundaries, this is not a limitation because a separate effort focused on determining the appropriate macroscale boundary conditions to apply to the upscaled problem essentially covers this region.

Under these circumstances, the closure problem solution simplifies to

$$\tilde{\psi}_\gamma(\mathbf{x},t) = \underbrace{\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} G(\mathbf{x},\mathbf{y},t-\tau)\mathcal{S}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma,\nabla\nabla\langle\psi_\gamma\rangle^\gamma)\,dV(\mathbf{y})\,d\tau}_{\text{influence of the volume sources}} + \underbrace{\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} G(\mathbf{x},\mathbf{y},t)\mathcal{I}(\mathbf{y})\,dV(\mathbf{y})}_{\text{influence of the initial condition}} + \underbrace{\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} G(\mathbf{x},\mathbf{y},t-\tau)\mathcal{G}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)\delta_{\gamma\kappa}(\mathbf{y})\,dV(\mathbf{y})\,d\tau}_{\text{influence of the interfacial sources}} \tag{5.14}$$

Again we have introduced the distribution $\delta_{\gamma\kappa}$ for notational convenience. It is useful to make a few modifications to this solution with the goal of ascertaining a general form for the solution. Because $\mathcal{S}$, $\mathcal{I}$, and $\mathcal{G}$ are linear functions of $\langle\psi_\gamma\rangle^\gamma$, $\nabla\langle\psi_\gamma\rangle^\gamma$ and $\nabla\nabla\langle\psi_\gamma\rangle^\gamma$, it is convenient to collect the contributions that are proportional to these three quantities. This yields a solution to the deviation problem that takes the form

$$\begin{aligned}\tilde{\psi}_\gamma(\mathbf{x},t) = &\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} \underbrace{\mathbf{K}_0(\mathbf{x},\mathbf{y},t-\tau)}_{\text{Kernel}} : \underbrace{\nabla\nabla\langle\psi_\gamma\rangle^\gamma\big|_{(\mathbf{x}+\mathbf{y},\tau)}}_{\text{Source}}\,dV(\mathbf{y})\,d\tau \\ &+ \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} \underbrace{\mathbf{K}_1(\mathbf{x},\mathbf{y},t-\tau)}_{\text{Kernel}} \cdot \underbrace{\nabla\langle\psi_\gamma\rangle^\gamma\big|_{(\mathbf{x}+\mathbf{y},\tau)}}_{\text{Source}}\,dV(\mathbf{y})\,d\tau \\ &+ \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} \underbrace{K_2(\mathbf{x},\mathbf{y},t-\tau)}_{\text{Kernel}} \underbrace{\langle\psi_\gamma\rangle^\gamma\big|_{(\mathbf{x}+\mathbf{y},\tau)}}_{\text{Source}}\,dV(\mathbf{y})\,d\tau \\ &+ \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} K_3(\mathbf{x},\mathbf{y},t-\tau)\,dV(\mathbf{y})\,d\tau\end{aligned} \tag{5.15}$$

where $\mathbf{K}_0$, $\mathbf{K}_1$, K_2, and K_3 are kernel functions arising from recombining terms in Eq. (5.14). Note that this solution for the closure is still assumed to be computed on the entire macroscopic domain, $\mathcal{V}_{\gamma,M}$. Although we have made efforts to eliminate the particular influence of the macroscopic boundaries (assuming that we are sufficiently far from these boundaries), we have imposed no constraints on the kernel functions themselves. Thus, to this point in the analysis the solution is fully nonlocal, and the solution for $\tilde{\psi}_\gamma(\mathbf{x})$ can, in principle, depend on the values of the source terms throughout the entire macroscopic volume.

5.2.4. Simplification 3: the existence of representative volumes

To this point in the analysis of the deviations quantities, we have sought a solution for $\tilde{\psi}_\gamma$ on the entire domain, $\mathcal{V}_M$. Mathematically, this makes sense: $\tilde{\psi}_\gamma$ is a field variable defined at every point in the domain, and the balance equations describing its evolution in time and space are derivable from the original (microscale) balance equations and the definitions of the averaging operation. However, recall that the motivation for computing $\tilde{\psi}_\gamma$ in the first place is so that we are able to close the averaged balance equation given by Eq. (4.13). The deviation quantities appear only in area or volume integrals whose support is the finite domain of the averaging volume (*i.e.*, the integrals are computed over either the volume $\mathcal{V}_\gamma(\mathbf{x})$ or the associated interfacial area, $\mathcal{A}_{\gamma\kappa}(\mathbf{x})$). Thus, for any location $\mathbf{x}$, we do not, in principle, need the solution for $\tilde{\psi}_\gamma$ over the entire domain to close the macroscopic balance, but only over the domain associated with the averaging volume.

This observation would be of little use under the conditions that scaling postulate 3 were invalid; this approximation essentially allowed us to replace the *actual* boundary conditions on the boundary of the macroscopic domain $(\mathcal{A}_{\gamma e,M})$ with periodic boundary conditions. Once we have accepted that this approximation is valid, then it becomes possible to consider computing the closure problem over volumes that are of the same dimensions as the averaging volume itself.

It is possible that for some highly heterogeneous media, the structure of each averaging domain $\mathcal{V}_\gamma(\mathbf{x})$ is unique enough that the volume and area integrals required to close the problem vary dramatically from point to point. For such cases, the idea that we need only to compute the closure over subvolumes $\mathcal{V}_\gamma(\mathbf{x})$ does not reduce the total degrees of freedom required to solve the problem (*i.e.*, we would still need to tessellate the domain, $\mathcal{V}_M$ with subvolumes whose size was on the order of $\mathcal{V}_\gamma(\mathbf{x})$, and then solve the closure over each of these sub-volumes).

In many instances, however, we hope to find that the microscale structure of the domain bears some kind of redundancy, such that the closure does not need to be computed uniquely for every subdomain of $\mathcal{V}_M$. Each of the kernel functions appearing in Eq. (5.18) is a microscale function. However, these functions appear in the final solution only in an integrated sense. Thus, we might propose

that, although the kernel functions themselves are random fields, they obey a scaling postulate such that the time–space integrals appearing in Eq. (5.18) are not sensitive to the particular realization that generates them (in the sense given by Eq. (5.16)). The idea here is that, although the dependent field variables $\langle\psi_\gamma\rangle^\gamma$ (and its gradients) may vary dramatically over the problem, the net effect of the Green's functions themselves does not vary dramatically from location to location. This is the concept of a *representative volume* that has been used in physics and in applications to porous media for many years [43, Section 113], [37], [10, Section 1.3.2], and [12, Section 6.1.3].

For convenience, we denote by M_i the spatial integral quantities appearing in Eq. (4.13), as identified above. A volume used for closure is called *representative* if the following definition holds (*cf.* Wood [76])

Definition. A sub-volume, $\mathcal{V}_\gamma(\mathbf{x})$ of the domain $\mathcal{V}_M$ is said to be *representative* when, for any n independent realizations of the volume $\mathcal{V}_\gamma^j$, $j \in \{1,\ldots,n\}$, the following is true for the integral quantities, M_i

$$\Delta Norm(M_i^j) \leqslant \varphi_i \tag{5.16}$$

Here j indexes the value of M_i for each realization, $\Delta Norm$ is any suitable measure of the difference among the integral quantities of the realizations (*e.g.,* the standard deviation of the integral quantity), and φ_i represents a parameter bounding the difference measure for the integral quantity M_i. As an example, note that the quantity $\mathbf{M}_1 = \langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma$ appears as an important term in Eq. (4.13) (and this term is related, ultimately, to the hydrodynamic dispersion). If one were to make, for example, 100 different realizations of the structure of the medium for the volume of media, $\mathcal{V}_\gamma(\mathbf{x})$, and the associated velocity field $\tilde{\mathbf{v}}_\gamma$, then we could compute the quantity $\mathbf{M}_1^j = \langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma|_j$, $j = 1,\ldots,100$. Each of these computations would correspond to a realization of the integral quantity, $\mathbf{M}_1$. A reasonable norm summarizing this quantity might be the standard deviation of the 100 realizations. Clearly, if this standard deviation were *small enough*, as based by some heuristic criterion, then the particular volume, $\mathcal{V}_\gamma(\mathbf{x})$, used for investigation would be of little interest. Media that meet this definition are frequently referred to as being *quasi-ergodic* [18, Section 2.12]. For systems that exhibit quasi-ergodic behavior, the particular configuration of a unit cell influences the appropriate integral measure only on the order of ϕ_i. With this definition in place, we can impose the following scaling postulate that allows the notion of a *representative* volume to be adopted for the purposes of closure, even for cases where the macroscale model is assumed to maintain time and space nonlocal behavior.

Scaling Postulate 3 (Existence of a Representative Volume). The kernel functions in the solution given in the closure solution (Eq. (5.18)) are representative in the following sense. For any particular functions $\langle\psi_\gamma\rangle^\gamma$, $\nabla\langle\psi_\gamma\rangle^\gamma$, and $\nabla\nabla\langle\psi_\gamma\rangle^\gamma$, the solution for $\tilde{\psi}_\gamma$ forms a set of identically prepared realizations of the system (*i.e.*, the geometry and parameter fields associated with the microscale balance equations adhere to the restrictions proposed by Eq. (5.16)).

Note that in the conventional presentation of the MVA approach, this postulate is stated by the restriction $\ell_\gamma \ll r_0$. The idea in this conventional presentation is that the expression given by Eq. (5.16) will be met under these conditions. Although this is probably a reasonable approximation to make, in principle one should check that Eq. (5.16) is actually met by computing the norm for a few realizations of the integral quantities under consideration.

The practical implications of this scaling law are significant. In essence, this allows one to solve for the Green's functions in a representative volume (which then generates the kernel functions $\mathbf{K}_0$, $\mathbf{K}_1$, K_2, and K_3) only once for a particular realization of the microscale system over a unit cell. The solution for any particular values of the source functions $\langle\psi_\gamma\rangle^\gamma$ and $\nabla\langle\psi_\gamma\rangle^\gamma$ are then found by simple convolution. Analytical solutions of the Green's functions can be obtained for simple geometries as shown in Appendix C, following the ideas reported by Ochoa-Tapia et al. [54]. Furthermore, for spatially periodic unit cells Wood [76] used a combination of Laplace and finite Fourier transforms in order to obtain an expression for the Green's functions related to dispersion in porous media. In Section 7 below, we present a detailed example of a nonlocal solution where the Green's functions must be computed numerically.

On the basis of scaling postulate 3, we solve the closure problem over a subset $\mathcal{V}(\mathbf{x})$ of the original domain $[\mathcal{V}_\gamma(\mathbf{x}) \subset \mathcal{V}_{\gamma,M}]$ (the domain of the averaging volume $\mathcal{V}(\mathbf{x})$ is assumed to be uniquely located by its centroid, $\mathbf{x}$) and impose the following boundary condition at the entrances and exits $[A_{\gamma e}(\mathbf{x})]$ of the representative volume

$$\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{l}_i,t) = \tilde{\psi}_\gamma(\mathbf{x},t), \quad \mathbf{x} \in A_{\gamma e}, \ \ i = 1,2,3. \tag{5.17}$$

Note that the periodic conditions that were applied to the macroscopic volume previously are now applied to the representative volume. As pointed out previously (*e.g.,* [76]), this scaling law does not imply that the porous medium is actually periodic. Rather, a periodic unit cell represents a *reasonable model* for the pore structure that, although abstracted from the real structure, is still consistent with our physical picture of a porous medium. It should be understood that it is an assumption that such a simplification can be made, and ultimately one should check to assure that the approximation yields reasonable results (one example of how this can be done is discussed in Section 7). When such a simplification is valid, the benefit is enormous. In essence, this approximation eliminates the need to compute the deviation quantities over the entire macroscopic domain, and this dramatically reduces the number of degrees of freedom embodied in the solution to the closure problem. In this way, our expression of the deviation fields given by Eq. (5.15) takes the form,

$$\begin{aligned}\tilde{\psi}_\gamma(\mathbf{x},t) = &\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} \underbrace{\mathbf{K}_0(\mathbf{x},\mathbf{y},t-\tau)}_{\text{Kernel}} \\ &: \underbrace{\nabla\nabla\langle\psi_\gamma\rangle^\gamma\big|_{(\mathbf{x}+\mathbf{y},\tau)}}_{\text{Source}} dV(\mathbf{y})\,d\tau + \int_{\tau=0}^{\tau=t} \\ &\times \int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} \underbrace{\mathbf{K}_1(\mathbf{x},\mathbf{y},t-\tau)}_{\text{Kernel}} \cdot \underbrace{\nabla\langle\psi_\gamma\rangle^\gamma\big|_{(\mathbf{x}+\mathbf{y},\tau)}}_{\text{Source}} dV(\mathbf{y})\,d\tau \\ &+ \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} \underbrace{K_2(\mathbf{x},\mathbf{y},t-\tau)}_{\text{Kernel}} \underbrace{\langle\psi_\gamma\rangle^\gamma\big|_{(\mathbf{x}+\mathbf{y},\tau)}}_{\text{Source}} dV(\mathbf{y})\,d\tau \\ &+ \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} K_3(\mathbf{x},\mathbf{y},t-\tau)\,dV(\mathbf{y})\,d\tau\end{aligned} \tag{5.18}$$

Despite this substantial simplification, we note that the average fields are contained in spatial and time integrals. This means that if $\tilde{\psi}_\gamma$ is substituted in its present form into the upscaled model (Eq. (4.13)), the result is a macroscale equation that is nonlocal in $\langle\psi_\gamma\rangle^\gamma$, $\nabla\langle\psi_\gamma\rangle^\gamma$, and $\nabla\nabla\langle\psi_\gamma\rangle^\gamma$. For systems that are to be represented by nonlocal macroscale balances, this would complete the averaging and closure step. The analysis of nonlocal closure problems will be discussed in additional detail in Section 7.

5.2.5. Simplification 4: localization

Traditionally, volume averaging has been used to develop models that are *local* in time and space. The assumptions required to generate a local model can be obtained directly from the nonlocal

solution given in Eq. (5.18). In short, one can obtain a local solution under conditions that the terms $\langle\psi_\gamma\rangle^\gamma$, $\nabla\langle\psi_\gamma\rangle^\gamma$, and $\nabla\nabla\langle\psi_\gamma\rangle^\gamma$ can be treated as if they were constants in the integrals that appear in Eq. (5.18). More formally, we can think of situations where the characteristic time and length scales for the kernel functions are sufficiently smaller than the corresponding time and length scales for the average of ψ_γ and its gradients. To understand under what conditions this is possible, a Taylor series expansion of $\langle\psi_\gamma\rangle^\gamma$ (and/or its derivatives) in time and space are introduced and then the corresponding length and time scale constraints are taken into account (*cf.* [73, Chapter 1]). It is possible to show, with a few limitations put on the structure of the microscale fields, that this assumption is valid for the when constraints are met of the form [73]

$$\frac{\ell}{L} \ll 1, \tag{5.19a}$$

$$\frac{t^*}{T^*} \ll 1. \tag{5.19b}$$

It is constructive to think of ℓ, L, t^* and T^* as being defined by appropriate integrals of the covariance functions for the field variable ($\langle\psi_\gamma\rangle^\gamma$ and its gradients) and of the kernel functions themselves. For example, the third term in Eq. (5.18) involves the scalar kernel function K_2 and the average field property, $\langle\psi_\gamma\rangle^\gamma$. The spatial scales for the kernel functions require a different approach to compute. However, recognizing that many of the kernel functions will be rapidly decreasing functions of the displacement from the origin, a reasonable length scale can be proposed. Suppose for the moment that we are interested in the length scale associated with a scalar kernel function, K. A reasonable length scale can be the derived from the second spatial moment of the kernel function. We propose the following. Let

$$\mathbb{S}_\gamma(\mathbf{x},t) = \frac{\int_{-\infty}^{\infty} K(\mathbf{x},\mathbf{x}+\boldsymbol{\lambda}w,t)w^2\,dw}{\int_{-\infty}^{\infty} K(\mathbf{x},\mathbf{x}+\boldsymbol{\lambda}w,t)\,dw} \tag{5.20}$$

where $\boldsymbol{\lambda}$ is a unit directional vector. Then one can associate a length scale to the kernel function K as follows

$$\ell_K(\mathbf{x},t;\boldsymbol{\lambda}) = \left\langle \mathbb{S}_\gamma^{\frac{1}{2}} \right\rangle^\gamma \tag{5.21}$$

The extension to vector and tensor valued kernel functions is straightforward. Because the Green's function represents the fundamental solution to the closure problem, we expect the quantity given by Eq. (5.21) to be approximately the same as the integral scale for $\tilde{\psi}_\gamma$; and, both of these quantities should be about the same as the integral scale for the indicator function, Φ_γ. In other words, it is generally safe to assume

$$\ell_\gamma \approx \ell_K \approx \ell_{\tilde{\psi}_\gamma} \tag{5.22}$$

and each of these quantities are mutually substitutable in the inequalities that constrain the analysis.

For the large length scale associated with ψ_γ, we have

$$L_{\langle\psi_\gamma\rangle^\gamma}(\mathbf{x},t;\boldsymbol{\lambda}) = \int_{w\in\mathbb{R}^+} \rho_{\langle\psi_\gamma\rangle^\gamma}(\mathbf{x},\mathbf{x}+\boldsymbol{\lambda}w)\,dw \tag{5.23}$$

where $\rho_{\langle\psi_\gamma\rangle^\gamma}$ is the autocorrelation function (see Section 3). With these definitions, Eq. (5.19a) would then be represented in terms of the ratio of integral scales

$$\frac{\ell_K}{L_{\langle\psi_\gamma\rangle^\gamma}} \ll 1. \tag{5.24}$$

Analogous arguments can be constructed to define the microscopic and macroscopic time scales t^* and T^*.

The practical impact of defining these length and time scales is that it allows one to assess the relative contribution of the two terms appearing in each of the convolutions that appear in Eq. (5.18). If the kernel functions fall off must more rapidly in time and space than do the source terms ($\langle\psi_\gamma\rangle^\gamma$, $\nabla\langle\psi_\gamma\rangle^\gamma$, and $\nabla\nabla\langle\psi_\gamma\rangle^\gamma$), then the source terms can be regarded as constants as far as computing the integral is concerned. With this condition in mind, we pose the following scaling law

Scaling Postulate 4 (Separation of Scales I). The characteristic length and time scales for the kernel functions appearing in the solution for $\tilde{\psi}_\gamma$ are sufficiently smaller than the corresponding length and time scales for the macroscopic source terms such that restrictions of the form

$$\frac{\ell_K}{L_{\langle\psi_\gamma\rangle^\gamma}} \ll 1, \quad \frac{t_K^*}{T^*_{\langle\psi_\gamma\rangle^\gamma}} \ll 1 \tag{5.25}$$

are valid (here, ℓ_K and t_K^* correspond to the length and time scales of the kernel functions, and $L_{\langle\psi_\gamma\rangle^\gamma}$ and $T^*_{\langle\psi_\gamma\rangle^\gamma}$ are the length and time scales for the corresponding source terms). Under these conditions, the source terms can be treated as if they were constants for the purposes of computing the solution for $\tilde{\psi}_\gamma$.

Under such circumstances, the solution for $\tilde{\psi}_\gamma$ is dramatically simplified. Eq. (5.18) can then be put in the form

$$\tilde{\psi}_\gamma(\mathbf{x},t) = \mathbf{A}_\gamma(\mathbf{x},t) : \nabla\nabla\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)} + \mathbf{b}_\gamma(\mathbf{x},t)\cdot\nabla\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)} + s_\gamma(\mathbf{x},t)\langle\psi_\gamma\rangle^\gamma\Big|_{\mathbf{x}} + \mathcal{P}(\mathbf{x},t). \tag{5.26}$$

where, as a matter of convenience we introduced the following definitions

$$\mathbf{A}_\gamma(\mathbf{x},t) = \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} \mathbf{K}_0(\mathbf{x},\mathbf{y},t-\tau)\,dV(\mathbf{y})\,d\tau \tag{5.27a}$$

$$\mathbf{b}_\gamma(\mathbf{x},t) = \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} \mathbf{K}_1(\mathbf{x},\mathbf{y},t-\tau)\,dV(\mathbf{y})\,d\tau \tag{5.27b}$$

$$s_\gamma(\mathbf{x},t) = \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} K_2(\mathbf{x},\mathbf{y},t-\tau)\,dV(\mathbf{y})\,d\tau \tag{5.27c}$$

$$\mathcal{P}(\mathbf{x},t) = \int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} K_3(\mathbf{x},\mathbf{y},t-\tau)\,dV(\mathbf{y})\,d\tau \tag{5.27d}$$

The variables $\mathbf{A}_\gamma$, $\mathbf{b}_\gamma$, s_γ, and $\mathcal{P}(\mathbf{x},t)$ are usually known as *closure variables* within the conventional MVA approach (see [73]).

6. Closed upscaled model

In the previous section, we developed a hierarchy of closures for the dependent variable $\tilde{\psi}_\gamma$ where the closure was sequentially simplified by approximations (as posed by the scaling postulates). With these closures in place, we can now consider how the closure schemes impact the resulting macroscopic model (*i.e.*, the closure allows us to eliminate the deviation terms by providing an explicit representation in terms of the sources and Green's functions for the problem). In this section, we describe how various closure approximations influence the macroscopic balance equations.

6.1. Closed model: fully nonlocal form

We have a closure available in Eq. (5.6) that contains very few restrictions. However, because few approximations have been imposed, the result is also quite complex. Nonetheless, one can substitute Eq. (5.6) into Eq. (4.13) to find a differential balance equation entirely in terms of $\langle\psi_\gamma\rangle^\gamma$ and its gradients.

Although such a model is, in principle, possible to construct, the model itself does not reduce the information content of the macroscale model as compared to the microscale representation. The macroscale problem essentially requires that a closure problem is computed to predict the quantity $\tilde{\psi}_\gamma$ pointwise throughout the domain. Because no scaling postulates regarding the regularity or

redundancy embedded in the microscale behavior are imposed, there is formally no way to avoid computing the solution for $\tilde{\psi}_\gamma$ for the entire macroscopic domain, $\mathcal{V}_M$ at the microscale level of description. There is, however, some overhead that is incurred in the process of averaging the equations; specifically, the macroscale balance now becomes an integro-differential equation involving both time and space convolutions. For such conditions, although averaging is technically possible to perform, it provides no benefits over computing the microscale solution directly. Although it is interesting to note that such models can be developed formally without additional limiting constraints, they are nonetheless not practical models for applications, and thus are discussed no further.

6.2. Closed model: simplified nonlocal forms

An interesting macroscopic model can be developed for conditions that represent the case between the fully nonlocal and localized closures. For this case, scaling postulates 0 through 3 are imposed, but localization (scaling postulate 4) is not imposed. The result is a nonlocal, integro-differential equation that applies at the macro scale. Because the resulting equation is extremely lengthy, rather than providing the entire equation in its explicit form we show here the result for closing the first unclosed term; the remaining terms are found by a similar substitution. The first unclosed term in Eq. (4.13) is the quantity $\langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma$. Substituting Eq. (5.18) into this term yields the closure

$$\begin{aligned}\mathbf{M}_1(\mathbf{x},t) &= \langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma\big|_{(\mathbf{x},t)}\\ &= \frac{1}{V_\gamma}\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\int_{\mathbf{z}\in\mathcal{V}_\gamma(\mathbf{y})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\mathbf{K}_0(\mathbf{x},\mathbf{y},t-\tau)\\ &\quad:\nabla_{\mathbf{z}}\nabla_{\mathbf{z}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{z},\tau)}dV(\mathbf{z})\,dV(\mathbf{y})\,d\tau + \frac{1}{V_\gamma}\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\\ &\quad\times\int_{\mathbf{z}\in\mathcal{V}_\gamma(\mathbf{y})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\mathbf{K}_1(\mathbf{x},\mathbf{y},t-\tau)\\ &\quad\cdot\nabla_{\mathbf{z}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{z},\tau)}dV(\mathbf{z})\,dV(\mathbf{y})\,d\tau + \frac{1}{V_\gamma}\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\\ &\quad\times\int_{\mathbf{z}\in\mathcal{V}_\gamma(\mathbf{y})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})K_2(\mathbf{x},\mathbf{y},t\\ &\quad-\tau)\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{z},\tau)}dV(\mathbf{z})\,dV(\mathbf{y})\,d\tau + \frac{1}{V_\gamma}\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\\ &\quad\times\int_{\mathbf{z}\in\mathcal{V}_\gamma(\mathbf{y})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})K_3(\mathbf{x},\mathbf{y},t-\tau)\,dV(\mathbf{z})\,dV(\mathbf{y})\,d\tau \qquad (6.1)\end{aligned}$$

Although such a scheme does allow one to develop a nonlocal macroscale equation, the resulting model is still extremely complex. The primary advantage to this model over the fully nonlocal model is that the concept of the representative volume allows one to compute the Green's functions that are associated with Eq. (6.1) for a single realization of a unit cell (via Eq. (5.9d)). However, the direct computation of Green's functions is itself a very complicated procedure. An example of computing the Green's functions in this way is presented in Section 7.

As an alternative, we note that scaling postulate 4 is generally not very restrictive. In a broad sense, the restrictions require only that the microscale fluctuations be defined by time and length scales that are sufficiently small compared to their macroscale counterparts. This is often a reasonable constraint to impose, especially in light of the similar constraint that has been imposed for the length scales associated with the parameter fields. If we are willing to impose such a constraint, then we can adopt the localized solution given by Eq. (5.26) for the deviations. Inserting this into the macroscale balance given by Eq. (4.13), we find a simplified (but still nonlocal) balance of the form

$$\begin{aligned}\frac{\partial\langle\psi_\gamma\rangle^\gamma}{\partial t} &= -\nabla\cdot(\langle\mathbf{v}_\gamma\rangle^\gamma\langle\psi_\gamma\rangle^\gamma) + \nabla\cdot\left(\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma\right) - k_1\langle\psi_\gamma\rangle^\gamma\\ &\quad-\nabla\cdot\mathbf{M}_1 + \nabla\cdot\left(\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\mathbf{M}_2\right) + \nabla\cdot\mathbf{M}_3 - k_s M_4 + \langle f\rangle^\gamma\\ &\quad-\Gamma_\gamma(\mathbf{x},t) + N(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma) \qquad (6.2)\end{aligned}$$

where the integral terms are specified by

$$\begin{aligned}\mathbf{M}_1(\mathbf{x},t) &= \langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma\big|_{(\mathbf{x},t)} = \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\mathbf{A}_\gamma(\mathbf{x}+\mathbf{y},t)\\ &\quad:\nabla_{\mathbf{y}}\nabla_{\mathbf{y}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dV(\mathbf{y}) + \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}\\ &\quad+\mathbf{y})\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\cdot\nabla_{\mathbf{y}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dV(\mathbf{y}) + \frac{1}{V_\gamma}\\ &\quad\times\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})s_\gamma(\mathbf{x}+\mathbf{y},t)\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dV(\mathbf{y})\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y}) \qquad (6.3a)\end{aligned}$$

$$\begin{aligned}\mathbf{M}_2(\mathbf{x},t) &= \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\\ &= \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\mathbf{A}_\gamma(\mathbf{x}+\mathbf{y},t)\\ &\quad:\nabla_{\mathbf{y}}\nabla_{\mathbf{y}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dA(\mathbf{y}) + \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}\\ &\quad+\mathbf{y})\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\cdot\nabla_{\mathbf{y}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dA(\mathbf{y}) + \frac{1}{V_\gamma}\\ &\quad\times\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})s_\gamma(\mathbf{x}+\mathbf{y},t)\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dA(\mathbf{y})\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y}) \qquad (6.3b)\end{aligned}$$

$$\begin{aligned}\mathbf{M}_3(\mathbf{x},t) &= \langle\tilde{\mathbf{D}}_\gamma\cdot\nabla\tilde{\psi}_\gamma\rangle^\gamma\big|_{(\mathbf{x},t)} = \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{D}}_\gamma(\mathbf{x}+\mathbf{y})\\ &\quad\cdot\nabla_{\mathbf{y}}\left[\mathbf{A}_\gamma(\mathbf{x}+\mathbf{y},t):\nabla_{\mathbf{y}}\nabla_{\mathbf{y}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}\right]dV(\mathbf{y})\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{D}}_\gamma(\mathbf{x}+\mathbf{y})\cdot\nabla_{\mathbf{y}}\left[\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\cdot\nabla_{\mathbf{y}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}\right]dV(\mathbf{y})\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{D}}_\gamma(\mathbf{x}+\mathbf{y})\cdot\nabla_{\mathbf{y}}\left[s_\gamma(\mathbf{x}+\mathbf{y},t)\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}\right]dV(\mathbf{y})\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{D}}_\gamma(\mathbf{x}+\mathbf{y})\cdot\nabla_{\mathbf{y}}\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y}) \qquad (6.3c)\end{aligned}$$

$$\begin{aligned}M_4(\mathbf{x},t) &= \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\\ &= \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{A}_\gamma(\mathbf{x}+\mathbf{y},t):\nabla_{\mathbf{y}}\nabla_{\mathbf{y}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dA(\mathbf{y})\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\cdot\nabla_{\mathbf{y}}\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dA(\mathbf{y})\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}s_\gamma(\mathbf{x}+\mathbf{y},t)\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)}dA(\mathbf{y})\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y}) \qquad (6.3d)\end{aligned}$$

This nonlocal model offers significant advantages over the more general form given above [with example term specified by Eq. (6.1)]. In particular, the fields $\mathbf{A}_\gamma$, $\mathbf{b}_\gamma$, s_γ, and $\mathcal{P}(\mathbf{x},t)$ are substantially easier to compute numerically than their corresponding Green's functions (see Section 1.4.4 in [73]). However, this nonlocal form is still an integro-differential equation, and such equations are

difficult to solve numerically (this is discussed in more detail in [76]). In the next section, we develop constraints indicating the conditions when fully local models are valid.

6.3. Closed model: localized solutions

The nonlocal terms that are given by Eqs. (6.3a)–(6.3d) can be simplified further when $\langle\psi_\gamma\rangle^\gamma$ and its gradients do not change much within the averaging domain. The arguments for this approximation can be constructed in analogous manner to those generated for the conditions of *quasi-stationarity* described in Appendix A. The most straightforward way to develop the associated constraints is to expand the macroscale functions of $\langle\psi_\gamma\rangle^\gamma$ in Taylor series. For example, expanding $\langle\psi_\gamma\rangle^\gamma|_{(\mathbf{x}+\mathbf{y},t)}$ about $\mathbf{x}$

$$\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x}+\mathbf{y},t)} = \langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)} + \mathbf{y}\cdot\nabla\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)} + \cdots \tag{6.4}$$

Noting that the maximum magnitude of $\mathbf{y}$ is r_0, then we are looking for a set of conditions of the form

$$\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)} \gg \mathbf{y}\cdot\nabla\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)} \tag{6.5}$$

or, as an explicit set of length-scale constraints

$$\frac{r_0}{L_{\langle\psi_\gamma\rangle^\gamma}} \ll 1 \tag{6.6}$$

The associated scaling postulate is stated as follows.

Scaling Postulate 5 (Separation of Scales II). The characteristic length scale, $L_{\langle\psi_\gamma\rangle^\gamma}$, for the macroscale quantity $\langle\psi_\gamma\rangle^\gamma$ and its gradients is much larger than the characteristic length for the support volume, r_0 (*i.e.*, $r_0 \ll L_{\langle\psi_\gamma\rangle^\gamma}$). Under these conditions, the macroscale quantities can be removed from volume integrals associated with the averaging volume.

Note that combining this with the length scale constraints that have been developed previously (scaling postulates 3 and 4) results in the classical idea of the separation of the three characteristic length scales that were identified in the introduction (*cf.* [73, Chapter 1]; Dagan [27, Section 1.10]), *i.e.*

$$\ell_K \ll r_0 \ll L_{\langle\psi_\gamma\rangle^\gamma} \tag{6.7}$$

A corollary of this scaling postulate is that the intrinsic averages of the deviation fields are zero; *i.e.*, $\langle\tilde{\psi}_\gamma\rangle^\gamma = 0$. This result arises after applying the intrinsic averaging operator to Eq. (3.18).

Under these conditions, a more classically-structured macroscale balance law can be developed. Although not necessary, for ease in presentation, we will consider here the case where the microscale diffusion tensor is a constant. This creates the following changes in the final closure of the macroscale balance.

1. The terms involving the source $\nabla\nabla\langle\psi_\gamma\rangle^\gamma$ in the closure problem are eliminated. This means that $\mathbf{A}_\gamma \equiv \mathbf{0}$.
2. All terms involving $\tilde{\mathbf{D}}_\gamma$ are zero. Thus, $\langle\mathbf{D}_\gamma\rangle^\gamma = \mathbf{D}_\gamma$, and $\mathbf{M}_3 = \mathbf{0}$.
3. The final macroscale balance equation involves terms with a maximum of two gradients of the macroscale concentration; thus, the macroscale balance law takes the same form as the microscale balance. When $\tilde{\mathbf{D}}_\gamma \neq \mathbf{0}$, the final form of the macroscale balance law would include terms proportional to the third gradient ($\nabla\nabla\nabla\langle\psi_\gamma\rangle^\gamma$) of the macroscale concentration. When spatial variations in the diffusion tensor are not negligible, the resulting macroscopic balance would indeed have such terms; they do not, however, appear with the constant tensor approximation.

With these approximations, the three remaining unclosed integral quantities identified in Eq. (4.13) can be expressed as follows

$$\begin{aligned}\mathbf{M}_1(\mathbf{x},t) &= \langle\tilde{\mathbf{v}}_\gamma\tilde{\psi}_\gamma\rangle^\gamma|_{(\mathbf{x},t)} = \left[\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y})\right]\\ &\quad\cdot\nabla\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)} + \left[\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})s_\gamma(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y})\right]\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)}\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y})\end{aligned} \tag{6.8a}$$

$$\begin{aligned}\mathbf{M}_2(\mathbf{x},t) &= \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\\ &= \left[\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right]\cdot\nabla\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)}\\ &\quad+\left[\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})s_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right]\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)}\\ &\quad+\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\end{aligned} \tag{6.8b}$$

$$\begin{aligned}M_4(\mathbf{x},t) &= \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\tilde{\psi}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\\ &= \left[\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right]\cdot\nabla\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)}\\ &\quad+\left[\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}s_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right]\langle\psi_\gamma\rangle^\gamma\Big|_{(\mathbf{x},t)}+\frac{1}{V_\gamma}\\ &\quad\times\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\end{aligned} \tag{6.8c}$$

In addition, notice that the non-local term in Eq. (6.2), N, takes the form

$$\begin{aligned}N(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma) &= -\nabla\cdot(\langle\tilde{\mathbf{v}}_\gamma\rangle^\gamma\langle\psi_\gamma\rangle^\gamma - \langle\tilde{\mathbf{D}}_\gamma\rangle^\gamma\cdot\nabla\langle\psi_\gamma\rangle^\gamma)\\ &\quad-\frac{k_s}{V_\gamma}A_{\gamma\kappa}\langle\psi_\gamma\rangle^\gamma - \nabla\cdot(\langle\mathbf{D}_\gamma\rangle^\gamma\cdot\varepsilon_\gamma^{-1}\nabla\varepsilon_\gamma\langle\psi_\gamma\rangle^\gamma)\end{aligned} \tag{6.9}$$

However, we have already accepted that the intrinsic average of the spatial deviations of a property is zero and we have neglected the spatial variations of ε_γ. In this way, Eq. (6.9) simplifies to,

$$N(\mathbf{x},t;\langle\psi_\gamma\rangle^\gamma) = -\frac{k_s a_v}{\varepsilon_\gamma}\langle\psi_\gamma\rangle^\gamma \tag{6.10}$$

where the interfacial area per unit volume, a_v, is defined as,

$$a_v = \frac{A_{\gamma\kappa}}{V} \tag{6.11}$$

Collecting terms that involve the same order of derivatives and regrouping, the macroscopic balance for $\langle\psi_\gamma\rangle^\gamma$ can be expressed by the conventional-looking equation

$$\begin{aligned}\underbrace{\frac{\partial\langle\psi_\gamma\rangle^\gamma}{\partial t}}_{\text{Accumulation}} &= -\underbrace{\nabla\cdot(\mathbf{V}_\gamma\langle\psi_\gamma\rangle^\gamma)}_{\text{Convection}} + \underbrace{\nabla\cdot(\mathbf{D}_\gamma^*\cdot\nabla\langle\psi_\gamma\rangle^\gamma)}_{\text{Hydrodynamic Dispersion}} - \underbrace{k_1\langle\psi_\gamma\rangle^\gamma}_{\text{Homogeneous Reaction}}\\ &\quad-\underbrace{k_{s,eff}\langle\psi_\gamma\rangle^\gamma}_{\text{Surface Reaction}} + \underbrace{F_\gamma}_{\text{Volumetric Source Term}} - \underbrace{\Gamma_\gamma}_{\text{Surface Source Term}}\end{aligned} \tag{6.12}$$

and the macroscopic parameters that appear are defined as follows.

$$\begin{aligned}\mathbf{V}_\gamma &= \langle\mathbf{v}_\gamma\rangle^\gamma + \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})}\tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})s_\gamma(\mathbf{x},t)\,dV(\mathbf{y})\\ &\quad-\mathbf{D}_\gamma\cdot\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})s_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\\ &\quad+\frac{k_s}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\end{aligned} \tag{6.13a}$$

$$\mathbf{D}^*_\gamma = \mathbf{D}_\gamma \cdot \left[\mathbf{I} + \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right] - \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} \tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\mathbf{b}_\gamma(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y}) \tag{6.13b}$$

$$k_{s,eff} = k_s\left[\frac{a_v}{\varepsilon_\gamma} + \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})} s_\gamma(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right] \tag{6.13c}$$

$$F_\gamma = \langle f\rangle^\gamma - \nabla\cdot\left[\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x})} \tilde{\mathbf{v}}_\gamma(\mathbf{x}+\mathbf{y})\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dV(\mathbf{y})\right] + \nabla\cdot\left[\mathbf{D}_\gamma\cdot\frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}(\mathbf{x}+\mathbf{y})\mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y})\right] - \frac{k_s}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathcal{P}(\mathbf{x}+\mathbf{y},t)\,dA(\mathbf{y}) \tag{6.13d}$$

Although Eq. (6.12) has required a number of approximations (with details given by scaling postulates 1–5), the approximations are nonetheless essentially those that are routinely specified for upscaling multiscale problems in which there is a clear separation of length scales. The result is a linear macroscopic balance equation that has substantial formal and intuitive appeal. Importantly, it is possible to extend our notions of upscaling to cases where fully localization (as specified by scaling postulates 4 and 5) is not imposed. In the next section, we provide an explicitly worked example for the case where scaling postulates 4 and 5 are not imposed. The result is a nonlocal equation; the cost of the generality of the nonlocal equation is that the resulting form is more complex than would be realized for the fully localized analogue.

7. A nonlocal example: diffusion in porous media

In this section, we present an example of a system for which the macroscale equation is nonlocal. We pursue an example to be as simple as possible and yet still illustrate the primary features of a nonlocal analysis. For that reason, we examine the problem of passive diffusion in a structured porous material.

Structured porous materials have a growing number of applications [26]. In particular, structured materials have seen widespread use in monolithic catalysis [74], gas-phase combustion [35], DNA purification [47], mixing and reaction [44], and biofilm support [77]. For our example, we will adopt a structure that is similar to some of the periodic arrays of posts that have been used in several applications (*e.g.,* Losey et al. [44], McMillan et al. [47] and Zhang et al. [77]). A representation of a periodic (square) array of posts in a microreactor is shown in Fig. 5. The governing equations for mass transfer at the microscale are

$$\frac{\partial c_{A\gamma}}{\partial t} = \nabla\cdot(\mathcal{D}_\gamma\nabla c_{A\gamma}), \quad \mathbf{x}\in\mathcal{V}_\gamma, \tag{7.1a}$$

$$B.C.1.\ -\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_{A\gamma} = 0, \quad \mathbf{x}\in\mathcal{A}_{\gamma\kappa}, \tag{7.1b}$$

$$B.C.2.\ -\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla c_{A\gamma} = \mathcal{F}(\mathbf{x},t), \quad \mathbf{x}\in\mathcal{A}_{\gamma\mathbf{e}}, \tag{7.1c}$$

$$I.C.\ c_{A\gamma} = \mathcal{I}(\mathbf{x}). \tag{7.1d}$$

Here, $c_{A\gamma}$ is the concentration of species A in the γ-phase and $\mathcal{D}_\gamma$ is the molecular diffusion coefficient, which is taken to be a constant. The derivation of transport equations involving inhomogeneous diffusion coefficients has a long tradition in the literature (*cf.* [5]). Note from Eq. (7.1b) that the solid surface has been assumed impermeable to transport of species A. This problem can be regarded as one of the simplest transport processes in porous media. It is thus convenient to study it as a benchmark problem for the application of the integral formulation presented above.

7.1. Nonlocal diffusion in a structured medium

We start the analysis by imposing the scaling postulate 0 (stationarity of the parameter fields), so that we can assume that the field Φ_γ is spatially stationary as measured by the averaging volume. The averaging procedure is relatively straightforward: the details of the derivation of the unclosed upscaled model are available in Chapter 1 (Section 1.2) of [73]. Essentially, the averaging involves two applications of the spatial averaging theorem, and the use of the no-flux boundary condition. For the case where ε_γ is assumed to be a constant (*i.e.*, a homogeneous porous medium), the resulting averaged mass balance equation is

$$\underbrace{\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla\cdot\left[\mathcal{D}_\gamma\left(\nabla\langle c_{A\gamma}\rangle^\gamma + \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})\tilde{c}_{A\gamma}\,dA(\mathbf{y})\right)\right]}_{\text{diffusion}} + \underbrace{\nabla\cdot\left[\frac{\mathcal{D}_\gamma}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})\langle c_{A\gamma}\rangle^\gamma\,dA(\mathbf{y})\right]}_{\text{macroscale nonlocal term}} \tag{7.2}$$

We have assumed scaling postulate 0, so the geometry (*i.e.*, Φ_γ) is spatially stationary. It is possible to show that in a spatially stationary geometry, the macroscale nonlocal term is identically zero (*cf.* [59]). The macroscale balance becomes particularly simple in this case

$$\underbrace{\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla\cdot\left[\mathcal{D}_\gamma\left(\nabla\langle c_{A\gamma}\rangle^\gamma + \frac{1}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})\tilde{c}_{A\gamma}\,dA(\mathbf{y})\right)\right]}_{\text{diffusion}} \tag{7.3}$$

In order to close Eq. (7.3) it is necessary to compute the deviation fields, $\tilde{c}_{A\gamma}$. With this aim, we subtract Eq. (7.3) from Eq. (7.1a) to obtain

$$\underbrace{\frac{\partial\tilde{c}_{A\gamma}}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla\cdot(\mathcal{D}_\gamma\nabla\tilde{c}_{A\gamma})}_{\text{diffusion}} - \underbrace{\nabla\cdot\left[\frac{\mathcal{D}_\gamma}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})\tilde{c}_{A\gamma}\,dA(\mathbf{y})\right]}_{\text{non-local diffusion}} \tag{7.4}$$

To make further progress from here, we must impose some assumptions. Thus, we adopt the following

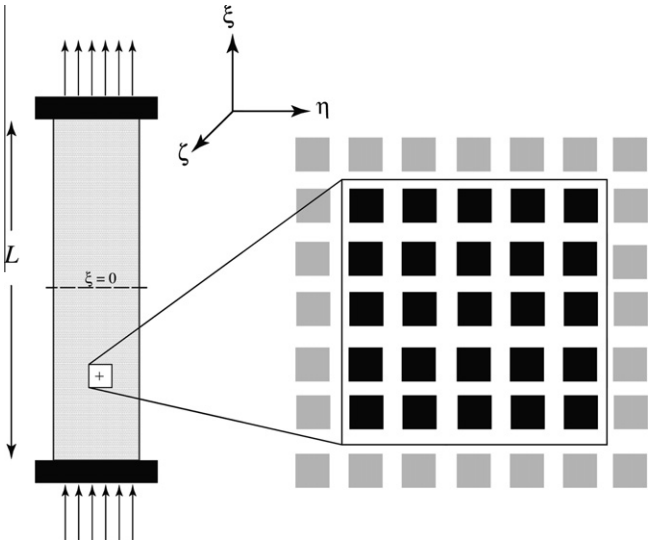

Fig. 5. A structured monolithic reactor with square pillars.

1. Scaling postulate 2 (influence of the macroscale boundary condition) and scaling postulate 3 (existence of a representative volume). Although we are interested in a nonlocal model for diffusion at the macroscale, we assume that the length scale of the influence of the nonlocal contributions in the closure problem is small compared to the domain size, so that we can consider a solution over a representative volume of media. Recall, imposing these two scaling postulates imply that we may replace the influence of the macroscopic boundary with a periodic condition.
2. Scaling postulate 4 (separation of time and length scales, I). This scaling law imposes the restriction that the closure is valid under the conditions

$$\frac{\ell_K}{L_{\langle c_{A\gamma}\rangle^\gamma}} \ll 1, \quad \frac{t_K^*}{T^*_{\langle c_{A\gamma}\rangle^\gamma}} \ll 1 \tag{7.5}$$

Note, however, that we have *not imposed the condition* $r_0 \ll L_{\langle c_{A\gamma}\rangle^\gamma}$. We have specifically avoided imposing this condition because our goal is to derive a nonlocal model for diffusion. Our averaging operations do not include averaging in time (as do, for example, some of the averages used in turbulence modeling). Because of this, the time constraint also implies that the closure problem can be treated as *quasi-steady*.

With these restrictions in place, the closure problem takes the form

$$\underbrace{\frac{\partial \tilde{c}_{A\gamma}}{\partial t}}_{\text{accumulation}} = \underbrace{\nabla\cdot(\mathcal{D}_\gamma \nabla \tilde{c}_{A\gamma})}_{\text{diffusion}} - \underbrace{\nabla\cdot\left[\frac{\mathcal{D}_\gamma}{V_\gamma}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}(\mathbf{y})\tilde{c}_{A\gamma}\,dA(\mathbf{y})\right]}_{\text{non-local diffusion}} \tag{7.6a}$$

$$-\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla\tilde{c}_{A\gamma} = \underbrace{\mathbf{n}_{\gamma\kappa}\cdot\mathcal{D}_\gamma\nabla\langle c_{A\gamma}\rangle^\gamma}_{\text{surface diffusive source}}, \mathbf{x}\in\mathcal{A}_{\gamma\kappa} \tag{7.6b}$$

$$\tilde{c}_{A\gamma}(\mathbf{x}+\mathbf{l}_i) = \tilde{c}_{A\gamma}(\mathbf{x}), \quad \mathbf{x}\in\mathcal{A}_{\gamma e}, i=1,2,3 \tag{7.6c}$$

$$I.C.\ \ \tilde{c}_{A\gamma} = \mathcal{I}(\mathbf{x}) - \langle c_{A\gamma}\rangle^\gamma \tag{7.6d}$$

These statements complete the closure problem.

7.2. Nonlocal quasi-steady closure for diffusion

To make the example concrete, we will examine the process of diffusion in a monolithic microreactor of the type shown in Fig. 5. Here, the medium is assumed to be structured, and is constructed of square pillars oriented in the ζ-direction. Such structured reactors are common (*e.g.,* [42]). At the macroscale, there is no net concentration flux in any direction other than the vertical one so that $\nabla\langle c_{A\gamma}\rangle^\gamma = (0,0,\partial\langle c_{A\gamma}\rangle^\gamma/\partial\xi)$. We consider the case where the reactor is loaded with a plane "delta" pulse at the midpoint perpendicular to the longitudinal axis of the reactor (*i.e.,* the pulse is located at $\xi = 0$). Then, at $t = 0$ the diffusion process begins. The question we want to answer is what the average concentration profile looks like as the system evolves from its initial condition.

To compute the closure problem, we need to define the geometry of the associated averaging volumes. Because the medium is itself periodic, the idea of a representative volume is true from a geometric standpoint. However, it is the *concentration field* that we are interested in, and thus a single period of the system is not necessarily *representative* in the sense of the definition given above. In this particular case, we need the condition expressed by Eq. (5.16) to be met. This creates some complexity in the problem because the size of the averaging volume chosen depends upon the integral quantities that appear on the right-hand side of Eq. (7.6b), and this, in turn, depends upon the average concentration, $\langle c_{A\gamma}\rangle^\gamma$, itself. Thus, the size of the averaging volume, in principle, would have to be done by iteration (*i.e.,* picking a representative volume size, computing the solution, and then checking to see if the constraint given by Eq. (5.16) is met). A representative volume for a nonlocal problem of this type may be on the order of several periods of the geometric structure. To start our iterative process, we assume an averaging volume as illustrated in Fig. 6.

For diffusion in porous media, there are many cases for which the effective diffusion coefficient does not exhibit time dependence on the time scales that we observe it. In the example here, we constrain the analysis to the quasi-steady state, *i.e.,* $\frac{\mathcal{D}_\gamma t^*}{\ell_\gamma^2} \gg 1$ [49]. In previous paragraphs we have put forward assumptions to *spatially* localize the closure problem based on length-scale constraints. However, in this example we proceed without spatially localizing the balance in order to point out the relevance of the integral formulation.

For an averaging volume, $\mathcal{V}(\mathbf{x})$, with centroid located at $\mathbf{x}$ (Fig. 6), the solution of the associated closure problem for the Green's function is specified by

$$\nabla\cdot\left[\mathcal{D}_\gamma\nabla_y G(\mathbf{y};\mathbf{z})\right] - \nabla_y\cdot\left[\frac{\mathcal{D}_\gamma}{V_\gamma}\int_{\mathcal{A}_{\gamma\kappa}(\mathbf{y})}\mathbf{n}_{\gamma\kappa}(\mathbf{w})G(\mathbf{w};\mathbf{z})\,dA(\mathbf{w})\right] = \delta(\mathbf{y}-\mathbf{z}), \quad \mathbf{y}\in\mathcal{V}_\gamma(\mathbf{x}) \tag{7.7a}$$

$$B.C.1. \quad -\mathbf{n}_{\gamma\kappa}(\mathbf{y})\cdot\mathcal{D}_\gamma\nabla_y G(\mathbf{y};\mathbf{z}) = 0, \quad \mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x}) \tag{7.7b}$$

$$B.C.2. \quad G(\mathbf{y}+\mathbf{l}_i;\mathbf{z}) = G(\mathbf{y};\mathbf{z}), \quad \mathbf{y}\in\mathcal{A}_{\gamma e}(\mathbf{x}), \ i=1,2,3 \tag{7.7c}$$

The Green's functions associated with this boundary value problem were determined numerically using the finite-element package COMSOL. For the range of ε_γ that we explored, it turned out that the Green's function decayed very rapidly within a single period. Thus, in practice, we could determine the Green's function using a single period, as illustrated in Fig. 8. However, the properties of the Green's functions will be very strongly problem-dependent. For example, for diffusion and convection in such a system where the Péclet number is much greater than unity, it is unlikely that a single period of the structured medium would have been sufficient to fully determine the Green's function; in that case, the Green's function would span a number of periods.

With the Green's function so determined, the formal solution for $\tilde{c}_{A\gamma}$ (see Appendix A) can now be specified by

$$\tilde{c}_{A\gamma}(\mathbf{y}) = -\underbrace{\int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})}\left[\mathbf{n}_{\gamma\kappa}(\mathbf{z})G(\mathbf{y};\mathbf{z})\cdot\mathcal{D}_\gamma\nabla_z\langle c_{A\gamma}\rangle^\gamma\big|_{\mathbf{z}}\right]dA(\mathbf{z})}_{\text{influence of the surface diffusive source}} \tag{7.8}$$

Nowhere in this solution have we invoked the length-scale constraint $r_0 \ll L_{\langle\psi_\gamma\rangle^\gamma}$. As pointed out by Wood [75], this length scale

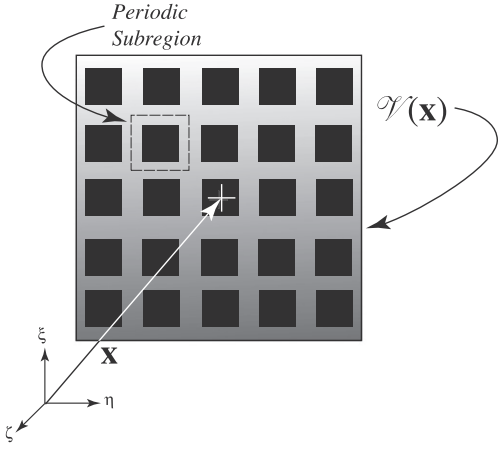

Fig. 6. Microscale structure of the medium within a representative volume.

constraint is the scaling law that is required in order to *localize* the problem. Without imposing this constraint, the problem is not restricted to cases where the averaging volume is necessarily much smaller than the large length scale. Correspondingly, the solution is valid under conditions where there are large gradients in the average concentration. The price to be paid for this additional capability, however, is that the solution is also now nonlocal. In such a solution, the macroscale and microscales are coupled via the gradients of the average concentration (as illustrated by Eq. (7.8)). Under these circumstances, a nonlocal representation and the associated computation of the Green's function is the most effective route to a solution.

To obtain the closed macroscopic model, we substitute the formal solution of the closure problem, given by Eq. (7.8), into Eq. (7.3); the result can be expressed for the general problem as follows

$$\frac{\partial\langle c_{A\gamma}\rangle^{\gamma}}{\partial t}=\nabla\cdot\left[\mathcal{D}_{\gamma}\left(\nabla\langle c_{A\gamma}\rangle^{\gamma}+\frac{1}{V_{\gamma}}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})}G(\mathbf{y};\mathbf{z})\mathbf{n}_{\gamma\kappa}(\mathbf{y})\mathbf{n}_{\gamma\kappa}(\mathbf{z})\cdot\nabla_{z}\langle c_{A\gamma}\rangle^{\gamma}\big|_{\mathbf{z}}\,dA(\mathbf{z})\,dA(\mathbf{y})\right)\right] \tag{7.9}$$

This, then, is the nonlocal form of the volume averaged equation for diffusion in a porous medium. Without the length-scale constraint $r_0 \ll L_{\langle c_{A\gamma}\rangle^{\gamma}}$, we have a more complicated solution that, correspondingly, has a wider range of applicability.

7.3. Methods for solution of the macroscale problem

One of the disadvantages of nonlocal forms, such as that given by Eq. (7.9), is that they are inherently implicit. The typical method for such implicit equations is simple iteration (although it is not guaranteed that such methods will converge). Nonetheless, simple iteration tends to be an effective approach for solving nonlocal problems, and an algorithm for computing the solution can be outlined as follows.

1. Solve the closure problem over a representative volume of media (as shown in Fig. 6). This process may have to be iterated to determine the appropriate size for determining the representative volume (*i.e.,* the Green's function needs to decay rapidly compared with the size of the averaging volume). An example of Green's functions computed for a the geometry adopted here (but with a variety of porosities) appears in Fig. 7.
2. Solve the macroscopic integro-differential balance equation (with appropriate boundary and initial conditions) for $\langle c_{A\gamma}\rangle^{\gamma}$ by assuming that the integral term is zero. This solution should be generated on a macroscale grid, with the grid size equal to the size of the averaging volume.
3. From this solution, compute $\nabla\langle c_{A\gamma}\rangle^{\gamma}$. Note that the functional shape of this term will not, in general, be linear. For example, with higher-order finite elements, the estimate of this term could be a polynomial of degree two or higher.
4. With $\nabla\langle c_{A\gamma}\rangle^{\gamma}$ available, compute the integral term appearing in Eq. (7.9) for each averaging volume in the domain. Note that this will require integration of the Green's function part-wise over the support domain of the averaging volume (*i.e.*, the domain shown in Fig. 6). Note that the term $\nabla\langle c_{A\gamma}\rangle^{\gamma}$ varies over the domain, and thus the integral must be computed as a sum of independent integrals over each periodic subregion in the volume.
5. Solve the macroscale integro-differential balance equation to generate an updated estimate for $\nabla\langle c_{A\gamma}\rangle^{\gamma}$.
6. Return to step 3, and continue until a heuristic convergence criterion (based, for example, on the sum of the square of the differences among subsequent solutions) is met.

In summary, for the problem above, we have illustrated how one can compute the associated Green's functions to obtain a closed nonlocal equation, and provided an algorithm for numerically solving the associated macroscale problem given by Eq. (7.9). As mentioned above, one significant disadvantage of this approach is that the problem is strongly implicit, and significant iteration may be need to be done to obtain a solution. Another disadvantage is that nonlocal problems, when discretized, yield matrixes that more non-zero entires than the corresponding local methods.

7.4. An approximation to the nonlocal macroscale balance equation

In this section, we consider a problem with a geometry similar to that above, but for which we can analytically compute a Green's function. Our goal is to examine a set of approximations to the nonlocal balance specified above, but where the solutions to both (1) the Green's function problem specified by Eqs. (7.7a)–(7.7c), and (2) the macroscopic balance given by Eq. (7.9) can be determined analytically. To that end, we propose the modified geometry of the form given by Fig. 9, where the media consists of cylindrical pillars spanning the reactor (in the ζ-direction) rather than square pillars.

We examine a particular approximation to the nonlocal equation that localizes the macroscopic scale equation in a way that still allows representing some of its nonlocal behavior. In short, this can

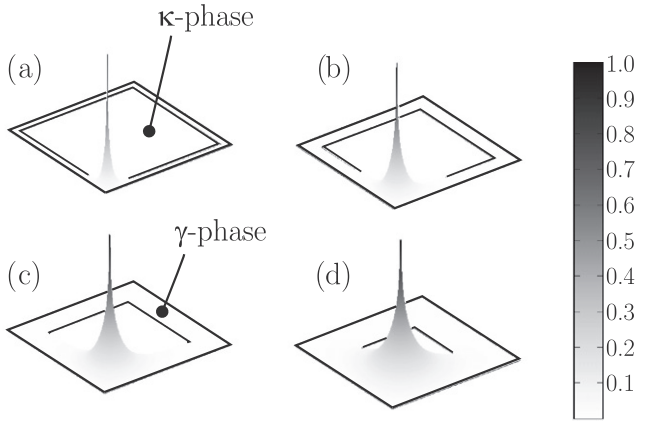

Fig. 7. Green's function for passive diffusion in porous media. (a) $\varepsilon_{\gamma}=0.2$, (b) $\varepsilon_{\gamma}=0.4$, (c) $\varepsilon_{\gamma}=0.6$ and (d) $\varepsilon_{\gamma}=0.8$.

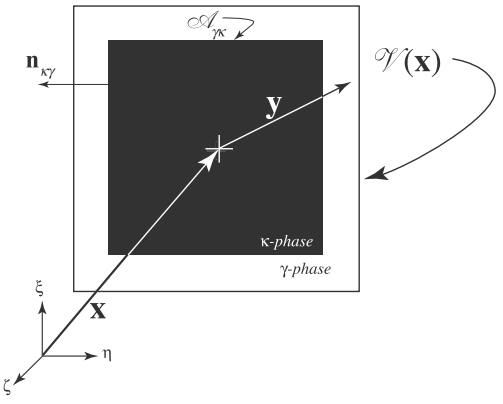

Fig. 8. Structure of a single period of the periodic geometry.

be done by considering a Taylor series expansion to the average concentration term that appears under the integral in Eq. (7.9). Although this formally "localizes" the problem, it does so at the expense of introducing additional terms involving higher-order derivatives to the balance equation.

Note that because our solutions to the nonlocal macroscale balance, Eq. (7.9), must be done numerically, it will generally be limited by the order of accuracy of the numerical method. For a problem like this, such accuracy will generally be, say, $\mathbf{O}(h^2)$, where h is the characteristic size of the partition function (for example, via a centered finite differencing scheme). Thus, if we consider approximations to the nonlocal balance equation that impose no more error than this, the resulting solution would contain no more error than the nonlocal one specified above.

Consider expanding the average concentration in a Taylor series around the centroid; this yields

$$\nabla\langle c_{A\gamma}\rangle^{\gamma}\big|_{\mathbf{x}+\mathbf{z}} = \nabla\langle c_{A\gamma}\rangle^{\gamma}\big|_{\mathbf{x}} + \mathbf{z}\cdot\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\big|_{\mathbf{x}} + \frac{1}{2}\mathbf{zz} : \nabla\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\big|_{\mathbf{x}} + \frac{1}{6}\mathbf{zzz}\vdots\nabla\nabla\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\big|_{\mathbf{x}} + \cdots \tag{7.10}$$

Introducing this expansion into the integral in Eq. (7.9) yields a macroscopic balance equation that contains spatial derivatives of all orders. This kind of averaged balance equation has a long history in physics [40], and has been proposed by a number of researchers reporting on porous media problems [17,55]. We are interested in a *first correction* to the macroscale diffusion equation. Thus, we truncate the Taylor expansion at the second-order term in $\mathbf{z}$. This results in the following fourth-order balance equation

$$\begin{aligned}\frac{\partial\langle c_{A\gamma}\rangle^{\gamma}}{\partial t} = {} & \nabla\cdot\left(\mathcal{D}_{\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma}\right) + \nabla\cdot\left(\frac{\mathcal{D}_{\gamma}}{V_{\gamma}}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})\mathbf{b}_{\gamma}(\mathbf{y})\,dA(\mathbf{y})\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma}\right) + \nabla\cdot\left(\frac{\mathcal{D}_{\gamma}}{V_{\gamma}}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})F_{\gamma}(\mathbf{y})\,dA(\mathbf{y})\cdot\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\right) + \nabla\\ & \cdot\left(\frac{\mathcal{D}_{\gamma}}{V_{\gamma}}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})\mathbf{s}_{\gamma}(\mathbf{y})\,dA(\mathbf{y}) : \nabla\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma}\right)\end{aligned} \tag{7.11}$$

where, for simplicity, we have introduced

$$\mathbf{b}_{\gamma}(\mathbf{y}) = \int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})} G(\mathbf{y};\mathbf{z})\,\mathbf{n}_{\gamma\kappa}(\mathbf{z})\,dA(\mathbf{z}) \tag{7.12a}$$

$$F_{\gamma}(\mathbf{y}) = \int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})} G(\mathbf{y};\mathbf{z})\,\mathbf{n}_{\gamma\kappa}(\mathbf{z})\cdot\mathbf{z}\,dA(\mathbf{z}) \tag{7.12b}$$

$$\mathbf{s}_{\gamma}(\mathbf{y}) = \frac{1}{2}\int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})} G(\mathbf{y};\mathbf{z})\,\mathbf{n}_{\gamma\kappa}(\mathbf{z})\cdot\mathbf{zz}\,dA(\mathbf{z}) \tag{7.12c}$$

If the magnitude of z is on the same order as h, then the approximation is accurate at $\mathbf{O}(h^2)$, and this localized approximation should be roughly no less accurate than the original nonlocal equation. Note that in this result, the first integral term on the right hand side of Eq. (7.11) is the term that arises conventionally in volume averaging when the length-scale constraints are met (*i.e.*, when the system is assumed to be local). The additional terms in this expression represent corrections to the transport equation to correct for nonlocal influences in the solution.

It is not difficult to show that, for symmetric periodic unit cells, the function F_{γ} is identically zero. This function would be nonzero for cases where the geometry of the periodic cell was non-symmetric; in that case, the term F_{γ} would allow for the anisotropic transport due to the asymmetry at the microscale. For the periodic geometry that we have adopted, the term $\mathbf{s}_{\gamma}$ is the first non-zero correction term to the macroscale transport equation. The macroscale transport equation can be put in the form

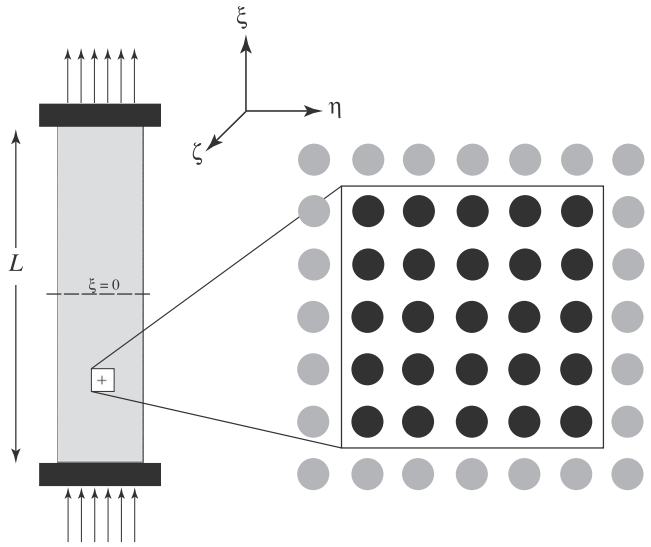

Fig. 9. Structure of a monolithic reactor with cylindrical pillars.

$$\frac{\partial\langle c_{A\gamma}\rangle^{\gamma}}{\partial t} = \mathbf{D}_{0,eff} : \nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} + \mathbf{D}_{2,eff}\nabla\vdots\nabla\nabla\nabla\langle c_{A\gamma}\rangle^{\gamma} \tag{7.13}$$

where the conventional effective diffusion tensor (zero order in moments of $\mathbf{z}$) is given by

$$\mathbf{D}_{0,eff} = \mathcal{D}_{\gamma}\left(\mathbf{I} + \frac{1}{V_{\gamma}}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})\mathbf{b}_{\gamma}(\mathbf{y})\,dA(\mathbf{y})\right) \tag{7.14}$$

and the second-order (in moments of $\mathbf{z}$) correction tensor is given by

$$\mathbf{D}_{2,eff} = \mathcal{D}_{\gamma}\left(\frac{1}{V_{\gamma}}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})}\mathbf{n}_{\gamma\kappa}(\mathbf{y})\mathbf{s}_{\gamma}(\mathbf{y})\,dA(\mathbf{y})\right) \tag{7.15}$$

In Eq. (7.13) the first two terms on the right-hand side represent the classical result obtained from local volume averaging with closure [73, Chapter 1]. The second term on the right-hand side represents the first correction to the equation, representing the nonlocal influence. This equation applies under the conditions when $r_0 \sim \mathbf{O}(L_{\mathbb{C}_{\gamma}})$ (here, $L_{\mathbb{C}_{\gamma}}$ the large length scale associated with the concentration field). Note that if the coordinate system can be aligned such that there are macroscopic gradients in the concentration in only the ξ-direction, then this averaged transport equation takes the form

$$\frac{\partial\langle c_{A\gamma}\rangle^{\gamma}}{\partial t} = D_{0,\xi\xi}\frac{\partial^2\langle c_{A\gamma}\rangle^{\gamma}}{\partial\xi^2} + D_{2,\xi\xi}\frac{\partial^4\langle c_{A\gamma}\rangle^{\gamma}}{\partial\xi^4} \tag{7.16}$$

Note that here a direction vector is assumed to have components (ζ,η,ξ) as indicated in, for example, Fig. 6. For reference below, the associated unit directional vectors are denoted $\mathbf{e}_{\zeta} = (1,0,0)$, $\mathbf{e}_{\eta} = (0,1,0)$, and $\mathbf{e}_{\xi} = (0,0,1)$.

7.5. Computation of the effective parameters

For diffusive problems in particular, it has been known for some time that the geometry can be significantly abstracted from the actual geometry, and yet still provide useful results. The archetypical example here is the solution developed by Rayleigh [60] for diffusion (conductance) for cylindrical obstacles in a medium. Rayleigh [60] considered a periodic array of spheres, and developed his solution in a convergent series. It is interesting to note that a third approximate method was proposed by Chang [15,16], where the domain was assumed to be a finite sphere with a Dirichlet condition imposed at the outer boundary; this method also yields results

that are consistent with the first-order approximation of the Rayleigh [60] result. An example of the geometry considered by Chang [15,16] appears in Fig. 10.

In Appendix C, we have developed the analytical solution for the Green's function within a cylindrical unit cell, adopting the conditions used by Chang [15,16]. In cylindrical coordinates, the result is

$$G(r,\theta;r_0,\theta_0) = b_0 - \sum_{n=1}^{\infty} \frac{\cos(n\theta)\cos(n\theta_0)+\sin(n\theta)\sin(n\theta_0)}{2n\pi r_0^n r^n \left[\left(\frac{2}{\ell_{ch}}\right)^{2n} + \left(\frac{1}{a}\right)^{2n}\right]} \times \begin{cases} \left(1+\left(\frac{r}{a}\right)^{2n}\right)\left(1-\left(\frac{2r_0}{\ell_{ch}}\right)^{2n}\right), & r<r_0 \\ \left(1+\left(\frac{r_0}{a}\right)^{2n}\right)\left(1-\left(\frac{2r}{\ell_{ch}}\right)^{2n}\right), & r>r_0 \end{cases} \tag{7.17}$$

Note that with this result, we can easily recover the classical solution given by Rayleigh [60]. To start, recall the definition

$$\frac{\mathbf{D}_{0,eff}}{\mathcal{D}_\gamma} = \mathbf{I} + \frac{1}{\varepsilon_\gamma \mathcal{V}} \int_{\mathbf{y}\in A_{\gamma\kappa}} \int_{\mathbf{z}\in A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa}(\mathbf{y})\mathbf{n}_{\gamma\kappa}(\mathbf{z}) G(\mathbf{y};\mathbf{z})\, dA(\mathbf{z})\, dA(\mathbf{y}) \tag{7.18}$$

Note that $D_{0,\xi\xi} \equiv \mathbf{e}_\xi \cdot \mathbf{D}_{0,eff} \cdot \mathbf{e}_\xi$. With this definition, a direct substitution of the Green's function immediately yields

$$\begin{aligned} \frac{D_{0,\xi\xi}}{\mathcal{D}_\gamma} &= 1 + \frac{1-\varepsilon_\gamma}{\varepsilon_\gamma \pi} \int_{\theta=0}^{\theta=2\pi} \int_{\theta_0=0}^{\theta_0=2\pi} \\ &\quad \times \cos\theta \cos\theta_0 G(a,\theta;a,\theta_0)\, d\theta_0\, d\theta \\ &= \frac{1}{2-\varepsilon_\gamma} \end{aligned} \tag{7.19}$$

This function is plotted in Fig. 11.

Similarly, the computation of the second effective parameter is also relatively straightforward. The $\xi\xi$-component of $\mathbf{D}_{2,eff}$ is given by

$$D_{2,\xi\xi} \equiv \mathbf{e}_\xi \cdot \mathbf{D}_{2,eff} \cdot \mathbf{e}_\xi = \frac{1}{2}\frac{\mathcal{D}_\gamma}{V_\gamma} \left(\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa}(\mathbf{x})} \int_{\mathbf{z}\in\mathcal{A}_{\gamma\kappa}(\mathbf{y})} G(\mathbf{y};\mathbf{z}) \left[\mathbf{e}_\xi \cdot \mathbf{n}_{\gamma\kappa}(\mathbf{y})\right] \left[\mathbf{n}_{\gamma\kappa}(\mathbf{z})\cdot\mathbf{z}\right] \left[\mathbf{z}\cdot\mathbf{e}_\xi\right] dA(\mathbf{z})\, dA(\mathbf{y}) \right). \tag{7.20}$$

Recalling that $\mathbf{e}_\xi \cdot \mathbf{n}_{\kappa\gamma}(\mathbf{y})$ is in all cases equal to $\cos\theta$, we have form Eq. (7.17), that

$$\frac{D_{2,\xi\xi}}{\mathcal{D}_\gamma} = -\frac{1-\varepsilon_\gamma}{2\varepsilon_\gamma N\pi} \frac{\left[1-\left(\frac{2a}{\ell_{ch}}\right)^2\right]}{\left[1+\left(\frac{2a}{\ell_{ch}}\right)^2\right]} \sum_{i=1}^{i=N} \int_{\theta_0=0}^{\theta_0=2\pi} \left[\mathbf{n}_{\kappa\gamma}(\mathbf{z})\cdot\mathbf{z}\right] \xi \cos(\theta_0)\, d\theta_0 \tag{7.21}$$

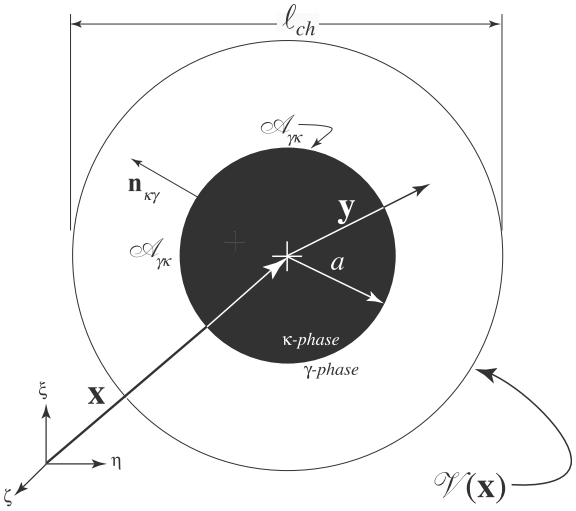

Fig. 10. The geometry considered by Chang [15,16].

For a simple unit cell, we find

$$\frac{D_{2,\xi\xi}}{\mathcal{D}_\gamma} = -\frac{1-\varepsilon_\gamma}{2(2-\varepsilon_\gamma)\pi} \int_{\theta_0=0}^{\theta_0=2\pi} \left[\mathbf{n}_{\kappa\gamma}(\mathbf{z})\cdot\mathbf{z}\right] \xi \cos(\theta_0)\, d\theta_0 \tag{7.22}$$

To make further progress, note that by definition $\mathbf{z}$ is on the $\mathcal{A}_{\gamma\kappa}$ surface. Hence

$$\mathbf{z} = a\cos\theta_0 \mathbf{e}_\xi + a\sin\theta_0 \mathbf{e}_\eta \tag{7.23}$$

and

$$\mathbf{n}_{\kappa\gamma} = \cos\theta_0 \mathbf{e}_\xi + \sin\theta_0 \mathbf{e}_\eta \tag{7.24}$$

Combining these results, we find $\mathbf{n}_{\kappa\gamma}(\mathbf{z})\cdot\mathbf{z} = a$ and $\xi = a\cos\theta_0$. Substituting this in Eq. (7.22) yields the final result,

$$\frac{D_{2,\xi\xi}}{a^2\mathcal{D}_\gamma} = -\frac{1-\varepsilon_\gamma}{2(2-\varepsilon_\gamma)\pi} \int_{\theta_0=0}^{\theta_0=2\pi} \cos^2(\theta_0)\, d\theta_0 = -\frac{1-\varepsilon_\gamma}{2(2-\varepsilon_\gamma)} \tag{7.25}$$

It can be easily demonstrated that the same result applies for the $\eta\eta$-component and that the $\zeta\eta$ and $\eta\zeta$ components are zero. The dependence of $D_{2,\xi\xi}$ with the porosity is also plotted in Fig. 11.

7.6. Macroscale solution in 1-dimension

As a final note about the application of the approximation to the nonlocal form, we discuss the solution to the localized higher-order expansion. Above we have discussed how we arrive at the macroscale equation of the form (in one-dimension)

$$\frac{\partial \mathbb{C}_\gamma}{\partial t} = D_{0,\xi\xi}\frac{\partial^2 \mathbb{C}_\gamma}{\partial \xi^2} + D_{2,\xi\xi}\frac{\partial^4 \mathbb{C}_\gamma}{\partial \xi^4} \tag{7.26a}$$

where for convenience, we have used the notation $\mathbb{C}_\gamma = \langle c_{A\gamma}\rangle^\gamma$, and we have taken the total mass in the system to be normalized to unity. Note that there are several challenges for applying such a higher-order equations, and Risken [61, Sections 4.3 and 4.6], pointed out the fact that the higher-order differential operators are not positive semidefinite [62], and the lack of physically-based boundary conditions that apply to the more widely-known partial differential equations. Although the properties and behavior such higher-order equations are an area of continuing research, Risken

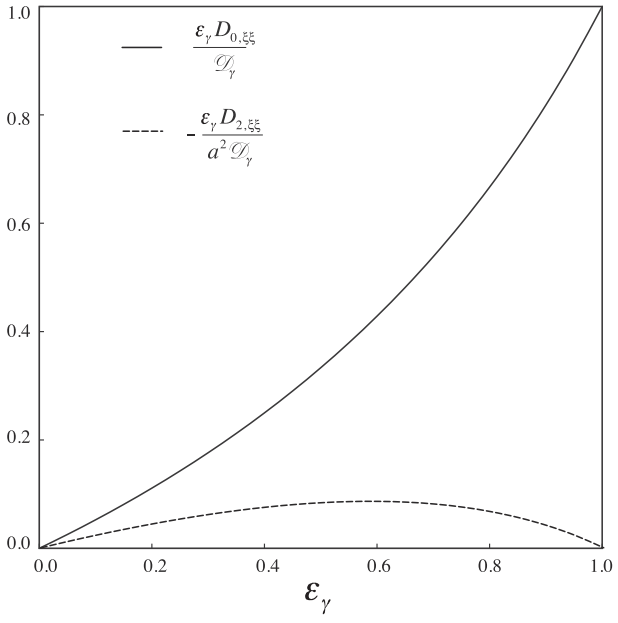

Fig. 11. Plots of $D_{0,\xi\xi}$ and $D_{2,\xi\xi}$ as a function of the volume fraction, ε_γ.

[61] and Risken and Vollmer [62] suggest that in many instances the effort is worthwhile.

To examine the behavior of Eq. (7.34b) in additional detail, we restrict ourselves to the case of an initial value problem in an infinite domain. The delta function will be taken as the initial condition (and other initial conditions can be attained by forming the convolution as per Duhamel's principle), and the other conditions will be that the concentration and its derivatives all approach zero as $|z| \to \infty$, *i.e.*,

$$I.C.\ \ \mathbb{C}_\gamma(\xi, t=0) = \delta(\xi) \tag{7.26b}$$

$$B.C.s\ \ \mathbb{C}_\gamma, \frac{\partial \mathbb{C}_\gamma}{\partial \xi}, \frac{\partial^2 \mathbb{C}_\gamma}{\partial \xi^2}, \frac{\partial^3 \mathbb{C}_\gamma}{\partial \xi^3} \to 0 \quad \text{as } |\xi| \to \infty \tag{7.26c}$$

7.6.1. Spatial moments of the concentration field

Before considering the direct solution to Eqs. (7.26a)–(7.26c), we will explore the preliminary step of determining the spatial moments of the solution. The consideration of spatial moments can be useful because they provide information about the global macroscale behavior in time for the solution, but are not nearly as difficult to compute as the concentration field itself. We can develop an equation for the pth moment of Eq. (7.34b) by multiplying through by powers of the moment arm distance, and integrating, *i.e.*,

$$\frac{\partial M_p}{\partial t} = \int_{-\infty}^{\infty} \xi^p D_{0,\xi\xi} \frac{\partial^2 \mathbb{C}_\gamma}{\partial \xi^2}\, d\xi + \int_{-\infty}^{\infty} \xi^p D_{2,\xi\xi} \frac{\partial^4 \mathbb{C}_\gamma}{\partial \xi^4}\, d\xi \tag{7.27}$$

where

$$M_p(t) \equiv \int_{-\infty}^{\infty} \xi^p \mathbb{C}_\gamma(\xi, t)\, d\xi \tag{7.28}$$

The zeroth moment indicates that Eq. (7.34b) is mass conservative, *i.e.*,

$$\begin{aligned}\frac{\partial M_0(t)}{\partial t} &= \int_{-\infty}^{\infty} \frac{\partial \mathbb{C}_\gamma}{\partial t}\, d\xi = \int_{-\infty}^{\infty} \left(D_{0,\xi\xi} \frac{\partial^2 \mathbb{C}_\gamma}{\partial \xi^2} + D_{2,\xi\xi} \frac{\partial^4 \mathbb{C}_\gamma}{\partial \xi^4} \right) d\xi \\ &= D_{0,\xi\xi} \frac{\partial \mathbb{C}_\gamma}{\partial \xi}\bigg|_{-\infty}^{\infty} + D_{2,\xi\xi} \frac{\partial^3 \mathbb{C}_\gamma}{\partial \xi^3}\bigg|_{-\infty}^{\infty} = 0,\end{aligned} \tag{7.29}$$

so that, with the initial condition given above, $M_0(t) = 1$. Note that because the initial condition is centered at $z = 0$, these moments are centered moments by definition. It is straightforward to verify by repeated use of integration by parts that the first through fourth moments are given by

$$M_1(t) = 0 \tag{7.30a}$$

$$M_2(t) = 2D_{0,\xi\xi} t \tag{7.30b}$$

$$M_3(t) = 0 \tag{7.30c}$$

$$M_4(t) = 12 D_{0,\xi\xi}^2 t^2 + 12 D_{2,\xi\xi} t \tag{7.30d}$$

Although Eqs. (7.30a)–(7.30d) are interesting, it is useful to put them in a form that represents deviations from the normal distribution. The first two nonzero cumulants of the solution are given by

$$\kappa_2(t) = M_2, \tag{7.31a}$$

$$\kappa_4(t) = M_4 - 3\kappa_2^2 \tag{7.31b}$$

with these definitions, the fourth moment is better re-expressed by a rearrangement of the fourth cumulants and normalizing by the second; this quantity is usually known as the kurtosis

$$\gamma(t) = \frac{\kappa_4}{\kappa_2^2} = 3 \frac{D_{2,\xi\xi}}{D_{0,\xi\xi}^2 t} \tag{7.32}$$

The kurtosis has the nice feature that, for the normal distribution, it is identically zero. In Fig. 12, the second moment (cumulant) and the kurtosis are plotted as a function of time. It is interesting to note that the second cumulant is exactly equal to that for the corresponding diffusion equation (*i.e.*, $D_{2,\xi\xi} \equiv 0$) for all time. In other words, the presence of the fourth-order derivative does not change the second moment at all. The situation is different for the fourth moment as measured by the kurtosis. In Fig. 12(b), one can observe that the kurtosis is initially negative, and over time this decays to zero (thus matching the normal distribution). From the first two nonzero moments, it appears that the solution to the fourth-order equation has a fourth-order moment that is different from the case of pure diffusion, but that it decays in time to the solution that would be predicted for pure diffusion with a diffusion coefficient of $D_{0,\xi\xi}$.

7.6.2. Analytical solution for the concentration

The solution to this problem is best found by Fourier transform. Denoting the Fourier transform by

$$\mathcal{F}(\mathbb{C}_\gamma) = \hat{\mathbb{C}}_\gamma(\alpha, \xi) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathbb{C}_\gamma(\xi, t) e^{-i\alpha\xi}\, d\xi, \tag{7.33}$$

then the transform of Eqs. (7.26a)–(7.26c) is

$$\frac{\partial \hat{\mathbb{C}}_\gamma}{\partial t} = -\alpha^2 D_{0,eff} \hat{\mathbb{C}}_\gamma + \alpha^4 D_{2,eff} \hat{\mathbb{C}}_\gamma \tag{7.34a}$$

$$I.C., \hat{\mathbb{C}}_\gamma(\alpha, t=0) = \frac{1}{\sqrt{2\pi}}. \tag{7.34b}$$

A single integration yields

$$\hat{\mathbb{C}}_\gamma(\alpha, t) = \frac{1}{\sqrt{2\pi}} e^{-\alpha^2 D_{0,\xi\xi} t} e^{\alpha^4 D_{2,\xi\xi} t}. \tag{7.35}$$

Defining then the inverse Fourier transform by

$$\mathcal{F}^{-1}(\hat{\mathbb{C}}_\gamma) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \hat{\mathbb{C}}_\gamma(\xi, t) e^{i\alpha\xi} d\alpha. \tag{7.36}$$

Then by the convolution theorem, we have that

$$\begin{aligned} g_1(\xi, t) * g_2(\xi, t) &= \int_{-\infty}^{\infty} g_1(\xi - \beta, t) g_2(\beta, t)\, d\beta \\ &= \mathcal{F}^{-1}(G_1(\alpha, t) G_2(\alpha, t)). \end{aligned} \tag{7.37}$$

Making the identifications $G_1(\alpha) = (2\pi)^{-\frac{1}{2}} e^{-\alpha^2 D_{0,\xi\xi} t}$ and $G_2(\alpha) = e^{\alpha^4 D_{2,\xi\xi} t}$, then the inverse Fourier transform gives the following results for $g_1(\xi, t)$ and $g_2(\xi, t)$

$$g_1(\xi, t) = \frac{1}{\sqrt{\pi}\sqrt{4 D_{0,\xi\xi} t}} e^{-\frac{\xi^2}{4 D_{0,\xi\xi} t}} \tag{7.38}$$

$$\begin{aligned} g_2(\xi, t) = \frac{1}{\pi(-D_{2,\xi\xi} t)^{\frac{3}{4}}} \Bigg\{ &\sqrt{-D_{2,\xi\xi} t}\, \Gamma\left[\frac{5}{4}\right] {}_0F_2\left[;\frac{1}{2}, \frac{3}{4}; -\frac{z^4}{256 D_{2,\xi\xi} t}\right] \\ &- \xi^2\, \Gamma\left[\frac{3}{4}\right] {}_0F_2\left[;\frac{5}{4}, \frac{3}{2}; -\frac{z^4}{256 D_{2,\xi\xi} t}\right] \Bigg\} \end{aligned} \tag{7.39}$$

The first function g_1 can be seen to be the conventional diffusion kernel. For the function g_2, recall that $D_{2,\xi\xi} \leqslant 0$. Note that for g_2 we must define the gamma function, Γ, by

$$\Gamma(\xi) = \int_0^{\infty} \beta^{\xi - 1} e^{-\beta}\, d\beta \tag{7.40}$$

and the generalized hypergeometric function, ${}_0F_2$ in three parameters (a, b, c), by [6]

$${}_0F_2[;a,b;c] = \sum_{n=0}^{\infty} \frac{\Gamma(a)\Gamma(b)}{\Gamma(a+n)\Gamma(b+n)} \frac{c^n}{n!}. \tag{7.41}$$

With these definitions, then, the solution to the approximation to the nonlocal macroscale concentration is given by

$$\mathbb{C}_\gamma(\xi, t) = \langle c_{A_\gamma} \rangle^\gamma = \int_{-\infty}^{\infty} g_1(\xi - \beta, t) g_2(\beta, t)\, d\beta. \tag{7.42}$$

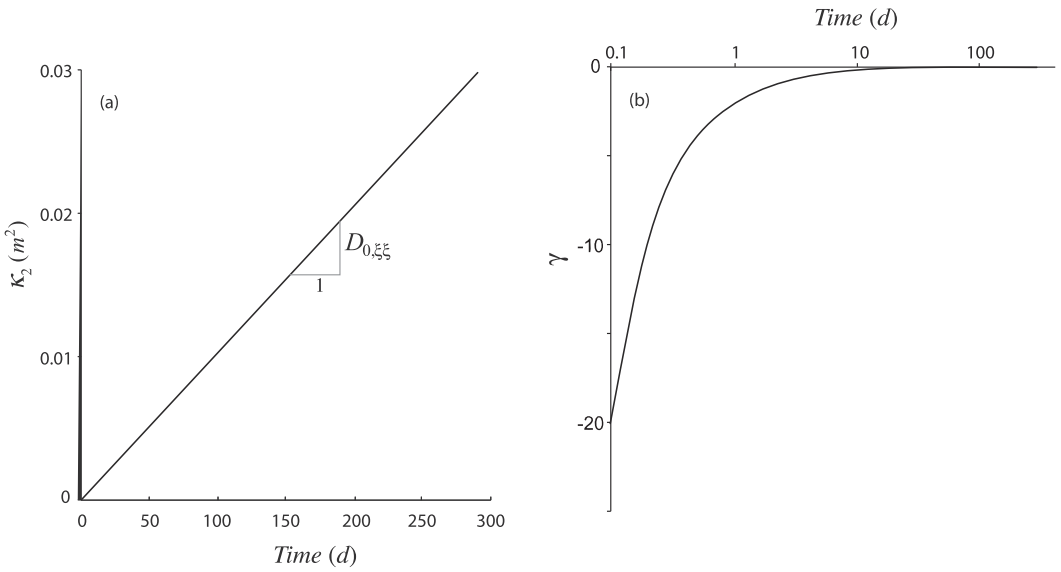

Fig. 12. Plots of (a) the second moment (cumulant) and (b) the kurtosis the fourth-order approximation to the nonlocal macroscale transport equation.

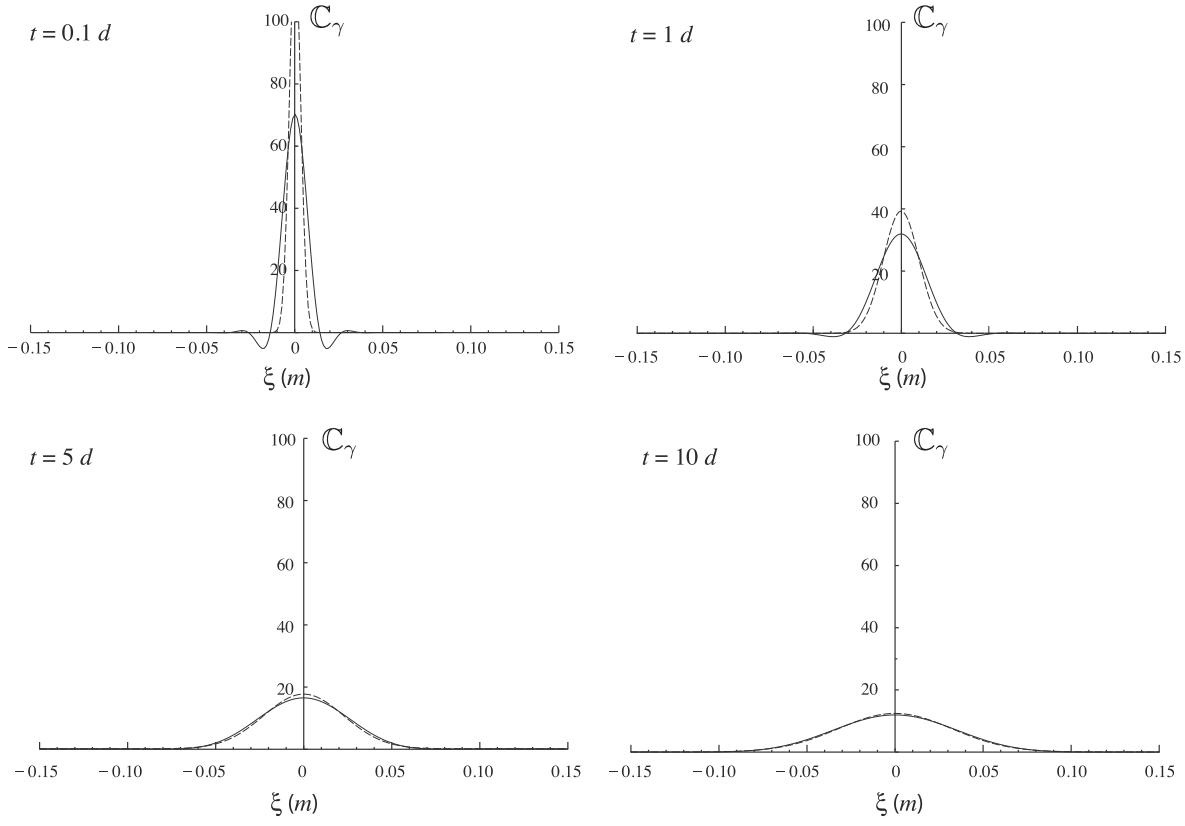

Fig. 13. Plots of the solution to the forth-order equation (Eq. (7.34b)) versus space for three values of time. For comparison, the solution of the second-order diffusion equation under equivalent conditions is shown by the dashed line. Note that the higher-order term contributes only at early time; as time increases, the solution approaches that predicted for ordinary diffusion.

In Fig. 13 we have plotted the solution given by Eq. (7.42) for several time values. For this solution, we used $\mathcal{D}_\gamma = 1 \times 10^{-9}$ m^2/s, $a = 1 \times 10^{-2}$ m, $\varepsilon_\gamma = 0.32$; this gave values of $D_{0,\xi\xi} = 5.1 \times 10^{-5}$ m^2/s and $D_{2,\xi\xi} = 5.1 \times 10^{-5}$ m^4/s. Solutions plotted represent times of $t = 0.1$, 1, 5, and 10 d.

There are several interesting features that can be observed in Fig. 13. First, note that the rate of spreading for the fourth order model is greater than that for the second order (diffusive) model at early times. As time increases, the profile for the fourth order approximation approaches that predicted for the purely local diffusive case. This is the response that we would hope to see for the higher-order model. When there are large gradients in the average concentration, the region of the concentration field, by definition, is such that $r_0 \approx L$; hence the concentration field is locally like a sharp front. Under these conditions, the concentration field in the region of the high spatial gradient does not sample a large volume

of the porous medium. Another way of thinking about this is that the transport process near the high gradient is not hindered by obstacles the way that transport is when the gradient in concentration is low (thus spread out over a large number of obstacles). Hence, we expect transport under high-gradient conditions to happen at a rate that is higher than the corresponding rate when the gradient is smaller and the front is more spread. In the example presented, the high-gradient conditions happen to be at early times. The observed increased rate of spreading at early times is, then, consistent with our expectations for the correction created by the higher-order terms.

Second, note that at early times the fourth-order equation predicts some concentrations near the tails of the concentration distribution that are negative. Although it is true that the fourth order equation does maintain mass conservation, it does not necessarily enforce the condition that the concentration be strictly positive. Admittedly, negative concentrations do not have a physical meaning in this context. In fact, due to a theorem of Pawula [56] (*cf.* Refs. [46,38]), it is not possible to represent any other continuous distribution other than Gaussian by a finite truncation. However, as pointed out by Risken and Vollmer [62], this does not mean that the solution given by the truncated representation is not useful. As mentioned above, the moments of the solution are correct to fourth order, and this is useful in itself.

8. Discussion and conclusions

In this work we have used an integral formulation based on Green's functions to formally solve the closure problems arising in the method of volume averaging applied to balance laws expressed by parabolic partial differential equations. The analysis shows that the associated Green's functions constitute the kernel of the closure variables, since they are responsible of capturing the essential aspects of the microscale processes. Hence the associated Green's functions play a significant role on the computation of the effective transport coefficients involved in upscaled models. However, this raises the issue about which function is more appropriate to be computed to determine the deviation fields. On the one hand, the integral formulation requires solving only one boundary-value problem, from which all closure variables can be computed. However, if no analytical expressions for the Green's functions are available, it is necessary to elaborate numerical routines where the concentrated source is located at each point of the fluid-phase. On the other hand, the closure variables solve boundary-value problems that usually share similar mathematical structures. Therefore, for cases where it is necessary to determine many closure variables, it is probable that only small modifications are needed to be made in a numerical code to compute each closure variable.

Specific conclusions reached in this work are summarized as follows.

1. A space and time nonlocal balance equation is possible to derive via volume averaging under reasonably nonrestrictive conditions. In the material presented in Sections 3 and 4, we have provided the details of such an analysis. The restrictions are only that (i) the statistics of the parameter fields associated with the balance laws be quasi-stationary in accordance with Eq. (4.8), (ii) that nonlocal contributions within the closure scheme itself can be neglected, and (iii) that the particular boundary conditions applied on external boundaries in the domain considered for closure do not significantly influence the resulting solution.
2. The closure scheme developed in this paper relies on the identification of Green's functions associated with the balance equations for the deviation quantities. The Green's function approach provides a solution for the deviation quantities in terms of time–space convolutions over the source terms that drive the development of the deviations. This formulation results in an inherently nonlocal result at the macroscale when the solutions to the deviations are re-introduced to the averaged balance laws to close them. One interesting observation that can be made at this juncture is as follows. Although a more robust (from the perspective of being able to represent various kinds of complex transport behavior) macroscale mode is produced when the time–space nonlocal terms are kept intact, such equations are also correspondingly more difficult to solve. In other words, the complexity of the problem is greater (as compared with the direct solution of the microscale equations) with the nonlocal formulation than would be true for, as an example, a purely local macroscale equation that was subjected to more rigorous restrictions regarding its range of validity. There is a trade off, then, between generality of the result of the upscaled equation on the one hand, and reduction of the amount of effort (or information) required to solve it on the other. In the worst possible case, one can, in principle, imagine developing a completely general balance equation for the average properties that contains essentially the same number of degrees of freedom (or complexity) as the original microscale problem.
3. Localized solutions to the closure problem (generating localized macroscale balance equations) can be developed under the conditions that the time and length scales associated with the kernel functions in the integral solution are much smaller than the analogous time and length scales associated with the macroscale source terms (terms involving $\langle\psi_\gamma\rangle^\gamma$, $\nabla\langle\psi_\gamma\rangle^\gamma$, or $\nabla\nabla\langle\psi_\gamma\rangle^\gamma$). Thus, under the conditions where a *separation of time and length scales between the microscale and the macroscale balances* exists, the source terms can be removed from under the integrals. As illustrated in Section 5.2.5, the integrals of the kernel functions themselves then take on the interpretation of conventional closure variables, where the solution to the deviation equation is expressed as a linear combination of the source terms and unknown coefficient functions.
4. An example of the development of a nonlocal balance law for the problem of diffusion in a porous medium was illustrated in Section 7. The form of the nonlocal problem and associated closure were presented, and the coupling between the two problems was noted. Even for the problem of simple diffusion, it was not possible to generate an analytical solution for the closure; hence, the Green's functions were computed analytically. With the Green's functions so computed, one can follow the algorithm presented in Section 7.3 to obtain a solution of the macroscopic-scale balance equations.
5. Because of the complexity associated with nonlocal solutions, we explored the potential to obtain local approximations to the nonlocal solution. This approximation process yields, in general, partial differential equations of infinite order. We examined a truncation to this problem which provides essentially the "first correction" to the local problem. The tradeoff is that a nonlocal (integral) equation is approximated by a higher-order partial differential equation, which has its own challenges for solution. Among these challenges is the result that, according to a theorem of Pawula [56], any such approximate solution is no longer positive-semidefinite. Although this may generate some unphysical behavior in parts of the domain of interest, the solutions still contain value. Not only can they help to explain overall qualitative behavior of the fully nonlocal solution (*e.g.,* finding that the nonlocal solution has smaller maximum concentrations at early time as compared with the local solution), but integral measures of the solution (in terms of cumulants) should be correct [62].

6. An analytical solution to the closure for a local approximation to a nonlocal diffusion equation was developed, and explicit formulas for the two effective parameters (the effective diffusivity and the effective parameter associated with the forth-order derivatives). It is particularly interesting to note that the approximate equation exhibited a second moment that was identical to the analogous equation for diffusion. However, the solution had a forth-order cumulant that was different than would have been obtained for pure diffusion. At early times, the approximation to the nonlocal equation predicted a nonzero kurtosis that decayed to zero with increasing time. The case of pure diffusion would have lead to a zero value for the forth-order cumulant for all time. Thus, the approximation to the nonlocal equation has the potential to include non-asymptotic behavior of a diffusive process at early times.

Acknowledgements

This work was supported in part by the National Science Foundation, Earth Sciences Directorate, Hydrology Program, under Grant 0711505 and NSF-BES program award 0310097. We thank Mark Porter for computing the Green's functions shown in Fig. 8, and the three anonymous reviewers who provided valuable input to earlier drafts of this work.

Appendix A. Spatial stationarity of the averages of the parameter fields

Suppose that we choose a simple form, for the purposes of example, for the second-order differential operator, $\mathcal{L}$

$$\mathcal{L}\psi_\gamma = \nabla\cdot(\mathbf{v}_\gamma(\mathbf{z})\psi_\gamma) + \nabla\cdot(\mathbf{D}_\gamma(\mathbf{z})\cdot\nabla\psi_\gamma). \tag{A.1}$$

Recall that the operator $\mathcal{L}_0$ is defined by

$$\mathcal{L}_0\psi_\gamma = \nabla\cdot(\langle\mathbf{v}_\gamma(\mathbf{z})\rangle^\gamma\psi_\gamma) + \nabla\cdot(\langle\mathbf{D}_\gamma(\mathbf{z})\rangle^\gamma\cdot\nabla\psi_\gamma), \tag{A.2}$$

and the *average* of $\mathcal{L}_0$ is defined by

$$\langle\mathcal{L}_0\psi_\gamma\rangle^\gamma = \langle\nabla\cdot(\langle\mathbf{v}_\gamma(\mathbf{z})\rangle^\gamma\psi_\gamma)\rangle^\gamma + \langle\nabla\cdot(\langle\mathbf{D}_\gamma(\mathbf{z})\rangle^\gamma\cdot\nabla\psi_\gamma)\rangle^\gamma. \tag{A.3}$$

Now, let $\mathbf{z}=\mathbf{x}+\mathbf{y}$, where $\mathbf{x}$ represents the centroid of the averaging volume, and $\mathbf{y}$ represents deviations from the centroid. Then, the average of the parameter fields can be expanded by Taylor series. For example, for $\langle\mathbf{v}_\gamma\rangle^\gamma$ we have

$$\langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}+\mathbf{y}} = \langle\mathbf{v}\rangle^\gamma\big|_{\mathbf{x}} + \mathbf{y}\cdot\nabla\langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}} + \frac{1}{2}\mathbf{y}\mathbf{y}:\nabla\nabla\langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}} + \cdots \tag{A.4}$$

Using this result in the first term on the right-hand side of Eq. (A.3) yields

$$\begin{aligned}\langle\langle\mathbf{v}_\gamma\rangle^\gamma\psi_\gamma\rangle^\gamma &= \frac{1}{V}\int_{\mathbf{y}\in V(\mathbf{x})}\langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}+\mathbf{y}}\Phi(\mathbf{x}+\mathbf{y})\psi_\gamma(\mathbf{x}+\mathbf{y})\,dV(\mathbf{y})\\ &= \frac{1}{V}\int_{\mathbf{y}\in V(\mathbf{x})}\langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}}\Phi(\mathbf{x}+\mathbf{y})\psi_\gamma(\mathbf{x}+\mathbf{y})\,dV(\mathbf{y}) + \frac{1}{V}\\ &\quad\times\int_{\mathbf{y}\in V(\mathbf{x})}\mathbf{y}\cdot\nabla\langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}}\Phi(\mathbf{x}+\mathbf{y})\psi_\gamma(\mathbf{x}+\mathbf{y})\,dV(\mathbf{y}) + \frac{1}{V}\\ &\quad\times\int_{\mathbf{y}\in V(\mathbf{x})}\mathbf{y}\mathbf{y}:\nabla\nabla\langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}}\Phi(\mathbf{x}+\mathbf{y})\psi_\gamma(\mathbf{x}+\mathbf{y})\,dV(\mathbf{y}) + \cdots\end{aligned} \tag{A.5}$$

In this last expression, the second integral can be dropped relative to the first term if the condition

$$\mathbf{y}\cdot\nabla\langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}} \ll \langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}}, \tag{A.6}$$

is met. In order to assess this inequality, we need first to develop an estimate for the quantity on the left-hand side. For our purposes, the required assumption is that the statistics of the parameter fields are quasi-stationary (*cf.* Ref. [18]). By this, we mean that the statistics are close enough to stationary in some sense that we can treat them as such. To make this idea more concrete, begin by assuming that the average $\langle\mathbf{v}_\gamma\rangle^\gamma$ is not stationary. Then, this quantity is a (random) function. To keep the notation simple, let us consider only the x-component of the velocity field. Assume that the average velocity field is smoothly varying, and let $\mathbb{V}_{\gamma,x} = \langle v_\xi\rangle^\gamma$. Then we have, by definition

$$\langle\mathbb{V}_\xi\rangle^\gamma\big|_{\mathbf{x}} = \frac{1}{V}\int_{\mathbf{z}\in V(\mathbf{x})}\langle v_\xi\rangle^\gamma\big|_{\mathbf{x}+\mathbf{z}}\,dV(\mathbf{z}) \tag{A.7a}$$

$$\sigma_{\mathbb{V}_\xi}(\mathbf{x}) = \left(\frac{1}{V}\int_{\mathbf{z}\in V(\mathbf{x})}\left[\mathbb{V}_\xi\big|_{\mathbf{x}+\mathbf{z}} - \langle\mathbb{V}_\xi\rangle^\gamma\big|_{(\mathbf{x}+\mathbf{z})}\right]^2 dV(\mathbf{z})\right)^{\frac{1}{2}} \tag{A.7b}$$

Further, assume that the spatial correlation matrix for $\mathbb{V}_\xi$ can be computed as described in Section 3.3, and is represented by $c_{\mathbb{V}_x}(\mathbf{x},\mathbf{x}+\mathbf{w})$. Then, the integral scale for any direction, $\boldsymbol{\lambda}$, can be defined by

$$L_{\mathbb{V}_\xi,\lambda}(\mathbf{x},\boldsymbol{\lambda}) = \int_{w\in\mathbb{R}} c_{\mathbb{V}_x}(\mathbf{x},\mathbf{x}+w\boldsymbol{\lambda})\,dw. \tag{A.8}$$

If one estimates the deviations of $\mathbb{V}_\xi$ to be on the order of $\sigma_{\mathbb{V}_\xi}$, then with these definitions one can estimate the gradient of the average parameter field by

$$\nabla\langle\mathbb{V}_\xi\rangle^\gamma = \mathbf{O}\left(\frac{\sigma_{\mathbb{V}_\xi}(\mathbf{x})}{L_{\mathbb{V}_\xi,\lambda}(\mathbf{x})}\right) \tag{A.9}$$

Estimating the value of $\mathbf{y}$ by r_0 and $\mathbb{V}_\xi$ by $\langle\mathbb{V}_\xi\rangle^\gamma$ using the results above, the inequality given in (A.6) can be estimated by

$$\sigma_{\mathbb{V}_\xi}\frac{r_0}{L_{\mathbb{V}_\xi}} \ll \langle\mathbb{V}_\xi\rangle^\gamma, \tag{A.10}$$

or, more compactly

$$C_{\mathbb{V}_\xi}\frac{r_0}{L_{\mathbb{V}_\xi}} \ll 1 \tag{A.11}$$

where the coefficient of variation is given by $C_{\mathbb{V}_\xi} \equiv \sigma_{\mathbb{V}_\xi}/\langle\mathbb{V}_\xi\rangle^\gamma$. Clearly, this kind of argument can be repeated for the other two terms in the velocity vector. Although there are times when one may want to maintain a characteristic length scale for each of three cardinal directions, in many instances we would like the restriction given in (A.10) to be the most conservative available. In this case, we can choose a single characteristic length scale by choosing the length scale that is associated with the direction $\boldsymbol{\lambda}$ that maximizes the left-hand side of the equality.

We explicitly assume that when the inequality (A.10) is valid, then each of the integrals beyond the first one on the right-hand side of Eq. (A.5) can be neglected. The result is that Eq. (A.5) can be approximated by

$$\begin{aligned}\langle\langle\mathbf{v}_\gamma\rangle^\gamma\psi_\gamma\rangle^\gamma\big|_{\mathbf{x}} &= \langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}}\frac{1}{V}\int_{\mathbf{y}\in V(\mathbf{x})}\Phi(\mathbf{x}+\mathbf{y})\psi_\gamma(\mathbf{x}+\mathbf{y})\,dV(\mathbf{y})\\ &= \langle\mathbf{v}_\gamma\rangle^\gamma\big|_{\mathbf{x}}\langle\psi_\gamma\rangle^\gamma\big|_{\mathbf{x}}\end{aligned} \tag{A.12}$$

The developments for the remaining terms in the original differential equation (Eq. A.1) follow along similar lines, and lead to identical constraints. Thus, when the constraint given by (A.10) is valid, the average of parameter fields can be removed from averages. Extending this development to the other parameter and source fields, these developments allow us to provide a concrete definition of the term *quasi-stationary* (after [18, Section 2.6]).

Definition. A random field, p_γ, is quasi-stationary in its *intrinsic spatial average*, $\mathbb{P}_\gamma = \langle p_\gamma \rangle^\gamma$, when, for an averaging volume characterized by a length scale r_0, the following constraint is met

$$\frac{\sigma_{\mathbb{P}_\gamma}}{\mathbb{P}_\gamma}\frac{r_0}{L_{\mathbb{P}_\gamma}} \ll 1. \tag{A.13}$$

Here it is to be understood that it may be desirable to choose the value of the characteristic length scale that maximizes the left-hand side of the inequality.

Appendix B. Solution to the nonlocal closure problem

The mathematical theory of nonlocal differential equations is still in its infancy. Although the equations remain linear, and in a practical sense their solution via numerical methods is reasonably straightforward, their mathematical status presents a very different problem. The question of existence and uniqueness of nonlocal integro-differential equations has been assessed for some relatively simple cases; some results can be found in the texts by Garroni and Menaldi [32] and by Andreu-Vaillo et al. [3]. On the basis of these works, we propose a solution to the nonlocal closure problem as

$$\begin{aligned}\tilde{\psi}_\gamma(\mathbf{x},t) = &\underbrace{\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} G(\mathbf{x},t;\mathbf{y},\tau)\mathcal{S}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma,\nabla\nabla\langle\psi_\gamma\rangle^\gamma)\,dV(\mathbf{y})\,d\tau}_{\text{influence of the net sources}}\\ &+\underbrace{\int_{\mathbf{y}\in\mathcal{V}_{\gamma,M}} G(\mathbf{x},t;\mathbf{y},0)\mathcal{I}(\mathbf{y};\langle\psi_\gamma\rangle^\gamma)\,dV(\mathbf{y})}_{\text{influence of the initial condition}}\\ &+\underbrace{\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{A}_{\gamma\kappa,M}} G(\mathbf{x},t;\mathbf{y},\tau)\mathcal{G}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)\,dA(\mathbf{y})\,d\tau}_{\text{influence of the interfacial sources}}\\ &+\underbrace{\int_{\tau=0}^{\tau=t}\int_{\mathbf{y}\in\mathcal{A}_{\gamma e,M}} G(\mathbf{x},t;\mathbf{y},\tau)\mathcal{Q}(\mathbf{y},\tau;\langle\psi_\gamma\rangle^\gamma,\nabla\langle\psi_\gamma\rangle^\gamma)\,dA(\mathbf{y})\,d\tau}_{\text{influence of the entrance and exit sources}}.\end{aligned} \tag{B.1}$$

In this expression, G is the Green's function for the integro-differential equation. The Green's function itself solves the following ancillary problem (*cf.* Garroni and Menaldi [32])

$$\frac{\partial G}{\partial t} = \nabla\cdot\left(-\mathbf{v}_\gamma G + \mathbf{D}_\gamma\cdot\nabla G\right) - k_1 G + \mathcal{N}(\mathbf{x},t;G) \tag{B.2a}$$

$$B.C.1\quad \mathbf{n}_{\gamma\kappa}\cdot(\mathbf{D}_\gamma\cdot\nabla G + \mathbf{v}_\gamma G) = -k_s G,\quad \mathbf{x}\in\mathcal{A}_{\gamma\kappa,M} \tag{B.2b}$$

$$B.C.2\quad \mathbf{n}_{\gamma e}\cdot(\mathbf{D}_\gamma\cdot\nabla G + \mathbf{v}_\gamma G) = 0 \tag{B.2c}$$

$$I.C.\quad G = \delta(\mathbf{x}-\mathbf{y},t-\tau) \tag{B.2d}$$

Here, δ is the Dirac's delta function. The Green's functions must also satisfy the causality principle

$$G(\mathbf{x},t;\mathbf{y},\tau) = 0,\quad \text{for } t<\tau. \tag{B.3}$$

Note that, although the ancillary problem for the Green's function is different from the local case, the solution to the problem take an identical mathematical form. We emphasize that the proposed solution is consistent with the work on the solution to nonlocal problems referenced above; however, we do not currently have a proof that Eqs. (B.2a)–(B.2d) has a solution that satisfies existence and uniqueness requirements.

Appendix C. Solution to the local closure problem

To obtain an analytical solution for the effective coefficients $D_{0,eff}$ and $D_{2,eff}$, we will adopt the geometry and conditions used by Chang [15,16]. Under this approximation to the geometry, the boundary-value problem for the concentration deviations can be expressed as follows.

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\tilde{c}_{A\gamma}}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2\tilde{c}_{A\gamma}}{\partial\theta^2} = 0,\quad \text{in the } \gamma\text{-phase} \tag{C.1a}$$

$$B.C.1\quad \frac{\partial\tilde{c}_{A\gamma}}{\partial r} = -\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial r}$$

$$= -\left(\cos\theta\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial\xi} + \sin\theta\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial\eta}\right),\quad \text{at } r=a \tag{C.1b}$$

$$B.C.2\quad \tilde{c}_{A\gamma} = 0,\quad \text{at } r=\ell_{ch}/2. \tag{C.1c}$$

The associated problem for the Green's function is

$$\frac{\partial}{\partial r}\left(r\frac{\partial G}{\partial r}\right) + \frac{1}{r}\frac{\partial^2 G}{\partial\theta^2} = \delta(r-r_0)\delta(\theta-\theta_0),\quad \text{in the } \gamma\text{-phase} \tag{C.2a}$$

$$B.C.1\quad \frac{\partial G}{\partial r} = 0,\quad \text{at } r=a \tag{C.2b}$$

$$B.C.2\quad G = 0,\quad \text{at } r=\ell_{ch}/2. \tag{C.2c}$$

Since we know that the eigenfunctions are located in the angular direction, we can propose the following expansions

$$G = b_0(r) + \sum_{n=1}^{\infty} b_n(r)\cos(n\theta) + \sum_{n=1}^{\infty} c_n(r)\sin(n\theta). \tag{C.3}$$

Substitution of this expression into Eq. (C.2a) yields

$$\begin{aligned}&\frac{d}{dr}\left(r\frac{db_0}{dr}\right) + \sum_{n=1}^{\infty}\left[\frac{d}{dr}\left(r\frac{db_n}{dr}\right) - \frac{n^2}{r}b_n\right]\cos(n\theta)\\ &+\sum_{n=1}^{\infty}\left[\frac{d}{dr}\left(r\frac{dc_n}{dr}\right) - \frac{n^2}{r}c_n\right]\sin(n\theta)\\ &= \delta(r-r_0)\delta(\theta-\theta_0).\end{aligned} \tag{C.4}$$

Integrating this expression from $\theta=0$ to $\theta=2\pi$ gives rise to

$$\frac{d}{dr}\left(r\frac{db_0}{dr}\right) = \frac{1}{2\pi}\delta(r-r_0). \tag{C.5}$$

The general solution of the above differential equation for $r\neq r_0$ is

$$b_0 = \begin{cases} C_1\ln r + C_2, & r<r_0\\ C_3\ln r + C_4, & r>r_0\end{cases}. \tag{C.6}$$

On the basis of the boundary conditions at $r=a$ and $r=\ell_{ch}/2$, we have that $C_1=0$ and $C_4=-C_3\ln\frac{\ell_{ch}}{2}$, thus

$$b_0 = \begin{cases} C_2, & r<r_0\\ C_3\ln\frac{2r}{\ell_{ch}}, & r>r_0\end{cases}. \tag{C.7}$$

Since the Green's function must be continuous at $r=r_0$, we can conclude that

$$C_2 = C_3\ln\frac{2r_0}{\ell_{ch}}, \tag{C.8}$$

so that Eq. (C.7) takes the form

$$b_0 = \begin{cases} C_3\ln\frac{2r_0}{\ell_{ch}}, & r<r_0\\ C_3\ln\frac{2r}{\ell_{ch}}, & r>r_0\end{cases}. \tag{C.9}$$

To determine the remaining integration constant, let us integrate Eq. (C.5) from $r=r_0^-$ to $r=r_0^+$ in order to obtain

$$\left(r\frac{db_0}{dr}\right)_{r=r_0^-}^{r=r_0^+} = \frac{1}{2\pi}, \tag{C.10}$$

from which it results that $C_3 = 1/2\pi$. Therefore, the first term in Eq. (C.3) is

$$b_0(r) = \frac{1}{2\pi}\begin{cases}\ln\frac{2r_0}{\ell_{ch}}, & r<r_0\\ \ln\frac{2r}{\ell_{ch}}, & r>r_0\end{cases}. \tag{C.11}$$

In order to determine b_n ($n \geqslant 1$), we multiply Eq. (C.4) by $\cos(m\theta)$ and integrate from $\theta = 0$ to $\theta = 2\pi$, this leads to

$$\frac{d}{dr}\left(r\frac{db_n}{dr}\right) - \frac{n^2}{r}b_n = \frac{\cos(n\theta_0)}{\pi}\delta(r - r_0), \quad \text{in the } \gamma\text{-phase}, \tag{C.12}$$

whose general solution is

$$b_n = \begin{cases} c_1 r^n + c_2 r^{-n}, & r < r_0 \\ c_3 r^n + c_4 r^{-n}, & r > r_0 \end{cases}. \tag{C.13}$$

After using the boundary conditions we find that

$$b_n = \begin{cases} c_2\left(r^{-n} + \frac{r^n}{a^{2n}}\right), & r < r_0 \\ c_4\left(r^{-n} - \left(\frac{\ell_{ch}}{2}\right)^{-2n} r^n\right), & r > r_0 \end{cases}. \tag{C.14}$$

Application of the continuity condition leads to

$$c_2\left(1 + \frac{r_0^{2n}}{a^{2n}}\right) = c_4\left(1 - \left(\frac{2r_0}{\ell_{ch}}\right)^{2n}\right). \tag{C.15}$$

Thus

$$b_n = \begin{cases} c_4 \dfrac{\left(1 - \left(\frac{2r_0}{\ell_{ch}}\right)^{2n}\right)}{\left(1 + \frac{r_0^{2n}}{a^{2n}}\right)}\left(r^{-n} + \frac{r^n}{a^{2n}}\right), & r < r_0 \\ c_4\left(r^{-n} - \left(\frac{\ell_{ch}}{2}\right)^{-2n} r^n\right), & r > r_0 \end{cases}. \tag{C.16}$$

To determine c_4, we use the jump condition

$$\left(r\frac{db_n}{dr}\right)_{r=r_0^-}^{r=r_0^+} = \frac{\cos(n\theta_0)}{\pi}, \tag{C.17}$$

in order to finally obtain

$$b_n = -\frac{\cos(n\theta_0)}{2n\pi r_0^n r^n\left[\left(\frac{2}{\ell_{ch}}\right)^{2n} + \left(\frac{1}{a}\right)^{2n}\right]} \begin{cases} \left(1 + \left(\frac{r}{a}\right)^{2n}\right)\left(1 - \left(\frac{2r_0}{\ell_{ch}}\right)^{2n}\right), & r < r_0 \\ \left(1 + \left(\frac{r_0}{a}\right)^{2n}\right)\left(1 - \left(\frac{2r}{\ell_{ch}}\right)^{2n}\right), & r > r_0 \end{cases}. \tag{C.18}$$

An equivalent result is obtained for a_n. Therefore, the Green's function is

$$G(r, \theta; r_0, \theta_0) = b_0 - \sum_{n=1}^{\infty} \frac{\cos(n\theta)\cos(n\theta_0) + \sin(n\theta)\sin(n\theta_0)}{2n\pi r_0^n r^n\left[\left(\frac{2}{\ell_{ch}}\right)^{2n} + \left(\frac{1}{a}\right)^{2n}\right]} \times \begin{cases} \left(1 + \left(\frac{r}{a}\right)^{2n}\right)\left(1 - \left(\frac{2r_0}{\ell_{ch}}\right)^{2n}\right), & r < r_0 \\ \left(1 + \left(\frac{r_0}{a}\right)^{2n}\right)\left(1 - \left(\frac{2r}{\ell_{ch}}\right)^{2n}\right), & r > r_0 \end{cases} \tag{C.19}$$

In order to derive the problem solution, we make use of the following form of Green's formula

$$\int_{A_\gamma}\left[\tilde{c}_{A\gamma}\nabla^2 G - G\nabla^2\tilde{c}_{A\gamma}\right] dA = \oint_{\partial A_\gamma} \mathbf{n}\cdot\left[\tilde{c}_{A\gamma}\nabla G - G\nabla\tilde{c}_{A\gamma}\right] d\sigma. \tag{C.20}$$

Or, in scalar form

$$\begin{aligned} &\int_{\theta=0}^{\theta=2\pi}\int_{r=a}^{r=\ell_{ch}/2}\left[\tilde{c}_{A\gamma}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial G}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 G}{\partial\theta^2}\right)\right. \\ &\left. - G\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\tilde{c}_{A\gamma}}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2\tilde{c}_{A\gamma}}{\partial\theta^2}\right)\right] r\,dr\,d\theta \\ &= \int_{\theta=0}^{\theta=2\pi} r\left[\tilde{c}_{A\gamma}\frac{\partial G}{\partial r} - G\frac{\partial\tilde{c}_{A\gamma}}{\partial r}\right]_{r=a}^{r=\ell_{ch}/2} d\theta \\ &+ \int_{r=a}^{r=\ell_{ch}/2}\frac{1}{r}\left[\tilde{c}_{A\gamma}\frac{\partial G}{\partial\theta} - G\frac{\partial\tilde{c}_{A\gamma}}{\partial\theta}\right]_{\theta=0}^{\theta=2\pi} dr. \end{aligned} \tag{C.21}$$

On the basis of the boundary-value problems for $\tilde{c}_{A\gamma}$ and G, we have that

$$\tilde{c}_{A\gamma}(r,\theta) = \int_{\theta_0=0}^{\theta_0=2\pi} aG(r,\theta;a,\theta_0)f(\theta_0)\,d\theta_0, \tag{C.22}$$

where,

$$f(\theta_0) = -\left(\cos\theta_0\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial x} + \sin\theta_0\frac{\partial\langle c_{A\gamma}\rangle^\gamma}{\partial y}\right) \tag{C.23a}$$

$$\begin{aligned} aG(r,\theta;a,\theta_0) &= \frac{a}{2\pi}\ln\frac{2r}{\ell_{ch}} \\ &- \sum_{n=1}^{\infty}\frac{\cos(n\theta)\cos(n\theta_0) + \sin(n\theta)\sin(n\theta_0)}{n\pi a^{n-1}r^n\left[\left(\frac{2}{\ell_{ch}}\right)^{2n} + \left(\frac{1}{a}\right)^{2n}\right]}\left(1 - \left(\frac{2r}{\ell_{ch}}\right)^{2n}\right). \end{aligned} \tag{C.23b}$$

References

[1] Adler P. Porous media: geometry and transports. London: Butterworth/Heinemann; 1992.
[2] Ahmadi A, Quintard M, Whitaker S. Transport in chemically and mechanically heterogeneous porous media - V. Two-equation model for solute transport with adsorption. Advances in Water Resources 1998;22(1):59–86.
[3] Andreu-Vaillo F, Mazón JM, Rossi JD, Toledo-Melero JJ. Nonlocal diffusion equations, mathematical surveys and monographs, vol. 165. Providence, RI: American Mathematical Society; 2010.
[4] Auriault JL. About the beavers and joseph boundary condition. Transport in Porous Media 2010;83:257–66.
[5] Barrer R. Measurement of diffusion and thermal conductivity constants in non-homogeneous media and in media these constants depend respectively on concentration or temperature. Proceedings of the Physics Society 1946;58:321–31.
[6] Bateman H. Higher transcendental functions, vol. 1. New York: McGraw-Hill; 1953.
[7] Battiato I, Tartakovsky DM. Applicability regimes for macroscopic models of reactive transport in porous media. Journal of Contaminant Hydrology 2011;120–121:18–26.
[8] Battiato I, Tartakovsky DM, Tartakovsky A, Scheibe TD. On breakdown of macroscopic models of mixing-controlled heterogeneous reactions in porous media. Advances in Water Resources 2009;32:1664–73.
[9] Baveye P, Sposito G. The operational significance of the continuum hypothesis in the theory of water movement through soils and aquifers. Water Resources Research 1984;20:521–30.
[10] Bear J. Dynamics of fluids in porous media. Elsevier; 1972.
[11] Benson DA, Wheatcraft SW, Meerschaert MM. Application of a fractional advection-dispersion equation. Water Resources Research 2000;36(6):1403–12.
[12] Beran M. Statistical continuum theories, monographs in statistical physics and thermodynamics, vol. 9. New York: Wiley; 1968.
[13] Berkowitz B, Cortis A, Dentz M, Scher H. Modeling non-fickian transport in geological formations as a continuous time random walk. Reviews of Geophysics 2006;44. RG2003-1–RG2003-49.
[14] Chandrasekhar S. Radiative transfer. London: Oxford University Press; 1950.
[15] Chang HC. Multiscale analysis of effective transport in periodic heterogeneous media. Chemical Engineering Communications 1982;15:83–91.
[16] Chang HC. Effective diffusion and conduction in two-phase media: a unified approach. AIChE Journal 1983;29:846–53.
[17] Chatwin PC. Cumulants of distribution of concentration of a solute dispersing in solvent flowing through a tube. Journal Of Fluid Mechanics 1972;51(JAN11):63–7.
[18] Christakos G. Random field models in earth sciences. San Diego: Academic Press, Inc.; 1992.
[19] Cushman J. Proofs of the volume averaging theorems for multiphase flow. Advances in Water Resources 1982;5:248–53.
[20] Cushman J, Ginn T. Nonlocal dispersion in media with continuously evolving scales of heterogeneity. Transport in Porous Media 1993;13:123–38.
[21] Cushman J, Ginn T. On dispersion in fractal porous media. Water Resources Research 1993;29(10):3513–5.
[22] Cushman J, Hu BX. A resumé of nonlocal transport theories. Stochastic Hydrology and Hydraulics 1995;9:105–16.
[23] Cushman J, Park M, Moroni M, Kleinfelter-Domelle N, O'Malley D. A universal field equation for dispersive processes in heterogenous media. Stochastic Environmental Research and Risk Assessment 2011;25:1–10.
[24] Cushman JH. On unifying the concepts of scale, instrumentation, and stochastics in the development of multiphase transport theory. Water Resources Research 1984;20:1668–76.
[25] Cushman JH, Bennethum LS, Hu BX. A primer on upscaling tools for porous media. Advances in Water Resources 2002;25(8–12):1043–67.
[26] Cybulski A, Moulijn J. Structured Catalysts and Reactors. Chemical Industries. Boca Raton: CRC/Taylor and Francis; 2006.

[27] Dagan G. Flow and transport in porous formations. Verlag, Berlin: Springer; 1989. the über omnitome of the Dagan approaches. Contains some derivation of the SC approach in Chapter 5.
[28] Dehghan M, Shakeri F F. Solution of parabolic integro-differential equations arising in heat conduction in materials with memory via He's variational iteration technique. Communications in Numerical Methods in Engineering 2008.
[29] Edelen D. Nonlocal field theories. In: Eringen AC, editor. Continuum physics, vol. IV. New York: Academic Press; 1976. p. 75–201.
[30] Eringen A. Nonlocal continuum field theories. New York: Springer; 2002.
[31] Galilei G. Two new sciences [Crew H, de Salvio A, Trans.]. New York: Dover; 1954 [Originally published by Elzevir, 1638].
[32] Garroni M, Menaldi J. Green functions for second order parabolic integro-differential equations. Pitman research notes in mathematics series, vol. 275. Harlow, Essex, UK: Longman Scientific and Technical; 1992.
[33] Gray W, Leijnse A, Kolar R, Blain C. Mathematical tools for changing spatial scales in the analysis of physical systems. Boca Raton, Florida: CRC Press; 1993.
[34] Gray W, Miller C, Schrefler B. Averaging theory for environmental flows: what have we learned? Advances in Water Resources 2013;51:123–38.
[35] Guettel R, Turek T. Assessment of micro-structured fixed-bed reactors for highly exothermic gas-phase reactions. Chemical Engineering Science 2009;65:1644–54.
[36] Howes FA, Whitaker S. The spatial averaging theorem revisited. Chemical Engineering Science 1985;40:1387–92.
[37] Hubbert MK. Darcy law and the field equation of the flow of underground fluids. Transactions of the American Institute of Mining and Metallurgical Engineers 1956;207:222–39.
[38] Kerscher M. Constructing, characterizing, and simulating gaussian and higher-order point distributions. Physical Review E 2001;64:056,109-1–056,109-12. http://dx.doi.org/10.1103/PhysRevE.64.056109.
[39] Koch DL, Brady JF. Nonlocal dispersion in porous-media-nonmechanical effects. Chemical Engineering Science 1987;42(6):1377–92.
[40] Kramers H. Brownian motion in a field of force and the diffusion model of chemical reactions. Physica 1940;7:284–304.
[41] Lions JL. Some methods in the mathematical analysis of systems and their control. Beijing: Kexue Chubanshe (Science Press); 1981.
[42] de Loos S, van der Schaaf J, Tiggelaar R, Nijhuis T, de Croon M, Schouten J. Gas-liquid dynamics at low reynolds numbers in pillared rectangular micro channels. Microfluid Nanofluid 2010;9:131–44.
[43] Lorentz H. The theory of electrons and its application to the phenomena of light and radiant heat. Leipzig: B.U. Teubner; 1909.
[44] Losey M, Jackman R, Firebaugh S, Schmidt M, Jensen K. Design and fabrication of microfluidic devices for multiphase mixing and reaction. Journal of Microelectromechanical Systems 2002;11(6):709–17.
[45] Lux J. A non-periodic closure scheme for the determination of effective diffusivity in real porous media. Transport in Porous Media 2010;82:299–315.
[46] Marcienkiewicz J. Sur une propriété de la loi de gau (on a property of the gauss law). Mathematische Zeitschrift 1939;44:612–8.
[47] McMillan W, Peterson K, Christel L, Northrup M. Proceedings of the 8th international symposium on microbial ecology. In: Bell C, Brylinsky M, Johnson-Green P, editors. Microbial biosystems: new frontiers. Halifax, Canada: Atlantic Canada Society for Microbial Ecology; 1999.
[48] Mori H. A continued-fraction representation of the time-correlation functions. Progress of Theoretical Physics 1965;34(3):399. , 416.
[49] Moyne C. Two-equation model for a diffusive process in porous media using the volume averaging method with an unsteady-state closure. Advances in Water Resources 1997;20:63–76.
[50] Neuman S, Tartakovsky DM. Perspectives on theories of non-fickian transport in heterogeneous porous media. Advances in Water Resources 2009;32:670–80.
[51] Neuman SP. Eulerian-lagrangian theory of transport in space-time nonstationary velocity fields: exact nonlocal formalism by conditional moments and weak approximation. Water Resources Research 1993;29:633–45.
[52] Neuman SP, Federico D. Multifaceted nature of hydrogeologic scaling and its interpretation. Reviews of Geophysics 2003;41:1014. http://dx.doi.org/10.1029/2003RG000130.
[53] Ochoa-Tapia J, Whitaker S. Momentum transfer at the boundary between a porous medium and a homogeneous fluid - I. Theoretical development. International Journal of Heat and Mass Transfer 1995;38(14):2635–46.
[54] Ochoa-Tapia JA, Stroeve P, Whitaker S. Diffusive transport in two-phase media: spatially periodic models and Maxwell's theory for isotropic and anisotropic systems. Chemical Engineering Science 1994;49:709–26.
[55] Pagitsas M, Nadim A, Brenner H. Projection operator analysis of macrotransport processes. Journal of Chemical Physics 1986;85:5238–45.
[56] Pawula R. Generalizations and extensions of the fokker–planck–kolmogorov equations. IEEE Transactions on Information Theory 1967;13:33–41.
[57] Peterson MA. Galileo's discovery of scaling laws. American Journal of Physics 2002;70:575–80.
[58] Polyanin A. Handbook of linear partial differential equations for engineers and scientists. Boca Raton, Florida: Chapman and Hall/CRC; 2002.
[59] Quintard M, Whitaker S. Transport in ordered and disordered porous media II: Generalized volume averaging. Transport in Porous Media 1994;14:179–206.
[60] Rayleigh LJWS. On the influence of obstacles arranged in rectangular order upon the properties of the medium. Philosophical Magazine 1892;34:481–9.
[61] Risken H. The Fokker–Planck equation: methods of solution and applications. Springer series in synergetics, 2nd ed., vol. 18. Berlin: Springer; 1989.
[62] Risken H, Vollmer H. On the application of truncated generalized fokker-plank equations. Zeitschrift für Physik 1979;B35:313–5.
[63] Sanchez-Palencia E. Non-homogeneous media and vibration theory. Lecture notes in physics, vol. 127. New York: Springer-Verlag; 1980.
[64] Sanchez-Vila X, Tartakovsky DM. Ergodicity of pumping tests. Water Resources Research 2007;43. W03,414-1–W03,414-5.
[65] Shapiro M, Brenner H. Greens-function formalism in generalized taylor dispersion theory. Chemical Engineering Communications 1987;55(1–6):19–27.
[66] Souadnia A, Didierjean S, Moyne C. Transient dispersion in porous media: a comparison between exact and approximate solutions in a case study. Transport in Porous Media 2002;47(3):245–77.
[67] Tartakovsky DM, Neuman S. Transient effective hydraulic conductivities under slowly and rapidly varying mean gradients in bounded three-dimensional random media. Water Resources Research 1998;34(1):21–32.
[68] Tartakovsky DM, Neuman SP. Transient flow in bounded randomly heterogeneous domains. 1. Exact conditional moment equations and recursive approximations. Water Resources Research 1998;34(1):1–12.
[69] Truesdell C. Mechanical basis of diffusion. Journal of Chemical Physics 1962;37(10):2336–44.
[70] Valdés-Parada F, Goyeau B, Ochoa-Tapia J. Jump boundary condition at a fluid-porous dividing surface: derivation of the closure problem. Chemical Engineering Science 2007;62:4025–39.
[71] Valdés-Parada FJ, Ochoa-Tapia JA, Alvarez-Ramirez J. Diffusive mass transport in the fluid-porous medium inter-region: closure problem solution for the one-domain approach. Chemical Engineering Science 2007;62:6054–68.
[72] Wen XH, Chen YM, Durlofsky LJ. Efficient 3d implementation of local-global upscaling for reservoir simulation. SPE Journal 2006;11(December):443–53.
[73] Whitaker S. The method of volume averaging. Kluwer Academic Publishers; 1999.
[74] Williams J. Monlith structures, materials, properties and uses. Catalysis Today 2001;69:3–9.
[75] Wood B. Taylor-Aris dispersion: an explicit example for understanding multiscale analysis via volume averaging. Chemical Engineering Education 2009;43:29–38.
[76] Wood BD. The role of scaling laws in upscaling. Advances in Water Resources 2009;32:723–36.
[77] Zhang C, Kang Q, Wang X, Zilles J, Müller R, Werth CJ. Effects of pore-scale heterogeneity and transverse mixing on bacterial growth in porous media. Environmental Science and Technology 2010;44:3085–92.
[78] Zhang Y, Benson DA, Meerschaert MM, LaBolle E. Space-fractional advection-dispersion equations with variable parameters: diverse formulas, numerical simulations, and application to the macrodispersion experiment site data. Water Resources Research 2007;43. W05,439-1–W05,439-1.
[79] Zwanzig R. Ensemble method in the theory of irreversibility. Journal of Chemical Physics 1960;33(5):1338–41.
[80] Zwanzig R. Memory effects in irreversible thermodynamics. Physical Review 1961;124:983–92.