

# Theory and Applications of Macroscale Models in Porous Media

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# Abstract

Systems dominated by heterogeneity over a multiplicity of scales, like porous media, still challenge our modeling efforts. The presence of disparate length- and time-scales that control dynamical processes in porous media hinders not only models predictive capabilities, but also their computational efficiency. Macrosopic models, i.e., averaged representations of pore-scale processes, are computationally efficient alternatives to microscale models in the study of transport phenomena in porous media at the system, field or device scale (i.e., at a scale much larger than a characteristic pore size). We present an overview of common upscaling methods used to formally derive macroscale equations from pore-scale (mass, momentum and energy) conservation laws. This review includes the volume averaging method, mixture theory, thermodynamically constrained averaging, homogenization, and renormalization group techniques. We apply these methods to a number of specific problems ranging from food processing to human bronchial system, and from diffusion to multiphase flow, to demonstrate the methods generality and flexibility in handling different applications. The primary intent of such an overview is not to provide a thorough review of all currently available upscaling techniques, nor a complete mathematical treatment of the ones presented, but rather a primer on some of the tools available for upscaling, the basic principles they are based upon, and their specific advantages and drawbacks, so to guide the reader in the choice of the most appropriate method for particular applications and of the most relevant technical literature.

**Keywords** Upscaling  $\cdot$  Porous media  $\cdot$  Volume averaging method  $\cdot$  Mixture theory  $\cdot$  Thermodynamically constrained averaging theory  $\cdot$  Homogenization theory  $\cdot$  Renormalization group theory

# **1** Introduction

One of the most significant challenges that porous media modelers across different disciplines continue to face is the "tyranny of scales", i.e., the disparity of temporal and spatial scales

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at which mass, momentum and energy transport are best understood (e.g., sub-pore to porescale, and seconds to days) and at which predictions are needed for practical applications. Such challenges cut across disciplinary boundaries as porous media are ubiquitous to a large number of engineering, environmental, biological, chemical and medical systems.

Due to their inherently multi-scale nature, transport phenomena in rigid and deformable porous media can be modeled at different scales. While the typical scale at which a given phenomenon is best described (in terms of model confidence, robustness and accuracy) is largely application dependent, it is often assumed that process dynamics at the pore scale is relatively well understood, i.e., one embraces the "continuum hydrodynamics" hypothesis and has confidence in the equations describing flow and transport at the pore-scale—e.g., the Navier-Stokes equation, and an advection-diffusion equation. Such a hypothesis, valid for Knudsen number less than 0.1 (Lasseux et al. 2016), i.e., when the molecular mean free path is much smaller than a characteristic length scale associated with the pore size, is generally satisfied for porous media that are not too "tight": in this respect, transport in tight formations, e.g., shales, or in engineered nanoporous materials presents additional challenges which will not be addressed in this review [we refer to Tartakovsky and Dentz (2019) for a review on the topic]. Although the concept of micro- and macro-scale is only relative (i.e., micro- and macro-scale indicate any two contiguous/adjacent scales) and not necessarily associated with any specific scale of reference, in the following we will consider the pore-scale as the scale of reference, i.e., the microscale, unless otherwise stated.

Although the ever-increasing computational power is helping to speed up the adoption of microscale models by practitioners, computational domains that can be modeled with modern-day pore-scale simulations are still frequently too small to generate useful predictions at the system scale (e.g., device or field scales in engineering or environmental systems, respectively). The heterogeneity of most natural porous media (e.g., oil reservoirs, aquifers) and technology products (carbon nanotubes assemblies, battery electrodes, water filters, food) and prohibitive computational costs render computational tools such as lattice-Boltzmann modeling (Leemput et al. 2007), smoothed particle hydrodynamics (Tartakovsky et al. 2007), conventional CFD (Wood et al. 2015), and other pore-scale simulations methods impractical as a predictive tool for scales that are many orders of magnitude larger than the pore scale. As a result, macroscale models are often the models of choice when a system level process assessment is necessary.

Macrosopic models (i.e., averaged representations of microscale processes) represent computationally efficient alternatives to microscale models in the study of flow and transport processes in porous media at the system, field, or device scale and are often treated as the foundational principles for system optimization and process design. In this respect, they are crucial elements guiding the decision process of practitioners, who are primarily interested in predictions and optimization of the overall system performance. Applications cover a broad range of fields in engineering, environmental and food sciences, biology, medicine, etc., which render virtually impossible the task of providing an exhaustive literature review. Here, we just list a few examples, for the sole purpose of demonstrating the cross-cutting nature of such problems across disciplinary boundaries. For example, engineering applications include, but are not limited to, the optimal design of electrochemical storage devices (Arunachalam et al. 2017; Zhang and Tartakovsky 2017b), sensors (Battiato et al. 2010), solar reactors (Valdés-Parada et al. 2011) and food texture (Zhao and Takhar 2017). Macroscale models have been historically used in subsurface hydrology (Bear 2018), e.g., for the optimization of remediation schemes for contaminant transport in the subsurface (Barry et al. 2002), predictions of the fate of fracking fluids during hydraulic fracturing (Malley et al. 2016), transport of fluids in pipelines (Picchi 2018), etc. More recently, they have been successfully extended to, e.g., ecohydrology applications, and for predictions of flow and transport in cities (Valdés-Parada et al. 2012) and canopy layers (Battiato and Rubol 2014; Rubol et al. 2016, 2018). Applications to biology and medicine include the study of swelling and deformation of cartilages (Lai et al. 1991), design of micromixers for lab-on-a-chip applications (Ling et al. 2018), study of transport in blood vessels (Battiato et al. 2017), calculations of effective properties of tissues (Wood et al. 2002), predictions of tumor growth (Sciumé et al. 2012, 2013), etc.

In many cases, macroscopic models were first formulated as empirical laws, e.g., Darcy's and the generalized Darcy's equation for single and multiphase flow (Darcy 1856; Hubbert 1957; Whitaker 1986; Blunt 2017), the Brinkman equation (Brinkman 1949; Durlofsky and Brady 1987), the advection–dispersion equation (Freeze and Cherry 1979; Bear 2018), etc., and then derived from the formal upscaling of microscale equations, with one of the first fundamental analysis provided by Taylor and Aris (Taylor 1953; Aris 1956). The discovery that formal mathematical techniques could be successfully employed to derive equations governing the dynamics of heterogeneous systems at different scales was extremely impactful: it led, on the one hand, to the development of many different upscaling methods and, on the other, to their application to a variety of problems spanning virtually any field of mathematical physics with applications to engineering, chemistry, medicine, sciences, etc.

The importance of understanding the quantitative connection between microscale processes and macroscale response through upscaling methods goes way substantially beyond the practical ability to formally derive upscaled equations for a specific application. Such mathematical tools (be them deterministic or stochastic, local or non-local) provide a framework (i) to rigorously track the hypothesis and approximations entailed in any given macroscale model and (ii) to establish a quantitative connection between pore-scale topology and effective parameters that goes beyond pure parametric fitting (Battiato and Tartakovsky 2011; Davit et al. 2013). The former consideration reminds one that macroscale models are only approximations (and not inviolable physical principles/laws) of the averaged response of the system at the microscale: as such, they should be cautiously handled within their conditions of validity to ensure their predictive capabilities and accuracy. In this context, it is important to highlight that the term "predictive" is used in the following sense: we refer to an upscaled model as "predictive," when its approximation error compared to the averaged pore-scale solution is bounded by the upscaling error. Furthermore, satisfaction of the former conditions is only sufficient, but not necessary, to ensure macroscale models accuracy, i.e., an upscaled model can still be accurate outside of such applicability conditions, although its accuracy cannot be a priori guaranteed (Battiato and Tartakovsky 2011; Boso and Battiato 2013). This is particularly important as, nowadays, the effort to achieve *purely predictive* understanding (in contrast to model fitting) across scales is indeed within reach even for highly heterogeneous systems like porous media, due to the development of improved theoretical frameworks and the ever-increasing computational power available. Moreover, the failures resulting from losing track of modeling assumptions can be dramatic in both social and economic terms (Semenenko 2003); examples range from miscalculation of oil recovery rates or contaminant migration (Um et al. 2005), to incorrectly estimating the elastic properties of carbon nanotubes patches (Deck et al. 2009). The second consideration emphasizes the possibility of either controlling macroscopic properties and system response by engineering microscale topology or estimating macroscale parameters from microscale topological data (e.g., Bhattad et al. 2011) as obtained by XCT scans, SEM images, etc. This provides a path to systematically incorporate data collected at the microscale for forward predictions of parameters at the macroscale, although problems associated with instrument resolution and subresolution porosity should be carefully handled (e.g., Korneev et al. 2018).

In light of the challenges shared by researchers in the porous media community, regardless of their specific field of focus, the purpose of this manuscript is to provide a basic introduction to some of the upscaling methods we are most familiar with, while providing specific application examples in disciplines ranging from food and chemical sciences to biological systems, etc. As distinct from other reviews of averaging methods (Miller et al. 1998; Wood 2000; Cushman et al. 2002; Neuman and Tartakovsky 2009; Davit et al. 2013), our purpose is threefold: (1) we focus on the basic features of various upscaling theories and present them for a non-expert audience, (2) we provide specific application examples and a brief summary of advantages and drawbacks for each method, and (3) we seek to bring together scientists from different backgrounds and raise awareness on some of the challenges porous media scientists still face as a community. For these reasons, the presentation below is purposefully less technical, but broader in terms of its interdisciplinary components, than other reviews on the topic.

The manuscript is organized as follows. Section 2 contains a brief discussion of common principles underlying upscaling tools. In Sect. 3, we provide an overview of some well-known macroscale equations, including Darcy and Darcy–Brinkman equations for single-phase flow, the diffusion and the advection–reaction–dispersion equations. Sections 4, 5, 6, 7 and 8 cover the method of volume averaging, mixture theory, the thermodynamically constrained averaging method, homogenization theory and renormalization group theory, respectively. In Sect. 9, we briefly mention additional methods and provide corresponding references. We conclude with Sect. 10, where limitations of macroscale models are discussed.

## 2 Classification of Upscaling Methods

To the best of our knowledge, a categorization of upscaling tools was first proposed by Cushman (1990) and then reviewed by Cushman et al. (2002). According to Cushman et al. (2002), there are two sets of complementary hierarchies: (1) structural-functional, and (2) discrete versus continuous. A porous medium is said to have structural hierarchy if it "can be decomposed into successively nested, interacting subunits" (Cushman et al. 2002), the most classical example of which is the idealized periodic system depicted in Figures 1 and 12. "Functional hierarchy, on the other hand, relates to hierarchical transport processes within the porous medium" (Cushman et al. 2002). As the authors point out, these two types of hierarchies are intimately connected, as obvious in the homogenization of, e.g., transport processes in periodic media, where such interrelation is made apparent through small-scale boundary conditions (functional hierarchical unit) at the unit cell level (structural hierarchical unit). While such a categorization is invaluable, it has been shown that the concept of geometric scale separation (related to structural hierarchical unit) is conceptually indivisible from the characteristic temporal scales governing pore-scale process dynamics (related to functional hierarchical unit) in the context of upscaling methods (Auriault and Adler 1995; Battiato et al. 2009; Wood 2009; Battiato and Tartakovsky 2011; Arunachalam et al. 2015). As a result, such a classification may be more formal than operational. Both functional and structural hierarchies may be either discrete or continuous: "in a discrete hierarchical medium there are a finite number of nested subprocesses (subunits), whereas in a continuous hierarchical medium no clear cut decomposition evinces. [...] The major conceptual difference between discrete hierarchical systems and continuous hierarchical systems is that, in the former, constitutive laws are local (e.g., in Darcy's law the flux is related to the gradient of potential via a material parameter which may be a function of time and space), while in the latter, constitutive laws are non-local (e.g., Darcy's law may take on a convolution form or involve higher-order gradients in potential)" (Cushman et al. 2002).

Since the purpose of this review is to provide a basic multi-disciplinary introduction to various upscaling methods, and their application to different fields ranging from food processing to biomechanics and hydrology, we will primarily focus on discrete hierarchical systems and on the demonstration of how to derive local macroscale equations by means of a few different methods. However, we would like to emphasize that the methods reviewed here, and applied to derive local macroscale equations, can be used with, often small, modifications to derive (spatial and/or temporal) non-local formulations as well.

Although the various methods are somewhat distinct, the essential goal of each of them is ostensibly the same: to formally generate macroscopic scale differential balance laws, and to complete these macroscale balances by a formal closure process. Regardless, there are some distinctions among the methods that can be used to establish some advantages and disadvantages to the method. All methods have in common the definition of the average of a (pore-scale, microscale) function over a support volume and the construction of an effective equation for such average quantities. For example, let u be a real-valued function on a pore-scale domain  $\Omega_1$  that exhibits rapid spatial oscillations. It describes a certain intensive quantity u (density, velocity, temperature, concentration, etc.) and satisfies a partial differential equation

$$\mathcal{L}_1[u] = f_1,\tag{1}$$

where  $\mathcal{L}_1$  is a differential operator  $(\nabla^2[\cdot]; \partial_t[\cdot] + \nabla^2[\cdot], \text{etc.})$ . The objective of any upscaling method is to obtain a partial differential equation for a spatially averaged u,  $\langle u \rangle$ , over a suitable support volume (e.g., a representative elementary volume in the volume averaging method, the unit cell in homogenization theory, etc.) of the form

$$\mathcal{L}_2[\langle u \rangle] = \langle f_1 \rangle \tag{2}$$

where  $\mathcal{L}_1[\cdot]$  and  $\mathcal{L}_2[\cdot]$  may be two different operators and, e.g., the local average of *u* can be defined as

$$\langle u \rangle |_{(\mathbf{x})} = \langle u \rangle (\mathbf{x}) = \frac{1}{|\mathcal{V}|} \int_{\mathbf{y} \in \mathcal{V}(\mathbf{x})} u(\mathbf{y}) d\mathbf{y}.$$
 (3)

The support volume  $\mathcal{V}(\mathbf{x}) \in \Omega_1$  "is a small, but not too small, neighborhood of point  $\mathbf{x}$  of the size of a representative elementary volume, REV (several hundred or thousand of pores)" (Hornung 1997, p. 1). The ambiguity in defining the size of an REV is typical. For example, in de Marsily (1986) "the size of the REV is defined by saying that it is

- Sufficiently large to contain a great number of pores so as to allow us to define a mean global property, while ensuring that the effects of the fluctuations from one pore to another are negligible. One may take, for example, 1 cm<sup>3</sup> or 1 dm<sup>3</sup>;
- Sufficiently small so that the parameter variations from one domain to the next may be approximated by continuous functions, in order that we may use infinitesimal calculus."

A necessary component of any upscaling method is based on the following observation: "It is well admitted that the existence of continuum behaviors that are macroscopically equivalent to finely heterogeneous media needs a good separation of scales. If l and L are the characteristic lengths at the local and the macroscopic scale, respectively, their ratio should obey"

$$\varepsilon = \frac{l}{L} \ll 1 \tag{4}$$

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(Auriault et al. 2005). Furthermore, most of the approximations needed to derive (2) from (1) originate from a *localization approximation*, i.e., exchanging the order of spatial integration/averaging and differentiation operators,

$$\langle \mathcal{L}_1[u] \rangle \approx \mathcal{L}_2[\langle u \rangle].$$
 (5)

Each method deals with such an approximation in a slightly different fashion. Nonlinearity of governing equations complicates the upscaling of most reactive transport phenomena since it often requires a linearization and/or other approximations, whose accuracy and validity, with a few exceptions, cannot be ascertained *a priori*. Additionally, even if based on different definitions of the averaging volume and on distinct mathematical tools, all upscaling methods require *closure assumptions* to decouple the average system behavior from the pore-scale information: the latter is exclusively incorporated into the upscaled equation through effective parameters that can be determined by laboratory experiments or numerical solution of a closure problem at the unit cell level.

In the following section, we present some of the equations governing flow and transport in porous media, including Darcy's and Darcy–Brinkman equations, the advection–reaction– dispersion equation, etc.

## 3 From First Principles to Effective Medium Theories: An Overview

We consider a porous medium consisting of a solid matrix  $\Omega_s$  and a fluid-filled pore space  $\Omega_1$ . We define  $\Omega := \Omega_s \cup \Omega_1$  and call it a *porous medium*. While upscaling methods can be used to connect any two adjacent scales, generally referred to as microscale and macroscale, here we will primarily discuss the connection between pore- (micro-) and macro-scale descriptions of transport processes in  $\Omega$ , although we will present, for demonstration only, one single example of upscaling from the dynamics of individual Brownian particles to effective diffusion. Furthermore, we emphasize that the mathematical machinery of upscaling techniques can be generally applied with little modifications to any two arbitrary adjacent scales.

Differently from the nomenclature used by Davit et al. (2013) and in line with that of Hornung (1997), here we will refer to the term *upscaling* as the process of deriving macroscale equations from microscale principles, and to the term *upscaling methods* as a broad class of analytical techniques devised for this scope, homogenization (by multiple-scale expansions) being one of them. Mathematical approaches to upscaling include the method of volume averaging (Whitaker 1999) and its modifications (Kechagia et al. 2002), generalizations of the method of moments (Shapiro and Brenner 1986, 1988; Shapiro et al. 1996), homogenization via multiple-scale expansions (Adler 1992; Hornung 1997), pore-network models (Acharya et al. 2005), and thermodynamically constrained averaging (Gray and Miller 2014). A number of other approaches to upscaling are reviewed by Brenner (1987), Wood (2000), Cushman et al. (2002), Neuman and Tartakovsky (2009), Davit et al. (2013), Grmela (2010), and are listed in more detail in Sect. 9.

In the following, we present some classical results from upscaling theories applied to flow and transport problems in porous media.

#### 3.1 Momentum Transport: From the Navier–Stokes Equations to Macroscale Laws

Momentum transport of a single-phase flow of an incompressible Newtonian fluid in the pore space  $\Omega_1$  of a rigid porous medium is described by the Navier–Stokes and the continuity

equations subject to appropriate boundary conditions on  $A_{ls}$ , e.g., the no-slip condition,

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v}\right) = \mu \nabla^2 \mathbf{v} - \nabla p, \quad \nabla \cdot \mathbf{v} = 0, \quad \mathbf{x} \in \Omega_1, \quad \text{and} \quad \mathbf{v} = \mathbf{0}, \quad \mathbf{x} \in A_{\text{ls}},$$
(6)

where  $\mathbf{v}(\mathbf{x})$  is the fluid velocity, *p* denotes the fluid dynamic pressure,  $\rho$  is the fluid density, and  $\mu$  is the dynamic viscosity. For small Reynolds numbers (smaller than 1, i.e., under creeping flow conditions), typical of many porous media flows, the inertial terms in the Navier–Stokes equation are negligible compared to the viscous terms: Eq. (6) simplifies to the Stokes equations subject to the no-slip boundary condition on  $A_{ls}$ ,

$$\mu \nabla^2 \mathbf{v} - \nabla p = 0, \quad \nabla \cdot \mathbf{v} = 0, \quad \mathbf{x} \in \Omega_{\mathrm{l}}, \qquad \mathbf{v} = \mathbf{0}, \quad \mathbf{x} \in A_{\mathrm{ls}}.$$
(7)

Upscaling of the Stokes equations (7) at the pore-scale to the macroscale has been the subject of numerous investigations, including those relying on multiple-scale expansions (Auriault and Adler 1995; Mikelic et al. 2006; Peter 2007; Marušić-Paloka and Piatnitski 2005, and references therein), volume averaging (Neuman 1977, and references therein), the method of moments, etc. These studies have demonstrated that Darcy's law, which was empirically established by Darcy (1856), and the continuity equation for  $\langle v \rangle$ ,

$$\langle \mathbf{v} \rangle = -\frac{\mathbf{K}}{\mu} \cdot \nabla \langle p \rangle, \quad \nabla \cdot \langle \mathbf{v} \rangle = 0, \quad \mathbf{x} \in \Omega,$$
 (8)

provide an effective representation of the pore-scale Stokes flow, e.g., (Hornung 1997, Eq. 4.7). Such upscaling procedures also enable one to formally define the permeability tensor **K** in (8) as the average of a suitably defined "closure variable"  $\mathbf{k}(\mathbf{y})$ , i.e.,  $\mathbf{K} = \langle \mathbf{k}(\mathbf{y}) \rangle$ . The latter is the unique solution of a local problem, e.g., Hornung (1997, pp. 46-47, Theorem 1.1) and Auriault and Adler (1995, Eq. 22), defined on a representative (unit) cell of the porous medium.

To describe flow through "hyperporous" media Brinkman (1949) introduced a modification of Darcy's law,

$$\nabla \langle p \rangle = -\mu \mathbf{K}^{-1} \langle \mathbf{v} \rangle + \mu_e \nabla^2 \langle \mathbf{v} \rangle, \tag{9}$$

where  $\mu_e$  is an effective viscosity "which may differ from  $\mu$ " (Brinkman 1949). The *raison d'etre* for such a modification was the necessity of obtaining an equation that was valid in the high permeability limit ( $|\mathbf{K}| \rightarrow \infty$ ) and that allowed for a direct coupling with the Stokes equations at interfaces separating Stokes flow (infinite permeability regions) and filtration flow (low-permeability regions). In Brinkman's words, "this equation has the advantage of approximating (8) for low values of **K** and (7) for high values of **K**."

After its introduction and its widespread use, an increasing research effort was devoted to the identification of domains of validity of both Darcy's and Brinkman's law (Lévy 1983; Auriault 2009; Durlovsky and Brady 2009, and references therein). Brinkman's intuition was mathematically proven later by Goyeau et al. (1997) and Auriault et al. (2005), who used, respectively, the method of volume averaging and homogenization by multiple-scale expansions to demonstrate that Brinkman's equation represents a higher-order approximation of Darcy's law when the separation of scales is poor. Poor-scale separation can be encountered in two typical situations. "The first one occurs when the porous medium is macroscopically heterogeneous, when the macroscopic characteristic length *L* associated with the macroscopic heterogeneities is not very large compared to the characteristic length *l* of the pores. For such media, length *L* can be estimated by  $L \approx K/|\nabla K|$ , where *K* is the permeability. When the macroscopic gradient of the permeability  $|\nabla K|$  is large, the ratio l/L may not be very small and the separation of scale is poor. The second typical situation corresponds to large gradients of pressure which are applied to macroscopically homogeneous media. The macroscopic characteristic length  $L \approx p/|\nabla p|$  associated with this gradient of pressure could be not very large compared to l" (Auriault et al. 2005). In a subsequent work, Auriault (2009) defines the applicability range of Darcy's and Brinkman's equations in terms of the geometric parameters of three classes of porous media: classical porous media characterized by connected porous matrix (e.g., capillary tubes), swarms of fixed particles with connected pore space, and fibrous media. It is finally concluded that the validity domain of Brinkman's equation corresponds to porous media with very large porosity and very small solid concentration.

Deviations from linear Darcy-type relationships of the type (8) and (9) occur when deviating from the creeping flow assumption, i.e., in the presence of non-negligible fluid inertial (yet, non-turbulent) effects or moderate Reynolds numbers. Andrade Jr. et al. (1998) demonstrated that departure from the classical Darcy's law in 2D disordered porous media could already be observed in a steady, inertial flow before a full transition to turbulence. This deviation was already experimentally observed by Forchheimer (1901) at the beginning of the twentieth century, who added a quadratic term to Darcy's equation to account for inertial effects at the microscale

$$-\nabla \langle p \rangle = \mu \mathbf{K}^{-1} \cdot \langle \mathbf{v} \rangle + \beta \rho \| \langle \mathbf{v} \rangle \| \langle \mathbf{v} \rangle$$
(10)

where  $\beta$  is an empirical coefficient that depends of the porous medium microstructure. Similar to the history of Darcy's equation, Forchheimer equation, first introduced heuristically, was theoretically derived many years later from its original inception. Many upscaling methods have been used to rigorously establish its relationship to the Navier–Stokes equation including, but not limited to, homogenization theory by matched asymptotic expansions (Giorgi 1997; Marušić-Paloka and Mikelic 2000), hybrid mixture theory (Hassanizadeh and Gray 1987) and the method of volume averaging (Whitaker 1996; Wood et al. 2020). Further generalizations of Darcy's equation to account for, e.g., gas slip and inertia effects are reviewed by Lasseux and Valdés-Parada (2017).

While different in their form, all the previous macroscale equations for momentum transport at the macroscale are all based on a separation of scale hypothesis ( $\varepsilon < 1$ ) and are obtained from the upscaling of the Navier–Stokes equations under different dynamical conditions (e.g., for creeping flow hypothesis, non-negligible inertial effects, etc.). This highlights one additional important feature of upscaling techniques, i.e., the ability to obtain a *family of macroscale models* from their corresponding pore-scale equations, once the underlying dynamics at the microscale is known or postulated (often expressed in terms of relevant dimensionless numbers—in this case, the Reynolds number).

## 3.2 Mass Transport: From Brownian Motion to Dispersion

In the following, we will briefly discuss the equations governing mass transport. We start with a sketch of the derivation of the diffusion equation from the motion of a Brownian particle in a fluid at rest, and later, we present the equations governing mass transport for reactive species at the macroscale.

*From Brownian Motion to Diffusion.* Einstein's paper on the effective/macroscale motion of a Brownian particle in a stationary liquid, one of his most cited works, is the first example of upscaling from the dynamics at the discrete particle level to the continuum scale (Ein-

stein 1905) [or its unabridged and unaltered republication in 1956 (Einstein 1956)]. Einstein demonstrated that the macroscopic representation of thermal molecular motion (i.e., Brownian motion) gives rise to the diffusion equation. In the following, we provide a sketch of his proof, as one example of the mathematical techniques (and necessary assumptions) needed to pass from a particle-scale description to an effective-scale representation.

Under the assumption that (i) each particle moves independently from other particles and that (ii) displacements of a given particle in different time intervals  $\tau$  are mutually independent processes (i.e.,  $\tau$  is small compared to the observation time, but large enough such that particle displacements at two consecutive time intervals can be considered uncorrelated), then the number dn of particles experiencing a 1D displacement (along the *X*-coordinate) that lies between  $\Delta$  and  $\Delta + d\Delta$  in a time interval  $\tau$  is

$$\mathrm{d}n = n\phi(\Delta)\mathrm{d}\Delta\tag{11}$$

where  $\int_{-\infty}^{+\infty} \phi(\Delta) d\Delta = 1$ , is a normalization condition,  $\phi$ , which differs from zero only for small values of  $\Delta$ , is the probability density function (pdf) of the particle displacements  $\Delta$ , and  $\phi(\Delta) = \phi(-\Delta)$ . If v = f(x, t) = n/dx is the particle density, i.e., the number of particles per unit volume (or unit length in a 1D space), then the number of particles found at time  $t + \tau$  between two plans perpendicular to the *X*-axis at locations *x* and x + dx is

$$f(x, t+\tau)dx = dx \int_{\Delta = -\infty}^{\Delta = +\infty} f(x+\Delta, t)\phi(\Delta)d\Delta.$$
 (12)

Since  $\tau$  and  $\Delta$  are very small,  $f(x, t + \tau)$  and  $f(x + \Delta, t)$  can be expanded in powers of  $\tau$  and  $\Delta$ , respectively, and (13) can be written as

$$f + \tau \frac{\partial f}{\partial t} = f \int_{\Delta = -\infty}^{\Delta = +\infty} \phi(\Delta) d\Delta + \frac{\partial f}{\partial x} \int_{\Delta = -\infty}^{\Delta = +\infty} \Delta \phi(\Delta) d\Delta + \frac{\partial^2 f}{\partial x^2} \int_{\Delta = -\infty}^{\Delta = +\infty} \frac{\Delta^2}{2!} \phi(\Delta) d\Delta.$$
(13)

Accounting for  $\phi$ 's normalization condition, while recognizing that the second term on the RHS is identically equal to zero since  $\phi$  is an odd function, leads to

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2},\tag{14}$$

where *D* is the effective diffusion coefficient and is defined as  $D := \tau^{-1} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2} \phi(\Delta) d\Delta$ and *f* corresponds to the molar concentration of a solute. Equation (14) is the classical diffusion equation satisfied by the particle density, i.e., the solute concentration. While the derivation proposed by Einstein is, to some extent, different from the methods discussed in the following, it does retain a critical feature of any upscaling procedure: the assumption that separation of scales (in this case, temporal ones) exists, i.e., that a "REV" in time of characteristic size  $\tau$  can be identified such that it is small compared to the observation (macroscale) time, but large enough such that particle displacements can be considered uncorrelated.

From Diffusion to Dispersion. Let us now move to a larger scale, i.e., the pore scale. Let us assume that the fluid saturating a porous medium contains a dissolved species  $\mathcal{M}$ , whose molar concentration  $c(\mathbf{x}, t) \, [\text{molL}^{-3}]$  at point  $\mathbf{x} \in \Omega_1$  and time t > 0 changes due to advection (due to fluid motion), molecular diffusion, homogeneous reaction in the liquid phase and heterogeneous reaction at the solid–liquid interface  $A_{\text{ls}}$ . The first three phenomena are described by an advection–diffusion–reaction equation,

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = \nabla \cdot (\mathbf{D} \nabla c) + R(c), \quad \mathbf{x} \in \Omega_1, \quad t > 0,$$
(15)

where the molecular diffusion coefficient **D** is, in general, a positive-definite second-order tensor. If diffusion is isotropic,  $\mathbf{D} = \mathcal{D}_m \mathbf{I}$  where  $\mathcal{D}_m [L^2 T^{-1}]$  is the diffusion coefficient and **I** is the identity matrix. The source term R(c) represents a generic homogeneous reaction occurring in the liquid phase. At the solid–liquid interface  $A_{\rm ls}$  impermeable to flow, mass conservation requires that mass flux of the species  $\mathcal{M}$  be balanced by net mass flux due to heterogeneous reaction occurring at the interface between solid and liquid phases, Q(c),

$$-\mathbf{n} \cdot \mathbf{D} \nabla c = Q(c), \qquad \mathbf{x} \in A_{\mathrm{ls}}.$$
 (16)

In addition to (16), flow and transport equations (7) and (15) are supplemented with boundary conditions on the external boundary of the flow domain  $\Omega$ . The upscaling of (15) and (16) leads to effective equations for the average concentration  $\langle c \rangle$ , generally written in the following form

$$\frac{\partial \langle c \rangle}{\partial t} + \langle \mathbf{v} \rangle \cdot \nabla \langle c \rangle = \nabla \cdot (\mathbf{D} \nabla \langle c \rangle) + \overline{R}(\langle c \rangle) + \overline{Q}(\langle c \rangle), \quad \mathbf{x} \in \Omega, \quad t > 0,$$
(17)

where  $\overline{R}(\langle c \rangle)$  and  $\overline{O}(\langle c \rangle)$  are effective reactive sources, and **D**\* is an effective dispersion coefficient. It is worth noticing that the source term  $\overline{Q}$  in (17) originates from the spatial upscaling of the boundary condition (16) under a specific set of assumptions as discussed in (Battiato and Tartakovsky 2011; Boso and Battiato 2013). A significant research effort and ingenuity has been devoted to the upscaling of various functional forms of R(c) and Q(c)relevant to engineering, chemical, biochemical, hydrological and other applications. Beside the requirement that geometric scale separation exists between the pore- (microscale) and the macroscale, a number of works have demonstrated that dynamic constraints, imposed on relevant dimensionless numbers, should be satisfied for the microscale equation (15) to be upscaled to the form of Eq. (17). For example, upscaling approaches that rely on characteristic dimensionless numbers (e.g., the Damköhler and Péclet numbers) can provide quantitative measures for the validity of various upscaling approximations. Auriault and Adler (1995) used multiple-scale expansions to establish the applicability range of advection-dispersion equation for a non-reactive solute in terms of Péclet number. Mikelic et al. (2006) provided a rigorous upscaled version of the Taylor dispersion problem with linear heterogeneous reaction. For flow between two parallel reacting plates they established the applicability range of the upscaled equation in terms of Damköhler and Péclet numbers. These results were later generalized, in the context of homogenization method, by Battiato and Tartakovsky (2011), who also demonstrated that bounds on dimensionless numbers can be successfully used to a priori assess macroscale models predictivity (Boso and Battiato 2013; Korneev and Battiato 2016; Ling et al. 2016) by defining applicability conditions of given macroscale models, and consequently employed as criteria for algorithm refinement techniques, where equations describing the same physics at different scales have to be coupled within the same simulation domain (e.g., Peszynska et al. 2000; Alexander et al. 2002, 2005; Battiato et al. 2011; Sun et al. 2012; Taverniers et al. 2014; Youzefzadeh and Battiato 2017). In the context of the method of volume averaging, Wood (2009) discussed the critical role that scaling laws have on the upscaling process. Similar concepts, necessary to guarantee that any closure relation is consistent with the second law of thermodynamics, and referred to as "permissibility conditions", have been formally elaborated in the thermodynamically constrained averaging theory (TCAT). Finally, such applicability/permissibility conditions or scaling laws (i) represent an additional layer of (dynamic) constraints (compared to the static constraints of geometric scale separation) that represent sufficient (but not necessary) conditions for any macroscale

model to be valid and (ii) should be upscaling method-independent as they should be exclusively controlled by the physics at the microscale only. Although there is no hard proof of the latter point, some studies (Battiato et al. 2009; Battiato and Tartakovsky 2011) appear to support this observation.

In the following sections, we provide an introduction to four different methods: the method of volume averaging (Sect. 4), mixture theory (Sect. 5), thermodynamically constrained averaging theory (Sect. 6), homogenization theory (Sect. 7) and renormalization group theory (Sect. 8). Each section is organized as follows: the first subsection describes the fundamentals of the technique and the most critical concepts; the second subsection shows a specific application of the method discussed; the last subsection provides a brief discussion of advantages and drawbacks. We emphasize that each section is stand-alone and can be read separately. The notation, unique to each method, was purposefully left unchanged (to the detriment of text uniformity) so to remain consistent with the already (large body of) published literature: this will help the interested reader in navigating the existing literature without unnecessary confusion due to inconsistent notation. Finally, due to space and time constraints, additional, yet not less relevant, methods are only briefly mentioned in Sect. 9.

## 4 Method of Volume Averaging

The method of volume averaging (MVA) is one of a suite of methods that are used to developed spatially smoothed representations of balance laws in porous materials. In this section, the approach commonly referred to as the method of volume averaging (MVA) is reviewed and discussed. The basic features of this method are well described in a number of resources (Whitaker 1999; Wood and Valdés-Parada 2013). Thus, our approach for this presentation will be to review the basic features more lightly and spend more focus on new developments in the method.

## 4.1 Fundamentals

## 4.1.1 Geometry and Topology

In this presentation, we will assume that there are two primary scales of interest and that these scales are well separated in the sense of having disparate characteristic length scales (these length scales can be thought of as finite integral scales as described in Wood and Valdés-Parada (2013). The larger of the two scales is usually called the *macroscale*, and the smaller of these the *microscale* regardless of the actual magnitude of the length scales involved. A schematic of a two-scale system is illustrated in Fig. 1.

Simplifying further, for this overview we assume that the medium of interest is composed of only two phases: a solid phase (the porous medium, referred to as the  $\kappa$ -phase) and a fluid phase (which could be a gas or liquid, and is referred to as the  $\gamma$ -phase).

Within the macroscopic domain  $\mathcal{V}^0$ , the system is composed of the union of three subdomains: The solid, the fluid and the interfacial area between the two phases. Symbolically,

$$\mathcal{V}^0 = \mathcal{V}^0_{\gamma} \cup \mathcal{A}^0_{\gamma\kappa} \cup \mathcal{V}^0_{\kappa} \tag{18}$$

The domain is compact, so we also consider the boundary with the external environment; this boundary is arbitrary, but, depending upon the applications involved, boundary data must be supplied there. Generally, this arbitrary boundary cuts across both the fluid and solid phases. Thus, the external boundary can be represented by



Fig. 1 a An averaging volume with centroid located at the position  $\mathbf{x}$ . **b** Details of the relationship among the vectors  $\mathbf{r}$ ,  $\mathbf{x}$ , and  $\mathbf{y}$ 

$$\mathcal{A}^0_{\rho} = \mathcal{A}^0_{\nu\rho} \cup \mathcal{A}^0_{\kappa\rho}. \tag{19}$$

In this notation, the superscript "0" indicates that these quantities are defined for the entirety of the macroscopic domain. These sets fully specify the macroscopic domain and its boundary.

Within this system, one can identify compact averaging volumes; typically, we assume that averaging volumes have a support domain with characteristic length scale  $r_0$ . A similar set of domains can be defined for any such averaging volume. Thus, we have

$$\mathcal{V}(\mathbf{x}) = \mathcal{V}_{\gamma}(\mathbf{x}) \cup \mathcal{A}_{\gamma\kappa}(\mathbf{x}) \cup \mathcal{V}_{\kappa}(\mathbf{x})$$
(20)

and

$$\mathcal{A}_{e}(\mathbf{x}) = \mathcal{A}_{\gamma e}(\mathbf{x}) \cup \mathcal{A}_{\kappa e}(\mathbf{x}).$$
<sup>(21)</sup>

Here, we have adopted the notation "( $\mathbf{x}$ )" to indicate that each averaging volume is located by its centroid at  $\mathbf{x}$ . This does not indicate that the *geometry* of the averaging volume domain changes with  $\mathbf{x}$  [although this is possible (Cushman 1983)]. Rather, it is indicated only as a coordinate that uniquely defines the support of any averaging operation.

There has been substantial discussion regarding the appropriate continuity conditions for the boundaries between phases and at the external boundaries within and bounding an averaging volume (e.g., Mls 1987). Although more general conditions can almost certainly be stated, it appears to be sufficient to require that boundaries have at least the characteristics of a Lipschitz function. In short, this simply means that the interface has (1) a unit normal defined everywhere except possibly a set of zero measure (i.e., there can be cusps or kinks on the interface, but these do not contribute to subsequent integrations) and (2) the derivative of a volume averaged quantity is well defined by the spatial averaging theorem (discussed in the following), except perhaps on a set of zero measure.

#### 4.1.2 The Averaging Process

Averages. The MVA was originally formulated using both compact, square-integrable  $C^{\infty}$  bump or test functions (Marle 1967), and also using compact discontinuous functions (Slattery 1967; Whitaker 1967). A popularly cited paper by Anderson and Jackson (1967) adopted an approach using non-compact, square-integrable  $C^{\infty}$  functions, which is useful only for cases of problems in unbounded domains.

The set of functions that include both the bump functions and the compact discontinuous functions has been informally referred to as *weighting functions* to distinguish them from proper  $C^{\infty}$  *test functions* that appear in the theory of distributions (Quintard and Whitaker 1994a, b, c, d). The conventional form of the superficial volume average is given as follows. For a field variable,  $\psi(\mathbf{r}, t)$  (and noting  $\mathbf{r} = \mathbf{x} + \mathbf{y}$ ), the volume average for the fluid phase as defined by Whitaker (1999) and Slattery (1999) has generally been presented as

$$\langle \psi_{\gamma} \rangle \Big|_{(\mathbf{x},t)} = \frac{1}{V} \int_{\mathbf{y} \in \mathcal{V}_{\gamma}(\mathbf{x})} \psi_{\gamma}(\mathbf{x} + \mathbf{y}, t) \mathrm{d}V(\mathbf{y})$$
 (22)

Here, the definitions of the averaging domain are illustrated in Fig. 1.

Averaging in the context of weighting functions. The domain of averaging is a compact spatial region indicated by  $\mathcal{V}_{\gamma}(\mathbf{x})$  as described above. For the classical theory, the weighting function is uniform and is given the value 1/V. However, any well-defined weighting functions can be considered. In particular, this expression can be re-written in a form that is consistent with conventional distribution theory, which is the approach we pursue here. To start, we first define an indicator function for the  $\gamma$ -phase

$$I_{\gamma}(\mathbf{x}) = \begin{cases} 1, & \mathbf{x} \in V_{\gamma} \\ 0, & \mathbf{x} \in V_{\kappa} \end{cases}$$
(23)

We will assume that w represents an appropriate compact  $C^{\infty}$  test function, conventional distribution theory allows the *superficial* volume average to be written in the form

$$\langle \psi_{\gamma} \rangle \Big|_{(\mathbf{x},t)} = \int_{\mathbf{y} \in \mathcal{V}(\mathbf{x})} w(\mathbf{y}) \psi_{\gamma}(\mathbf{x} + \mathbf{y}, t) I_{\gamma}(\mathbf{x} + \mathbf{y}) \mathrm{d}V(\mathbf{y})$$
(24)

where now w is a (fixed) symmetric  $[w(-\mathbf{y}) = w(\mathbf{y})] C^{\infty}$  test function (however, see the discussion below regarding the admissibility of non-smooth weighting functions w), noting in particular that now the integral is formed over the volume  $\mathcal{V}$  rather than only the  $\gamma$ -phase. In applications, weighting functions can serve to represent (1) the response of real instruments used in the measurement process (Baveye and Sposito 1984; Cushman 1984), (2) convenient domain restriction for the purposes of mathematical modeling (as in, for example, the boxcar weighting function mentioned previously), or (3) as a mollifying function used purposefully to smooth out undesirable oscillatory behavior, particularly in periodic models of media (Davit and Quintard 2017; Quintard and Whitaker 1994b). Note that although we pursue smooth functions here, there may be significant utility in the use of non- $C^{\infty}$  functions (Davit and Quintard 2017).

The definition given by Eq. (24) allows one to define the porosity by

$$\varepsilon_{\gamma}(\mathbf{x}) = \int_{\mathbf{y} \in \mathcal{V}(\mathbf{x})} w(\mathbf{y}) I(\mathbf{x} + \mathbf{y}) \mathrm{d}V(\mathbf{y}).$$
(25)

With this definition, the *intrinsic* volume average can then be specified by

$$\langle \psi_{\gamma} \rangle^{\gamma} \Big|_{(\mathbf{x},t)} = \frac{1}{\varepsilon_{\gamma}} \int_{\mathbf{y} \in \mathcal{V}(\mathbf{x})} w(\mathbf{y}) \psi_{\gamma}(\mathbf{x} + \mathbf{y}, t) I_{\gamma}(\mathbf{x} + \mathbf{y}) \mathrm{d}V(\mathbf{y}).$$
 (26)

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Fig. 2 Two closed-form,  $C^{\infty}$  test or weighting functions. These represent mollified versions of the boxcar and triangle weighting functions

We provide two examples of smooth functions based on the non-smooth boxcar and triangle weighting functions. On a superficial level, these functions are like their non-smooth counterparts; however, they have been convolved with a mollifying function so that the results are  $C^{\infty}$ . In short, the following two functions represent smoothed versions of the boxcar  $(w_{\Box})$  and the triangle  $(w_{\Delta})$  weighting functions (in one-dimension) smoothed with a  $C^{\infty}$  bump function, normalized to have a unit area and a total width of  $2r_0$ . In this expression,  $r_0$  is the characteristic length of the weighting function domain, and  $\epsilon_0$  is the characteristic dimension of the mollifying (smoothing) function (Fig. 2), whose width can be "tuned" depending upon application. These functions are  $C^{\infty}$  functions because the smoothing function is itself  $C^{\infty}$ ; the generic shape of these functions is illustrated in Fig. 2.

The spatial averaging theorem. A key component of the MVA is what is termed the spatial averaging theorem (SAT). The SAT was first proposed independently by a number of researchers in 1967 (Whitaker 1967; Slattery 1967; Anderson and Jackson 1967; Marle 1967), and it has been re-visited many times since (Mls 1987; Gray and Lee 1977; Veverka 1981; Cushman 1982; Howes and Whitaker 1985). Although geometrically oriented proofs are available (Whitaker 1985; Slattery 1999), the most successful proofs have relied on developments via distribution theory. Although Marle (1967) presented the spatial averaging theory in the context of distributions, the extension to three-dimensions was proposed without proof [although a rough proof was offered later, (Marle 1982a)]. The first proper proof via distribution theory appears to be that given by Cushman (1982). However, the essential feature is the interpretation of the gradient of the indicator function  $I(\mathbf{x})$ , which was developed earlier in a number of references (e.g., Schwartz 1966; Shilov 1968; Farassat 1977; Jones 1982; Kanwal 1983).

In the context of distribution theory, the SAT is straightforward to derive. Taking the gradient of both sides of Eq. (24), one finds (note: all gradient operators are with respect to the variable **x** unless otherwise indicated).

$$\nabla \langle \psi_{\gamma} \rangle \Big|_{(\mathbf{x},t)} = \int_{\mathbf{y} \in \mathcal{V}(\mathbf{x})} w(\mathbf{y}) \nabla [\psi_{\gamma}(\mathbf{x} + \mathbf{y}, t) I(\mathbf{x} + \mathbf{y})] \mathrm{d}V(\mathbf{y})$$
(27)

One now applies the product rule (in a distributional sense) to obtain

$$\nabla \langle \psi_{\gamma} \rangle \Big|_{(\mathbf{x},t)} = \int_{\mathbf{y} \in \mathcal{V}(\mathbf{x})} w(\mathbf{y}) I_{\gamma}(\mathbf{x} + \mathbf{y}) \nabla \psi_{\gamma}(\mathbf{x} + \mathbf{y}, t) \mathrm{d}V(\mathbf{y}) + \int_{\mathbf{y} \in \mathcal{V}(\mathbf{x})} w(\mathbf{y}) \psi_{\gamma}(\mathbf{x} + \mathbf{y}, t) \nabla I_{\gamma}(\mathbf{x} + \mathbf{y}) \mathrm{d}V(\mathbf{y})$$
(28)

Noting the identity (Gray and Lee 1977; Kanwal 1983)

$$\nabla I_{\gamma} = -\mathbf{n}_{\gamma\kappa} \delta_{\gamma\kappa}(\Sigma) \tag{29}$$

In this last expression,  $\delta_{\gamma\kappa}(\Sigma)$  is a surface-delta distribution (Kanwal 1983), where  $\Sigma = \{\mathbf{x} : \mathbf{x} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})\}$ . Thus, the final integral can be reduced, and the SAT expressed by

$$\langle \nabla \psi_{\gamma} \rangle \Big|_{(\mathbf{x},t)} = \nabla \langle \psi_{\gamma} \rangle \Big|_{(\mathbf{x},t)} + \int_{\mathbf{y} \in \mathcal{A}(\mathbf{x})} \mathbf{n}_{\gamma \kappa} w(\mathbf{y}) \psi_{\gamma}(\mathbf{x}+\mathbf{y},t) \mathrm{d}V(\mathbf{y})$$
(30)

Note that for periodic systems that have planes of symmetry in both the geometry and the field  $\psi_{\gamma}$ , the area integral may be identically zero.

#### 4.2 Applications

As described in the previous section, porous media systems that are *physically* periodic have some advantages that have made them viable options in applications (Kreutzer et al. 2006). As examples, it has been well known that periodic media have a generally lower pressure drop per unit length than random media (Pangarkar et al. 2008) and can also provide for a more efficient use of reactant in catalytic beds (Vervloet et al. 2013). Thus, the costs for pumping and catalyst materials for a structured medium may actually be lower than equivalent random media. Even modest increases in efficiency are often economically worthwhile in applications, so the consideration of physically periodic porous media is far from an abstract problem.

In the material that follows, we examine the upscaling of a physically periodic medium where the medium has a period that is finite. This problem presents some interesting complexities in upscaling despite the simplicity of the geometry. Although volume averaging is usually applied to the transient form of balance equations, here we make the simplification that we will be considering initially the steady-state solution of diffusion in a periodic medium.

To start, we consider the following problem of pure (dilute) steady diffusion in a periodic material with finite scale for the period.

$$\nabla \cdot \left( \mathcal{D}_{A\gamma} \nabla c_{A\gamma} \right) = 0, \quad \text{for } \mathbf{r} \in \mathcal{V}_{\gamma}(\mathbf{x}) \tag{31}$$

B.C. 1 
$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathcal{D}_{A\gamma} \nabla c_{A\gamma}) = 0, \quad \text{for } \mathbf{r} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})$$
 (32)

B.C. 2 
$$c_{A\nu} = \mathcal{F}_{\nu}(\mathbf{r}, t), \quad \text{for } \mathbf{r} \in \mathcal{A}_{\nu e}(\mathbf{x})$$
 (33)

Here  $\mathcal{D}_{A\gamma}$  is the (Fickian) molecular diffusion coefficient,  $c_{A\gamma}$  is the concentration, and  $\mathcal{F}_{\gamma}$  is a function that describes the concentration on the fluid-phase boundary of  $\mathcal{V}_{\gamma}$ . This set of equations applies to the microscale and describes the process of mass transfer via diffusion (under the dilute solution approximation) everywhere in the medium. Although the problems appears simple, the boundary conditions for the inlet and outlet (B.C. 2) essentially drive the problem, and they subvert the otherwise *simple* periodic geometric structure. Thus, the description of the diffusion process over the entire domain  $\mathcal{V}_{\gamma}$  is, in principle, a non-trivial problem.

The goal of volume averaging is that there is to identify and capitalize on statistical or geometric *redundancies* in the information content of complex systems. We will not pursue concrete notions of information content in this work (although these concepts can be made concrete), as the idea has enough intuitive appeal to convey the essential features of the upscaling process.

To proceed, we apply the averaging operations defined previously to both sides of the diffusion balance equation. Upon averaging this one time with application of the spatial averaging theorem, we find

$$\nabla \cdot \left( \mathcal{D}_{A\gamma} \langle \nabla c_{A\gamma} \rangle \right) + \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \cdot \left( \mathcal{D}_{A\gamma} \nabla c_{A\gamma}(\mathbf{x} + \mathbf{y}) \right) w(\mathbf{y}) \, \mathrm{d}A(\mathbf{y}) = 0.$$
(34)

Here, V is the measure of the domain  $\mathcal{V}$ . Note that because of the boundary condition at the fluid–solid interface, this expression is immediately reducible to

$$\nabla \cdot \left( \mathcal{D}_{A\gamma} \langle \nabla c_{A\gamma} \rangle \right) = 0. \tag{35}$$

Applying the spatial averaging theorem a second time yields the result

$$\nabla \cdot \left[ \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle + \mathcal{D}_{A\gamma} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa}(\mathbf{x} + \mathbf{y}) c_{A\gamma}(\mathbf{x} + \mathbf{y}, t) w(\mathbf{y}) \, \mathrm{d}A(\mathbf{y}) \right] = 0.$$
(36)

To make further progress, it is useful to define the deviation concentration by

$$c_{A\gamma}(\mathbf{x}) = \langle c_{A\gamma} \rangle^{\gamma} |_{\mathbf{x}} + \tilde{c}_{A\gamma}(\mathbf{x}).$$
(37)

In the remainder of the paper, we will not explicitly list the independent variables unless they are needed for clarity. Substituting this definition into the averaged balance equation yields

$$\nabla \cdot \left[ \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle + \mathcal{D}_{A\gamma} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \langle c_{A\gamma} \rangle^{\gamma} w(\mathbf{y}) \, \mathrm{d}A(\mathbf{y}) \right. \\ \left. + \mathcal{D}_{A\gamma} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \tilde{c}_{A\gamma} w(\mathbf{y}) \, \mathrm{d}A(\mathbf{y}) \right] = 0.$$
(38)

At this juncture, we can follow the example of Whitaker (1999, Chp. 1) which suggests expanding the average concentration as a Taylor series and then adopts a sequence of *geometric theorems* to make further simplifications. Typically, the center of mass of the  $\gamma$ -phase is assumed to be constant. However, for a periodic averaging volume, the center of mass fluctuates across the course of one period as the location of the  $\gamma$ -phase changes with respect to the centroid of the averaging volume. Although the conventional order-of-magnitude arguments will not allow us to simplify the problem (because these arguments are essentially a form of *spatial stationarity* criteria for the geometric structure of the  $\gamma$ -phase), we can adopt an approximate approach. For this, we suggest that the flux of the average concentration across the averaging volume can be well approximated by a linear function. Thus, the Taylor series is, explicitly, approximated by

$$\langle c_{A\gamma} \rangle^{\gamma} |_{(\mathbf{x}+\mathbf{y})} = \langle c_{A\gamma} \rangle^{\gamma} |_{(\mathbf{x})} + \mathbf{y} \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma} |_{\mathbf{x}}, \qquad (39)$$

where **y** is a set of vectors pointing to every location of the  $\gamma$ -phase relative to the centroid of the averaging volume. Introducing this approximation into Eq. (38), using the geometric theorems (Whitaker 1999, §1.3.1), and converting to the intrinsic average concentration yields the result

$$\nabla \cdot \left[ \varepsilon_{\gamma} \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma} - \underbrace{(\nabla \otimes \langle \mathbf{y} \rangle) \cdot \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma}}_{\text{correction term}} + \mathcal{D}_{A\gamma} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \tilde{c}_{A\gamma} w(\mathbf{y}) \, \mathrm{d}A(\mathbf{y}) \right] = 0.$$
(40)

Here, the outer product is defined by  $[\nabla \otimes \langle \mathbf{y} \rangle]_{ij} = \partial \langle y_j \rangle / \partial x_i$ . This result is identical to the that in Whitaker (1999, Eq. 1.3–24) except this example is steady state, and it retains

a first correction arising from the geometrical structure of the porous medium. Physically,  $\langle \mathbf{y} \rangle$  represents a vector pointing to the center of mass of the  $\gamma$ -phase within the averaging volume. Note that the superficial averaging operator is applied to  $\mathbf{y}$  as follows

$$\langle \mathbf{y} \rangle |_{\mathbf{x}} = \int_{\mathbf{r} \in \mathcal{V}(\mathbf{x})} w(\mathbf{r} - \mathbf{x}) \psi_{\gamma}(\mathbf{r}, t) I_{\gamma}(\mathbf{r}) dV(\mathbf{r})$$
(41)

where here we have used the relation  $\mathbf{y} = \mathbf{r} - \mathbf{x}$  to change the variables of integration.

When upscaling microscale balance equations, equivalent effective parameters (in this case the effective diffusion coefficient) must be calculated formulating a closure problem. The closure problem is a balance equation for the deviation concentrations occurring at the microscale. The first step in deriving the closure problem for this example requires using the product rule to expand the divergence operator. Doing this yields the expanded version of Eq. (40) as follows:

$$\nabla \cdot (\mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma}) + \varepsilon_{\gamma}^{-1} \nabla \varepsilon_{\gamma} \cdot \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma} - \varepsilon_{\gamma}^{-1} (\nabla \cdot \nabla \otimes \langle \mathbf{y} \rangle) \cdot \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma} - \varepsilon_{\gamma}^{-1} \nabla \otimes \langle \mathbf{y} \rangle : \mathcal{D}_{A\gamma} \nabla \nabla \langle c_{A\gamma} \rangle + \varepsilon_{\gamma}^{-1} \nabla \cdot \left[ \mathcal{D}_{A\gamma} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \tilde{c}_{A\gamma} w(\mathbf{y}) \, \mathrm{d}A(\mathbf{y}) \right] = 0.$$
(42)

The next step is to transform the intrinsic average concentration expression into one that describes the microscale deviation concentration. This is done by recalling that the deviation equation is defined as follows

$$\tilde{c}_{A\gamma}(\mathbf{x}) = c_{A\gamma}(\mathbf{x}) - \langle c_{A\gamma} \rangle^{\gamma} |_{\mathbf{x}}.$$
(43)

This leads to the notion of subtracting Eq. (42) from Eq. (31) and substituting this definition of the deviation concentration. The result of this is shown below.

$$\nabla \cdot (\mathcal{D}_{A\gamma} \nabla \tilde{c}_{A\gamma}) - \varepsilon_{\gamma}^{-1} \nabla \varepsilon_{\gamma} \cdot \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma} + \varepsilon_{\gamma}^{-1} (\nabla \cdot \nabla \otimes \langle \mathbf{y} \rangle) \cdot \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma} + \varepsilon_{\gamma}^{-1} \nabla \otimes \langle \mathbf{y} \rangle : \mathcal{D}_{A\gamma} \nabla \otimes \nabla \langle c_{A\gamma} \rangle^{\gamma} - \varepsilon_{\gamma}^{-1} \nabla \cdot \left[ \mathcal{D}_{A\gamma} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \tilde{c}_{A\gamma} w(\mathbf{y}) \, \mathrm{d}A(\mathbf{y}) \right] = 0$$

$$\tag{44}$$

with the boundary conditions given by

B.C. 1 
$$-\mathbf{n}_{\gamma\kappa} \cdot (\mathcal{D}_{A\gamma} \nabla \tilde{c}_{A\gamma}) = \mathbf{n}_{\gamma\kappa} \cdot (\mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma}), \quad \text{for } \mathbf{x} \in \mathcal{A}_{\gamma\kappa}$$
(45)

B.C. 2 
$$\tilde{c}_{A\gamma} = \mathcal{F}_{\gamma}(\mathbf{x}, t), \quad \text{for } \mathbf{x} \in \mathcal{A}_{\gamma e}.$$
 (46)

At this juncture, many of the remaining terms depend on the macroscale average concentrations. In order to fully decouple the microscale deviation concentration from the macroscale equation, constraints are typically defined to indicate the conditions for which various approximations are valid. Satisfying these constraints allows for the full decoupling of the deviation concentration from the average concentration. For diffusion problems, the of non-local diffusion term is negligible in the closure problem (Whitaker 1999; Wood and Valdés-Parada 2013), and it is neglected in further analysis . While we allow for the gradient of the average concentration to be significant, we require that the term  $\nabla \nabla \langle c_{A\gamma} \rangle^{\gamma}$  must be negligible; if it is not, then a third-order derivative term would arise in the macroscale equation, and this would create conceptual difficulties because third-order derivatives are not positive semi-definite operators. Making these assumptions yields a final result of the form

$$\nabla \cdot (\mathcal{D}_{A\gamma} \nabla \tilde{c}_{A\gamma}) - \varepsilon_{\gamma}^{-1} \nabla \varepsilon_{\gamma} \cdot \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma} + \varepsilon_{\gamma}^{-1} (\nabla \cdot \nabla \otimes \langle \mathbf{y} \rangle) \cdot \mathcal{D}_{A\gamma} \nabla \langle c_{A\gamma} \rangle^{\gamma} = 0.$$
(47)

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For the conditions explored here, it is clear that the volume diffusive source (involving the gradients of the porosity) is significant and cannot be neglected. Additionally, it is assumed that the second derivative of the center of mass is not negligible based on the observation that the center of mass oscillates significantly as the centroid of the averaging volume moves across the periodic domain. The simplified deviation balance takes the form

$$\nabla^2 \tilde{c}_{A\gamma} = \varepsilon_{\gamma}^{-1} \nabla \varepsilon_{\gamma} \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma} - \varepsilon_{\gamma}^{-1} (\nabla \cdot \nabla \otimes \langle \mathbf{y} \rangle) \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma}$$
(48)

At this juncture, we make the conventional arguments that the second boundary condition can be approximated, for the purposes of closure, by periodic conditions in the vertical and horizontal directions. This leaves two source terms in the problem: one arising from  $\nabla \langle c_{A\gamma} \rangle^{\gamma}$  in the balance equation, and one arising from  $\nabla \langle c_{A\gamma} \rangle^{\gamma}$  in the boundary condition. Thus, the integral solution for  $\tilde{c}_{A\gamma}$  will involve Green's functions that generate both area and volume integrals of  $\nabla \langle c_{A\gamma} \rangle^{\gamma}$ . When localized (Wood and Valdés-Parada 2013), this will give a solution with a single vector contracted with  $\nabla \langle c_{A\gamma} \rangle^{\gamma}$ . Thus, the localized closure variable takes the form

$$\tilde{c}_{A\nu}(\mathbf{r}) = \mathbf{b}(\mathbf{r}) \cdot \nabla \langle c_{A\nu} \rangle^{\gamma} |_{\mathbf{r}}$$
(49)

Substituting Eq. (49) into Eq. (48) and simplifying gives the following problem with boundary condition

$$\nabla^{2} \mathbf{b}_{\gamma} = \varepsilon_{\gamma}^{-1} \nabla \varepsilon_{\gamma} - \varepsilon_{\gamma}^{-1} \nabla \cdot \nabla \otimes \langle \mathbf{y} \rangle$$
B.C. 1
$$-\mathbf{n}_{\gamma\kappa} \cdot \nabla \mathbf{b}_{\gamma} = \mathbf{n}_{\gamma\kappa}, \quad \text{for } \mathbf{x} \in \mathcal{A}_{\gamma\kappa}$$
B.C. 2
$$\mathbf{b}_{\gamma}(\mathbf{r} + \mathbf{l}) = \mathbf{b}(\mathbf{r}), \quad \text{for } \mathbf{x} \in \mathcal{A}_{\mathbf{e}}$$
(50)

where  $\mathbf{n}_{\gamma\kappa}$  is the vector pointing from the  $\gamma$  to  $\kappa$  -phase (Fig. 2). Substituting Eq. (49) into Eq. (40) gives

$$\nabla \cdot \left[ \varepsilon_{\gamma} \mathcal{D}_{A\gamma} (\nabla \langle c_{A\gamma} \rangle^{\gamma} - \varepsilon_{\gamma}^{-1} \nabla \otimes \langle \mathbf{y} \rangle \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma} + \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \otimes \mathbf{b}_{\gamma} w(\mathbf{y}) \, \mathrm{d}A(\mathbf{y}) \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma}) \right] = 0.$$
(51)

The final closed problem can be put in the form

$$\nabla \cdot \left( \varepsilon_{\gamma} \mathbf{D}_{\text{eff}} \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma} \right) = 0 \tag{52}$$

where

$$\mathbf{D}_{\text{eff}} = \mathcal{D}_{A\gamma} \left( \mathbf{I} + \varepsilon_{\gamma}^{-1} \int_{\mathbf{y} \in \mathcal{A}_{\gamma\kappa}(\mathbf{x})} \mathbf{n}_{\gamma\kappa} \otimes \mathbf{b}_{\gamma} w_{\Delta}(\mathbf{y}) \, dA(\mathbf{y}) - \underbrace{\varepsilon_{\gamma}^{-1} \nabla \otimes \langle \mathbf{y} \rangle}_{\text{correction term}} \right).$$
(53)

We note that corrections to balance laws arising from changes in porosity have been suggested previously (Cushman et al. 2002; Valdés-Parada and Alvarez-Ramírez 2011; Bruna and Chapman 2015), though we are not aware of any that have considered the gradients of higher-order moments such as  $\langle y \rangle$  (Figs. 3, 4).

This example was implemented using a domain with a periodic array of squares as illustrated in Fig. 5. In this figure, the centroid of each square is located along the line  $(x_1, 0)$ ; similarly, all averaging volumes are located along this line. Note that any average property, then, is a continuous function of  $x_1$  (and, as defined here, does not depend upon  $x_2$ ). The geometric properties of the system (porosity, gradient of porosity, center of mass, etc.) were calculated using the mollified triangle function  $w_{\Delta}$  defined over two periods in the x-direction with  $\epsilon_0 = 0.05$ .



Fig. 3 The application of the mollified boxcar function  $(w_{\Box})$  over one and two periods for a simple periodic medium



Fig. 4 The application of the mollified triangle function  $(w_{\triangle})$  over one and two periods for a simple periodic medium

For all numerical solutions, the grid convergence index,  $GCI_G$ , and global convergence order,  $P_G$ , are reported in Table 1; these have been computed for the direct numerical simulation (DNS) of diffusion at the microscale, the numerical solution for the closure problem, and the numerical solution for the upscaled equation. The  $GCI_G$  provides a percent relative error estimate of the calculated solutions based upon Richardson's extrapolation. For each solution the estimated error is below 1%. The parameters for the simulations are summarized in Table 2. The DNS concentration profile was calculated using Eq. (31) over the macroscale domain



**Fig. 5** A periodic domain averaged using a mollified triangle function (illustrated above the region to which it is applied) with a width of two periods. The grayed regions represent two different averaging volumes (with centroids located at  $x_1$  and  $x'_1$ , respectively). Note that the average is a continuous function, defined for all values of  $x_1$ 

<b>Table 1</b> The global convergenceorder, $P_G$ , global GCI andaverage element size, $\bar{h}$ for theDNS solution, closure problem,and upscaled equations		PG	GCIG (%)	$ar{h}$ (m)
	$c_{A\gamma}$	2.89	$1.34 \times 10^{-3}$	$4.88 \times 10^{-5}$
	$\mathbf{b}_{\gamma}$	2.42	$5.13 \times 10^{-1}$	$4.81 \times 10^{-5}$
	$\langle c_{A\gamma} \rangle_{\rm C}^{\gamma}$	3.15	$1.78 \times 10^{-6}$	$1.00 \times 10^{-5}$
	$\langle c_{A\gamma} \rangle_{\rm NC}^{\gamma}$	3.79	$6.58  imes 10^{-8}$	$1.00 \times 10^{-5}$

and then intrinsically averaging the result using the mollified triangle function. Separately, the closure problem was solved across the microscale domain using Eq. (50). This solution was then used to calculate the effective diffusion coefficient as a function of x using the mollified triangle function as shown in Eq. (53) with and without the correction term. The effective diffusion coefficients exhibit oscillatory behavior (Fig. 6). However, the magnitude of the fluctuations is much larger for the effective diffusion coefficient calculated using the MVA with the correction term. The source of these fluctuations stems from the accounting for the change in the center of mass as the averaging volume slides across the microscale domain (Fig. 7).

Using the effective diffusion coefficients calculated using MVA, Eq. (52) was solved on a one-dimensional domain with Dirichlet conditions determined from the DNS solution at each boundary. The corrected MVA approach shows improved agreement over the MVA method without the correction term. To illustrate the quantitative differences between the MVA results with and without the correction term, the DNS concentration profile was subtracted from the two MVA concentration profiles (Fig. 8). It is noted that the approach utilizing the correction term reduces the maximum absolute error by about a factor of three. Interestingly, the behavior of the error differs between the MVA solutions with and without the correction term. The two solutions appear to both over- and underpredict the true concentration in a periodic manner. However, the magnitude of the error is reduced for the MVA solution that incorporates the additional correction term.

This correction improves the MVA solution because it better approximates the flux of mass through the averaging volume. We have observed that for uniform porous systems, the flux approximation appears to be well-enough converged using only the first few terms of the Taylor series. For average concentration profiles with large higher-order derivatives, this approach cannot be guaranteed to give an accurate solution. One way to mitigate this would be to increase the width of the averaging volume to smooth the average concentration. In doing this, a balance must be struck because increasing the size of the averaging volume

$L_X$	$1.4 \times 10^{-2} \text{ (m)}$	Macroscale domain length
$L_y$	$1.0 \times 10^{-3} \text{ (m)}$	Macroscale domain width
$c_{A\gamma}(x=0,y)$	$0\left(\frac{\mathrm{mol}}{\mathrm{m}^3}\right)$	Macroscale domain boundary conditions
$c_{A\gamma}(x=14,y)$	$1\left(\frac{\mathrm{mol}}{\mathrm{m}^3}\right)$	
$\frac{\partial}{\partial y}c_{A\gamma}(x, y=0)$	$0\left(\frac{\mathrm{mol}}{\mathrm{m}^4}\right)$	
$\tfrac{\partial}{\partial y}c_{A\gamma}(x,y=1)$	$0\left(\frac{\mathrm{mol}}{\mathrm{m}^4}\right)$	
$\mathcal{D}_{A\gamma}$	$10^{-9}\left(\frac{\mathrm{m}^2}{\mathrm{s}}\right)$	Microscale diffusion coefficient
εγ	0.4	Periodic cell $\gamma$ -phase porosity
$l_{\kappa}$	$7.75 \times 10^{-4}$ (m)	$\kappa$ -phase square side length
$l_p$	$1 \times 10^{-3} \text{ (m)}$	Period length
<i>r</i> <sub>0,<i>x</i></sub>	$2 \times 10^{-3}$ (m)	Averaging volume length
<i>r</i> <sub>0,y</sub>	$1 \times 10^{-3} \text{ (m)}$	Averaging volume width
€0	$2.5 \times 10^{-5}$ (m)	Mollifying function characteristic dimension

Table 2 The parameters used for the example MVA simulation



**Fig. 6** The effective diffusion coefficient for the periodic domain illustrated in Fig. 5. The corrected results illustrate significant periodic oscillations. These arise due to the significant changes in the center of mass of the geometric structure as the averaging volume translates longitudinally through the system

will lead to an increase in the amount of computation required to solve the closure problem. Assuming that the constraints stated in this analysis are met, for periodic systems it is clear that additional microscale information can be transferred through the upscaling process by including the first-order moment correction terms described above.

## 4.3 Advantages and Drawbacks

The major advantages of the MVA method can be summarized as follows:



Fig. 7 The concentration profiles over the entire macroscale domain (top) and the concentration profiles over one period (bottom). The DNS and MVA concentrations profiles with and without the correction terms are shown



Fig. 8 Observed differences between the DNS concentration profile and the MVA concentration profiles calculated with and without the correction term

- The method is based on the theory of PDE's coupled with distribution theory. This mathematical machinery is either already familiar to most researchers in hydrology or involves new concepts that can be learned with an existing mathematical background.

- The MVA has a clearly defined structure for both averaging and for closure. This means that it is relatively straightforward to apply to new problems.
- Closures in the MVA is done on finite-sized cells that have physical relevance. This is in contrast to, for example, classical homogenization theory in which a periodic cell of characteristic scale ε must be subjected to a limiting process in which ε tends to zero.
- The closure process in the MVA does not require the development of complex entropy constraints for closure.

Its disadvantages are the following:

- The MVA is sometimes not suitable for certain complex cases involving, for example, many coupled processes with large numbers of source terms. In such cases, the closures can become more complex than the original problem.
- The MVA has received less attention from mathematicians than has classical homogenization. Thus, its formal mathematical development (in the context of the conventional definition-theorem-proof) has not been fully outlined.

## **5 Hybrid Mixture Theory**

Mixture theories deal with studying displacement, velocities, momentum, energy exchange and other thermodynamic variables by applying the laws of continuum mechanics to a Ncomponent mixture. A mixture is composed of various dissolved constituents (also termed as species), each of which occupies the same spatial points. For example, in a mixture composed of salt and sugar dissolved in water of volume V, the total volume occupied by each component is V. At a spatial point **x** in the solution, each species–sugar, salt and water–would overlay each other. Mixture theories have applications in a wide range of fields spanning from food science and chemical engineering to civil engineering for applications such as sodium diffusion in cheese; polar compounds movement during frying; pesticide movement in soils; vapor diffusion in unsaturated porous soils; osmosis, etc. Mixture theories development initiated in 1960s when the laws of continuum mechanics were applied to mixture components to obtain the resulting transport and thermomechanical relations (Crochet and Naghdi 1966; Green and Steel 1966; Fulks et al. 1971; Bedford and Ingram 1971; Bowen 1976).

In porous media settings, mixture theories are extended to include solids and fluid phases (water, oil, vapors, etc.), each of which is composed of a given number of species. Laws of continuum mechanics are applied to both phases and species to study their movement and interactions. Mixture theories have been further extended by including the volume averaging of microscale thermodynamic quantities or field equations for porous media exhibiting scale hierarchy in their structures (Marle 1982b; Hassanizadeh and Gray 1979a). An example of multi-scale structures is a biological tissue that contains pores in cell membranes at the microscale, cell cytoplasm at the mesoscale and tissue at the macroscale. Inclusion of volume averaging of microscale field equations in mixture theories led to the development of hybrid mixture theory (HMT) that has been applied to a wide range of materials such as food gels, viscoelastic biopolymers in soybeans, pharmaceutical products, soils, plant tissue, cornstarch, etc., to study diffusion of constituents and thermomechanical characteristics (related to quality changes) in the product matrix. There are multiple theories describing mixtures as noted in references listed above. In this primer, we will introduce the mixture theory concept for a porous food system by focussing on hybrid mixture theory.

In this section, the equations are presented in indicial notation. Superscripts  $\alpha$  and  $\beta$  are used for general representation of a phase:  $\alpha$  and  $\beta$  = s, w, o, f, denote solid, water, oil

and fluid, respectively. The superscript index j = 1 to N denotes species, with their number varying from 1 to N. Thus, a phase mixture is composed of N number of species. A full list of symbols is provided in "Appendix."

## 5.1 Fundamentals

First, we will present the hybrid mixture theory (HMT)-based two-scale balance laws that describe species and fluid transport in a porous medium at macroscale. This will be followed by macroscale entropy inequality. In HMT, averaging is performed over microscale balance laws. The constitutive theory is formulated at the higher scales. A discussion of constitutive theory to obtain resulting relations will be presented. Next, an example of HMT's application to saturated viscoelastic biopolymers will be discussed.

*Mass Balance* The two-scale (macroscale) equations described below were obtained by averaging the microscale field equations. Further details on averaging are laid out by Hassanizadeh and Gray (1979b), Bennethum andf Cushman (1996a) and Cushman (1997). Additional details on the two-scale balance laws for species and phase transport are given in Bennethum et al. (2000). Macroscale relations were obtained by applying the averaging procedure described in Bennethum andf Cushman (1996a) to microscale field equations to obtain macroscale equations for two-scale theories. In three-scale theories, volume averaging is performed twice. First, the microscale field equations are averaged to obtain the mesoscale equations. The mesoscale field equations are averaged again to obtain their macroscale counterparts. The two-step averaging is performed for porous media showing three spatial scales (e.g., in a biological tissue, biopolymers in cell walls, membranes, etc., are at the microscale, cell cytoplasm is at mesoscale, and tissue is at the macroscale).

For presenting the central idea in a simpler manner, it will be assumed that interfaces and lines joining different phases do not contain thermomechanical properties. HMT-based equations including interfacial effects are described in Hassanizadeh and Gray (1979b), Achanta et al. (1994) and Bennethum and Cushman (1996b). In the following section, twoscale equations will be presented.

The macroscale mass balance equation for the *j*th species in the phase  $\alpha$  is (Achanta et al. 1994):

$$\frac{D^{\alpha_j}(\varepsilon^{\alpha}\rho^{\alpha_j})}{Dt} + \varepsilon^{\alpha}\rho^{\alpha_j}v_{l,l}^{\alpha_j} = \sum_{\beta\neq\alpha}{}^{\beta}\hat{e}^{\alpha_j} + \hat{r}^{\alpha_j}.$$
(54)

Unlike classical mass balance equation of one scale, the quantities on the right hand side are not zero. In multi-scale equations, such quantities appear at higher scales during the averaging procedure. These act as a source or sink term. The  $\varepsilon^{\alpha}$  multiplying with  $\rho^{\alpha_j}$  also emerged during averaging. Similar quantities appear in the laws of conservation of momentum, energy and entropy.

Since a phase is treated as a mixture, the form of phase balance equations depends upon the definition of phase variables (Klika 2014). We follow the definitions in Achanta et al. (1994) where the species balance equations are summed over N components to obtain phase balance equations of similar form.

Summing the above equation over N components gives the mass balance equation for phase  $\alpha$ :

$$\frac{D^{\alpha}(\varepsilon^{\alpha}\rho^{\alpha})}{Dt} + \varepsilon^{\alpha}\rho^{\alpha}v_{l,l}^{\alpha} = \sum_{\beta\neq\alpha}{}^{\beta}\hat{e}^{\alpha},$$
(55)

where the phase variables are related to the species variables by

$$\rho^{\alpha} = \sum_{j=1}^{N} \rho^{\alpha_j}, \qquad v_l^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j} v_l^{\alpha_j}, \tag{56}$$

$$C^{\alpha_j} = \frac{\rho^{\alpha_j}}{\rho^{\alpha}}, \qquad {}^{\beta} \hat{e}^{\alpha} = \sum_{j=1}^N {}^{\beta} \hat{e}^{\alpha_j}.$$
(57)

The following restrictions apply:

$$\sum_{\alpha} \varepsilon^{\alpha} = 1, \quad \sum_{j=1}^{N} \hat{r}^{\alpha_j} = 0, \quad \forall \alpha$$
(58)

$${}^{\beta}\hat{e}^{\alpha_{j}} + {}^{\alpha}\hat{e}^{\beta_{j}} = 0, \qquad \alpha \neq \beta, \quad \forall j.$$
(59)

The restriction (58) implies that the sum of volume fraction of phases in an REV is equal to one. The restriction (59) ensures that during chemical reactions, the mass lost by one component is gained by the other, i.e., the mass exchanged between the two phases remains conserved.

*Momentum Balance.* The macroscale momentum balance equation for the *j*th species in phase  $\alpha$ :

$$\varepsilon^{\alpha}\rho^{\alpha_{j}}\frac{D^{\alpha_{j}}v_{l}^{\alpha_{j}}}{Dt} - (\varepsilon^{\alpha}t_{lk}^{\alpha_{j}})_{,k} - \varepsilon^{\alpha}\rho^{\alpha_{j}}g_{l}^{\alpha_{j}} = \sum_{\beta\neq\alpha}{}^{\beta}\hat{T}_{l}^{\alpha_{j}} + \hat{i}_{l}^{\alpha_{j}}.$$
(60)

Summing this equation over the N components, we obtain the momentum balance equation for phase  $\alpha$ :

$$\varepsilon^{\alpha}\rho^{\alpha}\frac{D^{\alpha}v_{l}^{\alpha}}{Dt} - (\varepsilon^{\alpha}t_{lk}^{\alpha})_{,k} - \varepsilon^{\alpha}\rho^{\alpha}g_{l}^{\alpha} = \sum_{\beta\neq\alpha}{}^{\beta}\hat{T}_{l}^{\alpha}.$$
(61)

The relations between the phase and the species variables are:

$$t_{lk}^{\alpha} = \sum_{j=1}^{N} \left( t_{lk}^{\alpha_j} - \rho^{\alpha_j} u_l^{\alpha_j} u_k^{\alpha_j} \right), \qquad u_l^{\alpha_j} = v_l^{\alpha_j} - v_l^{\alpha}, \tag{62}$$

$$g_{l}^{\alpha} = \sum_{j=1}^{N} C^{\alpha_{j}} g_{l}^{\alpha_{j}}, \quad {}^{\beta} \hat{T}_{l}^{\alpha} = \sum_{j=1}^{N} \left( {}^{\beta} \hat{T}_{l}^{\alpha_{j}} + {}^{\beta} \hat{e}^{\alpha_{j}} u_{l}^{\alpha_{j}} \right).$$
(63)

The following restrictions apply to the momentum balance equations:

$$\sum_{j=1}^{N} \left( \hat{i}_{l}^{\alpha_{j}} + \hat{r}^{\alpha_{j}} u_{l}^{\alpha_{j}} \right) = 0, \quad {}^{\beta} \hat{T}_{l}^{\alpha_{j}} + {}^{\beta} \hat{e}^{\alpha_{j}} v_{l}^{\alpha_{j}} + {}^{\alpha} \hat{T}_{l}^{\beta_{j}} + {}^{\alpha} \hat{e}^{\beta_{j}} v_{l}^{\beta_{j}} = 0, \quad \alpha \neq \beta, \quad \forall j. \quad \forall \alpha$$

$$(64)$$

*Energy Balance*. The energy balance law for the *j*th species in the phase  $\alpha$  is:

$$\varepsilon^{\alpha}\rho^{\alpha_{j}}\frac{D^{\alpha_{j}}E^{\alpha_{j}}}{Dt} - \varepsilon^{\alpha}t_{kl}^{\alpha_{j}}v_{l,k}^{\alpha_{j}} - (\varepsilon^{\alpha}q_{l}^{\alpha_{j}})_{,l} - \varepsilon^{\alpha}\rho^{\alpha_{j}}h^{\alpha_{j}} = \sum_{\beta\neq\alpha}{}^{\beta}\hat{Q}^{\alpha_{j}} + \hat{E}^{\alpha_{j}}$$
(65)

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Summing this equation over the N components:

$$\varepsilon^{\alpha}\rho^{\alpha}\frac{D^{\alpha}E^{\alpha}}{Dt} - \varepsilon^{\alpha}t^{\alpha}_{kl}v^{\alpha}_{l,k} - (\varepsilon^{\alpha}q^{\alpha}_{l})_{,l} - \varepsilon^{\alpha}\rho^{\alpha}h^{\alpha} = \sum_{\beta\neq\alpha}{}^{\beta}\hat{Q}^{\alpha}.$$
 (66)

The relations between the phase and the species variables are:

$$E^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j} \left( E^{\alpha_j} + \frac{1}{2} u_l^{\alpha_j} u_l^{\alpha_j} \right), \tag{67}$$

$$q_{l}^{\alpha} = \sum_{j=1}^{N} \left[ q_{l}^{\alpha_{j}} + t_{kl}^{\alpha_{j}} u_{k}^{\alpha_{j}} - \rho^{\alpha_{j}} \left( E^{\alpha_{j}} + \frac{1}{2} u_{k}^{\alpha_{j}} u_{k}^{\alpha_{j}} \right) u_{l}^{\alpha_{j}} \right], \tag{68}$$

$$\rho^{\alpha}h^{\alpha} = \sum_{j=1}^{N} \rho^{\alpha_j} (h^{\alpha_j} + g_l^{\alpha_j} u_l^{\alpha_j}), \tag{69}$$

$${}^{\beta}\hat{Q}^{\alpha} = \sum_{j=1}^{N} \left[ {}^{\beta}\hat{Q}^{\alpha_{j}} + {}^{\beta}\hat{T}_{l}^{\alpha_{j}}u_{l}^{\alpha_{j}} + {}^{\beta}\hat{e}^{\alpha_{j}}\left(E^{\alpha_{j},\alpha} + \frac{1}{2}u_{l}^{\alpha_{j}}u_{l}^{\alpha_{j}}\right) \right].$$
(70)

The following restrictions apply to the energy balance equations:

$$\sum_{j=1}^{N} \left[ \hat{E}^{\alpha_j} + \hat{i}_l^{\alpha_j} u_l^{\alpha_j} + \hat{r}^{\alpha_j} \left( E^{\alpha_j} + \frac{1}{2} u_l^{\alpha_j} u_l^{\alpha_j} \right) \right] = 0, \quad \forall \alpha$$
(71)

*Entropy.* The second law of thermodynamics requires that the evolution of processes must proceed in such a way that the net internal entropy gained by the system increases. We begin by expressing an entropy balance law for each constituent of each phase:

$$\varepsilon^{\alpha}\rho^{\alpha_{j}}\frac{D^{\alpha_{j}}\eta^{\alpha_{j}}}{Dt} - (\varepsilon^{\alpha}\phi_{l}^{\alpha_{j}})_{,l} - \varepsilon^{\alpha}\rho^{\alpha_{j}}b^{\alpha_{j}} = \sum_{\beta\neq\alpha}{}^{\beta}\hat{\phi}^{\alpha_{j}} + \hat{\eta}^{\alpha_{j}} + \Lambda^{\alpha_{j}}.$$
 (73)

Summing the entropy balance equation over the N species:

$$\varepsilon^{\alpha}\rho^{\alpha}\frac{D^{\alpha}\eta^{\alpha}}{Dt} - (\varepsilon^{\alpha}\phi_{l}^{\alpha})_{,l} - \varepsilon^{\alpha}\rho^{\alpha}b^{\alpha} = \sum_{\beta\neq\alpha}{}^{\beta}\hat{\phi}^{\alpha} + \Lambda^{\alpha}.$$
(74)

The relations between the phase and the species variables are:

$$\eta^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j} \eta^{\alpha_j}, \quad \phi_l^{\alpha} = \sum_{j=1}^{N} (\phi_l^{\alpha_j} - \rho^{\alpha_j} u_l^{\alpha_j} \eta^{\alpha_j})$$
(75)

$$b^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j} b^{\alpha_j}, \quad {}^{\beta} \hat{\phi}^{\alpha} = \sum_{j=1}^{N} ({}^{\beta} \hat{\phi}^{\alpha_j} + {}^{\beta} \hat{e}^{\alpha_j} \eta^{\alpha_j, \alpha})$$
(76)

$$\Lambda^{\alpha} = \sum_{j=1}^{N} \Lambda^{\alpha_j} \tag{77}$$

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Restrictions on the entropy balance equations are:

$$\sum_{j=1}^{N} (\hat{r}^{\alpha_j} \eta^{\alpha_j} + \hat{\eta}^{\alpha_j}) = 0, \quad \forall \alpha$$
(78)

$${}^{\beta}\hat{\phi}^{\alpha_{j}} + {}^{\beta}\hat{e}^{\alpha_{j}}\eta^{\alpha_{j}} + {}^{\alpha}\hat{\phi}^{\beta_{j}} + {}^{\alpha}\hat{e}^{\beta_{j}}\eta^{\beta_{j}} = 0, \quad \alpha \neq \beta, \quad \forall j.$$

$$(79)$$

We assume that the system is at local thermal equilibrium, which causes different phases to have the same local temperature ( $T^{\alpha_j} = T^{\beta_j} = T$ .). The temperature is allowed to vary spatially. We also assume that the sources of entropy are solely due to heat flux and the body source of heat

$$\phi_l^{\alpha_j} = \frac{q_l^{\alpha_j}}{T}, \quad b^{\alpha_j} = \frac{h^{\alpha_j}}{T}.$$
(80)

A thermodynamic process satisfying (80) is called a simple thermomechanical process. In the energy balance equation (65), the internal energy,  $E^{\alpha_j}$ , is a function of the entropy,  $\eta^{\alpha_j}$ . Since entropy can not be directly measured from experiments, a Legendre transformation is performed on  $E^{\alpha_j}$  to convert it into the Helmholtz free energy,  $A^{\alpha_j}$ , which is a function of temperature

$$A^{\alpha_j} = E^{\alpha_j} - T\eta^{\alpha_j}.$$
(81)

Summing  $A^{\alpha_j}$  over the N components, we obtain the inner part of the total Helmholtz free energy:

$$A_{I}^{\alpha} = \sum_{j=1}^{N} C^{\alpha_{j}} A^{\alpha_{j}}.$$
 (82)

*Entropy Inequality.* All independent processes taking place inside a body must satisfy the axioms of mechanical and thermodynamic admissibility (see Eringen 1980). Equations of conservation of mass, momentum and energy ensure that the processes are mechanically admissible. To be thermodynamically admissible, the processes must satisfy the second law of thermodynamics (Grmela et al. 2013). This is imposed using entropy inequality, which states that the net rate of entropy generation in the universe is always greater than or equal to zero:

$$\Lambda = \sum_{\alpha} \Lambda^{\alpha} = \sum_{\alpha} \sum_{j=1}^{N} \Lambda^{\alpha_j} \ge 0$$
(83)

Eliminating  $h^{\alpha_j}$  between equations of energy and entropy balance and simplifying, we obtain:

$$\begin{split} \Lambda &= \sum_{\alpha} \Lambda^{\alpha} = -\sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{T} \left( \frac{D^{\alpha} A_{I}^{\alpha}}{Dt} + \eta^{\alpha} \frac{D^{\alpha} T}{Dt} \right) \\ &+ \sum_{\alpha} \frac{\varepsilon^{\alpha}}{T} \left( \sum_{j=1}^{N} t_{kl}^{\alpha_{j}} \right) d_{kl}^{\alpha} \\ &+ \sum_{\alpha} \frac{\varepsilon^{\alpha}}{T} \sum_{j=1}^{N} \left( t_{kl}^{\alpha_{j}} - \rho^{\alpha_{j}} A^{\alpha_{j}} \delta_{kl} \right) u_{k,l}^{\alpha_{j}} \end{split}$$

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4)

$$+\sum_{\alpha} \frac{\varepsilon^{\alpha} T_{,l}}{T^{2}} \left\{ q_{l}^{\alpha} + \sum_{j=1}^{N} \left[ -t_{kl}^{\alpha_{j}} u_{k}^{\alpha_{j}} + \left( A^{\alpha_{j}} + \frac{1}{2} u_{k}^{\alpha_{j}} u_{k}^{\alpha_{j}} \right) \rho^{\alpha_{j}} u_{l}^{\alpha_{j}} \right] \right\}$$

$$-\frac{1}{T} \sum_{\alpha} \sum_{j=1}^{N} \left[ (\varepsilon^{\alpha} \rho^{\alpha_{j}} A^{\alpha_{j}})_{,l} + \sum_{\beta \neq \alpha} {}^{\beta} \hat{T}_{l}^{\alpha_{j}} + \hat{i}_{l}^{\alpha_{j}} \right] u_{l}^{\alpha_{j}}$$

$$-\frac{1}{2T} \sum_{\alpha} \sum_{j=1}^{N} u_{l}^{\alpha_{j}} u_{l}^{\alpha_{j}} \left[ \sum_{\beta \neq \alpha} {}^{\beta} \hat{e}^{\alpha_{j}} + \hat{r}^{\alpha_{j}} \right]$$

$$-\frac{1}{T} \sum_{\alpha} \sum_{\beta \neq \alpha} {}^{\beta} \hat{T}_{l}^{\alpha} v_{l}^{\alpha,s}$$

$$-\frac{1}{T} \sum_{\alpha} \sum_{\beta \neq \alpha} {}^{\beta} \hat{e}^{\alpha} \left[ A_{l}^{\alpha} + \frac{1}{2} v_{l}^{\alpha,s} v_{l}^{\alpha,s} \right] \geq 0. \qquad (8)$$

The above equation includes the effect of heat, mechanical deformation, movement of species, chemical reactions and phase change effects in the system. For further details, please refer to Bennethum andf Cushman (1996a).

Constitutive Theory. In balance laws described above, the number of variables is greater than the number of equations. Thus, the system is not closed. To close the system, the nature of the porous material is included in the mathematical formulation via a constitutive theory. In hybrid mixture theory (HMT), the laws of conservation is upscaled from micro- to macroscale and the constitutive theory is formulated at the macroscale. At this step, a list of dependent and independent variables is formed at macroscale to include specific nature of the porous material and its constituents. Selection of variables in the list requires prior knowledge about the behavior of material being modeled, which comes from experimental observations in the field, and type of effects that need to be included. For example, to model the solid particles as elastic, the solid-phase strain tensor can be selected as one of the independent variable (Singh et al. 2003a), and for treating the solid polymers as viscoelastic, various order time derivatives of strain tensor can be selected as independent variables (Bennethum and Cushman 1996b; Singh et al. 2003c). During unsaturated transport in a biopolymeric matrix, both concentration (diffusive flow) and pressure gradients (Darcy flow) can cause movement of a fluid (an effect). Thus, both of these variables are included as independent variables in the constitutive theory. Additional details on unsaturated transport are given in Takhar (2014). Material time derivative of Helmholtz free energy,  $A^{\alpha_j}$ , which is a function of the list of selected independent variables, is computed and substituted in the entropy inequality given above.

The entropy inequality imposes restrictions on the system to ensure that the second law of thermodynamics is followed. This results in a large number of equilibrium, near-equilibrium and non-equilibrium relations. Initial derivations were made for two-scale saturated porous media with solid phase being elastic and the liquid phase being viscous (Hassanizadeh and Gray 1979a; Achanta et al. 1994).

Bennethum andf Cushman (1996a) extended this to three-scale porous media. The developed relations were solved for modeling drying of food gels (Achanta et al. 1997). Singh et al. (2003c) extended the theory to biopolymers by treating the solids as viscoelastic and liquids as viscoelastic at the microscale, and obtained temporally non-local relations at macroscale. Takhar (2014) used hybrid mixture theory to develop unsaturated transport relations for biopolymeric matrices. Boundary conditions for mixture theoretic equations may pose some challenges. When a domain is surrounded by a bulk medium, various fluid and species transport fluxes, and stresses on its boundary need to be balanced with the bulk medium. Thus, one needs to decide how those fluxes and stresses are split at the boundaries. Some experimental research is needed to split the mixture components related variables at the boundaries (Rajagopal and Tao 1995). For example, during unsaturated transport from a porous material containing two gases, one can utilize separate mass transfer boundary films for two components on the boundary. In hybrid mixture theory, the macroscale stresses are split based upon volume fractions of components ( $\varepsilon^{\alpha}$ ). For example for a solid–liquid mixture, the total stress on the boundary can be split using  $t_{kl} = \varepsilon^{s} t_{kl}^{s} + \varepsilon^{w} t_{kl}^{w}$ , where s and w denote solid and water, respectively (Schreyer-Bennethum 2007).

## 5.2 Applications

In this section, we will present two examples of hybrid mixture theory-based derivations--integrodifferential equation of Singh et al. (2003b) and unsaturated transport relations of Takhar (2014). After presenting the equations, solution of equations for drying and frying problems will be discussed. The equations presented below are based on the phase transport relations and constitutive theory presented in the preceding Fundamentals section.

## 5.2.1 Non-Fickian (or Non-Darcian) Transport in Biopolymers

Singh et al. (2003b) used three-scale hybrid mixture theory-based relations developed for viscoelastic biopolymers (Singh et al. 2003c) to obtain the following non-Fickian (or non-Darcian) fluid transport equation

$$\dot{\varepsilon}^{w} + (\varepsilon^{w} - 1) \left\{ D\varepsilon^{w}_{,k} - \int_{0}^{t} \left[ B_{c}G(t - \tau)\dot{\varepsilon}^{w}_{,k}(\tau)\mathrm{d}\tau \right] \right\}_{,k} = 0,$$
(85)

where *D* is the coefficient of diffusivity of the biopolymeric matrix, G(t) is the stress relaxation function, and  $B_c$  is the viscoelastic parameter. The integral term incorporates the effect of stress relaxation in the biopolymers on fluid transport and thus can describe non-Fickian transport. Wojciechowski (2011) discussed that in (85) permeability coefficient was assumed not be an explicit function of time due to which it can be moved inside the integral term. The indirect dependence of permeability on time via  $\varepsilon^w(t)$  was neglected in (Singh et al. 2003c)'s derivation. Equation (85) has also been shown to be well posed (Wojciechowski et al. 2014). The importance of stress relaxation on fluid transport in biopolymers undergoing glass transition has been realized in the polymer science literature (Astarita and Sarti 1978; Thomas and Windle 1980, 1982). However, its mathematical description was not complete in polymer science.

## 5.2.2 Fickian and Non-Fickian Transport in a Biopolymeric Matrix

The stress relaxation function, G(t), can be described using the generalized Maxwell model (Christensen 1982)

$$G(t) = G_0 + \sum_{1}^{n} G_i e^{-t/\lambda_i}$$
(86)

where  $G_i$  is the relaxation parameter, *n* is the number of terms in the stress relaxation function, and  $\lambda_i$  is the relaxation time. In the glassy state,  $\lambda_i \to \infty$ ,  $t/\lambda_i \to 0$ , and  $e^{-t/\lambda_i} \to 1$ . Thus,  $G(t) \rightarrow \sum_{i=1}^{n} G_i$ , which is not a function of time. In the rubbery state  $\lambda_i \rightarrow 0$ ,  $t/\lambda_i \rightarrow \infty$ , and  $e^{-t/\lambda_i} \rightarrow 0$ . Therefore,  $G(t) \rightarrow G_0$ , which is again independent of time. Thus, in glassy and rubbery states the integral term of (85) contributes a constant magnitude to the diffusivity term and can be merged with the diffusivity term (Singh et al. 2003b). However, near glass transition  $\lambda_i \sim t$ . Thus, near glass transition the integral term cannot be reduced to a time-independent term and contributes temporally non-local effects to fluid transport in biopolymers. Singh et al. (2003b) discussed that (85) describes Fickian transport in glassy and rubbery states of biopolymers, and non-Fickian transport near glass transition. They further verified this prediction by numerically solving (85) for drying of soybeans (Singh et al. 2004) and corn (Takhar 2011), both of which exhibit the glass transition phenomenon. The above equation is fully able to describe the non-Fickian transport in polymers undergoing glass transition states. The equation predicts that fluid transport in biopolymers is Fickian when they are in glassy or rubbery states, and non-Fickian when they are undergoing glass transition (Singh et al. 2003b). These predictions agree with experimental studies on dodecane transport in polymers (Kim et al. 1993), and drying of soybeans (Singh et al. 2004), pasta (Xing et al. 2007) and corn (Takhar 2011). Xing et al. (2007) used NMR imaging to measure moisture distribution across the cross section of a rubbery pasta undergoing drying in NMR tube. They observed that the moisture distribution profiles agree with the profile shapes predicted by (85).

Takhar (2011) and Takhar et al. (2011) solved (85) to calculate moisture gradients in corn kernels subjected to drying. Corn is a heterogeneous food material surrounded by a thin layer of pericarp that encloses soft endosperm, hard endosperm and germ. Each component has different coefficients of diffusivity and mechanical properties. In the midwest region of USA, corn is dried by the farmers in heated air dryers. It is important to calculate drying conditions, which lead to more uniform moisture gradients. Steep moisture gradients can cause steep strain and stress gradients, which can cause stress cracks in kernels. Cracked corn is prone to insect and microbial damage and poses explosion hazard in processing plants due to formation of dust. Figure 9 shows an example of moisture gradients in a corn kernel calculated by solving (85) (Takhar et al. 2011).

At 5 min of drying time, the highest moisture flux (proportional to moisture gradient) is observed at the top of a kernel, at the bottom left and under the pericarp toward outside. At longer drying times (1 and 5 h), the high moisture flux is observed in the soft endosperm toward top and in the region connecting soft endosperm and germ. Interestingly, similar observations in moisture gradient patterns were made using magnetic resonance imaging (MRI) by (Song et al. 1992). By calculating the moisture fluxes shown in Fig. 9, the moisture flow path inside corn was calculated (Takhar et al. 2011). Using real-world weather data, simulations were performed by varying the temperature–humidity combinations of the drying air to find conditions that lead to more uniform moisture gradients. Recommendations were made to dry corn to desired moisture levels while making it less prone to stress cracking.

## 5.2.3 Unsaturated Transport

Examples of unsaturated relations derived using hybrid mixture theory (Takhar 2014) include generalized Darcy's law that includes pressure driven (Darcy's law), concentration-driven (Fick's law) and non-Fickian (or non-Darcian) integral terms to include the effect of polymer



**Fig. 9** Calculated magnitude of moisture flux in a corn kernel dried at T = 67 °C, RH = 15% as a function of drying time Takhar et al. (2011) (Reprinted with permission from Elsevier)

relaxation; and near-equilibrium capillary pressure relations. The equations were solved to describe moisture, oil and vapor transport during frying of foods (Takhar 2014; Bansal et al. 2015, 2014); and water, vapor and heat transport during expansion of biopolymers exiting an extruder (Dit-u dompo and Takhar 2015). Here, we will present the generalized Darcy's law with memory effects and present its solution for calculating various pressures in a fried food.

The generalized Darcy's law of Takhar (2014) describing the flow of  $\alpha$  phase in a polymeric matrix is

$$v_{l}^{\alpha,s} = -\left[\frac{K^{\alpha}}{\mu^{\alpha}}\varepsilon^{\alpha}p_{,l}^{\alpha} + \varepsilon^{\alpha}D^{\alpha}\varepsilon_{,l}^{\alpha} + \varepsilon^{\alpha}\rho^{\alpha}\int_{0}^{t}\mathcal{M}^{\alpha}(t-\tau)\frac{\partial E_{MM,l}^{s}}{\partial\tau}\mathrm{d}\tau\right],\tag{87}$$

where the first term on the right hand side describes pressure driven flow, the second term describes concentration-driven flow, and the third term denotes flow due to conformational changes (strain) in the polymeric matrix. During unsaturated transport, both pressure and concentration gradients can cause flow in the polymeric matrix. Concentration-driven flow arises because a fluid in the porous matrix diffuses from regions of higher concentration to regions of lower concentration. In the vicinity of glass transition, the strain in the polymeric matrix adds a temporally non-local forcing term, which is denoted by the integral in above equation. Due to the involvement of integral, (87) has memory effect. Thus, the entire process history of mechanical changes in the polymers affect fluid flow at time *t*.

## 5.2.4 Application of Unsaturated Transport to Frying of Foods

Consumers have developed a taste for fried foods. The multi-billion dollar food industry aims at optimizing the process to obtain foods with lower levels of oil and undesirable compounds without compromising with taste and texture that consumers enjoy. However, it is tedious to optimize the process by purely experimental approaches due to complex interactions between the underlying mechanisms. Frying of foods is a highly transient process where the fluids, heat and species (chemicals formed in the matrix) move rapidly between the porous matrix and the surrounding oil medium. The physicochemical properties, such as porosity (Alam and



**Fig. 10 a** Gage pore pressure, and **b** oil content across the cross section of a fried food calculated using the unsaturated transport theory of (Takhar 2014) (Reprinted with permission from Elsevier)

Takhar 2016), thermal properties, diffusivity, permeability, hydrophilicity, hydrophobicity, of the matrix itself evolve rapidly during the process.

Takhar (2014) coupled (87) with the mass balance equation, multi-scale heat transfer equation, capillary pressure relation, binary-diffusion equation for air–vapor mixture, and other supporting relations and appropriate initial and boundary conditions to model the frying of foods.

Figure 10a elucidates calculated gage pore pressure across the cross section of French fries. Pore pressure was defined as the effective pressure experienced by the pore walls due to combined effect of various phases present inside pores. It was calculated using the equation  $P_{\text{pore}} = S_w P^w + S_g P^g + S_o P^o$  (Ehlers and Bluhm 2002). In the beginning of frying, pore pressure is positive (greater than atmospheric pressure). The pore pressure increases up to 20s as shown in the figure. Between 20s and 30s, the pore pressure starts reducing due to reduction in evaporation rate and increase in capillary pressure (see Takhar 2014 for details). Capillary pressure increases due to increase in suction potential of the matrix at lower water contents. By 50s, pore pressure becomes negative, thus creating a suction potential inside the fried food. As the pore space becomes available due to loss of vapors and water to the oil, the suction potential causes oil penetration in the material.

Figure 10 shows calculated oil content across the cross section of the French fry as a function of frying time. The figure shows that oil penetrates but remains in the surface layers. This has also been confirmed using dye penetration (Lalam et al. 2013) and MRI imaging experiments (Oztop et al. 2014) with high moisture foods. In comparison, in low-moisture foods such as rice crackers, the oil penetrates deeper inside the food (Bansal et al. 2014) as there is lower resistance to oil uptake due to less vapor formation. By performing simulations using hybrid mixture theory-based unsaturated transport equations, frying parameters have been identified that the industry can use to obtain foods that have lower fat content but have desirable textural and color attributes (Bansal et al. 2014, 2015).

## 5.3 Advantages and Drawbacks

In methods such as matched asymptotic expansion (Hornung 1997) and volume averaging in the sense of Whitaker (1977), constitutive theory is formulated at microscale, where material behavior may not be fully understood due to difficulty in devising microscale experiments. When the equations with material coefficients are upscaled to higher scales, material coefficients also get upscaled and they may not be easier to relate to experimentally determined properties. In addition, these approaches require well-defined microscale geometries. In hybrid mixture theory (HMT), the volume averaging is performed only on field equations laws of conservation to obtain their macroscale counterparts (meoscale and macroscale) (Cushman 1997). HMT requires only the existence of a representative elementary volume. The constitutive equations are formulated at the macroscale. The advantage of upscaling field equations before formulating the constitutive theory is that the material coefficients in equations show up at macroscale, where it is easier to devise experiments. However, the disadvantage is that the constitutive nature of different materials (e.g., elastic solid and viscous water) is not included at lower scales, but their combined behavior is addressed at higher scales (e.g., a viscoelastic solid–water mixture).

# 6 Thermodynamically Constrained Averaging Theory (TCAT)

TCAT is an upscaling technique that has evolved over the past 13 years as an alternative to earlier averaging methods, such as MVA and mixture theory, for macroscale model formulation (Gray and Miller 2005; Miller and Gray 2005). While some elements of TCAT overlap with hybrid mixture theory, several notable differences exist, which we use to distinguish the TCAT approach. These differences include the microscale formulation of thermodynamics and subsequent upscaling; the derivation of conditions that must hold at equilibrium to guide the formulation of the entropy inequality; the derivation and use of kinematic equations separate from conservation equations—reducing the closure problem; the formulation of state equations, based upon, for example, integral topological considerations; and the scale consistency afforded by the TCAT approach provides definitions for all macroscale variables in terms of microscale quantities—enabling microscale experimental and computational approaches to be used for model closure, evaluation and validation.

TCAT has been applied to a wide variety of single-fluid and two-fluid porous medium systems. Typically, a general approach is taken that results in a hierarchy of models of varying sophistication, and fidelity. A detailed description of the TCAT approach is available in the book by Gray and Miller (2014), and the reader interested in the development of this method is referred to the review paper by Gray et al. (2013), Gray and Miller (2005, 2014) and Miller et al. (2017, 2018a, b). The purpose of the following subsections is to summarize the TCAT approach for model building, its main components, applications, and its advantages and disadvantages.

## 6.1 Fundamentals

The foundational aspects of the TCAT approach that are needed for a complete understanding are available in the literature and will not be fully considered herein (Miller and Gray 2005, 2008; Gray and Miller 2013, 2014). To aid with clarity in the steps involved with TCAT model formulation, the objectives of the method are noted: (1) consistency of all quantities across scales; (2) inclusion of lower-dimensional entities such as interfaces and common curves; (3) a rigorous thermodynamic basis starting from the microscale; (4) the formulation of evolution equations, distinct from conservation equations, to aid closure; (5) the formulation of both exact and approximate forms of entropy production as archival expressions; (6)



Fig. 11 TCAT model formulation approach

general model hierarchies that support a range of models of a given class; (7) the formulation of permissibility conditions that closure relations must meet to be consistent with the second law of thermodynamics; (8) natural and explicit inclusion of physics known to be important at the microscale into larger-scale models; and (9) a path to use microscale experimental and simulation information to close, evaluate and validate larger-scale models.

In Fig. 11, we present TCAT model-building components and the general flow of the model-building process, which is depicted by the arrows. Restrictions and approximations are identified in purple ovals, microscale equations are marked in yellow rectangles, and their resulting macroscale entries are identified in maroon rectangles. These elements are combined to produce constrained and simplified entropy inequalities (EI), which lead to closure relations (blue rectangles) from which a hierarchy of closed parameterized models result (gray rectangle). We describe these elements in turn:

- In order to define the microscale system and its governing equations, a set of primary restrictions is adopted, which explicitly specify the entities (phases, interfaces, common curves), processes to be modeled, the applicability of a continuum mechanical approach, and a microscale thermodynamic theory to be relied upon (alternative thermodynamic theories are possible).
- As in other upscaling techniques, TCAT requires both the existence of a separation of characteristic length scales and the existence of an REV. However, averaging in TCAT is versatile enough so that combinations of macroscopic and megascopic averages in different spatial directions is possible.
- 3. An averaging operator is applied to all microscale equations, and the interchange of spatial integration and (temporal or spatial) differentiation is achieved using averaging theorems. The averaging process provides the macroscale versions of all microscale equations. The resulting equations are written in terms of average quantities with a clear connection to the microscale.
- 4. The averaged entropy balance equations for all entities, and species if a composition model, are summed to produce an entropy inequality (EI) for the system, which must be nonnegative in agreement with the second law of thermodynamics. Conservation and thermodynamic equations are connected to the EI using Lagrange multipliers, which enable the elimination of material derivative expressions. The role of this inequality is to identify flux–force pairs for dissipative processes that produce entropy, and to use these pairs to constrain permissible forms of closure relations.

- 5. Approximations of inaccessible quantities in the constrained EI allow for the production of a general simplified EI, which is in strict flux-force form. Secondary restrictions may also be applied, which reduce the complexity of the general simplified EI at the expense of limiting the class of models that may be considered. The simplified EI provides permissibility conditions on closure relations to complete a well-posed macroscale model. In this way, a given constrained EI can give rise to many simplified EIs (and therefore closure relationships) depending on the type of approximations and secondary restrictions that are made.
- 6. Besides the closure relations, the macroscale model is completed with the corresponding equations of state and evolution equations. The latter result from the averaging theorems and describe variations of geometrical properties such as the volume fractions, interfacial areas, common curve lengths and curvatures.
- 7. In order to compute the closure coefficients involved in the model, inverse modeling based upon microscale simulations or experimental data are required. This information is also needed to validate the model. However, Miller et al. (2018b), recently developed an *a priori* manner of predicting effective coefficients by following the rationale of the volume averaging method. If the model fails in its validation, it is possible to revisit the approximations made in the simplified EI in order to improve the macroscale model.

The TCAT approach does not need to be rendered in its entirety for each application. General, and available, conservation, balance, thermodynamic, potential and kinematic equations and EIs can be a starting point for model building. A simplified TCAT analysis is also possible in some instances with a loss of generality (Miller et al. 2017).

We will now describe the TCAT approach for two-fluid flow in porous media and note important aspects of this approach within this context. Technical details of the method for this specific application are presented in the following paragraphs. With respect to the macroscale two-fluid flow model hierarchy, the primary restrictions would include the entities present (three phases, three interfaces, one common curve), a specification that conservation and balance principles are applied to each entity for all quantities—rather than a species in an entity, the reliance on classical irreversible thermodynamics at the microscale, and the existence of a representative elementary volume (REV). All conservation, balance, potential and thermodynamic equations needed for this case have been derived both at the microscale and at the macroscale (Gray and Miller 2014).

A key aspect of the TCAT formulation for two-fluid flow is evolution equations, which are derived using the averaging theorems and are distinct from any conservation principle. The exact form of the evolution equations is typically not accessible, so approximations are applied to render a convenient solvable form. The approximations made can be evaluated for model systems in which microscale information exists. This is also the case for approximations made to derive the simplified EI, which is an important consequence of the consistent multi-scale derivation process. Evolution equations are formulated for changes in geometric extent measures, such as volume fractions, specific interfacial areas and specific common curve lengths. Together, the conservation equations, evolution equations and closure relations combine to yield a closed, solvable model, *i.e.*, a model with sufficient equations for the number of dependent macroscopic variables involved. Because the model forms are typically novel, some substantial work may be required to yield specific forms of the closure relations, including equations of state, and to evaluate and validate the utility of the approximations made to produce a solvable model. These aspects will become evident in the TCAT application that follows.

## 6.2 Applications

Macroscale TCAT model hierarchies have been derived for a variety of single- and multiphase flow and transport processes in porous media systems. Each of these model hierarchies provides the basis for the derivation of many specific model instances. All models have the desirable TCAT model characteristics, but work remains to generate, parameterize, evaluate, and validate specific forms of the closure relations needed for these new classes of models.

The first application of TCAT was to study single-phase flow in a porous medium (Gray and Miller 2006). The result of this work is ultimately the classical model for flow in porous media; however, by listing a set of assumptions involved in the derivations, interesting alternatives of this model may be envisaged. For example, the quasi-equilibrium assumption for the solid phase may be relaxed in order to produce a macroscale model that couples fluid and solid mechanics. Shortly afterward, two extensions of this work were presented: the first one was the paper by Jackson et al. (2009) about two-phase flow in homogeneous porous media. In this work, a hierarchy of three models were presented according to the level of assumptions involved in the derivations. The simplest model turned out to be equivalent to the classical one for two-phase flow in porous media. The second model included the influence of the interfaces, while the third one also included the influence of common curves. This study was later validated with lattice-Boltzmann simulations (Gray et al. 2015) and generalized to consider the issue of capillary dynamics (Gray and Miller 2011). The second extension of the work by Gray and Miller (2006) dealt with a study of flow at the megascale. The study carried out by Gray and Miller (2009c) departed from the same system considered earlier by Gray and Miller (2006), with the difference that the averaging was performed not within an REV but within the entire domain. For this reason, the spatial dependence within the domain was not resolved and the solution was formulated as boundary terms. The above works motivated Jackson et al. (2012) to carry out a study of the transition regions between two-fluid flow and species transport and a compositional single-fluid system. In addition, Gray and Miller (2009a) studied heat transport in single-fluid-phase saturated porous media; the resulting models encompass both thermal equilibrium and non-equilibrium conditions. In addition, multi-species mass transport in single-fluid-phase porous media was studied (Miller and Gray 2008; Gray and Miller 2009b). Gray and Miller (2009b) presented two different approaches, one in which a momentum equation for each entity is used along with constitutive relations for species diffusion and dispersion; in the second approach, a momentum equation for each entity is used. More recently, Rybak et al. (2015) have extended these analyses for the study of two-fluid flow and species transport.

Next we present an application of TCAT to formulate a two-fluid-phase flow model through a porous medium system. While the objectives of the TCAT model formulation process have been met for this general class of problem, the details of the formulation process are substantial and available in the literature (Jackson et al. 2009; Gray and Miller 2014). The constrained EI and the general simplified EI are each multi-page expressions, which can appear impenetrable to the non-specialist. Instead of either of these general expressions, we will begin with a somewhat simpler example of an isothermal system in which mass is not exchanged between entities, and the interfaces and common curve are massless. Applying these assumptions, the general simplified EI reduces to the secondarily restricted form that is expressed in a strict flux–force form of products of terms that can produce entropy away from equilibrium:
$$\sum_{\alpha \in \mathcal{I}_{\mathrm{f}}} \frac{1}{\theta} \left( \epsilon^{\overline{\alpha}} \mathbf{t}^{\overline{\alpha}} + \epsilon^{\overline{\alpha}} p^{\alpha} \mathbf{I} \right) : \mathbf{d}^{\overline{\alpha}} + \frac{1}{\theta} \left( \epsilon^{\overline{s}} \mathbf{t}^{\overline{s}} - \epsilon^{\overline{s}} \mathbf{t}^{s} \right) : \mathbf{d}^{\overline{s}}$$

$$+\sum_{\alpha\in\mathbb{J}_{\mathrm{I}}}\frac{1}{\theta}\left[\epsilon^{\overline{\alpha}}\mathsf{t}^{\overline{\alpha}}-\epsilon^{\overline{\alpha}}\gamma^{\alpha}\left(\mathsf{I}-\mathsf{G}^{\alpha}\right)\right]:\mathsf{d}^{\overline{\alpha}}$$

$$+\frac{1}{\theta} \left[ \epsilon^{\overline{wns}} \overline{t}^{\overline{wns}} + \epsilon^{\overline{wns}} \gamma^{wns} \left( I - G^{wns} \right) \right] : d^{\overline{wns}}$$

$$+\sum_{\alpha\in\mathfrak{I}_{\mathrm{f}}}\frac{1}{\theta}\left\{\nabla\left(\epsilon^{\overline{\alpha}}p^{\alpha}\right)-\epsilon^{\overline{\alpha}}\rho^{\alpha}\nabla\left(\mu^{\overline{\alpha}}+K_{E}^{\overline{\alpha}}+\psi^{\overline{\alpha}}\right)-\epsilon^{\overline{\alpha}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}}\right.$$

$$+\sum_{\kappa\in\mathfrak{I}_{c\alpha}^{-}}\overset{\alpha\rightarrow\kappa}{\mathbf{T}}\left\{\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)\right.$$

$$-\sum_{\alpha\in\mathfrak{I}_{\mathrm{I}}}\frac{1}{\theta}\left\{\nabla\cdot\left[\left(\mathsf{I}-\mathsf{G}^{\alpha}\right)\epsilon^{\overline{\alpha}}\gamma^{\alpha}\right]+\sum_{\kappa\in\mathfrak{I}_{\mathrm{c}\alpha}^{+}}\overset{\kappa\to\alpha}{\mathbf{T}}-\overset{\alpha\towns}{\mathbf{T}}\right\}\cdot\left(\mathbf{v}^{\overline{\alpha}}-\mathbf{v}^{\overline{s}}\right)$$

$$+ \frac{1}{\theta} \left\{ \nabla \cdot \left[ \left( \mathsf{I} - \mathsf{G}^{wns} \right) \epsilon^{\overline{wns}} \gamma^{wns} \right] - \sum_{\kappa \in \mathfrak{I}^+_{cwns}} \mathbf{T}^{\kappa \to wns} \right\}$$

$$+ \langle \mathbf{n}_{s} \cdot \mathbf{t}_{s}^{*} \cdot \mathbf{n}_{s} \mathbf{n}_{s} \rangle_{\Omega_{wns}, \Omega} \bigg\} \cdot \left( \mathbf{v}^{\overline{wns}} - \mathbf{v}^{\overline{s}} \right)$$

$$+\frac{1}{\theta}\left[\frac{D^{\overline{s}}\epsilon^{\overline{w}}}{Dt}-\chi_{s}^{\overline{ws}}\frac{D^{\overline{s}}\epsilon}{Dt}-\frac{\gamma^{wn}\hat{k}_{1}^{wn}\left(\epsilon^{\overline{wn}}-\epsilon_{eq}^{\overline{wn}}\right)}{\left(p_{w}^{wn}-p_{n}^{wn}\right)}\right]\left(p_{w}^{wn}-p_{n}^{wn}-\gamma^{wn}J_{w}^{wn}\right) \xrightarrow{g}$$

$$+\frac{1}{\theta}\frac{\mathrm{D}^{s}\epsilon}{\mathrm{D}t}\left[\chi_{s}^{\overline{ws}}p_{w}^{ws}+\chi_{s}^{\overline{ns}}p_{n}^{ns}+\chi_{s}^{\overline{ws}}\left(\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\right)_{s}^{ws}+\chi_{s}^{\overline{ns}}\left(\mathbf{n}_{s}\cdot\mathbf{t}_{s}\cdot\mathbf{n}_{s}\right)_{s}^{ns}\right]$$

$$+\chi_s^{\overline{ws}}\gamma^{ws}J_s^{ws}+\chi_s^{\overline{ns}}\gamma^{ns}J_s^{ns}$$

$$-\left(\frac{\epsilon^{\overline{wns}}}{\epsilon^{\overline{ws}}+\epsilon^{\overline{ns}}}\right)\left(\gamma_{wn}^{wns}\sin\varphi^{\overline{ws,wn}}-\gamma^{wns}\kappa_N^{\overline{wns}}-(\mathbf{n}_s\cdot\mathbf{t}_s^*\cdot\mathbf{n}_s)^{wns}\right)\right]$$

$$-\frac{1}{\theta}\left(\epsilon^{\overline{ws}} + \epsilon^{\overline{ns}}\right) \frac{D^{\overline{s}} \chi_{\overline{s}}^{\overline{ws}}}{Dt} \left[\gamma_{wn}^{wns} \cos \varphi^{\overline{ws,wn}} + \gamma_{ws}^{wns} - \gamma_{ns}^{wns} + \gamma^{wns} \kappa_{\overline{G}}^{\overline{wns}}\right]$$
<sup>13</sup>

where all terms are described in the nomenclature section. Lines 1–3 are the product of fluxes involving stress tensors and a deformation rate tensor. Lines 4–8 are products involving momentum transfer and relative velocities. Line 9 is an expression involving capillary pressure. Lines 10–12 involve the change in porosity in response to a balance of forces normal to the solid surface. Line 13 is a change in the wetted fraction of the solid phase resulting from forces on the common curve tangential to the surface of the solid. Line 14 is the entropy density production rate.

While (88) is much shorter than the general simplified EI for two-fluid flow, it can be used as a starting point to illustrate how secondary restrictions can reduce an EI. To do so, we can specify the following additional secondary restrictions: (1) the solid phase is fixed and incompressible, and thus, the porosity is constant in both time and space; (2) interface and common curve momentum are not resolved, and jump conditions for momentum transfer

between phases are assumed; (3) fluid pressures averaged over the fluid–fluid interface can be approximated by the intrinsic average of the fluid pressures; (4) phase densities are constant in space and time; (5) kinetic energy fluctuation terms are negligible for the slow flow considered; (6) the media are isotropic with respect to fluid flow; and (7) deviation terms involving pressures and potentials can be neglected. Under these conditions, the simplified EI is further reduced to

$$\sum_{\alpha \in \mathcal{J}_{\mathrm{f}}} \frac{1}{\theta} \left( \epsilon^{\overline{\alpha}} \mathbf{t}^{\overline{\alpha}} + \epsilon^{\overline{\alpha}} p^{\alpha} \mathbf{I} \right) : \mathbf{d}^{\overline{\alpha}} \qquad 1$$

$$+ \sum_{\alpha \in \mathcal{J}_{\mathrm{f}}} \frac{1}{\theta} \left[ \nabla \left( \epsilon^{\overline{\alpha}} p^{\alpha} \right) - \epsilon^{\overline{\alpha}} \rho^{\alpha} \nabla \left( \mu^{\overline{\alpha}} + \psi^{\overline{\alpha}} \right) - \epsilon^{\overline{\alpha}} \rho^{\alpha} \mathbf{g}^{\overline{\alpha}} + \mathbf{T}^{\overline{\mathbf{T}}} \right] \cdot \mathbf{v}^{\overline{\alpha}} \qquad 2$$

$$+ \frac{1}{\theta} \left[ \frac{\mathbf{D}^{\overline{s}} \epsilon^{\overline{w}}}{\mathbf{D}t} - \frac{\gamma^{wn} \hat{k}_{1}^{wn} \left( \epsilon^{\overline{wn}} - \epsilon^{\overline{wn}}_{eq} \right)}{\left( p^{w} - p^{n} \right)^{2}} \right] \left( p^{w} - p^{n} - \gamma^{wn} J_{w}^{wn} \right) \qquad 3$$

$$= \sum_{\alpha \in \mathcal{I}} \Lambda^{\overline{\alpha}} \ge 0 \quad \text{for } \kappa = \mathcal{I}_{\mathrm{f}} \setminus \alpha . \qquad (89)$$

The first three lines of (89) are each flux–force pair that can produce entropy. Since all fluxes are independent of other fluxes in the set, these lines can be considered individually and each of the lines must be greater than or equal to zero under all conditions. These lines thus form permissibility conditions for closure relation. Multiple sets of closure relations are possible that meet this requirement, which is consistent with the usual approximate nature of closure relations. We will formulate closure relations for each line in turn.

If one examines macroscale flow in a porous medium bulk, the effect of boundaries of the system is insignificant compared to those from boundaries between the fluid phases and the solid phase. This observation can be described as the fluids being macroscopically inviscid. Thus, the first line of (89) can be approximated using a zero-order approximation in which the flux in parenthesis is always zero, which can be written as

$$\mathbf{t}^{\overline{\alpha}} = -p^{\alpha} \mathbf{I} \quad \text{for } \alpha \in \mathcal{I}_{\mathrm{f}} \ . \tag{90}$$

A cross-coupled, first-order closure approximation for the second line of (89) results in the equation

$$\nabla\left(\epsilon^{\overline{\alpha}}p^{\alpha}\right) - \epsilon^{\overline{\alpha}}\rho^{\alpha}\nabla\left(\mu^{\overline{\alpha}} + \psi^{\overline{\alpha}}\right) - \epsilon^{\overline{\alpha}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}} + \mathbf{T}^{\alpha \to \kappa} = \hat{R}_{w}^{\alpha}\mathbf{v}^{\overline{w}} + \hat{R}_{n}^{\alpha}\mathbf{v}^{\overline{n}} \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} .$$
(91)

The cross-coupled form is posited based upon microscale studies that have shown the importance of momentum transfer across a fluid–fluid interface (Li et al. 2005). A first-order closure approximation applied to the third line of (89) yields

$$\frac{\mathbf{D}^{\overline{s}}\epsilon^{\overline{w}}}{\mathbf{D}t} - \frac{\gamma^{wn}\hat{k}_{1}^{wn}\left(\epsilon^{\overline{wn}} - \epsilon^{\overline{wn}}_{eq}\right)}{\left(p^{w} - p^{n}\right)} = \hat{c}^{wn}\left(p^{w} - p^{n} - \gamma^{wn}J_{w}^{wn}\right) \,. \tag{92}$$

This expression is based upon kinematics and shows the interrelationship among changes in volume fraction, interfacial area and capillary pressure. Each term in this equation vanishes at equilibrium.

The above three closure relations can be combined with conservation of mass and momentum equations for the fluid phases, equations of state and parametric relations for closure coefficients to produce a solvable model. We will examine the steps needed to do so. The conservation of mass equations for the fluid phases under the secondary restrictions applied to this model are

$$\frac{\partial \epsilon^{\overline{\alpha}}}{\partial t} + \nabla \cdot \left( \epsilon^{\overline{\alpha}} \mathbf{v}^{\overline{\alpha}} \right) = 0 \quad \text{for } \alpha \in \mathcal{I}_{\mathrm{f}} , \qquad (93)$$

and the conservation of momentum equations are

$$\frac{\partial \left(\epsilon^{\overline{\alpha}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\right)}{\partial t} + \nabla \cdot \left(\epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{v}^{\overline{\alpha}}\mathbf{v}^{\overline{\alpha}}\right) - \nabla \cdot \left(\epsilon^{\overline{\overline{\alpha}}}t^{\overline{\overline{\alpha}}}\right) - \epsilon^{\overline{\overline{\alpha}}}\rho^{\alpha}\mathbf{g}^{\overline{\alpha}} + \overset{\alpha \to \kappa}{\mathbf{T}}$$

$$= 0 \quad \text{for } \alpha \in \mathfrak{I}_{\mathrm{f}} \text{ and } \kappa = \mathfrak{I}_{\mathrm{f}} \setminus \alpha . \tag{94}$$

Equation (94) can be simplified by assuming slow flow and neglecting the first two terms, substituting Eq. (90) for the stress tensor, and subtracting Eq. (91) to eliminate the interfacial transfer of momentum term giving

$$\epsilon^{\overline{\alpha}}\rho^{\alpha}\nabla\left(\mu^{\overline{\alpha}}+\psi^{\overline{\alpha}}\right)+\hat{R}_{w}^{\alpha}\mathbf{v}^{\overline{w}}+\hat{R}_{n}^{\alpha}\mathbf{v}^{\overline{n}}=0\quad\text{for }\alpha\in\mathbb{J}_{\mathrm{f}}\;.$$
(95)

Applying the Gibbs–Duhem equation, converting the gravitational potential term to a gravitational acceleration vector, and dropping deviation terms associated with these quantities, in accordance with secondary restriction (7) yields

$$\epsilon^{\overline{\overline{\alpha}}} \nabla p^{\alpha} - \epsilon^{\overline{\overline{\alpha}}} \rho^{\alpha} \mathbf{g}^{\overline{\alpha}} + \hat{R}_{w}^{\alpha} \mathbf{v}^{\overline{w}} + \hat{R}_{n}^{\alpha} \mathbf{v}^{\overline{n}} = 0 \quad \text{for } \alpha \in \mathbb{J}_{\mathrm{f}} .$$
<sup>(96)</sup>

Equations (92), (93) and (96) are a set of nine equations with a corresponding set of unknowns given by

$$\mathcal{U} = \{ \epsilon^{\overline{\alpha}}, \mathbf{v}^{\overline{\alpha}}, p^{\alpha}, \epsilon^{\overline{wn}}, \epsilon^{\overline{wn}}_{eq}, J_w^{wn} \} \text{ for } \alpha \in \mathcal{I}_{\mathrm{f}} , \qquad (97)$$

which has a cardinality of 13 and leaving an equation deficit of four. This assumes that densities are specified, all quantities with a hat are measurable coefficients, the gravitational acceleration is known, and the interfacial tension between the fluids  $\gamma^{wn}$  is known.

To close the system of equations, the constraint on volume fractions can be used as follows:

$$\epsilon^{\overline{\overline{w}}} + \epsilon^{\overline{\overline{n}}} = \epsilon , \qquad (98)$$

and an equation of state for the mean curvature can be posited

$$J_w^{wn} = J_w^{wn}(\epsilon^{\overline{w}}, \epsilon^{\overline{wn}}) , \qquad (99)$$

the state equation can be inverted under equilibrium conditions giving

$$\epsilon_{\rm eq}^{\overline{wn}} = \epsilon_{\rm eq}^{\overline{wn}} \left( \frac{p^w - p^n}{\gamma^{wn}}, \epsilon^{\overline{w}} \right) \,, \tag{100}$$

a kinematic equation can be specified for the fluid–fluid interfacial area (Gray and Miller 2010, 2014)

$$\frac{\partial \epsilon^{\overline{wn}}}{\partial t} - J_w^{wn} \frac{\partial \epsilon^{\overline{w}}}{\partial t} + \nabla \cdot \left( \epsilon^{\overline{wn}} \mathbf{w}^{wn} \right) + \hat{k}_1^{wn} \left( \frac{p^n - p^w + \gamma^{wn} J_w^{wn}}{p^n - p^w} \right) \left( \epsilon^{\overline{wn}} - \epsilon_{\text{eq}}^{\overline{wn}} \right) = 0 ,$$
(101)

and a parameterization for the interfacial velocity is posited in a general functional form as

$$\mathbf{w}^{wn} = \mathbf{w}^{wn}(\mathbf{v}^{\overline{w}}, \mathbf{v}^{\overline{n}}) .$$
(102)

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In principle, this provides a closed solvable model for two-fluid flow, subject to the secondary restrictions that have been specified. Three items are worth further consideration: the need for specific (rather than general) functional forms, higher fidelity models, and the reduction of the formulated model to a simpler form. We will consider these topics briefly in turn.

Equations (99), (100) and (102) are specified in a general functional form, yet specific forms are needed to produce a solvable model. Efforts to determine a state equation for capillary pressure that includes interfacial areas has been ongoing for some time, and it has proved to be an elusive target. It is also reasonable to expect that the  $\hat{R}$  coefficients will depend upon the state of the system, just as relative permeabilities depend upon the state of the system (Miller et al. 1998).

Recent work has focused on deriving an equation of state for  $J_w^{wn}$ . Recall that the macroscale capillary pressure is  $-\gamma^{wn}J_w^{wn}$ . If  $\gamma^{wn}$  is a known measurable constant, then knowing  $J_w^{wn}$  also allows for the determination of the macroscale capillary pressure. It has been shown that the mean curvature can be described as (McClure et al. 2018)

$$J_w^{wn} = F(\epsilon^{\overline{n}}, \epsilon^{\overline{wn}}, \chi^{\overline{n}}) , \qquad (103)$$

where *F* is a function described by a general additive model (Wood 2006), and  $\chi^{\overline{n}}$  is the specific Euler characteristic of the non-wetting phase. This description is hysteretic-free, based upon integral topology, and has been confirmed with a large set of computational results across a wide range of porous media. In addition, this description is a state equation that holds under both equilibrium and non-equilibrium conditions. This work also shows that neglecting  $\chi^{\overline{n}}$  degrades the state equation to a form that would include significant error, although including  $\epsilon^{\overline{wn}}$  greatly reduces the error from using  $\epsilon^{\overline{n}}$  alone. Within the model formulated above, two choices are possible. First, one could neglect  $\chi^{\overline{n}}$  and accept the error of the approximation. Given an approximation for  $\mathbf{w}^{wn}$ , which must be consistent with the EI, the model would be completely closed and solvable, assuming approximations could be derived for the resistance coefficients in terms of the state variables—work that has not yet been undertaken. More ambitiously, to include  $\chi^{\overline{n}}$  one would need an additional evolution equation for this quantity, which is not yet available. Higher fidelity models could be formulated from the hierarchy by, for example, including common curves or relaxing some of the other restrictions made to deduce the subject model.

Lastly, one could further simplify the formulated model to reduce the complexity and concomitantly the fidelity and scope of the physics explicitly represented. This would require additional restrictions and approximations beyond those already specifically noted. For example, one could choose to ignore interfacial areas, which would be equivalent to hypothesizing that the interfaces are always at an equilibrium state, which is known to be a poor assumption from recent microfluidics experiments and pore-scale simulations (Gray et al. 2015). The second term in Eq.(92) would vanish; the set of unknowns given by (97) would not include either of the interfacial area terms; the expression for  $J_w^{wn}$  would not include interfacial area; Eq. (100) would not be required; and Eq. (101) could be ignored. The resultant model would resemble the traditional model for two-fluid flow, but it would include cross-coupling (Li et al. 2005) and a common form of the approximation for the relaxation rate of the fluid pressures to an equilibrium state (Celia et al. 2001). The many assumptions made that are known to be inaccurate would make this a relatively crude model, which is typical of current practice.

#### 6.3 Advantages and Disadvantages

The advantages of the TCAT approach include a firm connection between the microscale and larger scales; the natural incorporation of scale-consistent thermodynamics; the use of conservation equations for phases, interfaces, common curves and common points; the explicit emergence of quantities such as interfacial and common curve extents, tensions, and curvatures and contact angles at the macroscale; the substantial body of derived model component parts including conservation equations and entropy inequalities to guide the closure of new model instances from the several hierarchies of models that have been developed without a complete reformulation; and the ability to use microscale information to evaluate, verify and validate various components of macroscale models. A further significant advantage is the structured model-building approach, which provides a means to formulate models of a varying fidelity for a given application.

The disadvantages of the TCAT method are that the details of the approach are mathematically involved and substantial effort is needed to formulate and close a new mathematical hierarchy of models for a given class of application. This disadvantage is offset by the existence of model hierarchies for several different classes of models and the structured nature of the approach that allows reuse of various components needed to formulate a model. Perhaps the most significant disadvantage of the method is that the model formulations deviate from traditional approaches. Thus, the burdens of discovery are substantial. An example of this aspect of TCAT model building can be seen in the application provided, where a completely new description of a capillary pressure state equation was needed and has been derived, which required some substantial effort. Similar efforts will be needed for resistance coefficients, interfacial velocities and the Euler characteristic evolution equation. Only when all such closure relations are generated in specific form, evaluated and validated will a complete, rigorous model be fully closed and solvable. Adding common curve components would require additional specific model-building components. A challenge that TCAT and many other upscaling techniques face is the use of closure relations for boundary conditions, which may come from numerical or laboratory experiments. In this regard, the recent proposition made by Klika and Krause (2018) that it is possible to choose boundary conditions such that all forces but one vanish, while keeping the system outside of equilibrium, deserves some consideration. In addition, the applications mentioned above are restricted to deterministic systems at some scale. Certainly, transport processes involving more complicated situations than those allowed by the Onsager cross-coupling and CIT can arise in porous media systems and these can be studied using cross-coupling approaches. In this regard, the use of functional constraints as those suggested by Klika et al. (2017) may be a potential aid. Lastly, the applications of this approach have been so far restricted to porous media systems and extensions to other systems that are still hierarchical in nature are desirable.

## 7 Homogenization Theory

### 7.1 Fundamentals

Homogenization by two-scale expansions (or its generalization to multiple-scale expansions) is also referred to as periodic homogenization, since it is based on the hypothesis that a porous medium  $\Omega$  with characteristic dimensionless length scale 1 can be represented microscopically by a collection of spatially periodic "unit cells" *Y* with a characteristic length  $\varepsilon$ , such that the scale separation parameter



**Fig. 12** (Left) Conceptual representation of the homogenization approach (after Battiato 2016). (Right) Applicability conditions of macroscale model (138) in terms of dimensionless numbers *Pe* and *Da*. The shaded region indicate conditions under which (138) represents averaged pore scale within upscaling errors of order  $O(\varepsilon^2)$ 

$$\varepsilon \ll 1,$$
 (104)

See Fig. 12. Although the assumption of periodicity of the porous medium is not always realistic, particularly for natural porous media, spatially periodic representations of microstructures of porous media are routinely used to derive macroscopic properties and effective models of phenomena taking place in disordered media that lack such periodicity (Nitsche and Brenner 1989, Section 2). Recent studies have also relaxed the periodicity hypothesis (Bruna and Chapman 2015). The unit cell  $Y = \mathcal{B} \cup \mathcal{G}$  consists of the pore space  $\mathcal{B}$  and the impermeable solid matrix  $\mathcal{G}$  that are separated by the smooth surface  $\Gamma$ . The pore spaces  $\mathcal{B}$  of each cell Yform the multi-connected pore space domain  $\mathcal{B}^{\varepsilon} \subset \Omega$  bounded by the smooth surface  $\Gamma^{\varepsilon}$ .

In homogenization theory by multiple-scale expansions (see Hornung 1997), a homogenized equation for a pore-scale (dimensional) quantity  $\hat{\psi}$  is obtained by determining the following limit,

$$\langle \hat{\psi} \rangle = \langle \lim_{\varepsilon \to 0} \hat{\psi}_{\varepsilon} \rangle, \tag{105}$$

where  $\psi_{\varepsilon}$  is the sequence (indexed by  $\varepsilon$ ) of solutions of the microscale equation

$$\mathcal{L}[\hat{\psi}] = f, \quad \mathbf{x} \in \mathcal{B}^{\varepsilon} \tag{106}$$

with either constant coefficients in the highly irregular periodic flow domain  $\mathcal{B}^{\varepsilon}$  (since from a mathematical point of view,  $\Omega$  is a periodically perforated domain, i.e., it has many small holes which represent solid obstacles that the fluid cannot penetrate), or equivalently, with periodically oscillating coefficients in a regular domain  $\Omega$ , composed of both the solid matrix  $\mathcal{G}$  and the pore space  $\mathcal{B}$ . The passage between these two equivalent representations is accomplished by introducing an indicator (membership) function as detailed in Hornung (1997)).

The limit is determined through the following steps:

Step 1. For any microscale variable, perform a two-scale asymptotic expansion that is an ansatz of the form,

$$\hat{\psi}_{\varepsilon}(\mathbf{x},t) := \hat{\psi}(\mathbf{x},\mathbf{y},t) = \sum_{m=0}^{\infty} \varepsilon^m \hat{\psi}_m(\mathbf{x},\mathbf{y},t) = \hat{\psi}_0(\mathbf{x},\mathbf{y},t) + \varepsilon \hat{\psi}_1(\mathbf{x},\mathbf{y},t) + \varepsilon^2 \hat{\psi}_2(\mathbf{x},\mathbf{y},t) + \cdots$$
(107)

wherein each function  $\hat{\psi}_m(\mathbf{x}, \mathbf{y}, t)$  in this series depends on two variables,  $\mathbf{x}$ , the macroscopic (or slow) variable, and  $\mathbf{y}$ , the microscopic (or fast) variable defined as

$$\mathbf{y} = \frac{\mathbf{x}}{\varepsilon},\tag{108}$$

and  $\hat{\psi}_m(\mathbf{x}, \mathbf{y}, t), m = 0, 1, \dots$ , are *Y*-periodic in **y**.

Step 2. Insert the ansatz (107) in Eq. (1) satisfied by  $\psi_{\varepsilon}$  while accounting for the following relation for the spatial derivatives,

$$\nabla \hat{\psi}_{\varepsilon} = \nabla_{\mathbf{x}} \hat{\psi} + \varepsilon^{-1} \nabla_{\mathbf{y}} \hat{\psi}. \tag{109}$$

Step 3. Identify and collect terms of like-powers of  $\varepsilon$ . This leads to a cascade of equations for each term  $\hat{\psi}_m(\mathbf{x}, \mathbf{y}, t)$ . In general, averaging with respect to  $\mathbf{y}$  yields the homogenized equation for  $\psi_0$ . Specifically, three averages are generally defined:

$$\langle \hat{\psi}_{\varepsilon} \rangle \equiv \frac{1}{|Y|} \int_{\mathcal{B}(\mathbf{x})} \hat{\psi}_{\varepsilon} d\mathbf{y}, \quad \langle \hat{\psi}_{\varepsilon} \rangle_{\mathcal{B}} \equiv \frac{1}{|\mathcal{B}|} \int_{\mathcal{B}(\mathbf{x})} \hat{\psi}_{\varepsilon} d\mathbf{y}, \text{ and } \langle \hat{\psi}_{\varepsilon} \rangle_{\Gamma} \equiv \frac{1}{|\Gamma|} \int_{\Gamma(\mathbf{x})} \hat{\psi}_{\varepsilon} d\mathbf{y}$$
(110)

are three local averages (function of **x**) over the pore space  $\mathcal{B}(\mathbf{x})$  or the solid-liquid boundary  $\Gamma$  in the unit cell  $Y(\mathbf{x})$  centered at **x**. In (110),  $\langle \psi_{\varepsilon} \rangle = \hat{\phi} \langle \hat{\psi}_{\varepsilon} \rangle_{\mathcal{B}}$  and  $\hat{\phi} = |\mathcal{B}|/|Y|$  is the porosity. A closure problem needs to be formulated to be able to close the system of equations and define effective parameters.

Step 4. "Another step is required to rigorously justify the homogenization result obtained heuristically with this two-scale asymptotic expansion" (Hornung 1997, p. 238), i.e., to prove the two-scale convergence, as outlined in the mathematics literature on homogenization. However, generally such proofs are available only for linear partial differential equations, although most of the engineering and science applications deal with highly nonlinear problems.

The steps previously outlined reflect the classical application of homogenization theory by two-scale expansions (free of proofs), which is generally performed on dimensional equations (except for the spatial variables, x and y, that are dimensionless). The focus on dimensionless spatial variables only is probably due to two factors: the first proofs of two-scale convergence were developed for Poisson equation (which does not contain timescales) and the focus (shared by all upscaling communities) on separation of geometric length scales, a *conditio* sine qua non the upscaling procedure itself would not be possible. The recognition of the importance of temporal scales (i.e., of the dynamic features of the system, besides its staticgeometric-characteristics) is much more recent. Originally introduced by Auriault and Adler (1995), and later further developed in a number of other works (Battiato and Tartakovsky 2011; Boso and Battiato 2013; Korneev and Battiato 2016), the method of homogenization, performed on dimensionless equations has demonstrated to be particularly powerful (as we will show in Applications Section) in (i) deriving families of upscaled equations under different dynamical conditions (i.e., for different values of dimensionless numbers) and (ii) a priori identifying applicability regimes of macroscale equations based on the order of magnitude of dimensionless numbers.

We will now outline few modifications needed in the context of multiple-scale expansion in order to handle multi-temporal scales as controlled by the dimensionless numbers  $\Pi_j$ ,  $j = \{1, \dots, N\}$ . Let us assume that transport in a porous medium occurs because of N + 1 processes (e.g., diffusion, advection, reaction, electromigration, etc.). Then, N + 1

characteristic timescales  $\hat{t}_j$ ,  $j = \{0, ..., N\}$  can be defined once the physical domain and its boundary conditions are defined. Let  $\hat{t}$  be a macroscale dimensional time, and  $\tau := \hat{t}/\hat{t}_0$ a dimensionless macroscale time, defined by normalizing  $\hat{t}$  with the reference timescale  $\hat{t}_0$ . Then, we can define the following dimensionless temporal scales:

$$\tau_j := \frac{\hat{t}}{\hat{t}_j} = \Pi_j t, \quad \text{with} \quad \Pi_j = \frac{\hat{t}_0}{t_j}, \quad j = \{1, \dots, N\}$$
(111)

Then, expansion (107) can be re-written accounting also for slow and fast temporal scales as

$$\psi_{\varepsilon}(\mathbf{x},t) := \psi(\mathbf{x},\mathbf{y},t,\tau_1,\ldots,\tau_N) = \sum_{m=0}^{\infty} \varepsilon^m \hat{\psi}_m(\mathbf{x},\mathbf{y},t,\tau_1,\ldots,\tau_N)$$
(112)

and, in Step 2, the temporal derivatives must be accounted as follows

$$\frac{\partial \psi_{\varepsilon}}{\partial t} = \frac{\partial \psi}{\partial t} + \Pi_j \frac{\partial \psi}{\partial \tau_j}, \quad j = \{1, \dots, N\},\tag{113}$$

where Einstein summation is implied whenever a repeated index is present. Finally, by setting

$$\Pi_j := \varepsilon^{\alpha_j},\tag{114}$$

which provides a definition of  $\alpha_j$  once  $\varepsilon$  is defined and  $\Pi_j$  is fixed, one can (i) relate spatial and temporal scale dimensionless parameters,  $\varepsilon$  and  $\Pi_j$ , respectively, and (ii) explore the form of the upscaled equations for different values of the exponents  $\alpha_j$ , which determine the system behavior, as outlined in the following section, we show that bounds on the order of magnitude of  $\Pi_j$  are necessary to guarantee that both spatial and temporal scales are properly separated for a continuum-scale equation to be formulated.

#### 7.2 Applications

Homogenization theory has been applied to a large variety of problems in physics, engineering, environmental sciences, since its first elaboration and application to the study of composite materials in the 1970 and 1980s. The theoretical foundations of the approach were first developed in two seminal papers by Spagnolo (1968) and Sanchez-Palencia (1970) (see also Bakhvalov and Panasenko 1989). Within a homogenzation framework, researchers have studied the mechanical response of composite materials, such as bones (Hollister and Kikuchi 1994), transport in electrochemical systems (Ciucci and Lai 2011; Groot 2012; Finden 2012; Davit et al. 2013; Salvadori et al. 2014; Arunachalam et al. 2015), evolving microstructures (Peter 2009), design of nanoporous materials (Zhang and Tartakovsky 2017a).

In the following, we will show how homogenization applied to dimensionless equations can be employed not only to derive upscaled equations, but also their applicability conditions. We will consider two examples:

Homogenization of nth-order heterogeneous reactions in porous media. To demonstrate the method, we choose a simpler problem which, however, highlights some of the critical features of homogenization. We focus specifically on transport in a fully saturated porous medium of a solute that undergoes a nonlinear heterogeneous reaction once it reaches a threshold concentration value, at which it precipitates on the solid matrix to form a crystalline solid. The fluid contains a dissolved species  $\mathcal{M}$ , whose molar concentration  $\hat{c}_{\varepsilon}(\hat{\mathbf{x}}, \hat{t}) \text{ [molL}^{-3}]$  at point  $\hat{\mathbf{x}} \in \hat{\mathcal{B}}^{\varepsilon}$  and time  $\hat{t} > 0$  changes due to advection (as governed by the Stokes equation),

molecular diffusion, and a nonlinear heterogeneous reaction at the solid-liquid interface  $\hat{\Gamma}^{\varepsilon}$ . These processes are described by an advection–diffusion equation,

$$\frac{\partial \hat{c}_{\varepsilon}}{\partial \hat{t}} + \hat{\mathbf{v}}_{\varepsilon} \cdot \hat{\nabla} c_{\varepsilon} = \hat{\nabla} \cdot (\hat{\mathbf{D}} \hat{\nabla} \hat{c}_{\varepsilon}), \qquad \hat{\mathbf{x}} \in \hat{\mathcal{B}}^{\varepsilon}, \quad \hat{t} > 0,$$
(115)

where the molecular diffusion coefficient  $\hat{\mathbf{D}}$  is isotropic,  $\hat{\mathbf{D}} = \hat{\mathcal{D}}_m \mathbf{I}$  and  $\hat{\mathcal{D}}_m [L^2 T^{-1}]$  is the diffusion coefficient and  $\mathbf{I}$  is the identity matrix. Whenever the concentration  $\hat{c}_{\varepsilon}$  exceeds a threshold value  $\bar{c}$ , a heterogeneous reaction  $n\mathcal{M}\leftrightarrow\mathcal{N}_{(s)}$  occurs, in which n molecules of the solute  $\mathcal{M}$  precipitate in the form of one molecule of a crystalline solid  $\mathcal{N}_{(s)}$ . At the solid–liquid interface  $\hat{\Gamma}^{\varepsilon}$  impermeable to flow, mass conservation requires that, (e.g., Morse and Arvidson 2002, Eq. 5)

$$-\mathbf{n} \cdot \hat{\mathbf{D}} \hat{\nabla} \hat{c}_{\varepsilon} = \hat{k} (\hat{c}^a_{\varepsilon} - \overline{c}^a), \qquad \hat{\mathbf{x}} \in \hat{\Gamma}^{\varepsilon}, \quad \hat{t} > 0,$$
(116)

where **n** is the outward unit normal vector of  $\hat{\Gamma}^{\varepsilon}$ ,  $\hat{k} [L^{3a-2}T^{-1}mol^{1-a}]$  is the reaction rate constant,  $a \in \mathbb{Z}^+$  is related to the order of reaction *n* (Morse and Arvidson 2002, Eq. 6), and the threshold concentration  $\overline{c}$  represents the solubility product (Morse and Arvidson 2002). The previous equations can be cast in dimensionless form

$$\frac{\partial c_{\varepsilon}}{\partial t} + \nabla \cdot (-\mathbf{D}\nabla c_{\varepsilon} + Pe\mathbf{v}_{\varepsilon}c_{\varepsilon}) = 0, \quad \mathbf{x} \in \mathcal{B}^{\varepsilon}, \quad t > 0,$$
(117)

subject to

$$-\mathbf{n} \cdot \mathbf{D} \nabla c_{\varepsilon} = Da\left(c_{\varepsilon}^{a} - 1\right), \quad \mathbf{x} \in \Gamma^{\varepsilon}, \quad t > 0.$$
(118)

where

$$c_{\varepsilon} = \frac{\hat{c}_{\varepsilon}}{\bar{c}}, \quad \mathbf{x} = \frac{\hat{\mathbf{x}}}{L}, \quad \mathbf{v}_{\varepsilon} = \frac{\hat{\mathbf{v}}_{\varepsilon}}{U}, \quad \mathbf{D} = \frac{\hat{\mathbf{D}}}{D}, \quad p = \frac{\hat{p}\ell^2}{\hat{v}UL},$$
 (119)

are dimensionless quantities, D and U are characteristic values of **D** and  $\mathbf{v}_{\varepsilon}$ , and  $\ell$  is a characteristic length at the pore-scale, respectively. Furthermore, we define three timescales associated with diffusion  $(\hat{t}_D)$ , reactions  $(\hat{t}_R)$  and advection  $(\hat{t}_A)$  as

$$\hat{t}_D = \frac{L^2}{D}, \quad \hat{t}_R = \frac{L}{\hat{k}\bar{c}^{a-1}}, \quad \hat{t}_A = \frac{L}{U}.$$
 (120)

Ratios between these timescales define the dimensionless Damköhler ( $Da = \hat{t}_D/\hat{t}_R$ ) and Péclet ( $Pe = \hat{t}_D/\hat{t}_A$ ) numbers,

$$Da = \frac{L\hat{k}\overline{c}^{a-1}}{D}$$
 and  $Pe = \frac{UL}{D}$ . (121)

We now follow the steps as outlined in the previous section. Step 1. We start by representing the concentration  $c_{\varepsilon}(\mathbf{x}, t)$  in (117) as  $c_{\varepsilon}(\mathbf{x}, t) := c(\mathbf{x}, \mathbf{y}, t, \tau_r, \tau_a)$ . The latter is expanded into an asymptotic series in powers of  $\varepsilon$ ,

$$c(\mathbf{x}, \mathbf{y}, t, \tau_r, \tau_a) = \sum_{m=0}^{\infty} \varepsilon^m c_m(\mathbf{x}, \mathbf{y}, t, \tau_r, \tau_a),$$
(122)

wherein  $c_m(\mathbf{x}, \mathbf{y}, t, \tau_r, \tau_a)$  (m = 0, 1, ...) are Y-periodic in y. Finally, we set

$$Pe = \varepsilon^{-\alpha} \quad \text{and} \quad Da = \varepsilon^{\beta},$$
 (123)

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with the exponents  $\alpha$  and  $\beta$  determining the system behavior. For example, transport due to advection and dispersion at the pore scale is not homogenizable if  $\alpha \ge 2$  (Auriault and Adler 1995, Sec. 3.5, Tab. 1).

Step 2. Substituting (122) and (123) into (117) and (118), while accounting for (109) and (113), yields

$$\varepsilon^{-2} \Big[ \nabla_{\mathbf{y}} \cdot (-\mathbf{D} \nabla_{\mathbf{y}} c_{0} + \varepsilon^{1-\alpha} c_{0} \mathbf{v}_{0}) \Big] + \varepsilon^{-1} \Big\{ -\nabla_{\mathbf{x}} \cdot \mathbf{D} \nabla_{\mathbf{y}} c_{0} - \nabla_{\mathbf{y}} \cdot \mathbf{D} (\nabla_{\mathbf{y}} c_{1} + \nabla_{\mathbf{x}} c_{0}) \\ + \varepsilon^{1-\alpha} \Big[ \frac{\partial c_{0}}{\partial \tau_{a}} + \varepsilon^{\alpha+\beta} \frac{\partial c_{0}}{\partial \tau_{r}} + \nabla_{\mathbf{x}} \cdot (c_{0} \mathbf{v}_{0}) + \nabla_{\mathbf{y}} \cdot (c_{1} \mathbf{v}_{0} + c_{0} \mathbf{v}_{1}) \Big] \Big\} \\ + \varepsilon^{0} \Big\{ \frac{\partial c_{0}}{\partial t} - \nabla_{\mathbf{x}} \cdot \mathbf{D} (\nabla_{\mathbf{x}} c_{0} + \nabla_{\mathbf{y}} c_{1}) - \nabla_{\mathbf{y}} \cdot \mathbf{D} (\nabla_{\mathbf{x}} c_{1} + \nabla_{\mathbf{y}} c_{2}) \\ + \varepsilon^{1-\alpha} \Big[ \frac{\partial c_{1}}{\partial \tau_{a}} + \varepsilon^{\alpha+\beta} \frac{\partial c_{1}}{\partial \tau_{r}} + \nabla_{\mathbf{x}} \cdot (c_{1} \mathbf{v}_{0} + c_{0} \mathbf{v}_{1}) \\ + \nabla_{\mathbf{y}} \cdot (c_{1} \mathbf{v}_{1} + c_{0} \mathbf{v}_{2} + c_{2} \mathbf{v}_{0}) \Big] \Big\} = \mathcal{O} (\varepsilon) , \quad \mathbf{y} \in \mathcal{B}.$$
(124)

Similarly, boundary condition (118) can be written as

$$\varepsilon^{-1}(-\mathbf{n}\cdot\mathbf{D}\nabla_{\mathbf{y}}c_{0}) + \varepsilon^{0} \Big[-\mathbf{n}\cdot\mathbf{D}(\nabla_{\mathbf{x}}c_{0} + \nabla_{\mathbf{y}}c_{1}) - \varepsilon^{\beta}(c_{0}^{a} - 1)\Big] \\ + \varepsilon\Big[-\mathbf{n}\cdot\mathbf{D}(\nabla_{\mathbf{x}}c_{1} + \nabla_{\mathbf{y}}c_{2}) - \varepsilon^{\beta}c_{0}^{a-1}c_{1}\Big] = \mathcal{O}(\varepsilon^{2}), \quad \mathbf{y} \in \Gamma.$$
(125)

Step 3 The objective of this portion of the analysis is to find solutions for the functions  $c_0$ ,  $c_1$ , etc. (here we are looking for an approximation of the average concentration at the second order, and therefore we stop at terms of order  $\mathcal{O}(\varepsilon^2)$ ). In the following, we will only highlight the critical steps, while all the details of the derivation (rich of technical nuances) are available in "Appendix" of Battiato and Tartakovsky (2011). At the highest order, i.e.,  $\mathcal{O}(\varepsilon^{-2})$ , from (124) and (125) one obtains

$$\nabla_{\mathbf{y}} \cdot (-\mathbf{D}\nabla_{\mathbf{y}}c_0 + \varepsilon^{1-\alpha}c_0\mathbf{v}_0) = 0, \quad \mathbf{y} \in \mathcal{B}, \text{ subject to } -\mathbf{n} \cdot (\mathbf{D}\nabla_{\mathbf{y}}c_0) = 0, \quad \mathbf{y} \in \Gamma.$$
(126)

The homogeneity of (126) ensures that this boundary value problem has a trivial solution, i.e., that  $c_0$  is independent of **y**,

$$c_0 = c_0(\mathbf{x}, t, \tau_r, \tau_a), \quad \text{for any } \alpha < 2.$$
(127)

At order  $\mathcal{O}(\varepsilon^{-1})$ , one obtains

$$-\nabla_{\mathbf{y}} \cdot \mathbf{D}(\nabla_{\mathbf{y}} c_{1} + \nabla_{\mathbf{x}} c_{0}) + \varepsilon^{1-\alpha} \Big[ \frac{\partial c_{0}}{\partial \tau_{a}} + \varepsilon^{\alpha+\beta} \frac{\partial c_{0}}{\partial \tau_{r}} + \nabla_{\mathbf{x}} \cdot (c_{0} \mathbf{v}_{0}) + \nabla_{\mathbf{y}} \cdot (c_{1} \mathbf{v}_{0} + c_{0} \mathbf{v}_{1}) \Big] = 0, \quad \mathbf{y} \in \mathcal{B}.$$
(128)

subject to the boundary condition

$$-\mathbf{n} \cdot \mathbf{D}(\nabla_{\mathbf{x}} c_0 + \nabla_{\mathbf{y}} c_1) - \varepsilon^{\beta}(c_0^a - 1) = 0, \quad \mathbf{y} \in \Gamma.$$
(129)

Mathematical manipulation of (128) [detailed in Appendix A.2 of Battiato and Tartakovsky (2011)] leads to

$$\varepsilon^{1-\alpha} \Big[ (\mathbf{v}_0 - \langle \mathbf{v}_0 \rangle_{\mathcal{B}}) \nabla_{\mathbf{x}} c_0 - \varepsilon^{\alpha+\beta-1} \mathcal{K}^* (c_0^a - 1) + \mathbf{v}_0 \nabla_{\mathbf{y}} c_1 \Big] - \nabla_{\mathbf{y}} \cdot \mathbf{D} (\nabla_{\mathbf{y}} c_1 + \nabla_{\mathbf{x}} c_0) = 0,$$
(130)

which, together with (129), forms a boundary value problem for  $c_1$ . Due to the linearity of (130), we look for a solution in the form

$$c_1(\mathbf{x}, \mathbf{y}, t, \tau_r, \tau_a) = \boldsymbol{\chi}(\mathbf{y}) \cdot \nabla_{\mathbf{x}} c_0(\mathbf{x}, t, \tau_r, \tau_a) + \overline{c}_1(\mathbf{x}, t, \tau_r, \tau_a),$$
(131)

where  $\chi(\mathbf{y})$  is an unknown closure variable to be determined, which is *Y*-periodic. The postulation of (131) is one of the critical step in any upscaling, since it postulates the relationship between deviation fields (in this case  $c_1$ ) and macro-scale gradients ( $\nabla_{\mathbf{x}}c_0$ ). Also, depending of the form of the equation for  $c_1$ , (131) could contain convolution terms, which would lead to upscaled non-local equations (Hui and Oskay 2013). Substitution of (131) into (130) and (129) leads to the following cell problem for the closure variable  $\chi(\mathbf{y})$ :

$$\begin{bmatrix} -\nabla_{\mathbf{y}} \cdot \mathbf{D}(\nabla_{\mathbf{y}} \boldsymbol{\chi} + \mathbf{I}) + \varepsilon^{1-\alpha} \mathbf{v}_{0} \cdot \nabla_{\mathbf{y}} \boldsymbol{\chi} \end{bmatrix} \cdot \nabla_{\mathbf{x}} c_{0}$$
  
=  $\varepsilon^{1-\alpha}(\langle \mathbf{v}_{0} \rangle_{\mathcal{B}} - \mathbf{v}_{0}) \cdot \nabla_{\mathbf{x}} c_{0} + \varepsilon^{\beta} \mathcal{K}^{*}(c_{0}^{a} - 1), \quad \mathbf{y} \in \mathcal{B};$  (132a)

subject to  $\langle \boldsymbol{\chi} \rangle = 0$  and

$$-[\mathbf{n} \cdot \mathbf{D}(\nabla_{\mathbf{y}} \boldsymbol{\chi} + \mathbf{I})] \cdot \nabla_{\mathbf{x}} c_0 = \varepsilon^{\beta} (c_0^a - 1), \quad \mathbf{y} \in \Gamma.$$
(132b)

It is worth noticing that (132) is not satisfactory in its current form:  $\chi$ , the microscale closure variable, depends on source terms at the macro-scale (specifically  $\nabla_{\mathbf{x}} c_0$  and  $c_0$ ), i.e., microand macro-scales are fully coupled if no additional constraints (besides  $\varepsilon \ll 1$ ) are satisfied; this represents a contradiction with the postulation (131) where we require  $\chi$  to be function of **y** only. This inconsistency is resolved by imposing the following constraints on the exponents  $\alpha$  and  $\beta$  (or Pe and Da), so to guarantee that macroscale source terms are of higher order (i.e., smaller) than any other term. This leads to the following conditions on the dimensionless Damköhler and Peclet numbers

1. 
$$Pe < \varepsilon^{-2}$$
,

2. 
$$Da/Pe < \varepsilon$$

3. 
$$Da < 1$$
,

which are visually represented in Fig. 12 (Right). Such conditions guarantee that pore-scale concentration is well homogenized at the unit cell level: this imposes bounds on the relative speed between different microscale mass transport processes. Under these conditions, the closure variable  $\chi(\mathbf{y})$ , with zero mean  $\langle \chi \rangle = \mathbf{0}$ , is defined as a solution of the local problem

$$-\nabla_{\mathbf{y}} \cdot \mathbf{D}(\nabla_{\mathbf{y}} \mathbf{\chi} + \mathbf{I}) + \varepsilon \operatorname{Pe} \mathbf{v}_0 \nabla_{\mathbf{y}} \mathbf{\chi} = \varepsilon \operatorname{Pe} \left( \langle \mathbf{v}_0 \rangle_{\mathcal{B}} - \mathbf{v}_0 \right), \qquad \mathbf{y} \in \mathcal{B},$$
(133a)

$$-\mathbf{n} \cdot \mathbf{D}(\nabla_{\mathbf{y}} \mathbf{\chi} + \mathbf{I}) = 0, \qquad \qquad \mathbf{y} \in \Gamma.$$
(133b)

Having identified the conditions that guarantee homogenizability, we proceed to derive the effective transport equation by looking at the following order. Collecting  $\mathcal{O}(\varepsilon^0)$  terms in (124) and (125), one obtains

$$\frac{\partial c_0}{\partial t} - \nabla_{\mathbf{x}} \cdot \mathbf{D} (\nabla_{\mathbf{x}} c_0 + \nabla_{\mathbf{y}} c_1) - \nabla_{\mathbf{y}} \cdot \mathbf{D} (\nabla_{\mathbf{x}} c_1 + \nabla_{\mathbf{y}} c_2) + \varepsilon^{1-\alpha} \Big[ \frac{\partial c_1}{\partial \tau_a} + \varepsilon^{\alpha+\beta} \frac{\partial c_1}{\partial \tau_r} + \nabla_{\mathbf{x}} \cdot (c_1 \mathbf{v}_0 + c_0 \mathbf{v}_1) + \nabla_{\mathbf{y}} \cdot (c_1 \mathbf{v}_1 + c_0 \mathbf{v}_2 + c_2 \mathbf{v}_0) \Big] = 0, \quad \mathbf{y} \in \mathcal{B},$$
(134)

with the boundary condition

$$-\mathbf{n} \cdot \mathbf{D}(\nabla_{\mathbf{x}} c_1 + \nabla_{\mathbf{y}} c_2) - a\varepsilon^{\beta} c_0^{a-1} c_1 = 0, \quad \mathbf{y} \in \Gamma.$$
(135)

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Integrating (134) over  $\mathcal{B}$  with respect to y, using the boundary condition (135), and combining with (131), leads to

$$\frac{\partial \langle c_0 \rangle_{\mathcal{B}}}{\partial t} + \varepsilon^{1-\alpha} \frac{\partial \langle c_1 \rangle_{\mathcal{B}}}{\partial \tau_a} + \varepsilon^{1+\beta} \frac{\partial \langle c_1 \rangle_{\mathcal{B}}}{\partial \tau_r} = \nabla_{\mathbf{x}} \cdot (\phi^{-1} \mathbf{D}^* \nabla_{\mathbf{x}} c_0) - a \varepsilon^{\beta} \mathcal{K}^* c_0^{a-1} \langle c_1 \rangle_{\Gamma} - \phi^{-1} \varepsilon^{1-\alpha} \nabla_{\mathbf{x}} \cdot (c_0 \langle \mathbf{v}_1 \rangle + \overline{c}_1 \langle \mathbf{v}_0 \rangle), \quad (136)$$

where

$$\mathbf{D}^* = \langle \mathbf{D}(\mathbf{I} + \nabla_{\mathbf{y}} \mathbf{\chi}) \rangle + \varepsilon \, Pe \, \langle \mathbf{\chi} \mathbf{k} \rangle \nabla_{\mathbf{x}} p_0. \tag{137}$$

The previous equation can be further and finally rearranged in an effective advection– dispersion–reaction equation, which approximates averaged pore-scale processes up to errors of order  $\varepsilon^2$ 

$$\phi \frac{\partial \langle c \rangle_{\mathcal{B}}}{\partial t} = \nabla \cdot (\mathbf{D}^* \nabla \langle c \rangle_{\mathcal{B}} - Pe \langle c \rangle_{\mathcal{B}} \langle \mathbf{v} \rangle) - \varepsilon^{-1} \phi Da \mathcal{K}^* (\langle c \rangle_{\mathcal{B}}^a - 1), \quad \mathbf{x} \in \Omega,$$
(138)

where the effective dispersion coefficient  $\mathbf{D}^*$  is defined by (137) and  $\mathcal{K}^* = |\Gamma|/|\mathcal{B}|$ . The procedure outlined above allows one to derive, not only a family of macroscale equations (for different values of the dimensionless numbers), but importantly dynamic conditions under which scales can be separated, i.e., the applicability conditions of Fig. 12 (Right). These conditions, if satisfied, guarantee what is the maximum predictive error of macroscale models.

*Macroscale models of transport in Li-ion batteries*. Similar analyses can be conducted for virtually any porous media system. One such example is transport in Li-ion batteries. The battery community has heavily relied on the seminal work by Newman and Tiedemann (1975) where macroscopic ion transport equations were first formulated. The Newman model, as it came to be known, has been widely used in the context of battery management systems for optimal battery performance over its life cycle, as a physics-based alternative to electric circuit models. The original model was later generalized to account for concentrated solutions (Doyle et al. 1993; Doyle and Newman 1995), thermal effects (Thomas and Newman 2003) and capacity fade due to solid electrolyte interphase (SEI) growth (Ploehn et al. 2004; Smith et al. 2011; Pinson and Bazant 2013), just to mention a few. However, the inability of the model to predict average battery performance, e.g., charge and discharge cycles at high C-rates, the rate at which a battery is discharged relative to its maximum capacity, remained a big drawback. Although heuristically well known, the performance of the classical Newman model could not be *a priori* assessed for different operation conditions or battery chemistries.

The procedure previously outlined can be successfully used for this purpose as shown in Arunachalam et al. (2015). In the following, we briefly discuss the most relevant results by Arunachalam et al. (2015), and skip the derivations, since the highly nonlinear nature of Li-ion transport in electrochemical systems significantly complicates the homogenization process.

Due to space constraints, here we will present only the equations governing Li-ion transport in the electrolyte phase only. The full set of equations (including transport in the electrode phase can be found in Arunachalam et al. (2015)). The dimensionless form of mass and charge transport in the electrolyte of a Li-ion battery is given by

$$\frac{\partial c_{\varepsilon}^{e}}{\partial t} = \nabla \cdot \left[ (\mathbf{D}^{e} + \lambda t_{+}^{2} P e_{e} \mathbf{K}^{e} / c_{\varepsilon}^{e}) \nabla c_{\varepsilon}^{e} + 2 P e_{e} t_{+} \mathbf{K}^{e} \nabla \phi_{\varepsilon}^{e} \right], \quad \mathbf{x} \in \mathcal{B}^{\varepsilon}$$
(139a)

$$0 = \nabla \cdot [(\lambda t_{+} \mathbf{K}^{e} / c_{\varepsilon}^{e}) \nabla c_{\varepsilon}^{e} + 2 \mathbf{K}^{e} \nabla \phi_{\varepsilon}^{e}], \quad \mathbf{x} \in \mathcal{B}^{\varepsilon}$$
(139b)

subject to

$$\mathbf{n}_{e} \cdot \left[ (\mathbf{D}^{e} + \lambda t_{+}^{2} P e_{e} \mathbf{K}^{e} / c_{\varepsilon}^{e}) \nabla c_{\varepsilon}^{e} + 2 P e_{e} t_{+} \mathbf{K}^{e} \nabla \phi_{\varepsilon}^{e} \right] = D a_{e} f(c_{\varepsilon}^{e}, c_{\varepsilon}^{s}, \phi_{\varepsilon}^{s}, \phi_{\varepsilon}^{e}), \quad (140a)$$

$$\mathbf{n}_{e} \cdot \left[ \left( P e_{e} \lambda t_{+} \mathbf{K}^{e} / c_{\varepsilon}^{e} \right) \nabla c_{\varepsilon}^{e} + 2 P e_{e} \mathbf{K}^{e} \nabla \phi_{\varepsilon}^{e} \right] = D a_{e} f(c_{\varepsilon}^{e}, c_{\varepsilon}^{s}, \phi_{\varepsilon}^{s}, \phi_{\varepsilon}^{s}), \tag{140b}$$

on  $\Gamma^{\varepsilon}$ , respectively, where  $c_{\varepsilon}^{e} := \hat{c}_{\varepsilon}^{e}/\hat{c}_{max}^{s}$  and  $\phi_{\varepsilon}^{e} := \hat{\phi}_{\varepsilon}^{e}F/(2RT)$ , are the dimensionless Li-ion concentration and electrostatic potential in the electrolyte,  $\hat{c}_{max}^{s}$  is the maximum concentration of lithium that can be stored in the active particle,  $t_{+}$  is the transference number,  $\lambda := 1 + \frac{d \ln f_{\pm}}{d \ln(\hat{c}_{\varepsilon}^{e}/\hat{c}_{max}^{s})}$  is assumed constant, and  $f_{\pm}$  is the activity coefficient. In (139) and (140), the dimensional space and time scales are non-dimensionalized by the macroscopic length L and the diffusion time in the electrolyte phase  $\hat{t}_{D_{e}}$ , respectively, i.e.,  $\mathbf{x} = \hat{\mathbf{x}}/L$  and  $t_{e} = \hat{t}/\hat{t}_{D_{e}}$ ;  $\mathbf{D}^{e} = \hat{\mathbf{D}}^{e}/D^{e}$  and  $\mathbf{K}^{e} = \hat{\mathbf{K}}^{e}/K^{e}$  are the dimensionless interdiffusion coefficient and the electrolyte. Also,

$$f(c_{\varepsilon}^{e}, c_{\varepsilon}^{s}, \phi_{\varepsilon}^{e}, \phi_{\varepsilon}^{s}) = 2\sqrt{c_{\varepsilon}^{e}c_{\varepsilon}^{s}(1 - c_{\varepsilon}^{s})} \sinh(\phi_{\varepsilon}^{s} - \phi_{\varepsilon}^{e} - U)$$
(141)

where  $c_{\varepsilon}^{s}$  and  $\phi_{\varepsilon}^{s}$  are the dimensionless Li-ion concentration and electrostatic potential in the active particles,  $U = F\hat{U}/(2RT)$  is the dimensionless open circuit potential, F and R are the Faraday and the universal gas constants; T is temperature. Furthermore, transport processes occurring at the pore-scale include heterogeneous reaction on the electrode-electrolyte interface  $\hat{\Gamma}^{\varepsilon}$ , and ion diffusion and migration in the (electrode and) electrolyte phases, ( $\hat{S}^{\varepsilon}$  and)  $\hat{B}^{\varepsilon}$ . The characteristic timescales associated with the heterogeneous reaction, ionic diffusion and ionic migration over a macroscopic length scale L are

$$\hat{t}_R = \frac{LF}{k}, \quad \hat{t}_{D_e} = \frac{L^2}{D^e}, \quad \hat{t}_{M_e} = \frac{F^2 L^2 \hat{c}_{\max}^s}{RT K^e},$$
(142)

respectively. In (142),  $D^e = O(\hat{\mathbf{D}}^e)$  and  $K^e = O(\hat{\mathbf{K}}^e)$ , are characteristic values of the interdiffusion and electric conductivity tensors  $\hat{\mathbf{D}}^e$  and  $\hat{\mathbf{K}}^e$  in the electrolyte, respectively. We define the dimensionless Damköhler and electric Péclet numbers as

$$Da_e := \frac{\hat{t}_{D_e}}{\hat{t}_R} = \frac{Lk}{FD^e} \quad \text{and} \quad Pe_e := \frac{\hat{t}_{D_e}}{\hat{t}_{M_e}} = \frac{RTK^e}{F^2D^e\hat{c}_{\max}^s}.$$
 (143)

They provide information about the relative magnitude of ion transport processes in the electrolyte and the electrode phases.

Lithium transport in the electrolyte phase described by (139a)–(140b) can be homogenized, i.e., approximated up to order  $\varepsilon^2$ , by the following effective mass and charge transport equations

$$Pe_{e}\nabla_{\mathbf{x}} \cdot [(\lambda t_{+}\mathbf{K}^{e\star\star}/\langle c^{e}\rangle)\nabla_{\mathbf{x}}\langle c^{e}\rangle_{\mathcal{B}} + 2\mathbf{K}^{e\star\star}\nabla_{\mathbf{x}}\langle \phi^{e}\rangle_{\mathcal{B}}]$$
  
=  $2\eta\varepsilon^{-1}\mathcal{K}^{\star}Da_{e}f(\langle c^{e}\rangle_{\mathcal{B}}, \langle c^{s}\rangle_{s}, \langle \phi^{e}\rangle_{\mathcal{B}}, \langle \phi^{s}\rangle_{s}),$  (144)

and

$$\eta \partial_t \langle c^e \rangle_{\mathcal{B}} = \nabla_{\mathbf{x}} \cdot \left[ (\mathbf{D}^{e^{\star\star}} + \varepsilon^{-\alpha} \lambda t_+^2 \mathbf{K}^{e^{\star\star}} / \langle c^e \rangle) \nabla_{\mathbf{x}} \langle c^e \rangle_{\mathcal{B}} + 2\varepsilon^{-\alpha} t_+ \mathbf{K}^{e^{\star\star}} \nabla_{\mathbf{x}} \langle \phi^e \rangle_{\mathcal{B}} \right] + 2\eta \varepsilon^{-1} \mathcal{K}^{\star} Da_e f(\langle c^e \rangle_{\mathcal{B}}, \langle c^s \rangle_s, \langle \phi^e \rangle_{\mathcal{B}}, \langle \phi^s \rangle_s),$$
(145)

where

$$f(\langle c^e \rangle_{\mathcal{B}}, \langle c^s \rangle_s, \langle \phi^e \rangle_{\mathcal{B}}, \langle \phi^s \rangle_s) = 2\sqrt{\langle c^e \rangle_{\mathcal{B}} \langle c^s \rangle_s (1 - \langle c^s \rangle_s)} \sinh(\langle \phi^s \rangle_s - \langle \phi^e \rangle_{\mathcal{B}} - U)$$
(146)

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provided the following conditions are met:

- 1.  $\varepsilon \ll 1$ ,
- 2.  $Da_e < 1$ ,
- 3.  $Pe_e < 1$ ,
- 4.  $Da_e/Pe_e < 1$ ,

In (145) and (144), the dimensionless effective reaction rate constant in the electrolyte phase  $\mathcal{K}^{\star}$  is determined by the pore geometry,  $\mathcal{K}^{\star} = |\Gamma|/|\mathcal{B}|$ , and the dispersion tensors are given by  $\mathbf{D}^{e\star} = \langle \mathbf{D}^e(\mathbf{I} + \nabla_y \chi^e) \rangle_e$ , and  $\mathbf{K}^{e\star} = \langle \mathbf{K}^e(\mathbf{I} + \nabla_y \chi^e) \rangle_e$ . The closure variable  $\chi^e(\mathbf{y})$ has zero mean,  $\langle \chi^e \rangle_e = 0$ , and is defined as a solution to the local problem  $\nabla_y \cdot (\nabla_y \chi^e +$ I) = 0, y  $\in \mathcal{B}$ , subject to  $\mathbf{n}_e \cdot (\nabla_{\mathbf{y}} \mathbf{\chi}^e + \mathbf{I}) = 0$ ,  $\mathbf{y} \in \Gamma$ . Constraints (1)-(4) ensure the separation of scales. While constraint (1) is almost always met in practical applications since the pore size is generally much smaller that the electrode dimension, constraints (2)-(4)depend on the relative importance of the diffusion, electromigration and reaction mechanisms, i.e., they impose constraints on the transport regimes that can be appropriately modeled by the macroscale equations (145). Constraints (2)-(4) are plotted in Fig. 13(Left), where the light blue area represents a region where all conditions are satisfied. Figure 13(Left) shows the values of Pe and Da for a variety of common Li-ion battery chemistries. The phase diagram allows one to *a priori* assess for which chemistries macroscale models of the type of (145) are accurate (empty symbols) or not (solid symbols) representations of averaged porescale processes. Furthermore, the impact of C-rate on macroscale models predictivity can be assessed: different C-rates primarily impact the temperature range at which the battery is operated: experimental evidence shows significant cell temperature variations in terms of C-rate. The analysis is conducted for three different C-rates: low (C/25), medium (1C)and high (10C). Following experimental data, the temperature increase, starting from room temperature, can be estimated as follows: from 298 to 299 K, from 298 to 306 K and from 298 to 333 K at a discharge C-rate of C/25, 1C and 10C, respectively. In turn, temperature variations can greatly affect transport parameters in the electrolyte phase, specifically, k(reaction rate constant),  $D^e$  (the electrolyte diffusion coefficient) and  $K^e$  (the electrolyte conductivity coefficient). In Fig. 13(Right), we plot the variation of Da and Pe as a function of temperature for different C-rates (C/25 top, 1C center, 10C bottom) for the same chemistry (lithium manganate cathode). The analysis demonstrates that operating the battery at high C-rates may drive the system out of the applicability conditions. This can be explained as follows: when the influence of temperature on k is much more pronounced than on  $D^e$  and  $K^e$ , as for a battery operating at high C-rates, the diffusion transport mechanism is no longer the dominant mode of transport. As a result, Li-ion concentration in the electrolyte is not uniformly distributed inside the unit cell and the homogenized transport equations do not accurately capture transport at the microscale.

#### 7.3 Advantages and Drawbacks

Homogenization theory is an elegant tool to obtain macroscale models. As any other method, however, it presents advantages and drawbacks. One of the primary advantages (probably related to its origin in the applied math community) lies in its formal elegance (including the possibility of rigorously proving two-scale convergence proofs), clear, rigorous and easily traceable assumptions and its inherent ability to create a complete and self-consistent upscaling theory (for a given application) which includes (1) macroscale model, (2) its conditions of applicability and (3) a rigorous estimate of the order of magnitude of the upscaling error. All these elements can be used to both validate macroscale models and/or build predictive



**Fig. 13** (Left) Applicability conditions of the macroscale model (145) (shaded region), and data points corresponding to the most common Li-ion battery chemistries. The analysis allows one to a priori establish for which chemistries macroscale models of the type of (145) are accurate (empty symbols) or not (solid symbols). (Right) Analysis of the impact that C-rate has on the applicability conditions for a given chemistry: variation with temperature of dimensionless parameters  $\alpha$  and  $\beta$  in lithium manganate cathode batteries for three different C-rate of discharge, C/25 (top), 1C (middle) and 10C (bottom). An increase in C-rate induces higher operating temperature variations inside a battery: as a result the system can be driven outside the applicability regime region. Adapted from (Arunachalam et al. 2015)

understanding of dynamic processes across scales. It is worth noticing that the applicability conditions (as well as the homogenization method, in general) are rigorously derived from consistency arguments only, and do not require, unlike other methods, a priori physical intuition of the system under consideration, i.e., a "wrong choice" in collecting orders will lead to a mathematical inconsistency: in this respect, the method is suited for scientists/engineers/mathematicians who may be new to a specific application and have not yet developed a deep physical grasp of the process. Some of the primary drawbacks of the method include: (i) the hypothesis of periodicity (which could be numerically relaxed, to the detriment of rigor, by including a buffer zone or using mirroring techniques), (ii) the non-obvious generalization to account for non-local effects (Hu and Oskay 2018, 2019), (iii) its more difficult use in the formulation of multi-scale numerical algorithms, and (iv) often, the lack of rigorous two-scale convergence proofs for most nonlinear problems of interest in engineering, medical and environmental applications. We emphasize though that despite the unit cell is often represented as containing a single grain, this need not to be the case, and unit cells (although periodic) of arbitrary complexity could be chosen, see, e.g., (Korneev and Battiato 2016).

### 8 Renormalization Group Theory

Renormalization group theory provides more of a strategy than a method for dealing with physical systems at different scales. It has found a wide range of applications including in statistical mechanics and quantum field theory (Wilson and Kogut 1974), quantum electro-

dynamics (Gell-Mann and Low 1954) and turbulence (Yakhot and Orszag 1986). In some applications, renormalization group theory has made a major impact, best signified by the Nobel Prize being awarded to Kenneth Wilson for his work on critical phenomena and renormalization group theory (Wilson 1983). In the context of porous media, renormalization group theory has been applied to upscaling permeability (King 1989; Hristopulos and Christakos 1999) (see (Hristopulos 2003) for a review in the context of hydrology), gravity driven flow (Chen et al. 1991), and dispersion (O'Malley and Cushman 2012a, b). These three applications in porous media highlight the versatility of renormalization group theory. In one case (upscaling permeability), it helps us understand the constitutive properties of a porous medium. In another (gravity driven flow), it helps us understand fluid flow through a porous medium. In yet another (dispersion), it helps us understand mass transport in a porous medium. We note that renormalization group can be carried out in either real space or frequency space [e.g., contrast (King 1989) with Hristopulos and Christakos (1999)].

In this section, we will illustrate the basic concepts of the renormalization group theory by studying its use in the context of dispersion. An application of renormalization group theory to dispersion in the human bronchial tree will be considered. Subsequently, we will discuss some of the advantages and disadvantages of applying renormalization group theory in the field of porous media.

#### 8.1 Fundamentals

There are two key ingredients in an application of renormalization group theory. The first is a set of renormalization operators. The second is a set of objects that the operators act on. For example, in the context of upscaling the permeability, the objects that the operator acts on would be a collection of small-scale permeabilities. In this same context, the operator would transform a set of permeabilities at, say, the centimeter scale into an effective permeability (or set of effective permeabilities) at, say, the meter scale.

The physical intuition of these operators is that they change the scale at which the system is being studied or observed. In this sense, the renormalization operator can be viewed as an upscaling operator when it changes the scale to a larger scale. The nomenclature "renormalization group" is used because these operators often (but not always) follow the rules associated with the mathematical concept of a group (Dummit and Foote 2004). These rules state that there is an identity operator, that the composition of two operators is an operator in the group (called closure), that every operator has an inverse, and that composition of operators is associative. In more detail, the closure rule states that if A and B are two operators in the renormalization group, then the composition of A and B (denoted AB) is also an operator in the renormalization group. This means that an operator can be applied repeatedly, so if the operator is an upscaling operator it can go to larger and larger scales. For example, in the context of upscaling permeabilities, if A is the operator that goes from the centimeter to meter scale (i.e., it upscales by a factor of 1000) then B = AA would also be an operator in the group. The operator would scale from the centimeter scale to the kilometer scale (since each of two applications of A would increase the scale by a factor of 1000).

Our focus here will be on applying renormalization group theory in the context of dispersion. The renormalization group operators will act on stochastic processes that describe the dispersion of a particle as a function of time. The action of the renormalization group operators on a stochastic process is defined by

$$L_{p,r}X(t) = \frac{X(rt)}{r^p}$$
(147)

where  $L_{p,r}$  is a renormalization group operator and X(t) is a stochastic process. The stochastic process, X(t), would be defined by

$$X(t) = \int_0^t v'(t) \mathrm{d}t \tag{148}$$

where the motion of the particle is defined by a Lagrangian velocity  $v(t) = \bar{v}(t) + v'(t)$ ,  $\bar{v}(t)$  is the mean velocity, and v'(t) is the fluctuating velocity. The fluctuating velocity term can arise in porous media for different reasons depending on the application. For dispersion in hydrologic transport, it is often due to an insufficiently (and/or inaccurately) resolved velocity field arising from a lack of information about the hydraulic conductivity, boundary conditions, etc. For dispersion in the human bronchial tree, which we will explore in more detail in the subsequent subsection, it is due to the fact that different particles take different branches as they move through the bronchial tree.

It is worth nothing the connection between Eqs. (147) and (148) and the central limit theorem from probability theory. The classical central limit theorem states that the distribution of a sum of independent, identically distributed random variables converges to a normal distribution when normalized appropriately. The sum of random variables in this context is analogous to the integral in Eq. (148), and the normalization is analogous to the division by  $r^p$  in Eq. (147). Renormalization group approaches are often successful for essentially the same reason that the central limit theorem is useful. The central limit theorem is useful because it enables us to approximate a sum of many random variables with potentially complex distribution of these random variables do not matter, because they are wiped out by the summation. Similarly, small-scale information that is unimportant is often wiped out by a renormalization group operator that goes to a larger scale while essential information related to the larger scale is retained. See (Bouchaud and Georges 1990) for a more in-depth discussion of the central limit theorem perspective in the context of dispersion.

The operator,  $L_{p,r}$ , rescales both the temporal and spatial dimensions of the dispersive process, X(t), but in different ways. We can think of  $p \ge 0$  as being fixed and r > 0 as determining the extent of the upscaling. A bigger value of r would imply that  $L_{p,r}$  is upscaling to a larger scale. The value of p controls how much the spatial dimension is dilated in relation to the dilation of the temporal dimension. Note that

$$L_{p,r}L_{p,s}X(t) = L_{p,r}\left[\frac{X(st)}{s^{p}}\right] = \frac{X(rst)}{(rs)^{p}} = L_{p,rs}X(t)$$
(149)

so we see that the closure property is satisfied. The other properties of groups can be readily verified. The family of operators,  $L_{p,r}$ , also satisfy the other rules required of groups.

Let B(t) be a simple stochastic process, where B(0) = 0 and at each integer value of t, B either increases by 1 or decreases by 1. Consider the action of  $L_{p,r}$  on B(t) as visualized in Fig. 14. If p is too small (e.g., p = 1/4 in the figure), then as r increases  $L_{p,r}B(t)$  becomes increasingly erratic. For example, the time it takes for  $L_{1/4,r}B(t)$  to exit the figure's field of view decreases as r increases. On the other hand, if p is too large (e.g., p = 3/4 in the figure), then as r increases,  $L_{p,r}B(t)$  becomes increasingly flat. The case of p = 1/2 is "just right." That is, as r increases,  $L_{1/2,r}B(t)$  begins to maintain a consistent statistical character. In fact, as  $r \to \infty$ ,  $L_{1/2,r}B(t)$  approaches a Brownian motion (Karlin 2014). Since  $L_{1/2,r}$  applied to a Brownian motion produces a Brownian motion, we say that Brownian motion is a fixed point of  $L_{1/2,r}$ . Finding the value of p that is "just right" provides information about how the dispersive process scales in space and time.



**Fig. 14** The action of the renormalization group operator,  $L_{p,r}$ , on the stochastic process B(t) for various values of p and r. The values of p include 1/4 (top), 1/2 (middle), and 3/4 (bottom). The values of r include 10, 10<sup>2</sup>, 10<sup>3</sup> and 10<sup>4</sup> going from left to right

In the case of B(t), the limiting behavior as  $r \to \infty$  was to approach a fixed point. In general, a stochastic process may not approach a fixed point for any value of p. Given an arbitrary stochastic process, X(t), let

$$S = \left\{ p \ge 0 : L_{p,r} X(t) \to 0, \forall t \right\}$$

$$(150)$$

$$\hat{p} = \inf S \tag{151}$$

where  $L_{p,r}X(t) \to 0$  implies convergence in distribution as  $r \to \infty$ . We say that X(t) is  $\hat{p}$ -dispersive. If *S* is the empty set, we say that X(t) is  $\infty$ -dispersive. If X(t) = B(t), then  $S = (1/2, \infty)$ . This can be seen mathematically via the central limit theorem or more intuitively via Fig. 14. From this, we can conclude that B(t) is 1/2-dispersive. The intuition behind the value of  $\hat{p}$  is that a larger value of  $\hat{p}$  implies a faster dispersive process. Classical Fickian dispersion (which may be seen as anomalous in porous media Cushman and O'Malley (2015)) is 1/2-dispersive. Superdiffusive processes would have  $\hat{p} > 1/2$  and subdiffusive processes would have  $\hat{p} < 1/2$ .

#### 8.2 Application

We now consider an application of the renormalization group approach described in the previous subsection to dispersion in the human bronchial tree. The bronchial tree has a fractal, self-similar structure (Bassingthwaighte et al. 2013) which enables the renormalization group analysis to be performed analytically. Studying dispersion from this perspective can help us

understand the role of the bronchial tree in the vascular system, which is to disperse oxygen into the acini where molecular diffusion transfers the oxygen into the blood Weibel (1984). We will show that this dispersive process is 0-dispersive. This means that it can be regarded as a very slow dispersive process. The bronchial tree spreads out the oxygen within a finite volume while causing it to slow (nearly to a halt from the perspective of advection), thereby enabling the diffusive process that the acini and alveoli are designed for to become the dominant process.

We consider a model of the bronchial tree that has the topological properties as the bronchial tree and the essential geometric properties. Figure 15 shows a depiction of the tree with two possible paths through the tree depicted in red and blue. Topologically, it is a binary tree. Geometrically, at each branch in the tree the diameter is reduced via the recurrence relation

$$d_{n+1}^3 = \frac{d_n^3}{2} \tag{152}$$

so  $d_n = 2^{-n/3} d_0$ . Assuming that the flux of air coming into a branch must be balanced by the flux out of its two child branches. The velocity must follow the same rule,  $v_n = 2^{-n/3} v_0$ . As one descends the tree, the cross-sectional area increases and the velocity slows. We also assume that the length of a branch is proportional to the diameter,  $l_n = 2^{-n/3} l_0$ , where the constant of proportionality is  $l_0/d_0$ .

Now let X(t) be some projection (onto a one-dimensional space) of the position of a particle advecting through the tree in Fig. 15 that starts at the origin. For example, X(t) could be the horizontal position of the particle. Note that the time it takes for the particle to traverse a branch at the *n*th level is constant,

$$\frac{v_n}{l_n} = \frac{2^{-n/3}v_0}{2^{-n/3}l_0} = \frac{v_0}{l_0}$$
(153)

Therefore,  $X(nv_0/l_0) - X([n-1]v_0/l_0)$  is the horizontal displacement that occurs while traversing the *n*<sup>th</sup> branch. This implies that

$$|X(nv_0/l_0)| = |\sum_{i=1}^{n} X(iv_0/l_0) - X([i-1]v_0/l_0)|$$
  

$$< \sum_{i=1}^{n} |X(iv_0/l_0) - X([i-1]v_0/l_0)|$$
  

$$\leq \sum_{i=1}^{n} l_i$$
  

$$= \sum_{i=1}^{n} 2^{-n/3} l_0$$
  

$$\leq \sum_{i=1}^{\infty} 2^{-n/3} l_0$$
  

$$= \frac{l_0}{2^{1/3} - 1}$$
(154)

Hence,  $X(t) \in [-\frac{l_0}{2^{1/3}-1}, \frac{l_0}{2^{1/3}-1}]$  at all times, t.



**Fig. 15** A tree with the same branching structure as the human bronchial tree is shown. Two possible paths from the root to a leaf in the tree are highlighted in red and blue

We now show that X(t) is 0-dispersive using Eqs. (150) and (151). A number, p is in S if  $P(|L_{p,r}X(t)| > \epsilon) \to 0$  as  $r \to \infty$  for all  $\epsilon > 0$ . Since  $X(t) \in [-\frac{l_0}{2^{1/3}-1}, \frac{l_0}{2^{1/3}-1}]$ , it must follow that

$$P\left(|X(t)| > \frac{l_0}{2^{1/3} - 1}\right) = 0 \tag{155}$$

for any t. Therefore,

$$P\left(|L_{p,r}X(t)| > \frac{l_0}{r^p(2^{1/3} - 1)}\right) = 0$$
(156)

Given an  $\epsilon > 0$  we then have that

$$P\left(|L_{p,r}X(t)| > \epsilon\right) = 0 \tag{157}$$

so long as p > 0 and is sufficiently large that  $\epsilon > \frac{l_0}{r^{p}(2^{1/3}-1)}$ . This implies that  $P(|L_{p,r}X(t)| > \epsilon) \to 0$  as  $r \to \infty$  for all  $\epsilon > 0$  given that p > 0. Hence if p > 0,

 $p \in S$ , so that  $\hat{p} = \inf S = 0$ . The conclusion is that X(t) is 0-dispersive, as claimed. Intuitively, this implies that the macroscale model of dispersion within the human bronchial tree is a very slow dispersive process, since 0-dispersive processes are the slowest class of dispersive processes.

#### 8.3 Advantages and Drawbacks

Renormalization group theory has advantages and drawbacks in comparison to other methods for upscaling. One strength is that since it is more of a strategy than a method, it can be applied in a variety of contexts and ways. However, its application may require some cleverness to construct renormalization group operators that are suitable for a given application. In the context of upscaling hydraulic conductivity, a renormalization group approach has been found to outperform perturbative methods, especially when there is high uncertainty (Hristopulos and Christakos 1999). A drawback of the approach is that it is not an algorithm for solving a physical problem. Renormalization group theory has made fundamental contributions in areas such as quantum physics where there is a relatively parsimonious and universal description of the relevant physics. In contrast, porous media problems often do not have a parsimonious description (since heterogeneity must often be described in detail) and the different physics are required in different situations. This could limit the applicability of renormalization group methods in such settings.

## 9 Miscellaneous Methods

The literature on upscaling techniques has been extremely prolific, be it on the development of upscaling methods, or their specific application to an extremely wide variety of processes spanning virtually any science, engineering, medical and environmental field. Besides the techniques described in this review, there is a plethora of methods, which we have not discussed. These include diagrammatic methods (Christakos et al. 1995; Hristopulos and Christakos 1997), multiscale methods from the GENERIC point of view (Grmela 2010), continuous time random walks (Montroll and Scher 1973; Scher and Montroll 1975; Berkowitz and Scher 1998), space transforms (Christakos and Hristopulos 1997), and conditioning (Tartakovsky and Neuman 1998; Tartakovsky et al. 1999). Integral transform methods, fractional approaches, central limit approaches, Taylor-Aris-Brenner moment methods, spectral integral approaches, fast Fourier transform and Greens functions methods, projection operator methods, stationary and non-stationary stochastic convective type approaches are all reviewed by Cushman et al. (2002): their suggested application for any given class of problems (characterized by the type of process under investigation, e.g., fluid flow, solute transport and matrix deformation, as well as the type of solid matrix in which the process occurs, e.g., deterministic periodic, stochastic periodic or continuously evolving) is provided in their Table 2. This review, combined with those by Brenner (1987) and Cushman et al. (2002) (whose Table 2 provides a specific summary of the recommended upscaling techniques for different classes of problems), Neuman and Tartakovsky (2009) and Davit et al. (2013), should provide a quite comprehensive, yet still not exhaustive, review of most upscaling methods.

## 10 Limitations of Macroscale Models: Complexity, Accuracy, Predictivity

Macroscale models, embraced by researchers since the nineteenth century, have been instrumental in societal and technological advances (Darcy). However, any mathematical model is an idealization of a real system at a specified scale. Assumptions and/or simplifications upon which such models (e.g., macroscopic models) are based enable their formulation, analytical and/or numerical treatment and, consequently, their use as predictive tools. Such hypotheses, which any model is built upon, cannot (and should not) be disentangled from the model itself (as a shadow provides the physical context to the object it represents), since they define the theoretical and practical boundaries of models' applicability, and guard one from unnecessary disappointments of poor model performance, predictivity and accuracy (Wood 2009; Battiato et al. 2009; Golfier et al. 2009; Battiato and Tartakovsky 2011; Arunachalam et al. 2015). So, tracking upscaling assumptions must be embraced as an integral process of any upscaling tool, and not as an unpleasant side effect or a necessary evil. All upscaling methods have built in tools (e.g., scaling laws for MVA, applicability conditions for homogenization, permissibility conditions in TCAT, etc.) to track modeling assumptions and establish under which conditions the error between the averaged microscale and the macroscale solutions is guaranteed to be bounded by the upscaling error prescribed by any given averaging technique.

As pointed out before, besides the well-recognized, and widely discussed, constraint of geometric scale separation (i.e.,  $\varepsilon \ll 1$ ), other (dynamic) conditions, often not as appreciated, yet equally important, must be satisfied for macroscale models to be (mathematically) valid. This ensures that macroscale models are:

- Accurate, i.e., they represent averaged microscale processes within the bounds of the upscaling error,
- Predictive, i.e., once parametrized, they can be used for fit free predictions under different dynamical and boundary conditions while retaining accuracy.

The concepts of accuracy and predictivity are particularly important since they have critical implications both on macroscale model validation and application: How can a macroscale model (existent or derived) be validated? The obvious answer is by a direct comparison with the corresponding averaged microscale model. Yet, since macroscale equations are themselves approximations of microscale processes, what is the allowable error that one should accept to conclude that the model is indeed validated? For numerical validation, it is needed that the numerical error be bounded by the upscaling error, i.e., the discretization scheme of choice should be of the minimum order necessary to guarantee that the numerical error does not overcome the upscaling error.

Such an approach in the use of upscaling tools and deployment of macroscale models paves the way to achieve purely predictive understanding of dynamics across scales.

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the other co-authors; DO reviewed renormalization group theory; CTM and FJV-P provided the overview on the thermodynamically constrained averaging theory; PST reviewed hybrid mixture theory; BDW and PTF-V provided the overview of the volume averaging method. All authors have reviewed and provided feedbacks on the manuscript structure and content.

# **11 Appendix: Notation**

## 11.1 Hybrid Mixture Theory

## Latin Symbols

- $A^{\alpha_j}$ Helmholtz free energy of the *i*th component in the  $\alpha$  phase [J/kg]
- $A^{\alpha}$ Total Helmholtz free energy of the  $\alpha$  phase computed in volume V (= $A_L^{\alpha} M^{\alpha}$ ) [J/kg]
- Inner part of the Helmholtz free energy of the  $\alpha$  phase [J/kg]  $A^{\alpha}_{I}$
- Viscoelastic parameter [m<sup>3</sup> s/kg]  $B_c$
- $b^{\alpha_j}$ External entropy source for the *j*th component in the  $\alpha$  phase [J/(kg s K)]
- $b^{\alpha}$ External entropy source for the  $\alpha$  phase [J/(kg s K)]
- $C^{\alpha_j}$ Mass concentration of the *j*th component in the  $\alpha$  phase (=  $\rho^{\alpha_j} / \rho^{\alpha}$ ) [dimensionless]
- D Coefficient of diffusivity [m<sup>2</sup>/s]
- $d^{lpha}_{kl}_{\ eta \, \hat{e}^{lpha_j}}$ Rate of deformation tensor of the  $\alpha$  phase [s<sup>-1</sup>]
- Net mass transfer from the phase  $\beta$  to the *j*th component in the  $\alpha$  phase [kg/(m<sup>3</sup> s)]
- $\beta \hat{e}^{\alpha}$ Net mass transfer from the phase  $\beta$  to the phase  $\alpha$  [kg/(m<sup>3</sup> s)]
- $E^{\alpha_j}$ Internal energy of the *i*th component in the  $\alpha$  phase [J/kg]
- $E^{\alpha}$ Internal energy of the  $\alpha$  phase [J/kg]
- $\hat{E}^{\alpha_j}$ energy gained by the *i*th component from other components in the same phase  $[J/(m^3s)]$
- $E^s_{MM}$ Trace of Lagrangian strain tensor of the solid phase [dimensionless]
- $g_l^{\alpha_j}$  $g_l^{\alpha}$  $g_l^{\alpha}$  $G^w$ Gravitational force on the *i*th component in the  $\alpha$  phase  $[m^2/s]$
- Gravitational force on the  $\alpha$  phase [m<sup>2</sup>/s]
- Gibbs free energy [J/kg]
- G(t)Stress relaxation function for the viscoelastic biopolymers [Pa]
- $G_i$ With *i* from 0 to *N*, relaxation parameters for the Generalized Maxwell model [Pa]
- $h^{\alpha_j}$ Net external energy source for the *j*th component in the  $\alpha$  phase [J/(kg s)]
- $h^{\alpha}$ Net external energy source for the  $\alpha$  phase [J/(kg s)]
- $\hat{i}_l^{\alpha_j}$ Momentum transfer to the *j*th component due to interaction with other components in the same phase  $[N/m^3]$
- $p^{\alpha}$ Thermodynamic pressure in the  $\alpha$  phase [Pa]
- Total thermodynamic pressure for the particle (solid+liquid) [Pa] р
- Pα Classical pressure of the  $\alpha$  phase [Pa]
- $q_l^{\alpha_j}$ Heat flux vector for the *j*th component in the  $\alpha$  phase [J/(m<sup>2</sup> s)]
- $q_l^{\alpha}$ Heat flux vector for the  $\alpha$  phase [J/(m<sup>2</sup> s)]
- Total heat flux vector for the particle (solid+liquid)  $[J/(m^2 s)]$  $q_l$
- $\beta \hat{O}^{\alpha_j}$ Net heat gained by the *j*th component in the phase  $\alpha$  from the phase  $\beta$  [J/(m<sup>3</sup> s)]
- $\beta \hat{O}^{\alpha}$ Net heat gained by the phase  $\alpha$  from the phase  $\beta$  [J/(m<sup>3</sup> s)]
- $\hat{r}^{\alpha_j}$ Mass production of the *j*th component in phase  $\alpha$  due to chemical reactions within the phase  $[kg/(m^3 s)]$
- $S^{\alpha}$ Degree of saturation for the  $\alpha$  phase [dimensionless]

- REV Representative elementary volume
- Time [s]
- $t \\ t_{kl}^{\alpha_j}$ Stress tensor of the *j*th component in the phase  $\alpha$  [Pa]
- $t_{kl}^{\alpha}$ Stress tensor of the phase  $\alpha$  [Pa]
- Total stress tensor of the particle (solid+liquid) [Pa] t<sub>kl</sub>
- $T^{\alpha_j}$ Temperature of the *j*th component in the phase  $\alpha$  [K]
- Т Temperature [K]
- $^{\beta}\hat{T}_{i}^{\alpha_{j}}$ Momentum transfer to the *i*th component in the phase  $\alpha$  due to mechanical interactions with the phase  $\beta$  [N/m<sup>3</sup>]
- $\beta \hat{T}_{I}^{\alpha}$ Momentum transfer to the phase  $\alpha$  due to mechanical interactions with the phase  $\beta$  $[N/m^3]$
- $u_{k}^{\alpha_{j}} v_{l}^{\alpha_{j}} \\ v_{l}^{\alpha} \\ x_{k}^{\alpha} \\ X_{K}^{\alpha}$ Diffusion velocity of the *i*th component in the phase  $\alpha$  [m/s]
- Velocity of the *i*th component in the phase  $\alpha$  [m/s]
- Velocity of the  $\alpha$  phase [m/s]
- Eulerian coordinate in the  $\alpha$  phase [m]
- Lagrangian coordinate in the phase  $\alpha$  [m]

## **Greek Symbols**

- $\delta_{kl}$ Kronecker delta function in Eulerian coordinates
- Kronecker delta function in Lagrangian coordinates  $\delta_{KL}$
- $\varepsilon^{\alpha}$ Volume fraction of the phase  $\alpha$  [dimensionless]
- $\eta^{\alpha_j}$ Entropy of the *j*th component in the  $\alpha$  phase [J/(kg K)]
- $n^{\alpha}$ Entropy of the  $\alpha$  phase [J/(kg K)]
- $\hat{n}^{\alpha_j}$ Entropy gained by the *i*th component in a phase by interaction with other components in the same phase  $[J/(m^3 s K)]$
- Kα Permeability of the porous matrix for phase  $\alpha$  [m<sup>2</sup>]
- Net entropy production for the *j*th component in the  $\alpha$  phase [J/(m<sup>3</sup> s K)]  $\Lambda^{\alpha_j}$
- $\Lambda^{\alpha}$ Net entropy production in the  $\alpha$  phase [J/(m<sup>3</sup> s K)]
- Net entropy production in the system at mesoscale  $[J/(m^3 \text{ s } \text{K})]$ Λ
- Relaxation time for *i*th element of generalized Maxwell model [s] λi
- Memory function in the generalized Darcy's law for biopolymers [m<sup>5</sup>/(kg s)]  $\mathcal{M}$
- $\rho^{\alpha_j}$ Density of the *j*th component in the  $\alpha$  phase [kg/m<sup>3</sup>]
- Density of the  $\alpha$  phase [kg/m<sup>3</sup>]  $\rho^{\alpha}$
- $\phi_l^{\alpha_j}$ Entropy flux vector for the *j*th component in the  $\alpha$  phase [J/(m<sup>2</sup> s K)]
- Entropy flux vector for the  $\alpha$  phase [J/(m<sup>2</sup> s K)]  $\phi_{I}^{\alpha}$
- $\beta \hat{\phi}^{\alpha_j}$ Entropy transfer to the *j*th component in the  $\alpha$  phase from the  $\beta$  phase [J/(m<sup>3</sup> s K)]
- $\beta \hat{\phi}^{\alpha}$ Entropy transfer to the  $\alpha$  phase from the  $\beta$  phase [J/(m<sup>3</sup> s K)]

# Subscripts

k. l Coordinate indices

# Superscripts

Solid phase S

- w Water (or liquid) phase
- f Fluid phase
- $\alpha, \beta$ General representation of phases
- A given component of species i

# Special Symbols

- $D^{\alpha_j}$ Material derivative of a function with respect to velocity of *i*th component in the  $\alpha$ Dt phase  $[s^{-1}]$
- $D^{\alpha}$ Material derivative of a function with respect to velocity of the  $\alpha$  phase [s<sup>-1</sup>] Dt

 $v_l^{\alpha,s}$ Velocity of the  $\alpha$  phase relative to the solid phase  $(=v_I^{\alpha} - v_I^s)$  [m/s]

# 11.2 Thermodynamically Constrained Averaging Theory

# **Roman Letters**

- $\hat{c}^{wn}$ Capillary pressure relaxation rate coefficient
- d Rate of strain tensor
- F A generalized additive function
- G Geometric orientation tensor
- Gravitational acceleration vector g
- L Identity tensor
- $\mathcal{I}^+_{c\alpha}$ Index set of entities connected to the  $\alpha$  entity that are of a higher dimension than the  $\alpha$  entity
- Index set of fluid phases  $J_{\mathbf{f}}$
- $J_w^{wn}$ Mean curvature of the *wn* interface
- Kinetic energy term due to velocity fluctuations  $K_E$
- $\hat{k}_1^{wn}$ Interfacial area relaxation coefficient
- Outward unit normal vector from entity  $\alpha$  $\mathbf{n}_{\alpha}$
- Fluid pressure р
- $\hat{R}_{\substack{\alpha \to \kappa \\ \mathbf{T}}}$ Resistance coefficient
  - Transfer rate of momentum from the  $\alpha$  to the  $\kappa$  entity
  - Stress tensor t
- t\* Solid-phase stress tensor corresponding to the action of a common curve on the solid phase
- time t
- U Set of unknowns
- Velocity v
- $\mathbf{w}^{wn}$ Velocity of the fluid-fluid interface

# **Greek Letters**

- Interfacial or curvilinear tension γ
- $\epsilon$ Porosity

- $\epsilon^{\overline{\alpha}}$  Specific entity measure of the  $\alpha$  entity (volume fraction, specific interfacial area)
- $\theta$  \_\_\_\_\_ Temperature
- $\kappa_{\overline{G}}^{\overline{wns}}$  Geodesic curvature of the common curve
- $\kappa_N^{\overline{wns}}$  Normal curvature of the common curve
- *Λ* Entropy density production rate
- $\mu$  Chemical potential
- $\rho$  Mass density
- $\chi^{\overline{n}}$  Euler characteristic of the non-wetting phase
- $\chi_s$  Wetted fraction of the solid phase

 $\varphi^{\overline{ws,wn}}$  Contact angle between the ws and wn interfaces

- $\psi$  body force potential per unit mass (e.g., gravitational potential)
- $\Omega$  Spatial domain

# Subscripts and Superscripts

- eq An equilibrium state
- *n* Index that indicates a non-wetting phase
- *ns* Index that indicates the non-wetting–solid phase interface
- s Index that indicates a solid phase
- *w* Entity index corresponding to the wetting phase
- wn Index that indicates the wetting-non-wetting phase interface
- wns Index that denotes the common curve
- ws Entity index corresponding to the wetting-solid interface
- $\alpha$  General entity index qualifier
- $\kappa$  General entity index qualifier

## **Other Mathematical Symbols**

- Above a superscript refers to a density weighted macroscale average
- = Above a superscript refers to a uniquely defined macroscale average
- D/Dt Material derivative

## Abbreviations

- EI Entropy inequality
- REV Representative elementary volume
- TCAT Thermodynamically constrained averaging theory

# 11.3 Homogenization Theory

- $\mathcal{B}$  Pore space domain in the unit cell Y
- $|\mathcal{B}|$  Volume of  $\mathcal{B}$  [L<sup>3</sup>]
- $\mathcal{B}^{\varepsilon}$  Pore space domain in the porous medium  $\Omega$
- $c_{\varepsilon}$  Dimensionless pore-scale aqueous concentration of species C [-]
- $\hat{c}_{\varepsilon}$  Pore-scale aqueous concentration of species C [mol L<sup>-3</sup>]

$\langle c_{\varepsilon} \rangle$	Average of $c_{\varepsilon}$ over the unit cell Y
$\langle c_{\varepsilon} \rangle_{\mathcal{B}}$	Average of $c_{\varepsilon}$ over the pore volume $\mathcal{B}$
$\langle c_{\varepsilon} \rangle_{\Gamma}$	Average of the quantity $c_{\varepsilon}$ over the solid-liquid interface $\Gamma$
$\overline{c}$	$:= \sqrt[n]{k_d/k}$ , threshold aqueous concentration of species C [mol L <sup>-3</sup> ]
$\overline{c}^n$	:= solubility product of species C
D	dimensionless molecular diffusion coefficient defined by (119) [-]
$\mathcal{D}$	Molecular diffusion coefficient $[L^2 T^{-1}]$
$\mathcal{D}_0$	Characteristic value of $\mathcal{D}$ , [L <sup>2</sup> T <sup>-1</sup> ]
D*	Dimensionless dispersion tensor defined by (137)
Da	$:= \hat{t}_d / \hat{t}_r$ , Damköhler number defined by (121)
${\mathcal G}$	Solid matrix domain in the unit cell <i>Y</i>
k	Reaction rate of the forward heterogeneous reaction $C \rightarrow S$
$k_c$	reaction rate of the backward homogeneous reaction $A + B \leftarrow C$ .
$k_d$	Reaction rate of the backward heterogeneous reaction $C \leftarrow S$
k	Closure variable defined by (??)
K	$:= \langle \mathbf{k}(\mathbf{y}) \rangle$ , permeability tensor
$\mathcal{K}^{\star}$	Effective reaction rate constant defined by (??)
l	Characteristic length of the periodic unit cell Y
L	Characteristic length of macroscopic porous medium domain $\Omega$
n	Heterogeneous reaction order, [-]
$\hat{p}$	Fluid dynamic pressure, $[ML^{-1}T^{-2}]$
Pe	Péclet number defined by (121)
t	$:= \hat{t}/\hat{t}_{d}$ , dimensionless time [–]
$\hat{t}_{a}$	Advection timescale [T]
$\hat{t}_{d}$	Diffusion timescale [T]
Îri	$i = \{1, 2, 3\}$ , reaction timescales [T]
U	Characteristic velocity associated with $\hat{\mathbf{v}}_{c}$ [TL <sup>-1</sup> ]
V <sub>c</sub>	Dimensionless pore-scale fluid velocity [–]
Ŷs	Pore-scale fluid velocity [T $L^{-1}$ ]
x	Spatial coordinate of the pore space $\mathcal{B}_{s}$
v	Spatial coordinate of the unit cell Y
Ŷ	Spatially periodic unit cell
Y	Volume of the spatially periodic unit cell $[L^3]$
α	Coefficient for the definition of $Pe = \varepsilon^{-\alpha}$
β	Coefficient for the definition of $Da = \varepsilon^{\beta}$
ε	$:= \ell/L$ , scale separation coefficient [–]
$\hat{\phi}$	Unit cell porosity [–]
Г	Solid–liquid interface in the unit cell <i>Y</i>
$\Gamma^{\varepsilon}$	Solid–liquid interface in the porous medium $\Omega$
$\mu$	Fluid dynamic viscosity [M $L^{-1} T^{-1}$ ]
$\Omega$	Porous medium domain
$\psi$	General dimensionless pore-scale function
$\psi_m$	<i>Y</i> -periodic terms of order <i>m</i> for the multiple-scale expansion of $\psi$
$\psi_{arepsilon}$	$\psi$ defined in $\mathcal{B}_{\varepsilon}$
1/c	Dimensional value of $\psi$ in $\mathcal{B}_{s}$

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