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Effective medium equations for fractional Fick's law in porous media

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Abstract

This paper studies reaction–diffusion phenomena in disordered porous media with non-Fickian diffusion effects. The aim is to obtain an effective medium equation of the concentration dynamics having a fractional Fick's law description for the particles flux. Since the methodology is based on a volume averaging approach, a fractional spatial averaging theorem is developed to interchange averaging integration and fractional differentiation. Model structure simplifications are made on the basis of an order of magnitude analysis from physical insights. The closure problem associated with the effective diffusivity definition is also developed, showing that the macroscale diffusion parameter is affected by (i) the scaling from mesoscales to macroscales, and (ii) by the disordered structure of the porous medium.
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1. Introduction

Chemical reaction is commonly coupled to transport phenomena in many natural and industrial systems. At certain length scales, an equation widely used to describe the process is the traditional reaction–diffusion equation section

$$\frac{\partial c}{\partial t} = \mathscr{D}\boldsymbol{\nabla}^2 c + R(c),$$

where c is a given particle concentration, $\mathscr{D}$ is the diffusion coefficient, and $R(c)$ is a reaction rate. The underlying hypothesis behind this reaction–diffusion model is that the transport mechanisms are constitutive properties equivalent to the average of unmeasurable transport properties at arbitrarily small scales, and so the parameters of the model are scale independent. That is, the transport mechanisms are invariant under spatial scaling, implying that the model is able to describe the transport process at any spatial and time scales. This corresponds to Fickian behavior, which is valid when the particle jump size (i) is uncorrelated in time,

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and (ii) has finite mean and variance [1–3]. For non-reactive solutes, (i.e., $R(c) = 0$), the fundamental solutions to the Fickian diffusion over time will be Gaussian densities with (finite) means and variances based on the transport coefficient $\mathscr{D}$. However, field and experimental measurements have shown that the standard Fickian diffusion equation typically underestimates concentrations in the leading and/or trailing edges tracer plumes [5–7]. Application of the standard framework to describe field data reveals an apparent scale-dependence of dispersity, not consistent with Fickian transport, complicating the prediction of plume evolution in time and space [3]. Since non-Gaussian breakthrough curves are often observed, at least one of the conditions implying Fickian transport is failing [3,4]. Violation of the uncorrelated jump assumption leads to enhanced diffusion, which is faster than Gaussian analytical solution predictions [8]. Most non-Fickian transport theories are based on the effects of long-range temporal correlations due, for instance, to solute sorption or preferential pathways. Recently, it has been suggested that non-Gaussian plumes can be explained by a violation of the finite-variance assumption [4,9,10]. Schumer et al. [3] have shown that non-Gaussian distributions with heavy leading edges can be the result of the infinite-variance particle jump distributions that arise during the transport in disordered porous media. They demonstrated that a fractional Fick's law, as suggested by Schumer et al. [3,4], is a governing equation for solute transport in porous media in cases where temporally correlated velocity fields do not dominate the transport process. In this way, Fickian dispersion can only occur in homogeneous media.

Scaling problems are encountered when Fickian models are applied to non-Fickian processes. In fact, the infinite-variance assumption leading to non-Fickian transport implies that the Fickian transport properties at a given spatial scale are not necessarily the same at macroscales, leading to scale-dependent transport parameters. For instance, from a Fickian perspective, a large particle that jumps at mesoscales could be interpreted as normal (Fickian) particle jumps at macroscales by virtue of an average effect. Hence, there is a scaling problem for this kind of particle transport. This is particularly important for interpreting lab-scale experimental measurements. In fact, experiments are carried out at relatively small spatial and temporal scales, and measurements arising from such should recover the transport behavior at real scales. Wrong interpretation of transport coefficients can lead to, e.g. malfunctioning of industrial equipments or failures in the preservation of aquifers perturbed by contaminants. To address this scaling problem, consider a process involving diffusion and surface reaction in a heterogeneous (porous) medium at characteristic length scales described in Fig. 1. Suppose that there are only two phases present in the particle; namely, the solid (κ) and fluid phase (γ). The solid phase is assumed to be impermeable and bounded by a surface where a chemical reaction takes place. Therefore, the chemical reaction occurs only at the surface of the solid phase. The conservation equation that governs the transport process in the γ-phase is given by

$$\frac{\partial c_\gamma}{\partial t} + \boldsymbol{\nabla} \bullet \mathbf{N}_\gamma = 0 \text{ in the } \gamma\text{-phase,} \tag{1}$$

where c_γ and $\mathbf{N}_\gamma$ are the concentration and the molar flux of the reactant in the γ-phase, respectively. Assume heterogeneous, first order, irreversible chemical reaction on the catalyst surface. The corresponding interfacial
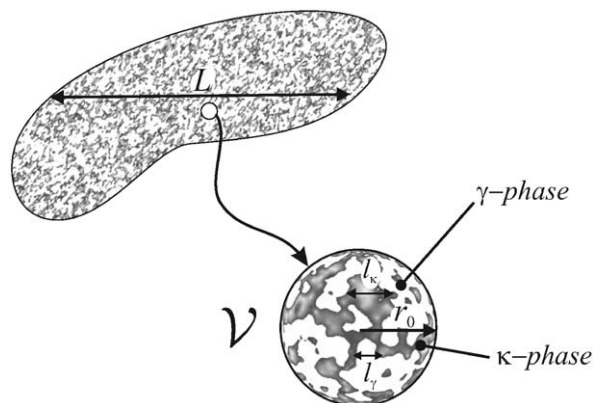

Fig. 1. Porous medium and averaging volume with characteristic lengths.