



# High-performance computing of flow and transport in physically reconstructed silica monoliths

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## ABSTRACT

This work presents an approach towards resolving hydrodynamic flow in real porous media by carrying out direct numerical simulations in the reconstructed macroporous (flow-through) domain of a silica monolith. The macroporous domain of a  $60\ \mu\text{m} \times 60\ \mu\text{m} \times 12\ \mu\text{m}$  segment of a  $100\ \mu\text{m}$  i.d. capillary silica monolith was reconstructed by confocal laser scanning microscopy. A  $60\ \mu\text{m} \times 12\ \mu\text{m} \times 12\ \mu\text{m}$  segment of the reconstructed domain was then used as the 3D matrix for simulation of fluid flow by the lattice-Boltzmann method on a high-performance computing platform. Excellent agreement is observed between the experimental and simulated Darcy permeabilities without any assumptions or further adjustments on the monolith morphology. The flow velocity field is analyzed in detail, including longitudinal and transverse velocity distributions, the occurrence of negative longitudinal velocities, as well as the beginning transition to the viscous-inertial flow regime. The presented methodology promises great potential for resolving the key relationships between morphology and band broadening in monolithic columns for HPLC applications.

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## 1. Introduction

Fluid flow and dispersion processes in natural and synthetic porous media arise in numerous fields of science and engineering, ranging from soil and food science to petroleum and chemical engineering [1–6]. The high-surface-area materials used in diverse applications of industrial and environmental technologies are characterized by different physicochemical and morphological properties, depending on their main purpose. For example, due to the reduced dynamic viscosity of gases at elevated temperatures, solid phase catalysts for gas reactions usually are highly ordered microporous media with a monomodal pore size distribution. The stationary phases in HPLC, on the other hand, preferably have a hierarchically structured, interconnected pore space with macropores for convective mass transport through the column and mesopores (often also micropores) that offer the required surface area accessible *via* diffusion-limited mass transfer. This morphology with ideally bimodal pore size distributions in HPLC has conventionally been realized

by packing micrometer-sized mesoporous particles into columns [7].

Monoliths have found a number of applications, *e.g.*, as ceramic supports for high-temperature heterogeneous solid phase–gas phase catalysis (especially as automotive exhaust gas catalysts and in industrial gas purification), as condensators, and in HPLC [8–17]. The appeal of using monolithic stationary phases characterized by a hierarchically structured pore space for chromatographic separations is related to the feasibility of achieving high-speed separations by a relatively low column backpressure and fast mass transfer kinetics, which, to some extent, is similar to the performance of solid core-porous shell particles [18]. During the past decade, the potential advantages of monolithic over particulate packed beds have provoked increased interest in monolith design, fabrication, and application, along with the theoretical and numerical analysis of the involved transport and separation processes [15].

The analysis and modeling of mass transport in chromatographic columns is based either on *phenomenological* (macroscopic) or *microscopic* approaches to represent the involved processes. The former approach is based on the classical transport equations supplemented with constitutive equations describing the transport and phenomenological (macroscopic) coefficients and parameters. In this approach, all microscopic structural and mor-

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phological parameters of stationary phases are accounted for *implicitly* by introducing phenomenological characteristics, such as the total and external porosities, the pore size distribution, specific surface area, rate constants of mass transfer kinetics, *etc.* Such an implicit incorporation of microscopic characteristics on a macroscopic scale requires an accurate knowledge of the specific equilibrium thermodynamics and equilibration kinetics involved. The phenomenological models are specifically concerned with a description at the system scale rather than the pore scale, *i.e.*, macroscopic properties are defined as averages of the corresponding microscopic quantities [19–21]. Having derived the macroscopic equations and suitable phenomenological transport properties, one arrives at the classical description of the system as continuum or piecewise-continuum [5]. Models based on the macroscopic approach were and still are widely applied because of their convenience and relative familiarity in engineering practice. The models presented in the works of Scheidegger [22], Saffman [23], Bear [3], Carbonell and Whitaker [24], Eidsath et al. [25], Koch and Brady [26,27], Plumb and Whitaker [28,29], Brenner and Edwards [30], Torquato et al. [31], and Tartakovsky et al. [32] all belong to the group of the macroscopic models of mass transport in porous media. The macroscopic moment-analysis model of chromatographic separations in a monolithic stationary phase, recently developed by Miyabe et al. [33], appears to be the most comprehensive interpretation of plate height data that theory can nowadays provide.

However, the phenomenological approach has an intrinsic disadvantage. It requires to involve a number of macroscopic characteristics of mass transport in porous media that are very difficult (or even impossible) to be accessed directly. Instead, relevant characteristics are estimated by semi-empirical relationships [15], but their validity is not experimentally confirmed for the whole range of chromatographic parameters. Further, these relationships do not account for effects related to the anisotropy and heterogeneity of the system at the mesoscopic scale.

Actually, an accurate description of mass transport in porous media can be obtained by *explicit* incorporation of information at the pore level. In fact, one can formulate transport phenomena in the form of piecewise-continuous equations for momentum and mass transfer in the solid and liquid phases, along with corresponding initial and boundary conditions at the interface between the two phases. However, just the precise determination of the solid–liquid boundary is a very difficult practical task, as this interface is typically very irregular and topologically complex in porous media. Moreover, if this boundary is known, solving such a boundary-value problem remains mathematically intractable or requires enormous amounts of computational resources to be resolved numerically, with the exception of some model porous media with a simple spatial structure [34].

Therefore, the pore structure of random porous media is frequently approximated by bundles or networks of cylindrical pores. This simplifies the formal description of transport in a porous medium. The pioneering idea to model a porous medium as a network of randomly distributed points in space connected to one another for studying transport in the material dates back to the work of Bjerrum and Manegold in 1927 [35]. However, the computational resources available back then did not enable extensive numerical simulations. The first relatively extensive computations employing a 3D network representation of the pore space in a random medium were carried out by Owen in 1952 [36]. He used a network approach to calculate the formation factor of a porous body. Later, from 1960 to 1990, a similar approach was proposed and realized to simulate permeability, conductivity, and the formation factor, as well as to investigate the relationship between them (see p. 1455 in [5] for a list of references to some of the numerous papers in this field). The first paper related to an application of

the pore network model to simulate hydrodynamic dispersion in porous media was reported by Sahimi and Imdakm in 1988 [37]. They assumed the porous medium as a bundle of interconnected capillary tubes with distributed effective radii. Hydrodynamic dispersion in an individual tube was calculated according to the Taylor–Aris model, while the Monte-Carlo random-walk approach was used to calculate the system-averaged dispersion coefficient. Their results showed that the morphology of a porous medium strongly affects dispersion.

In 1999, Meyers and Liapis [38] proposed a structural model of a monolith based on topological mapping onto a cubic lattice network of interconnected cylindrical pores with a given size distribution. Their results also indicate that transport phenomena in the porous medium are strongly affected by parameters characterizing its morphology (pore size distribution, pore interconnectivity). Another model of monolithic beds for studying mass transport, involving the kinetics of adsorption/desorption, was proposed by Miyabe and Guiochon in 2002 [39]. It assumes a material structure with a porous cylinder (containing the mesopores) located in the center of a coaxial, cylindrical macropore as unit element. In 2003, Vervoort et al. [40] proposed a simplified, highly ordered structural model of silica monoliths. It assumes the monolith skeleton as a conjunction of a spatially periodic tetrahedral structure of monosized cylindrical tubes.

The aforementioned structural models of porous media cannot, in fact, be classified as truly microscopic ones. Though the transport phenomena in these models are simulated at the microscopic (individual-pore) level, the underlying pore-level morphological characteristics (*e.g.*, porosity, pore diameter, tortuosity, pore interconnectivity, *etc.*), introduced into the models, were derived from macroscopic averaging information obtained from experimental techniques, including mercury intrusion and nitrogen adsorption, inverse size exclusion chromatography, scanning and transmission electron microscopy, nuclear magnetic resonance (NMR), X-ray tomography, or confocal laser scanning microscopy (CLSM). However, some of these experimental techniques give *direct* information on the 3D geometrical structure of natural and synthetic porous media, *e.g.*, sandstones, rocks, or packed beds. This information can then be employed for numerical simulations of mass transport in these materials. This approach belongs to the concept of *explicit* or *direct* numerical simulations, where one seeks to account for and model *all* important parameters and phenomena *explicitly* rather than in a meanfield or average procedure, including the volumetric representation of the morphology of the studied system [41]. In 1994, Spanne et al. [42] used a stack of X-ray tomography images of a Fontainebleau sandstone to simulate Stokes flow by a finite-difference method. The pixel size was  $10\ \mu\text{m} \times 10\ \mu\text{m}$  and the distance in the reconstructed images between consecutive tomographic sections was  $10\ \mu\text{m}$ . The simulated fragment had a physical dimension of  $3.03\ \text{mm} \times 3.03\ \text{mm} \times 1.0\ \text{mm}$  and consisted of  $303 \times 303 \times 100$  voxels. However, the relative difference between simulated and experimental hydraulic permeabilities was around 50%. In 1999, Manz et al. [43] reported the results of a direct comparison between the measured (by dynamic NMR microscopy) and simulated (using the lattice-Boltzmann method) velocity fields and dispersion characteristics in a fragment of a cylindrical packed bed of 10 mm i.d. filled with 1-mm glass beads. They used the spatial matrix obtained by NMR imaging of the real sphere packing in their simulations. The spatial resolution was  $86\ \mu\text{m}$  and the digitalized fragment used for the flow simulations ( $10\ \text{mm} \times 10\ \text{mm} \times 1.72\ \text{mm}$ ) contained around  $2.7 \times 10^5$  voxels. Recently, Piller et al. [44] employed high-resolution X-ray tomography to acquire the 3D structure of a  $2.7\ \text{mm} \times 2.7\ \text{mm} \times 2.7\ \text{mm}$  fragment of a real reservoir rock from a deep oil exploration. They obtained a cubic volume image with an edge length of 600 voxels at a resolution of  $4.5\ \mu\text{m}$ , and then used it to simulate laminar flow

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