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Modelling ordered packed beds of spheres: The importance of bed orientation and the influence of tortuosity on dispersion

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ABSTRACT

Ordered packing has previously been considered for porous media applications in the industrial and analytical worlds, with implementation constrained only by the lack of feasible fabrication methods. Additive manufacturing now provides the answer to this limitation, which leads to the novel domain of customized ordered packing and a variety of optimized geometries. In this work, the chromatographic behaviour of ordered configurations of particles was described using computational fluid dynamics methods based on the Lattice Boltzmann Model. The model was first validated by matching van Deemter trends for ordered and random packings shown in previous research. The influence of rotations of the ordered configurations was then considered, indicating that orientational changes with respect to the main flow axis can strongly affect minimum plate height. In particular, it is demonstrated that targeted rotations of ordered packings can reduce axial dispersion while improving transverse dispersion, thus improving chromatographic performance. This principle is clearly shown in a strong linear correlation between tortuosity and plate height, offering an additional parameter to enable *a priori* control of the performance of ordered packings. Furthermore, rotation of the packing does not change porosity or surface area and has a relatively small effect on permeability. Thus, highly permeable packings with poor dispersion can be improved in terms of chromatographic impedance by simple rotation of the packing orientation. This work further demonstrates the advantages of ordered packings over randomly packed beds, and introduces new perspectives on the development of chromatographic structures with improved performance.

1. Introduction

The stationary phase in traditional liquid chromatography columns is composed of randomly packed beads. Packing processes are strongly dictated by manufacturing capability, and variants of slurry packing are almost universally applied in both industrial and analytical column production [1–3]. Until now, slurry packing has been the exclusive method by which chromatography columns are produced, with the resulting disordered packing simply regarded as an unavoidable outcome. However, column-to-column variability is often observed, mainly resulting from the random nature of this fabrication step, thus impacting product consistency [4,5]. Accordingly, all columns undergo stringent quality control and validation procedures to ensure random packing is free from major defects that would lead to a number of issues such as channelling, stagnation regions or other non-ideal flow behaviours, which negatively impact chromatographic performance [6].

Schure et al. were the first to challenge the concept of randomly arranged particles, and speculated about the advantages of ordered packings in chromatographic columns [7]. Using the Lattice Boltzmann Method (LBM), they demonstrated that the height equivalent to a theoretical plate (HETP) for a face centred cubic (FCC) packing of spheres was considerably lower than that for randomly packed spheres over a broad range of reduced velocities. There has been only a handful of computational studies since Schure's initial research, e.g. ordered packings of ellipsoidal particles [8,9] or pillar arrays [10,11], yet all of these studies have consistently demonstrated that ordered packings have the capability to outperform random arrangements of spherical particles. The tangible improvement in chromatographic performance is mainly related to a reduction in eddy dispersion in ordered packings. Despite the promise of such theoretical results, technical and financial constraints have precluded the manufacture of columns with precisely ordered packings until now.

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An imminent paradigm shift in column manufacturing is now offered by additive manufacturing technology (AM, or 3D printing), as it enables the creation of complex geometries with high precision. 3D printing was recently employed by Fee et al. to fabricate perfectly ordered column packings, revolutionizing the design and production of chromatographic stationary phases [12]. Later, Nawada et al. evaluated the performance of 3D printed beds of ordered particles, thus experimentally validating the trends predicted by the above computational studies [13]. The exponential growth we are currently witnessing in the 3D printing arena indicates that AM methods with improved resolution, reduced printing times, and enlarged build sizes will soon be available, making the printing of chromatographic stationary phases a reality at industrial scale. Clearly, AM now provides a completely new context for computational studies of perfectly ordered column configurations. Computational Fluid Dynamics (CFD) applied to hypothetical arrangements of particles is no longer an academic speculation but rather offers a predictive tool to help identify suitable geometries for chromatographic operations in a time and cost-efficient manner [14]. Identical geometries can later be fabricated using AM tools to finally obtain physical replicas of improved chromatographic packings.

Among the CFD methods currently available, the LBM is currently preferred when modelling complex geometries such as porous media [7,10,11,15]. The LBM efficiently handles a high proportion of fluid/solid boundaries in the simulation domain, allowing the generation of accurate results in much shorter simulation times than do conventional CFD tools based on the Navier-Stokes equations [16,17].

The possibilities offered by AM, coupled with the computing capabilities of the LBM, provide a renewed impetus in the exploration of the performance of ordered morphologies of packed beds. In this work, we employed a new approach for the LBM to measure *in silico* column metrics such as HETP, pressure drop and tortuosity. This approach was first validated against prior research results for random and ordered sphere packings. Different configurations for ordered packings were then considered, including various packing arrangements and relative orientations with respect to the main direction of flow. This report highlights, for the first time, key aspects that should be taken into account when designing new ordered morphologies for packed bed columns. For example, we propose the use of flow tortuosity of the porous lattice (based upon the fluid phase velocities) as an indicator of column performance. Such observations will help direct CFD investigations towards higher performing morphologies that can be potentially fabricated through AM and experimentally tested.

2. Theory and description of computational methods

2.1. Hardware & software

Simulations were performed using a variety of parallel computing systems. The largest simulations were performed using 1024 nodes of an IBM Blue Gene/P (IBM, NY, USA) (four cores running in virtual node mode), while smaller simulations used two nodes of a Power 755 cluster (IBM, NY, USA) (32 cores per node). These systems were both operated under the New Zealand eScience Infrastructure (NeSI).

Palabos (FlowKit Ltd., Lausanne, Switzerland), an open source C++ library, was selected to solve the mathematical framework of the LBM. Palabos is fully parallelized and thus extremely efficient on cluster computing [18]. A front-end script was prepared to use the Palabos library, generate the domain and solve the system's governing equations. Flow field data from simulations were stored in visualization toolkit (.vtk) files and post-processed using Paraview (Kitware Inc., NY, USA), while data from the advection-diffusion process were written to text files (.txt) and analysed using spreadsheets designed to calculate the appropriate performance metrics (Section 2.5).

2.2. Lattice Boltzmann method

To simulate fluid flow and dispersion in the mobile phase of the domain, the LBM was used. The LBM is a method that has been the subject of rapid development in the last decade because of its suitability for simulating complex geometry flow fields, such as those in porous media [16,17,19].

This approach considers a fluid as a collection of particles, unlike the standard Navier-Stokes approach, which considers a fluid body as a continuum. The LBM uses a probability density function (PDF) to convert the discrete particle system into a continuous variable, which is subsequently discretized into a homogenous grid to perform the numerical iterative solution procedure. Macroscopic variables may then be calculated as moments of the PDF. Although the LBM is based on a rarefied gas system, it may be extended to liquid systems by artificially manipulating the Mach number to approach a compressibility limit.

Further details on the LBM parameters used are noted in Section 2.4.

2.3. Domain and boundary conditions

The domain was spatially discretized using a homogeneous mesh, comprised of 30^3 nodal points per spherical particle (mesh independence study described in Section 3.1). Two superimposed lattices were applied, the first to resolve the steady-state velocity field and the second applied subsequently to resolve the advection-diffusion field.

Both random and ordered packings were considered in this work. All packings were generated from spherical particles with a uniform diameter of 200 μm, i.e. the minimum diameter that can be currently achieved reliably in some commercial 3D printers [20]. The position of each spherical particle is identified by the location of its centre, which in turn depends upon the packing configuration.

- *Random packings*: an external code was used to generate the centre locations [21] which were imported into Palabos to create the random packings. Five different random packings were generated and employed for the simulations. Packings were $7{d_p}^3$ in size, where d_p is the sphere diameter. Simulation results were averaged over the five independent packings.
- *Ordered packings*: both particle arrangement and orientation of the packings with respect to the main direction of the flow were considered. Three arrangements, Simple Cubic (SC), Body Centred Cubic (BCC) and Face Centred Cubic (FCC), all based on a cubic unit cell, were generated. The cubic cells were investigated for [001], [011] and [111] orientations, where the main direction of the flow is aligned with the z axis (Fig. 1). The notation in this work uses the Miller Index to denote the axial direction with respect to the standard cubic cell packing. The rotations of the unit cell were produced using rotation matrices on the coordinates of the sphere centres of the standard [001] configuration, a result equivalent to changing the direction of flow with respect to the packing. It is worth noting that, for the same particle diameter, the size of the cubic unit cell as well as the number of particles contained in the unit cell varied amongst the configurations considered (Table 1).

Simulations were run on appropriate multiples of the representative unit cells. A single unit cell was used in the transverse directions (x and y), with periodic boundary conditions applied across all four transverse boundaries. The unit cell was repeated

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