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# Intraparticle and interstitial flow in wide-pore superficially porous and fully porous particles

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## HIGHLIGHTS

- Models of fully porous and superficially porous particles are constructed.
- Extensive fluid flow is calculated within and around these particles in packed beds.
- Velocities within these wide pore particles show significant internal flow.
- Perfusion chromatography can be performed with these particles.
- Course-grained theory agrees with the fluid velocities.

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## ABSTRACT

Using a synthetic particle model, viscous fluid flow through packed beds of porous particles is directly simulated at the pore scale (1000 Å) using the lattice Boltzmann method to characterize intraparticle and interstitial flow. Synthetic particle models are derived from synthesis conditions, scanning electron and focused ion-beam microscopy. A fully porous particle (FPP) and a superficially porous particle (SPP), derived from the FPP, both with the same external surface, are studied. Packed beds of random packings and body-centered cubic packings of the SPP and FPP models were generated by a Monte Carlo procedure that employs random translation and rigid-body rotation of the particles.

Detailed velocity distributions are presented for the interstitial and intraparticle regions of the packed beds and within the particles. These results confirm that porous particle packed beds are heterogeneous systems which require extensions to classical theory for correctly predicting the resistance to flow. It is shown that SPPs require less pressure than FPPs to maintain the same flow velocity. For the random SPP and FPP packed beds, the particle hull mass flux is ≈ 10% of the interstitial flux and ≈ 3% of the total volumetric flux in the flow direction through the SPP hull. The calculated intraparticle pore velocities confirm that an internal flow, characteristic of "perfusion" chromatography, exists within the porous shell that can enhance biomolecular separations.



## 1. Introduction

Many of the newer particles utilized in liquid chromatography (LC) use core-shell particles, also known as superficially porous particles (SPPs) (DeStefano et al., 2008; Schuster et al., 2012, 2013; Wagner et al., 2012, 2017; Schure and Moran, 2017). These particles contain a nonporous core with a porous shell on the outside. This is in contrast to fully porous particles (FPPs) which have been traditionally used in LC, and "pellicular" particles (Horváth and Lipsky, 1969), which have thicker shells than modern SPPs and were introduced in the late 1960s. Many questions still exist about SPPs, including understanding the flow-field inside and outside of the particle in wide-pore SPP materials. The work reported herein attempts to explain some of these questions.

A number of large-scale simulation studies have examined the microscopic details of solute transport through a packed bed of nonporous particles (Maier et al., 1998, 2000, 2003; Kandhai et al., 2002; Bijeljic et al., 2004; Sullivan et al., 2005). This

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technology has also been used to study chromatographic column processes (Schure et al., 2002; Schure and Maier, 2006; Hlushkou et al., 2007; Khirevich, 2011). In all of these studies, the chromatographic particle is a nonporous sphere enabling the study of fluid-phase mass transport; the positions of these particles are explicitly stated in the packed bed by using particle packing software to construct the bed.

No transport models have been developed previously that explicitly define a detailed pore structure at the particle level. In cases where transport is to be discussed for porous particles, stochastic, coarse-grained effects are utilized to predict transport under random diffusion (Spaid and Phelan, 1997; Kandhai et al., 2002; Daneyko et al., 2015). In this and all other scenarios used in simulating packed beds for studying LC, it has been assumed that fluid flow ceases in the particle phase as the pore size is much too small, typically $\leqslant$ 400 Å, to permit flow through any of the particle pore structure. This would justify the assumption of a purely diffusive transport of solutes into and out of the intraparticle pore space.

It is well-recognized that particles with large connecting porous networks, often with pore sizes on the order of $\geqslant$ 5000 Å, have a significant internal convective flow (Lloyd and Warner, 1990; Afeyan et al., 1991; Rodrigues et al., 1993; Frey et al., 1993; Rodrigues, 1997; de Neuville et al., 2014; Wu et al., 2015); this is often referred to as "perfusion" and is characteristic of wide-pore materials. In one of these works (Frey et al., 1993) particles were referred to as "gigaporous" when the pore diameter to particle diameter ratio is $> 0.01$. The particles studied here fit that definition.

Previous studies have not examined the microfluidic details of the surface and internal flow of wide-pore particles with pore diameters $\geqslant$ 1000 Å. If there is flow into (and out of) wide-pore particles, this would enhance diffusion. The extent of convective flow in and around the pore surface of a porous particle is extremely hard to ascertain by experiment, although single particle measurements have been made (Pfeiffer et al., 1996).

A number of investigations have examined the internal flow in porous particles. For example, in a well-known study (Neale et al., 1973), Brinkman's equation (Brinkman, 1947, 1949; Durlofsky and Brady, 1987) was used as the basis to predict the permeability of porous particle beds. These authors calculated *bed* permeability as a function of the interstitial porosity for various values of $\beta$, the nondimensional *particle* permeability. Their results show that for $\beta > 100$, the particle permeability has little effect on the bed permeability, and this is the range in which the simulations in this paper are relevant.

Gritti et al. (2007) measured the porosity and permeability of SPP and FPP packed columns. Although they found the SPP column less permeable than the FPP, the differences in diameter and interstitial porosity of their SPP and FPP columns complicate a direct comparison. The Kozeny-Carman (KC) equation (Carman, 1937; Giddings, 1965; Neue, 1997; Quinn, 2014) was also used to predict permeability based on particle size and interstitial porosity. (Note that this approach would predict the same permeability for SPP and FPP particles of the same diameter in columns of the same interstitial porosity.) They found the SPP column permeability less than predicted by theory and less than the prediction for the FPP column. They suggested that the greater rugosity of the SPP, which is a measure of the deviation from a purely spherical surface and also referred to as surface roughness, might play a role in understanding the permeability, but they did not propose a specific physical explanation. Yet in another study (Ismail et al., 2016), the SPP and FPP particle diameters and interstitial porosities were more similar than those studied by Guiochon and coworkers, mentioned above, and it was found that the SPP column was 22% more permeable than the FPP column.

A porous particle can be regarded as a rough sphere by ignoring intraparticle flow. The effect of surface roughness on packed bed pressure drop has been studied in several contexts. It has been found (Crawford and Plumb, 1986) that the pressure drop increases with increasing surface area and roughness of nonporous particles. However, it was demonstrated (Eisfeld and Schnitzlein, 2001) that increased porosity associated with rough particles counteracted this effect. Others (Nemec and Levec, 2005; Allen et al., 2013) have suggested that this effect can be attributed to departures from sphericity rather than surface roughness. Nonetheless, the surface roughness literature highlights the importance of accounting for porosity and surface area within the porous particle structure.

The influence of SPP morphology on pore-level flow can be studied with high resolution fluid mechanics if a model of the SPP or FPP can be formulated. For studying wide-pore materials, computer simulation of the model can yield useful and realistic information on fluid flow. One of the benefits of simulation is that differences can be eliminated in particle surface geometry when comparing SPP and FPP packed beds. This makes it possible to evaluate theoretical approaches, such as the KC equation, for predicting porous particle flow properties. Differences in permeability between SPP, FPP and solid-sphere beds are discussed in the work presented here, including the contrast of some theoretical predictions with calculations reported herein.

In this paper a synthetic particle model derived from synthesis conditions, electron microscopy and particle simulation techniques, described below, are used to study the detailed flow near, into and out of the particle. Both SPP and FPP morphologies can be produced as sphere models, which are included as supplemental files. The surface area and pore volume of the sphere models are in close agreement with experimental particles made in the laboratory. Calculation of a high-resolution flow field in the interstitial and intraparticle pore regions of the models is therefore considered a simulation of flow through the experimental particles. Specific attention is given here to understanding the permeability, mass and volumetric flux and detailed flow field that exist both internal and external to the particle.

## 2. Experimental and computational methods for particles

### 2.1. Experimental methods and techniques

A number of silica SPPs were prepared using the layer-by-layer method (Hayes et al., 2014) to put porous shells on nonporous cores. The porous shell is composed of silica sol particles with average radius $r_{sol} = 0.0575$ μm. The average core radius $r_c = 1.65$ μm and the thickness of the shell, $L_s$, is $\approx 0.58$ μm. These parameters are utilized for the construction of the synthetic particle, as described below in Section 2.2. The particle diameter is the mean value of 70 particles, each with two orthogonal measurements taken utilizing scanning electron microscopy (SEM) (Reimer, 2013). SEM images were obtained using a Zeiss (Jena, Germany) Auriga 60 high resolution SEM with integrated focused ion beam (FIB) (Yao, 2007) at the University of Delaware (Newark, DE).

A number of these parameters are summarized in Table 1 for both experimental and synthetic particles. For the experimental particles, dividing the standard deviation by the mean gives a relative variation in mean diameter of 4.6%, a relatively narrow size distribution. One of the SPP systems was chosen for further study, with label 1030-27-D-SPP, a 1000 Å mean pore diameter SPP.

Experimental surface areas and pore volumes were measured with a Micromeritics (Norcross, GA) Tristar II instrument using the $N_2$ BET adsorption method for surface area determination (Brunauer et al., 1938) and the BJH method for pore volume