Understanding flow and diffusion in porous networks combining electron tomography and pore-scale simulations

Reich, S.[1], Reisinger, A.E.[1], Schlabach, S.[2,3], Baranau, V.[1], Svidrytski, A.[1], Hlushkou, D.[1], Stoeckel, D.[1], Höltzel, A.[1], Tallarek, U.[1] and Kübel, C.[2,3]

[1] Philipps-Universität Marburg, Germany, [2] KIT, Germany, [3] KNMF, Germany

Disordered hierarchical porous media play a crucial role as fixed bed supports for a wide range of applications from separation techniques such as HPLC to heterogeneous catalysis. To understand and ultimately optimize their performance, the relationship between morphology and transport properties has to be established. The key is a statistically meaningful, quantitative description of the pore structure across length scales linked to pore-scale simulations to determine the flow and diffusion properties using realistic models for the macro [1] and mesopores [2].

In our work, we focus on porous silica monoliths where the flow properties are dominated by the macropore morphology and the diffusion properties by the mesopore morphology. The macropore morphology was systematically varied during sol-gel synthesis, which was quantitatively characterized by 3D slice&view techniques in the FIB [3]. Similarly, macro pore differences of the core and the walls of an HPLC column were quantitatively reconstructed in 3D (Fig. 1) and used to model the flow differences in these regions, which limit the HPLC separation performance [1].

At the mesoscale, an isomorphic series of silica monoliths with varying average pore diameter (12 to 26 nm) was the basis for a quantitative analysis of hindered diffusion. HAADF-STEM tomographic reconstruction followed by advanced image processing was used to reconstruct a statistically relevant volume of the different monoliths, which was segmented to form realistic experimental models of the pore structure (Fig. 2). Hindered diffusion, explicitly taking into account the solute vs. pore size ratio, was simulated for all models to derive a quantitative expression of the hindrance factor, which describes the degree to which diffusion through a material is hindered compared to the diffusion in the bulk liquid depending on the size ratio. The result is a master curve describing hindered diffusion without specific surface interactions for all materials with comparable morphology, which potentially encompasses all sol-gel processed mesoporous silicas.

Details on the image acquisition at different length scales, reconstructed microstructure morphology and the flow & diffusion simulations will be presented and the crucial role of the combination of experiment and modelling discussed.

References

1. Reising, A. E., Schlabach, S., Baranau, V., Stoeckel, D. & Tallarek, U. Analysis of packing microstructure and wall effects in a narrow-bore ultrahigh pressure liquid chromatography column using focused ion-beam scanning electron microscopy. *J. Chromatogr. A* **1513,** 172 - 182 (2017).

2. Reich, S.-J. *et al.* Hindrance Factor Expression for Diffusion in Random Mesoporous Adsorbents Obtained from Pore-Scale Simulations in Physical Reconstructions. *Ind. Eng. Chem. Res.* online (2018). doi:10.1021/acs.iecr.7b04840

3. Stoeckel, D. *et al.* Morphological Analysis of Disordered Macroporous - Mesoporous Solids Based on Physical Reconstruction by Nanoscale Tomography. *Langmuir* **30,** 9022 - 9027 (2014).

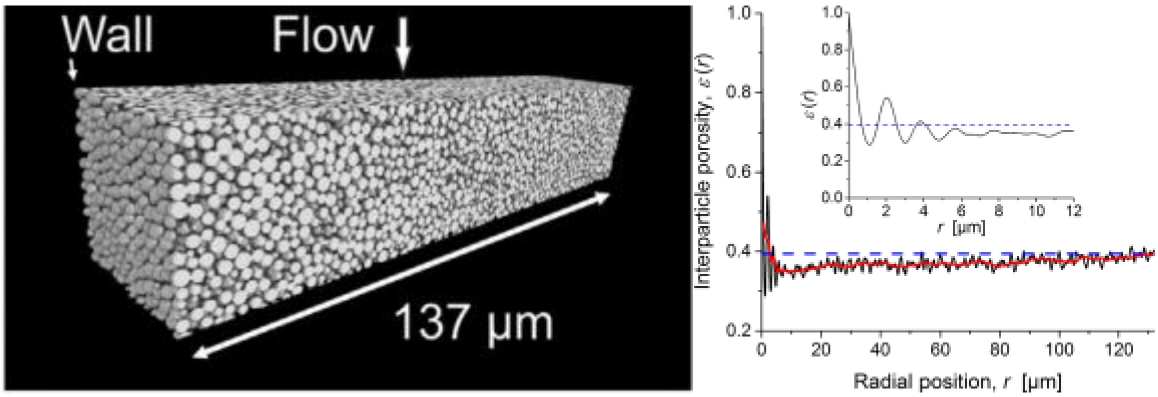

Figure 1: a) FIB slice&view reconstruction of the macropores in an HPLC colum and b) distribution of the local void volume fraction as a function of distance from the column wall. From Ref. [1].

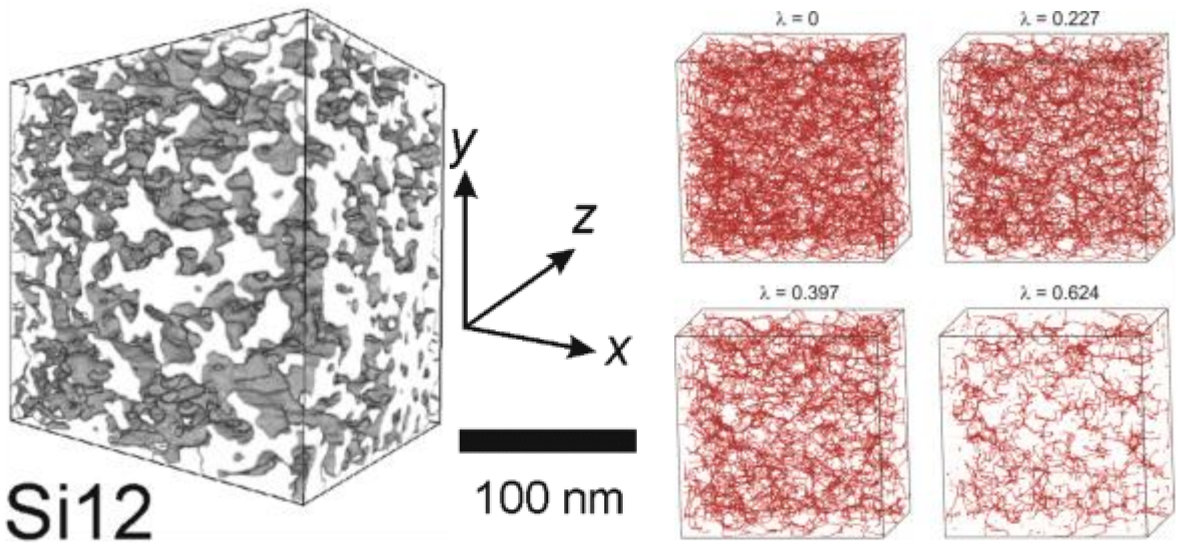

Figure 2: a) Electron tomographic reconstruction of the mesopore space in a silica monolith and b) modelling of the accessible pore network for tracers of different size λ. From Ref. [2].