

Colloquium of the SFB 716

May 17th, 2018 | 4 pm

University of Stuttgart
Campus Vaihingen
Allmandring 3
Room 1.079

The Collaborative Research Center (SFB) 716 invites to the upcoming colloquium. In this lecture series guest speakers and members of our subprojects inform about their results regarding dynamic simulation of systems with large particle numbers.

TALK

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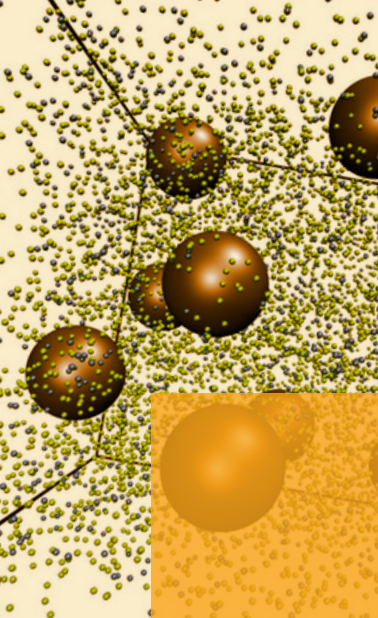
Simulation of Transport in Hierarchically Porous Materials: From Solute-Surface Interaction to Hindered Diffusion to Hydrodynamic Dispersion

The ability to simulate transport properties like diffusion and hydrodynamic dispersion coefficients as well as performance factors (retention or selectivity) in hierarchically porous materials is a key challenge and of paramount importance to the understanding and design of functional devices. This addresses continuous-flow reactors, desalination membranes, battery electrodes, as well as fixed-bed adsorption and separation columns.¹

We resolve this issue by pore-scale simulations of advection, diffusion, sorption and partitioning using a multiscale reconstruction approach that provides realistic models for surface chemistry (and resulting liquid-phase organization on the single-pore level) as well as for the 3D morphology of mesopore and macropore spaces in hierarchical (macro-mesoporous) materials. In particular, molecular dynamics simulations take account for the pore shape, surface functionalization, liquid phase composition, and solute structure and quantify solvent/solute distribution and mobility on the single mesopore

level.^{2,3} In the next step, the mesopore network is reconstructed by electron tomography to serve as model for simulations of hindered diffusion of (finite-size) solutes using a random-walk approach.⁴ This leads to very accurate hindrance factor expressions for diffusion that substantially improve expressions based on an idealized single-pore geometry.⁵ The combination of the molecular dynamics and random-walk simulations offers access to long-time diffusion coefficients covering the impact of surface chemistry, solvent composition, and solute structure, as well as the entire mesopore space morphology resulting from a specific material preparation route.

The effective mesopore scale dynamics (revealing diffusion, retention, and selectivity) is subsequently coupled with the advection-diffusion dynamics in the macropore space of the hierarchically structured materials, e.g., the interstitial macropores in a packing of particles or the flow-through macropores of a monolith. Fluid flow is simulated using the lattice-Boltzmann method⁶ and care is taken for solvent and solute exchange between the stagnant pools in the mesopores and flowing fluid in the macropores



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of the material.⁷ In this way, diffusion, sorption and partitioning in the mesopores is connected to the fluid flow dynamics in the macropores, which allows to calculate effective dispersion coefficients for solvent and solutes in the long-time limit. These coefficients can be studied systematically as a function of the average velocity^{7,8} with explicit variation of surface modification, solvent composition, solute structure as well as mesopore space and macropore space characteristics (e.g., porosity, pore size distribution, order vs. disorder) through fine-tuned experimental synthesis or computer-generation.

In this approach, the simulations do not just corroborate experimental findings but take the lead in the targeted design of bed morphologies and surface functionalization for boosted material performance in demanding applications.

Read more:

- (1) C. P. Haas, T. Müllner, R. Kohns, D. Enke & U. Tallarek (2017) High-performance monoliths in heterogeneous catalysis with single-phase liquid flow. *React. Chem. Eng.* 121:8416–8426.
- (2) S. M. Melnikov, A. Höltzel, A. Seidel-Morgenstern & U. Tallarek (2013) How ternary mobile phases allow tuning of analyte retention in hydrophilic interaction liquid chromatography. *Anal. Chem.* 85:8850–8856.
- (3) J. Rybka, J. Kärger & U. Tallarek (2017) Single-molecule and ensemble diffusivities in individual nanopores with spatially dependent mobility. *ChemPhysChem* 18:7416–7426.

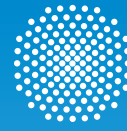
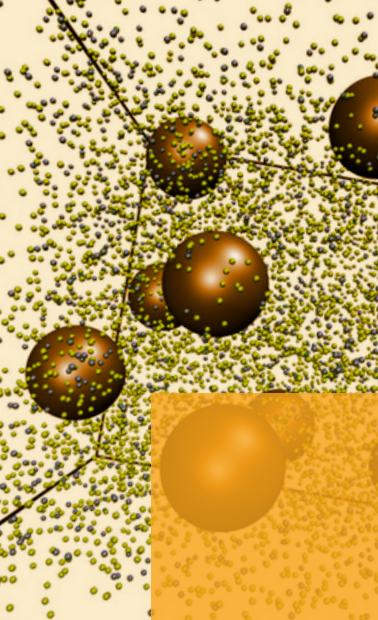
- (4) D. Hlushkou, A. Svidrytski & U. Tallarek (2017) Tracer-size-dependent pore space accessibility and long-time diffusion coefficient in amorphous, mesoporous silica. *J. Phys. Chem. C* 121:8416–8426.

- (5) S.-J. Reich, A. Svidrytski, D. Hlushkou, D. Stoeckel, C. Kübel, A. Höltzel & U. Tallarek (2018) Hindrance factor expression for diffusion in random mesoporous adsorbents obtained from pore-scale simulations in physical reconstructions. *Ind. Eng. Chem. Res.* 57:3031–3042.

- (6) S. Khirevich, I. Ginzburg & U. Tallarek (2015) Coarse- and fine-grid numerical behavior of MRT/TRT lattice-Boltzmann schemes in regular and random sphere packings. *J. Comput. Phys.* 281:708–742.

- (7) A. Daneyko, D. Hlushkou, V. Baranau, S. Khirevich, A. Seidel-Morgenstern & U. Tallarek (2015) Computational investigation of longitudinal diffusion, eddy dispersion, and trans-particle mass transfer in bulk, random packings of core-shell particles with varied shell thickness and shell diffusion coefficient. *J. Chromatogr. A* 1407:139–156.

- (8) U. M. Scheven, S. Khirevich, A. Daneyko & U. Tallarek (2014) Longitudinal and transverse dispersion in flow through random packings of spheres: A quantitative comparison of experiments, simulations, and models. *Phys. Rev. E* 89:053023.



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TALK

Frank Maier,
Maofeng Dou

Subproject C.9

Institute for
Computational
Physics (ICP)

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Electronic Features of Functionalized Nanopores

Nanopore materials are used for performing single-molecule experiments and detect the translocating molecules through electronic means.

It has been proposed, that functionalizing the nanopores with small molecules could potentially enhance the electronic signals used for the detection. Along these lines, we have used diamond-like molecules to functionalize electrodes embedded into a nanopore. Based on quantum-mechanical calculations we could show that such a setup shows indeed very localized electronic current peak for each DNA unit, a nucleotide, in the pore.

In order to quantify this finding we have defined the sensitivity of such a functionalized nanopore. This was also found to strongly depend on whether a DNA nucleotide is natural or modified. This allows for a clear detection of mutated DNA, as well. This proof of principles study needs to be supplemented by effects, such as the presence of a solvent environment and dynamics.

Accordingly, we extend our simulations using a QM/MM approach in order to investigate the influence of these effects on the sensitivity of our nanopores.

In the end, we discuss the details of this approach and our first results.