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

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The ability to simulate transport properties like diffusion and hydrodynamic dispersion coefficients as well as performance factors (e.g., retention and 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 method[6] and care is taken for solvent and solute exchange between the stagnant pools in the mesopores and flowing fluid in the macropores 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.

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