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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Multiscale simulation of sorption and diffusion in porous media

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(Received: 2023/06/13, Published online: 2023/06/24)

Transport in surface-functionalized porous media involves time and length scales ranging from solute–surface interactions to tortuous diffusion in hierarchical pore spaces. Realistic multiscale simulations therefore combine molecular-level information of the interfacial dynamics with porosity models from tomographic reconstructions to investigate the relationships between surface functionality, pore space morphology, and effective transport. Although multiscale simulations of transport in porous media have advanced in recent years, connecting the different modeling scales is still challenging and requires suitable linker schemes.

We illustrate multiscale simulations with a focus on reversed-phase liquid chromatography (RPLC), the most important chemical separation and purification technique today. RPLC is a multiscale process taking place inside a macro–mesoporous, often silica-based adsorbent, the chromatographic bed. An aqueous–organic liquid is pumped through the bed to separate analytes based on differential retention by the hydrophobically-modified silica surface. The hydrophobic modification typically consists of long alkyl chains. Mass transport through the bed combines advective flow in the macropore space with pore liquid diffusion in the mesopore space and surface diffusion along the soft surface of the bonded phase. We previously presented a bottom-up approach that considers analyte distribution and mobility at the functionalized solid–liquid interface, as received from molecular dynamics (MD) simulations in an RPLC mesopore model, in Brownian dynamics (BD) diffusion simulations implemented in a macro–mesoporosity model of the bed [1]. This simulation approach traces the impact of subtle changes in the interfacial dynamics on the effective diffusion coefficient in the interconnected mesopore space (D_{meso}) and finally the effective diffusion coefficient in the entire chromatographic bed (D_{bed}). The approach was later extended by the lattice-Boltzmann method to include fluid flow in the macropore space of the bed to study the influence of mass transfer resistance in the stagnant mobile phase (inside the mesopores) on longitudinal and transverse dispersion coefficients [2]. Through our multiscale simulation approach we have already demonstrated that the key interfacial phenomena of RPLC, namely analyte partitioning into and adsorption onto the bonded-phase chains as well as surface diffusion along the bonded-phase chains, significantly influence the effective diffusion and dispersion coefficients in the chromatographic bed [1, 2]. In this work, we investigate the effect of relevant surface chemistry parameters in stationary-phase design on effective diffusion coefficients, namely length and ligand density of the surface-tethered alkyl chains [3].

Figure 1 provides an overview of the multiscale simulation approach. MD simulations (Figure 1A) characterize the interfacial dynamics at the single-mesopore level by analyte density $\rho(z)$ and surface-parallel diffusivity profiles $D_{\parallel}(z)$. The information contained in $\rho(z)$ and $D_{\parallel}(z)$ is translated into a distance map assigning analyte density and diffusion coefficient values according to the distance from the solid silica surface. Analyte transport in the mesopore space is simulated with BD simulations (Figure 1B), specifically with a random-walk particle-tracking (RWPT) method. Probabilistic-reflection and time-splitting schemes are applied to capture analyte travel over different distances from the surface. These linker schemes ensure that random walkers in the RWPT simulation, sampling the mesopore space to indicate D_{meso}, retain the information about $\rho(z)$ and $D_{\parallel}(z)$. At the top level (Figure 1C), we simulate the exchange (i.e., mass transfer) of analyte molecules between mesopore space and macropore space of the bed. To progress from D_{meso} to D_{bed}, we adapt an effective-homogeneous-medium representation of the mesopore space in the explicit macropore space morphology, with the probabilistic-reflection and time-splitting (linker) schemes now applied to the interface between these two spatial domains.

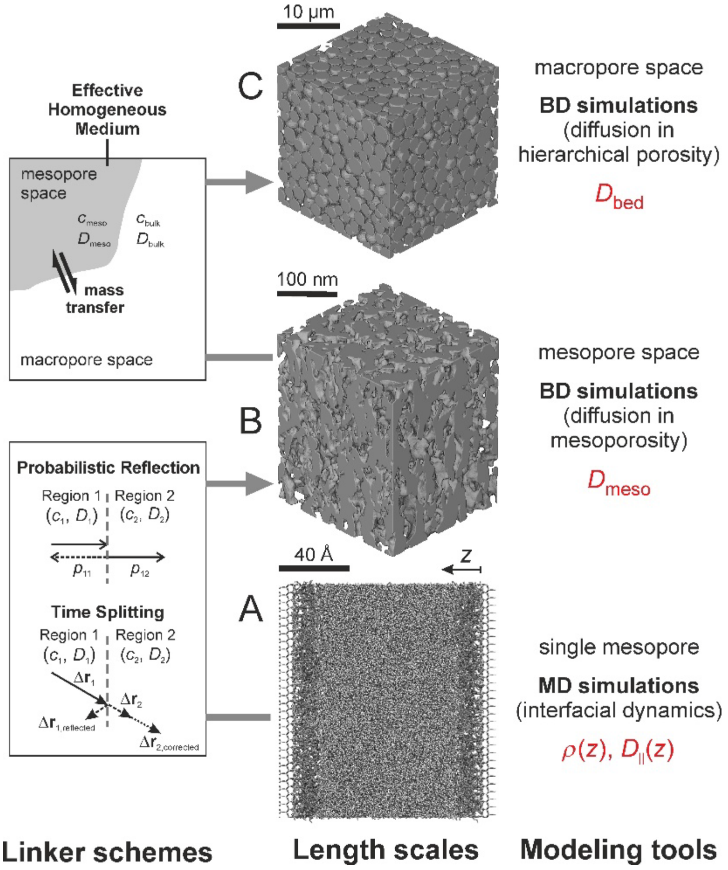

Fig. 1. Multiscale approach to the simulation of effective mesopore space and bed diffusion coefficients (D_{meso} and D_{bed}) in a hierarchically porous silica adsorbent with a functionalized surface. Reproduced with permission from [3].

It has been found [3] that at the single-mesopore level the pore-averaged analyte diffusivities reflect analyte-specific retention properties as well as the surface chemistry. Longer chains and, to a much lesser degree, higher ligand density favor fast surface diffusion and thus the main mode of analyte transport. At the mesopore space level, analyte diffusivities become significantly reduced from the surface tortuosity inside the random mesoporous silica. Additionally, a mobility-reducing overlap between interfacial regions from opposite pore walls develops locally at pore necks and other constrictions in the irregularly shaped mesopore space. At the bed level, surface chemistry effects are hardly detectable any more. The stronger an analyte is retained by the RPLC solid–liquid interface inside the mesopores, the slower becomes the mass transfer between the pore space hierarchies and the lower is the bed diffusivity. Diffusive mass transport through the column is limited by the analyte properties that govern RPLC retention rather than by the surface chemistry of the stationary phase.

References

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