Random Walks in Porous Media –
Diffusion under Confinement, and What It Means for Catalyst and Membrane Analysis and Design

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Molecular transport in nanoporous materials is important to a variety of chemical engineering applications, including catalysis, separation, and controlled release and uptake of chemicals. In nanopores, interactions of the diffusing molecules with the pore walls dominate the diffusion process, so that diffusivities differ from those in a bulk fluid. This can be useful to, e.g., control selectivity in separation processes, but it can also lead to undesired reductions in catalytic rates in heterogeneous catalysis.

We will discuss methods to calculate the *influence of pore geometry and chemical structure of the pore walls on diffusion in nanopores*. Examples are the effects of: (1) surface roughness on Knudsen diffusion of gases in mesopores, (2) network topology and adsorption site distribution on diffusion in zeolites and other microporous materials, (3) confinement and surface charge distribution on diffusion in nanopores.

In short pores, an incorrect analysis based on the mean-square displacement of molecules may bias diffusion results, even qualitatively. Diffusion might appear anomalous while, in fact, it follows Einstein's diffusion law. A first-passage time analysis gives correct and more complete information on diffusion in nanopores than a mean-square displacement analysis. Different origins for a power-law dependence of the residence time in nanopores are reviewed. They vary widely, from fractal surface roughness to chemical heterogeneity, collective motion, or trapping along pore walls induced by fluctuations.

In chemical engineering applications, we are most interested in macroscopic results, on the scale of a membrane, adsorbent or catalyst particle. To nevertheless include heterogeneity (which could be microscopic or macroscopic) on macroscopic transport requires *multiscale methodologies* that enable us to bridge wide ranges of length and time scales. We will illustrate how a combination of statistical mechanical and coarse-graining methods on modern computational platforms allow us to do this within reasonable computational times, taking diffusion in zeolites as an example.

Finally, since molecular transport plays such an important role in engineering applications and is strongly structure-dependent, our ability to investigate its influence at nano- and macro-scales brings up the question whether materials could be designed to tune molecular transport to enhance transport-dependent properties, such as membrane permeation and selectivity, or catalyst yield and stability? Considerable advances in materials science allow putting such designs to practice, and we have proposed a *nature-inspired chemical engineering* (NICE) approach – taking guidance from trees, lungs and protein channels – to optimize hierarchical transport networks and nanopore designs.