192d Multiscale Modeling for Bridging Disparate Scales of Diffusion in Polycrystalline Microporous Membranes

Mark A. Snyder and Dionisios G. Vlachos

Microporous (e.g., zeolite) materials have been the focus of intense research over the past several decades for applications in adsorption and catalysis. The more recent development of techniques for growing oriented zeolite thin films (e.g., [1-4]) coupled with their ordered crystalline microstructure, nanometer-sized pores, and cation tunability, make them attractive for control and manipulation of molecules in nanotechnology applications (e.g., high-resolution gas separation, chemical sensors). While the current paradigm for modeling permeation through zeolite membranes focuses almost exclusively on perfect single-crystal membranes, fluorescence confocal optical microscopy (FCOM) studies [5, 6] have revealed the polycrystalline nature of these thin films. Indeed, discrepancies between theory and experiment are often tacitly attributed to such polycrystallinity, underscoring the need for development of structure-properties relations for realistic membrane systems.

Here, we employ multiscale stochastic kinetic Monte Carlo (KMC) methods [7] and continuum mesoscopic theories, e.g., [8-10] to bridge the disparate scales associated with molecular transport in microporous thin films. We specifically focus on the rich test bed system of benzene diffusion in NaX zeolite membranes, characterized by a mixture of strong and weak adsorbate-adsorbate interactions and strongly corrugated potential energy surface. Employing a hierarchically parameterized [11] molecular model of benzene in NaX, we carry out gradient KMC simulation of permeation through thin (sub-micron) single crystal membranes. Despite the thin system size, these simulations yield apparent activation energies in good agreement with laboratory experiments. They also reveal molecular level insight into near-boundary nonlinearities resulting from truncated adsorbate-adsorbate potentials, limitations of the Darken approximation, and potentially complex non-unique functionality and multiplicity of the transport diffusivity for strongly interacting adsorbates. To more quantitatively assess the role of polycrystallinity in membrane performance, we also perform gradient KMC simulations of benzene flux through NaX membranes of varying polycrystallinity. We show that only a moderate number of grain boundaries can reduce flux by nearly an order of magnitude below single crystal predictions.

To overcome the computational limitations of conventional KMC, we derive a topology-specific mesoscopic model via rigorous coarse-graining of the parameterized lattice representations of benzene in NaX. The resulting continuum model retains molecular level details of diffusion dynamics and adsorbate-adsorbate interactions while accessing larger length and time scales required for prediction of macroscopic permeation properties. Here, we assess the accuracy of these new mesoscopic theories by direct comparison with gradient KMC simulations in the limit of thin membranes and with experimental permeation data for realistically thick membranes. Finally, we illustrate how the resulting device-level mesoscopic models provide the framework necessary to capture diffusion through microporous membranes, and begin to elucidate structure-properties relations for these complex systems.

References

1. Hedlund, J., J. Porous Mater., 7(2000), 455-464.

2. Nikolakis, V., et al., J. Membrane Sci., 184(2001), 209-219.

3. Lai, Z., et al., Science, 300(2003), 456-460.

4. Gump, C.J., et al., Ind. Eng. Chem. Res., 40(2001), 565-577.

5. Snyder, M.A., et al., Microporous and Mesoporous Materials, 76(2004), 29-33.

6. Bonilla, G., et al., J. Membrane Sci., 182(2001), 103-109.

7. Snyder, M.A., et al., Comput. Chem. Eng., 29(2005), 701-712.

8. Vlachos, D.G. and M.A. Katsoulakis, Physical Review Letters, 85(2000), 3898-3901.

9. Snyder, M.A., et al., Chem. Eng. Sci., 58(2003), 895-901.

10. Lam, R., et al., Journal of Chemical Physics, 115(2001), 11278-11288.

11. Snyder, M.A. and D.G. Vlachos, Molecular Simulation, 30(2004), 561-577.