4ca Multiscale Elucidation of Structure-Properties Relations for Molecular Transport in Polycrystalline Thin Films

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Despite advances in computational power and algorithm efficiency, invaluable fundamental insight from current molecular models remains limited to a narrow range of short length and time scales. In light of such limitations, a recent U.S. Department of Energy (DOE) initiative [1] has put forth a roadmap directing development of multiscale approaches to address science and engineering problems that are currently "out of reach" due to strongly coupled disparity in scales. Among the roadmap targets is the rational design of materials for applications such as molecule sensing, high-resolution gas separations, and nanoscale materials templating. Realization of such materials applications demands comprehensive development of structure-properties relations. Concomitant challenges derive from the strongly coupled scales associated with molecular transport in the presence of material polycrystallinity (i.e., grain boundaries) and strong adsorbate-adsorbate forces.

The ordered crystalline microstructure, nanometer-sized pores, cation tunability, and established techniques for thin film fabrication (e.g., [2]) make microporous materials (e.g., zeolites) attractive for such applications. The current paradigm for modeling molecular transport in zeolite thin films focuses almost exclusively on *single-crystal* systems characterized by relatively *weak adsorbate-adsorbate forces*. Many systems of practical interest, however, are characterized by *strongly interacting* adsorbates and *substantial polycrystallinity*. This poster will provide an overview of parallel theoretical and experimental efforts taken towards the development of structure-properties relations for transport in realistic microporous thin films:

I. Multiscale modeling of diffusion of strongly interacting molecular species in microporous membranes

Strong coupling between scales associated with transport in polycrystalline microporous films plagues conventional molecular simulations and leads to the break down of phenomenological continuum theories (e.g., generalized Maxwell-Stefan). In this research, we develop and employ multiscale stochastic kinetic Monte Carlo (KMC) methods [3] and continuum mesoscopic theories, e.g., [4-6], to bridge these disparities in scale. The rich test-bed system of benzene in NaX zeolite will be employed as an example application of these multiscale techniques. The approach first employs a hierarchical technique to rationally parameterize complex molecular models of host-guest systems [7]. Despite limitations to thin (sub-micron) systems, subsequent gradient KMC simulations of permeation through single crystal and polycrystalline membranes are in good agreement with laboratory experiments (i.e., apparent activation energies of permeation). In addition, they reveal molecular level insight into the role of crystal terminations, strong adsorbate-adsorbate potentials [8], underlying diffusion mechanisms, and nanoscopic defects in permeation through thin polycrystalline films.

To overcome the computational limitations of conventional KMC, we derive a topology-specific mesoscopic model via rigorous coarse-graining of the parameterized lattice representations. 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. The accuracy of mesoscopic theories has been shown in the past for a range of prototype systems (e.g., [4-6, 9]). Here, we assess the accuracy of these new mesoscopic theories, derived for more complex systems, by direct comparison with gradient KMC simulations in the limit of thin membranes and with experimental permeation data for realistically thick membranes. Ultimately,

this multiscale approach yields device-level mesoscopic models that begin to elucidate structure-properties relations for these complex systems.

II. Novel non-destructive characterization of thin film polycrystallinity for elucidating structure-properties relations

Our gradient KMC simulations predict substantial sensitivity of permeation to only moderate membrane polycrystallinity. This underscores the need for quantitative characterization of microporous membrane polycrystallinity for development of predictive models of membrane permeation. Fluorescence confocal optical microscopy (FCOM) studies [10, 11] involving selective adsorption of dye molecules in polycrystalline features have highlighted the extent of this polycrystallinity in zeolite membranes. Quantitative interpretation of FCOM images, however, has remained relatively elusive.

This poster summarizes newly developed protocols for pushing the limits of FCOM as a quantitative, non-destructive materials characterization technique. These protocols involve rational screening of dye molecules via molecular mechanics calculations for *a priori* assessment of steric compatibility and energetic interactions with zeolitic (e.g., silicalite-1 and NaX) pores and dominant crystal surfaces. Novel standards with nanometer scale features are also fabricated and imaged to calibrate feature size and density with fluorescence intensity and its spatial decay. Such protocols, in conjunction with correlative FCOM and SEM studies [11] using separate and sequential adsorption of dyes, quantify the size and distribution of polycrystalline features, and link them directly to the crystal morphology. In this poster, these protocols are applied to both siliceous silicalite-1 and, for the first time, NaX zeolite membranes. Comparison of characteristic polycrystallinity is employed to explain variations in separation performance associated with membrane orientation (in the case of silicalite-1) and growth conditions. Ultimately, we illustrate the capabilities of more quantitative, non-destructive FCOM imaging for elucidating structure-properties relations for polycrystalline zeolite membranes.

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