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Molecular Transport in Nanostructured Materials: a Hierarchical Approach to Design Nanostructured Materials

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PROJECT SUMMARY:

Nanostructured materials obtained by self-assembly or as quenched, nonequilibrium structures exhibit remarkable membrane properties that can be exploited for separations technologies. Although natural membranes with nanoscale microstructure are common, the rational design and application of synthetic, nanostructured membranes for separations in the chemical and pharmaceutical industries, etc., are relatively new. For example, nanoporous carbons are exception in that they exhibit ideal separations of O_2/N_2 as high as 30:1, making them candidates for gas separations and membrane reactors. Although previous transition state models of separation and sorption suggested this high selectivity may be a consequence of shape selective transport (an entropic effect) through the complex structure, more recent analyses strongly suggest that the effect is actually due to specific penetrant-matrix interactions affecting the transition state (i.e. enthalpic in origin). At the heart of this controversy and the inability to predict mass transport in nanostructured materials is a general lack of understanding of the molecular mechanisms of transport. Indeed, compared to our ability to predict (and thus design devices around) transport in liquids and gases, or in large pores with Knudsen and surface diffusion, our basic scientific understanding of molecular transport in dense, nanostructured materials is quite limited. The primary difficulties in modeling this transport, often termed *configurational* diffusion, are that the penetrants are in continuous, intimate contact with the membrane matrix material and the matrix often has a complex topology with multiple length scales (e.g. polymer glasses). Both of these characteristics result in *anomalous* diffusion.

The goal of this proposal is to understand and quantitatively predict the transport of small molecules through nanostructured materials by an *ab initio* hierarchical approach. This will be achieved by combining quantum mechanics with statistical mechanics and molecular dynamics simulations to accurately predict thermodynamic solubilities and short-time tracer diffusivities in model nanostructured membranes. Novel methods for predicting the nanostructure of NPCs will be developed and validated. The information from this molecular modeling will be used within the context of generalized hydrodynamics and transition state theory to predict macroscopic permeability. These predictions will be validated by comparison to ongoing experiments on

supported nanoporous carbon membranes and supported polymer-inorganic membranes. The results will provide a rational framework for designing nanostructured membranes to meet current and future challenges in separation science.

The research thrust will start with idealized models for nanoporous carbons (Schwarzites) and move toward real nanoporous carbons and polymer-loaded, nanoporous silicates. The project includes active industrial collaboration and support, largely because of the potential uses for nanostructured membranes in gas separations, reverse osmosis, water purification, biomolecule separations, packaging, selective sensors, and fuel cells. In all these cases, controlling the selective transport (or blockage) of small molecules is critical to the membrane performance. Chemistry and Chemical Engineering students at the B.S., Ph.D. and postdoctoral levels will be trained synergistically in skills and knowledge appropriate to address challenges in transport and material structure in a wide variety of nanotechnology applications.

GOALS & EXPECTED RESULTS

The goal of this project is to provide a predictive, coherent theoretical description of configurational diffusion from first principles. A novel, hierarchical approach will connect ab initio quantum mechanical calculations to mesoscopic diffusivities and thermodynamic solubilities. Specific applications to be considered include gas separation in nanoporous carbons and permeation through polymers confined in mesoporous silica. The results will have application in a wide range of technologies, but most specifically for the rational design of membranes used in separation processes.

Proposed Work

Nanostructured membranes are exciting new materials that promise unique and controllable separation technologies. Two specific examples are the remarkable separation of O_2/N_2 obtained using nanoporous carbons (NPCs) and the effects of confinement in nanometer-scale cavities on the selectivity of glassy polymers for gas separations. Our objective is to investigate membranes composed of materials without well defined “pores”, i.e. systems in which diffusion pathways are of a size comparable to that of the molecular penetrants. Permeation through these materials is controlled by thermodynamic solubility and diffusion through the membrane matrix. There is no bulk phase of the penetrant and the penetrant is in constant molecular contact with the matrix; thus, the thermodynamic and transport processes are governed by penetrant-matrix interactions and by the diffusion pathways afforded by the matrix. The latter is often denoted as *configurational* or *micropore* diffusion to distinguish it from Knudsen, surface, and bulk diffusion typical in membranes containing pores larger than the penetrant. Due to the *complexity* of the matrix and intimate contact with the penetrant, the molecular mechanisms of diffusion are poorly understood, and consequently methods for the accurate prediction of transport in nanostructured materials are severely limited. By “complexity” we mean that diffusion in nanostructured materials requires consideration of length scales from the atomistic to the mesoscopic (micron) and time scales from femtoseconds to milliseconds. As a consequence, to date the reliable prediction of membrane performance from knowledge of the molecular structure of the membrane and penetrant-matrix interaction is not possible, and the rational engineering of nanostructured membranes to effect a desired separation is not feasible.

Controversy surrounds the molecular mechanisms of the high selectivity obtained in NPCs, which are now capable of achieving ideal selectivities of 30:1 (O_2/N_2), 178:1 (He/N_2), and 333:1 (H_2/N_2). For example, in the separation of nitrogen from oxygen over NPC the conventional reasoning is that since the extents of adsorption are nearly the same, the separation is kinetic in nature. Further, this kinetic separation is attributed to the geometric differences between the gases. However, recent analyses of permeation data on NPCs via Transition State Theory (TST) demonstrate that the entropic differences resulting from molecular size and shape

effects are not large enough to produce a two order of magnitude difference in the macroscopic diffusivity. Rather, we conclude that the enthalpy of the transition state is primarily responsible for the selectivity. Hence, models for activated transport in NPCs must focus on the use of accurate interaction potential functions, such as those afforded by *ab initio* methods. This is just one example of the unresolved problems in the modeling and prediction of transport of small molecules in NPC. Hydrogen and hydrocarbons, alkenes and alkanes all offer similar problems, as well as interesting competitive diffusion effects as mixtures in NPCs. To solve these and other problems of configurational diffusion in nanoporous membranes requires new approaches and more sophisticated potential functions.

Given the need for predicting configurational diffusion in many new areas that exploit nanostructured materials, we propose a hierarchical theoretical approach to provide a new and accurate *molecular* understanding of diffusive mass transfer in nanostructured materials. This group of investigators has broad theoretical and experimental experience that will be focused on unraveling the key aspects of permeation through model, nanostructured carbonaceous membranes. Our goal is to develop a predictive theoretical framework that can be applied to more realistic NPCs. We will also extend this approach to nanostructured silica/polymer composites. Our task is to predict the performance of a membrane unit operation, which in turn requires predicting the solubility and long-time diffusivities of the permeants. These quantities can be computed using Transition State Theory and/or Generalized Hydrodynamics with knowledge of the structure of the membrane combined with molecular simulations. Molecular simulations provide information about short-time diffusion, (nanosecond time and nanometer length scales) but cannot, at present, predict actual diffusion rates in nanostructured materials because these involve much longer time (micro- to milli-seconds) and length (microns to millimeter) scales. Molecular simulations require accurate potential functions as inputs; we will use a new approach developed by Doren to obtain these potentials. As the potentials that will be used in molecular dynamics simulations will be obtained from direct, quantum mechanical *ab initio* computations, this hierarchical approach provides an *ab initio* method for predicting membrane performance. A guide to the information flow within this hierarchical approach is illustrated in Figure 1.

Hierarchy of Length and Time Scales.

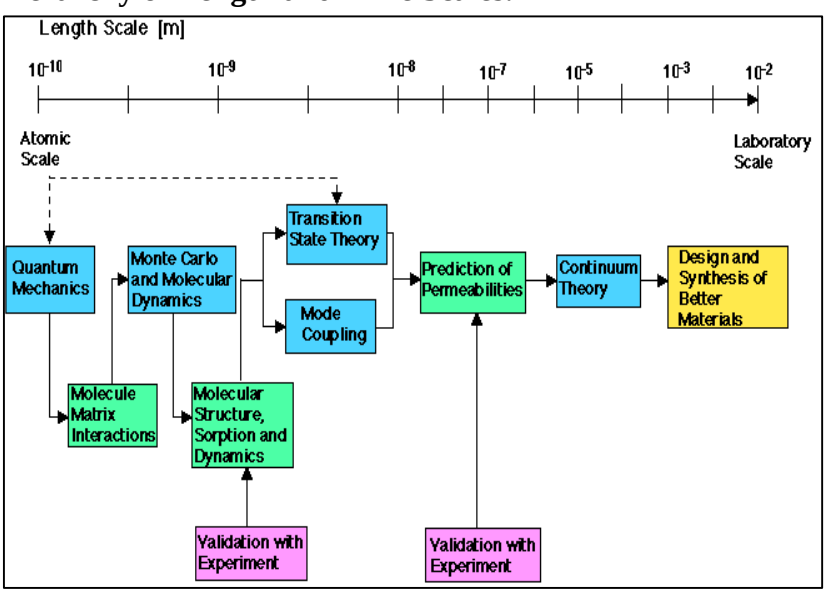

Figure 1. Information Flow: Computational quantum mechanics will be used as a basis for new and more accurate potential functions, which in turn can be used to produce far more realistic molecular dynamics simulations than are presently possible. The analysis of the trajectories provides short time diffusivities and establishes the transition state geometries. Both results can be extended to macroscopic length scales and to longer times via both generalized hydrodynamics and transition state theory.