CROSS-CUTTING COMPUTATION

Meeting the challenges posed by the needs for innovative solutions to carbon capture cannot be met by experimentation alone. Cutting across all possible solutions—whether using membranes, liquid solutions, solid sorbents, or other as yet unknown approaches—appropriate and innovative computation and modeling approaches will be needed to make significant strides in our understanding of routes that more effectively reduce CO_2 emissions. Starting with existing technologies, such as large-scale separation processes, predictions of thermodynamic equilibria and the transport of gaseous target molecules in liquid substrates or solid materials are essential for design and optimization of carbon capture technologies. Even in these established approaches, such data are not always available. For example, though it is common to find measurements of pure component adsorption isotherms in the literature, isotherms for mixtures of gases are less often available for optimization and design. This lack of information often promotes untested approximations of, say, ideal behavior of the mixture to be adopted in the absence of reliable data or predictions of mixture behavior. As methodologies for carbon capture advance, turning to new and different choices of materials and conditions, and different characteristic length and time scales, the relevant thermodynamic, transport and kinetic data are even less likely to be available.

This situation creates a strong driving force to turn to molecular simulations (such as Molecular Dynamics and Monte Carlo–based techniques) and other larger-scale computational routes (whether coarse-grained, PDE- or stochastic simulation-based approaches) to provide predictions of properties that enable new carbon capture processes to be designed and optimized. Molecular-scale simulations rely on the availability of accurate molecular interactions. While many intermolecular potential models are available for small molecules such as CO_2, O_2, N_2, and water, cross-interactions with the new materials that could be considered for carbon capture (e.g., carbon nanotubes, porous materials, polymers and others) may not be available. Parameterizing these interactions invariably requires quantum chemical calculations and knowledge of the interaction between the guest molecule and host molecules. For ordered crystalline materials, the host structure is well understood; however, for many complex materials, including amorphous materials, these structures are often poorly characterized and new means to create representative structures of amorphous materials are needed. Once the required parameters are available, molecular simulations can readily be carried out to determine thermodynamic equilibria and transport of guest molecules at process conditions. Coarse-grained and other mesoscopic simulation techniques also have a significant role to play. Molecular simulations can take advantage of explicit representation of each atom in the system by simpler objects ("beads" or other geometric shapes, for example) that retain the essential geometry and interactions of the particles. Such representations allow consideration of far larger system sizes and time evolutions are appropriate to bridge the gap between representations of atomic-level and macroscopic processes and hence allow a more facile comparison to experimental data (where such data exist). Unfortunately, the lack of ready access to parameters for coarse-grained simulations is even more acute than for molecular simulation and deserves more attention by the community. Similarly,

deterministic and, increasingly, stochastic simulation approaches are needed to describe reaction-diffusion processes relevant to many carbon capture technologies at scales that facilitate comparisons to experiments.

Up to this point, molecular simulation has largely played a traditional role of providing insight into the mechanistic understanding of known materials and processes and offering the ability to optimize both. However, there is tremendous potential for computer simulation to play a more extensive and predictive role in the design of novel materials in advance of experimentation. Once the capability exists to predict macroscopic properties of materials accurately through the use of representative intermolecular and coarse-grained potential models and appropriate simulation techniques, the process of reverse-engineering, or "inverse design," can be initiated in which simulation provides candidate materials that satisfy desired properties or characteristics. Techniques, such as Reverse Monte Carlo and genetic search algorithms, are two such existing approaches, but more innovative search techniques will surely be needed. Inverse design constitutes a 'grand challenge' for molecular simulation, but one that has the potential to provide enormous benefit to the carbon capture community, particularly in discovering materials that may be unexpected candidates that would not have been uncovered by more traditional routes of searching known classes of materials with suitable properties.

There are thus three sets of challenges and opportunities for advancing the capabilities for carbon capture using theoretical, computational and modeling tools:

- Creation of a molecular toolbox of simulation methods and models to describe guest (gas solute) and host interactions and the host structure of complex non-crystalline materials
- The prediction of thermodynamics and transport properties, especially absorption, adsorption, and diffusion
- *De novo s*earch and discovery of novel materials

Section I: Expanding the molecular toolbox for guest-host interactions and host structure materials

Current Status

The range of potential models and simulation techniques, a virtual "molecular toolbox," is critically needed to simulate the broad range of dissimilar molecular interactions and complex material structures that are found in future carbon materials.. While there have been great strides in the advancement of computational tools and methods over the past couple of decades, further advances in the development of molecular models and techniques will be crucial to accelerate the discovery of carbon capture materials that will efficiently separate CO_2 at levels necessary beyond 2020.

Complex molecular interactions.

The availability of accurate force fields that define inter-molecular interactions is key to the success of molecular simulations in predicting the thermodynamic and transport properties of materials. However, accurate potentials are not always readily available for materials of interest and for mixtures, even for relatively simple gases from a molecular

standpoint. Progress will require a better understanding of the interactions of key targeted gas species or "guests," *e.g.,* CO_2, CH_4, N_2, O_2, H_2O, *etc.*, with complex materials such as ionic liquids, polymers, MOFs, carbon nanotubes, and other as yet untried materials. In order to predict adsorption isotherms, it is insufficient only to characterize the local interactions with, for example, one well-defined metal site or ionic molecule. The primary current method to obtain intermolecular potential parameters for advanced carbon capture material is to use standard literature potentials for CO_2 and other available potentials for the material such as zeolites, polymers, or ionic liquids. There has been some use of a combination of quantum mechanical calculations and literature potentials in the framework of molecular simulations. Other methods include matching some intermolecular parameters to experimental isotherm data.

For example, if we consider the adsorption of CO_2 within a metal organic framework (MOF), selectivity for CO_2 is not only determined by the interaction with the exposed metal site, but also with the topology of the framework. This environment requires knowledge of accurate charge distributions and dispersive interactions beyond the accuracy that is currently available. Today, this problem is commonly addressed empirically by selective inclusion of experimental data. Examples exist where one can rely on the availability of isotherms from existing data to fit to parameters in the models, but these are scarce. A further complication to the use of experimental data comes from the fact that these isotherms are invariably not measured at conditions actually used in separation processes. Moreover, these isotherms are typically determined for pure substances; isotherms for mixtures are essentially unknown for systems relevant to carbon capture. Similarly in polymers, ionic liquids, and other novel carbon capture materials, it is important to accurately characterize not only the local molecule-molecule interactions, but these interactions in the context of the environment, including charge distributions and dispersive interactions. Truly predictive models, ones that do not require the fitting of intermolecular parameters to experimental data, need to be available to allow for the screening of potential carbon dioxide absorbing and adsorbing materials.

Complex material structures.

In addition to the need for improved characterization and prediction of the intermolecular interactions between the guest gas molecule and the host lattice of a crystalline material, a better, molecular-level, understanding of the structure of carbon capture materials is needed. Simulations of solid materials with rigid structures can be made relatively easily. However, for materials with amorphous or flexible molecular structures, finding even a suitable initial configuration that relates to the real material is much more challenging. The structure of materials with a high degree of ordering can be characterized quite readily through scattering techniques and the structures transferred to molecular models. The situation is less straightforward for polymeric systems, which are typically highly heterogeneous, as illustrated in

Figure ***1***. Differences in process conditions may contribute to macromolecular structure differences and inhomogeneities in the polymer. The driving forces leading to these heterogeneous structures are not currently well known. The non-equilibrium state of

glassy polymers often cannot be predicted because it depends on the processing conditions used to create the material. The situation is further complicated by the need to represent dominating physical and chemical characteristics, such as diffusion, porosity, tortuosity, and density of the polymer or polymer blend.

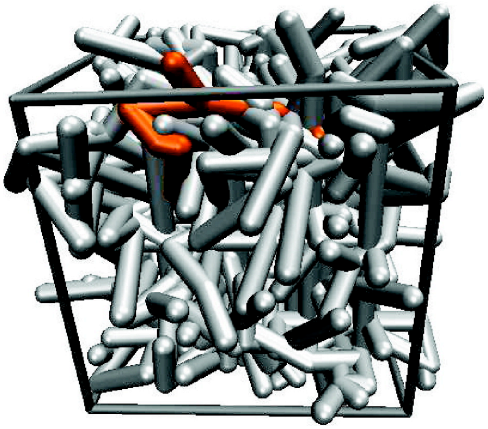

Figure 1: A snapshot from a coarse-grained simulation of an entangled DNA polymer system. Image source: (Dambal et al. 2009)

An area of new development in the field of carbon capture material development is the potential use of composite and mixed-matrix materials. These composite materials may include a large number of potential material and chemical combinations such as carbon nanotubes, composite polymer nanoparticles, and copolymers. These composite materials can exhibit complex structures, see Figure 2, and complex materials chemistry. Developing a rational approach for selecting composites or mixed-matrix materials and optimization their performance would provide a way to narrow down the immense number of potential combinations of materials that could, in principle, be incorporated into the composites to a smaller set of candidates with the most promising properties.

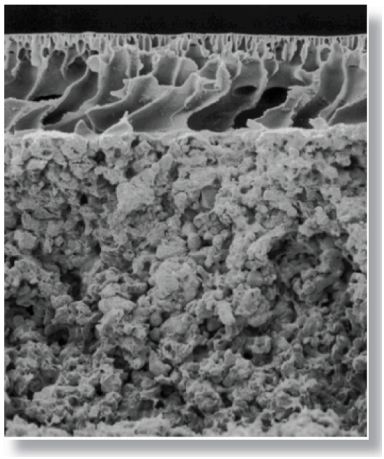

Figure 2: Scanning electron microscopy image of a poly-benzimidazole (PBI)-based polymeric-metallic composite membrane cross-section. The polymeric selective layer is the thin skin at the surface of the composite structure. Image source: (National Energy Technology Laboratory 2008)

Basic Science Challenges and Opportunities

Along with its many challenges, this cross-cutting Priority Research Direction also presents many opportunities. These opportunities and challenges are fundamental in nature, with the ability to inform and influence the design of materials at the macroscale.

Complex molecular interactions.

The development of classical potentials informed by quantum calculations and experiment is one of the most important and fundamental pre-requisites to facilitate a scale-up of use of molecular simulations for materials design for carbon capture. Every atomistic, molecular, and coarse-grained model has, at its heart, intermolecular interaction potentials. As the need increases to scale simulations to longer time scales and to larger systems, computationally efficient, yet accurate, potential functions and parameters will be needed. Researchers are currently limited by the trade-off between accuracy and scale, each resulting in increased computational expense. To facilitate the development of novel carbon capture materials, these intermolecular interaction potentials will also enable the prediction of absorption isotherms for separated gases and gas mixtures.

One current challenge in the development and use of classical intermolecular interaction potentials is the lack of quantitative prediction of dispersive interactions and charge distributions for candidate capture materials. Ionic liquids, MOFs, and zeolites all contain unique charge distributions due to the presence of electronegative or electropositive moieties. These charge distributions are central to the unique absorption properties and must be accurately characterized in order to facilitate molecular simulations with predictive capabilities. Intermolecular potentials for polymers also have limited accuracy when they contain rigid, associating, or polar moieties (see review by Theodorou, 2006).

Beyond the coulombic and dispersive interactions that can be represented using classical intermolecular potentials there exists a research opportunity that includes the use of appropriate quantum calculations in situations where this level of theory is essential, including situations involving reactive interactions. These reactive systems will include effects of electron transfer beyond polarization, will result in the formation and destruction of covalent bonds and thus must be calculated using quantum calculation methods. Advances in quantum mechanically based approaches or hybrid approaches that can represent liquid phases and which are computationally tractable are particularly necessary.

Complex material structures.

For a crystalline material, the major disruptions to the repeating crystal pattern are found at grain boundaries or defects, and these are often well characterized. In contrast, for amorphous materials with no discernable, long-range order, even the concept of defects is unclear, and few if any "gold standard" structures of representative amorphous materials exist. For materials with complex structures, particularly amorphous, composite, mixed-matrix, or even nano-structured fluids, the ability to construct molecular configurations as a starting point for a molecular simulation that are representative of the real material is itself a tremendous challenge. However, huge opportunities exist to integrate experimental and computational methods to build representative models of non-crystalline materials. By characterizing the complex material structure through x-ray scattering or nano-scale spectroscopic techniques, as outlined in the XXXX section, and coupling this structural information to the molecular models it may be possible to build realistic descriptions of some of these complex materials.

The combination of representative nano-scale materials structure for complex materials and accurate molecular interactions will provide a significant enabling of the prediction of structural property changes due to process changes, including instances where perturbations to the material structure is prompted by the presence of CO_2 or other guests. The broader challenge will be to develop predictive capabilities for increasingly complex materials, for which 'gold standard' structures for amorphous (or other complex) materials may well be essential.

It is known that processing conditions can have large effects on the overall properties of self-organized material, yet the use of simulation to capture materials processing is underutilized. This situation provides an incentive to develop novel carbon capture materials through *in silico* modeling of the effects of *processing* techniques and *processing* conditions on nano- or micro-structures of these materials.

Materials with such complex structures, as described above, will become increasingly more difficult to simulate using atomistic methods and it will be essential that atomic- or nano- structured descriptions are subsequently linked to multiscale models capable of representing a link to macroscale and experimentally accessible data. This would certainly improve the performance of membrane approaches to carbon capture which typically involve composites or mixed matrices and which may involve more exotic materials in the future. Developing a rational approach for selecting a material and optimizing its performance is ultimately an opportunity for computational methods to assist in the design of novel materials for carbon capture.

Section II: Thermodynamic and transport properties: Absorption/adsorption and diffusion

The successful development of the variety of technologies for carbon capture is crucially dependent on the achieving the desired *selectivities* for separating gaseous mixtures of CO_2/N_2, CO_2/H_2, CO_2/CH_4, and O_2/N_2, among others. Addition of other species, such as H_2O and SO_2, often introduce further complications. The separation selectivities are dictated by a combination of two factors: (1) absorption or adsorption selectivity, and (2) diffusion selectivity. For optimum separation both these factors need to complement each other.

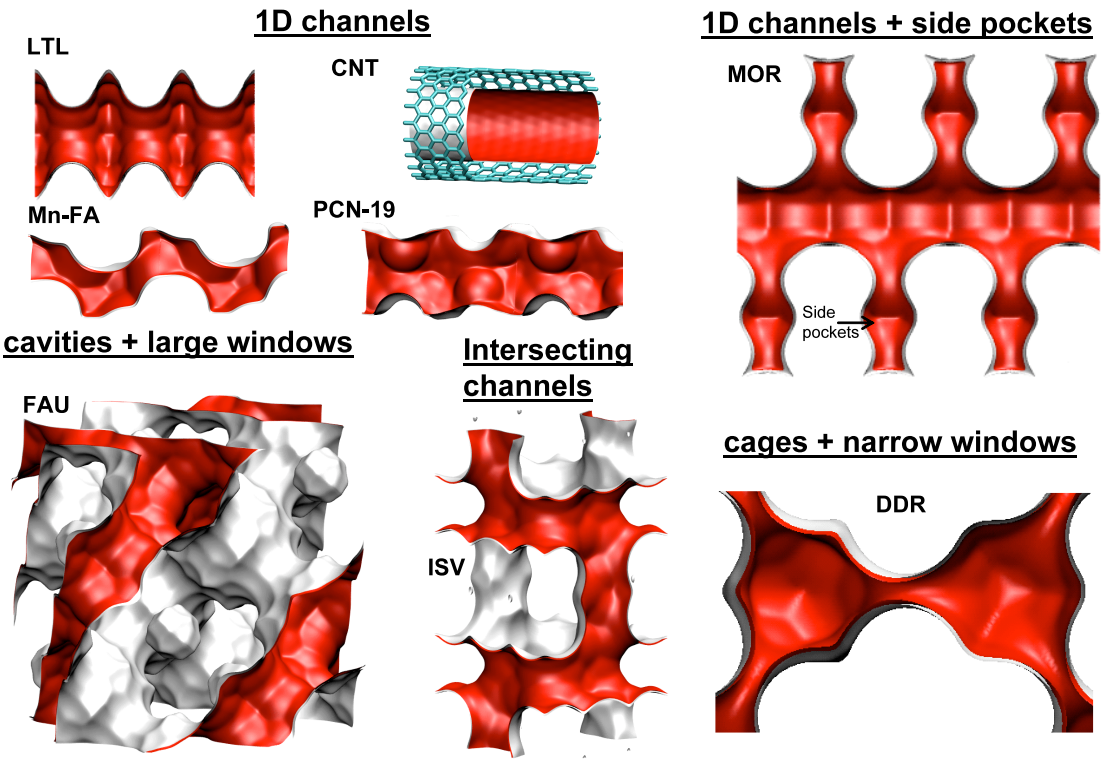

Figure 3. Examples of the variety of channel topologies and connectivities in zeolites, MOFs, and CNTs. Reprinted with permission from (Krishna, 2009). Copyright 2009 American Chemical Society.

Current Status

The sorption selectivity depends on the thermodynamic equilibrium between the bulk gas phase mixture and the liquid, polymeric, or crystalline solid material. The diffusion selectivity is dictated by the rates of transport of guest molecules within the host material. Both sorption and diffusion selectivities are dependent on a variety of factors such as the distribution of active sites, framework charges, presence of cations, pore size, pore topology, and connectivity. For ordered crystalline microporous materials such as zeolites (crystalline aluminosilicates), carbon nanotubes (CNTs), and metal-organic frameworks (MOFs), there is a wide variety of channel sizes, topologies and connectivities, as illustrated in Figure 3. Reliable estimations of phase equilibria, in combination with mixture diffusion, are an essential requirement for process development and design. In practice, such estimations are not possible purely on the basis of experiments because mixture isotherms and diffusivities are more difficult to access experimentally. Use of molecular simulation techniques such as Monte Carlo (MC), simulations in the Grand-Canonical (GC) ensemble, Molecular Dynamics (MD), Kinetic Monte Carlo (KMC), and Transition State Theory (TST) offer potent alternatives. However, the data accruing from such simulations need coarse-graining to obtain parameters that are required for use in more commonly used continuum models for describing mixture adsorption and diffusion, such as the Ideal Adsorbed Solution Theory (IAST), and the Maxwell-Stefan (M-S) diffusion formulation. At present, only for ordered perfect crystalline materials, with rigid

structures, such as zeolites and MOFs, can these thermodynamic and transport properties be predicted with a reasonable degree of confidence.

Basic Science Challenges and Opportunities

When accurate force fields are available, together with detailed atomic structural information, it is possible to obtain simulation data on the required mixture isotherms and diffusivities inside the "bulk" material. However, just understanding these bulk systems is not sufficient for understanding the behaviors of materials as used in separations. For example, in actual applications these bulk materials need to be integrated in a separation device. The presence of any such device will create a gas/material interface, which can be an additional barrier for the transport. Recent work has shown that the surface of crystalline materials have different transport properties than the crystal interiors. Such surface resistances influence separation selectivities, and there is a need to develop the proper simulation tools for its determination. Modeling of the interfaces between gases and ionic liquids also need similar attention and analysis.

In addition, one needs to have an understanding of the role of defects, impurities, and other surface characteristics that cause deviations from the bulk properties of the materials. As these effects exceed, by many orders of magnitude, the longest time and length scales that can be simulated with conventional algorithms, reliable coarse-grained models have to be developed that can incorporate these effects and make the link between the atomic scale of a material and the continuum scale used in process design. Such a strategy typically consists of several interconnected levels, each level addressing phenomena over a specific window of length and time scales, receiving input from finer-grained levels and providing input to coarser-grained ones (Theodorou, 2006). These models should be able to provide a better link between molecular diffusion and macroscopic transport through materials.

Observations that targeted gas molecules change the properties of the materials are also a particular interest. For example, CO_2 and H_2O have been found to induce structural changes in the host crystalline structure and similar observations have been made for adsorption-induced swelling of polymer materials. The development of appropriate simulation methods that take into account structural changes is an important challenge, which requires an accurate description of phase changes of the host material. Ultimately, a better understanding of these effects should result in separation concepts that take advantage of these phase changes to reduce the energy costs of an adsorption/desorption cycle in a separation process

Section III: *In silico* search and discovery of novel materials

Current Status

The majority of current research activities involving theory, modeling, and simulation of chemical systems related to carbon capture are aimed at predicting properties of

experimental systems. This approach focuses on materials and structures, which are often constrained by being easy to synthesize or closely related to other known materials. Clearly, there is considerable unexplored territory to look for structures beyond these constraints and which may provide unexpected and more optimal solutions for carbon capture applications.

The grand opportunity offered by computational techniques is to transform the portfolio of possible applications to include prediction or design of new chemical systems *de novo*. Such *in silico*-designed materials could be the result of either rational design or systematic search and could offer more nearly optimal properties for a given application or process. Carbon capture research could also greatly benefit from a "reverse engineering" approach through unorthodox or novel applications of existing or new computational tools, which could be used to discover materials that closely match a desired set of properties. Computational-based discovery has the potential advantage of being able to find optimal materials among known classes (*e.g.,* the best amine for liquid capture, or the best metal oxide framework for a membrane application). This approach could also discover novel materials not related to any currently known chemical systems.

Basic Science Challenges and Opportunities

The problem of identification of the best molecule or material for a given application is common across areas of chemistry. The most advanced approaches to molecular discovery are in use in the drug discovery field, where they are known by the name 'cheminformatics.' Cheminformatics is an area of chemistry focused on storing and processing data representing large sets of chemical structures. Given the success and wide implementation of cheminformatics techniques in pharmaceutical industry, it is intriguing to ask if similar approaches, could be developed to discover unimagined systems of material(s) and/or processing techniques that are particularly suitable for carbon capture.

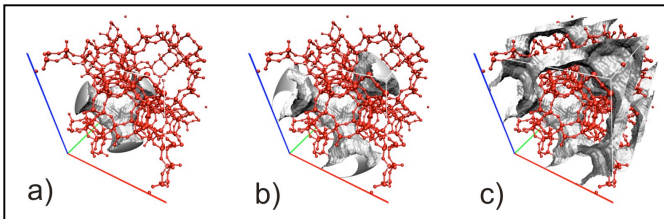

Figure 4. Partial differential equations (PDE)-based techniques can be used to automatically analyze 3D structures of porous materials. This Figure shows how PDE-based front propagation method is used to map accessible void space inside porous material. (Haranczyk, M.; Sethian, J. A. Proc. Natl. Acad. Sci. U. S. A. 2009, 106, 21472) Reprinted with permission

Two different approaches for the *in silico* discovery of new materials can be envisioned: virtual screening and inverse design. *Virtual screening* starts with a database of possible structures, which are then prioritized according to an assumed/estimated measure of the extent to which they meet set points of desired properties. *Inverse design*, in contrast,

requires knowledge of some or all of the relationships between properties and structure. This knowledgebase is then used to directly predict structures with a given (desired) property.

Discovery by screening The critical part of discovery by virtual screening is the availability of structural databases. For example, commercially available databases (or databases of commercially available compounds) can be screened to identify new amines to scrub CO_2. Extending these databases to materials that have *not yet* been synthesized would allow us to explore the limits of maximum achievable performance. In drug design, generation of virtual libraries of drug candidates is relatively straightforward, as it requires merging organic fragments to produce relatively small molecules. Similar search strategies for inorganic materials, in contrast, lead to a combinatorial explosion of a number of structures that would have little chemical relevance. Developing design strategies for databases of hypothetical materials that have a reasonable chance of being synthesized remains a key challenge [Deem *et al.*]. The generation of a database of hypothetical materials is the first step to discovery of novel materials. Another anticipated challenge involves the screening of such databases to identify structures with closer to optimal performance. Given the very large number of pore structures these screening strategies have to rely on algorithms that can characterize the pore topologies (see Figure 4). Molecular simulations techniques are too time consuming to screen the many million structures and screening strategies need to be developed to find the optimal material.

Discovery by inverse design. The concept of inverse design represents an exciting and largely unexplored opportunity to identify optimal materials for carbon capture applications, and many other design targets. Given a known 'property-structure' relationship, one could envision algorithms that generate novel materials or molecules that directly satisfy the constraint of producing a desired property. For example, if the desired property requires, say, a nanoporous material with a well defined pore topology, the inverse design algorithms would generate, chemically accessible, structures that have exactly the desired property.

Guided Synthesis. In the last two subsections, two approaches to facilitate the discovery of novel materials have been presented. These virtual materials would, however, need to be capable of synthesis before it would be possible to verify their performance experimentally. Thus, the design of realistic synthesis pathway for such hypothetical, search-generated, materials will present another considerable challenge for computational techniques. The synthesis of three-dimensional solid-state materials involves a much better understanding of guided nucleation processes will be needed, *e.g.,* how structure-directing agents or templates affect the nucleation barriers to create a variety of solid-state forms of matter. Additionally, more study is needed to understand how solution or processing conditions (solvents, aging, and environmental factors) and composition affect the self-assembly processes. Finally, computational elucidation of the principles behind hierarchical assembly is still a considerable challenge. It is insufficient simply to know how to create/synthesize a desired molecular structure; competing thermodynamic and

kinetic pathways that create undesired or unexpected structures must be inhibited or avoided.

IMPACT AND CONCLUSIONS

The cross-cutting research directions above will have considerable impact in facilitating and expanding the usefulness of computer simulation techniques (from *ab initio* to continuum-based approaches) to predict solutions for carbon capture scenarios. The provision of accurate transferable force fields and materials structures forms the bedrock of subsequent studies of specific candidate materials and processes for carbon capture. Better descriptions of these complex host materials and gas-host interactions will be essential for the calculation of phase equilibria, isotherms, estimates of permeability and the selectivity for a specific solute (CO_2 or O_2, say), and the nature of fluid-fluid and fluid-solid interfaces.

Molecular simulations might be used to derive theoretical "upper bounds" for the anticipated separation selectivity for a given class of materials (e.g. ionic liquids, crystalline solids, polymers). Such an upper bound can help experimentalists in setting targets for materials development. For any given separation task, can molecular simulations help us decide *a priori* which class of materials is likely to be more effective?

New algorithm development and the development of the area of "inverse design" will play a key role in the expansion of computer simulation and modeling for carbon capture processes. The development of improved simulation techniques and coarse-grained models to handle mixture adsorption and diffusion inside complex materials will have a significant influence on the way we model adsorption and diffusion in diverse areas in the chemical process industries. These models are of special value in process optimization studies in order to determine the right set of process conditions to achieve maximum separation selectivities. Accurate models for adsorption and diffusion will also aid process development by cutting down the time required for commercialization. Broad searches through chemical space for novel materials offer the enticement of suggesting candidate systems with desirable properties and/or optimal operating conditions.

An exciting example of such a new technology might be designated as "a zero cost [carbon] capture toolkit," which would facilitate the discovery of materials for carbon capture. For example, electric power plants have low-grade energy, which contribute little, if any, to the overall efficiency of producing electricity. Can materials be developed that use this heat for the carbon-capture process? Can material be developed release the captures CO2 by unconventional switching mechanism, such as light or pH changes, as opposed to traditional separations that release captured materials by a pressure or temperature swing? A suitably constructed search might identify novel and perhaps optimized materials processing routes using novel swing techniques. An even more inspiring example is the possibility to discover novel carbon sequestration solutions that have not yet been even conceptualized. It is possible to imagine a "polymeric" form of CO_2, which would be an oxidized, non-volatile form of carbon, which is less stable than gaseous CO_2.

But all of these advances will also have extensive corollary benefits in application areas well beyond carbon capture, from providing better descriptions of polymers and amorphous or porous materials for semiconductor applications, including photovoltaics, to studies of geothermal energy, where many of the same gas solutes encased in rock structures share the same modeling challenges. The availability of thermodynamic and transport properties could be of immediate benefit to process designers. Thus, the general availability of reliable intermolecular force fields and structural representations of complex materials will be an enormous asset to the scientific community in general. Studies of thermodynamic and transport properties for these complex materials systems, once disseminated, should also spur advances in related areas of catalysis and separations.

Perhaps the broadest benefit to the materials community, and its most challenging, is the idea of completely predictive *in silico* design. Such strategies would have broad and profound implications on the state of our general knowledge of materials discovery, synthesis and processing. For example, systematic studies of materials could lead to information on trends that expose new relationships between changes of properties and a concomitant variation of chemical structures. This information is destined to be more useful than simply discovering a particular material as it is likely to spur the foundation of new theories and models describing the composition of chemical space as well as describing composition/function relationships. Such theories and models can be applied quite generally to discover other types of materials beyond the scope of this Report and its emphasis on O_2 - and CO_2 - separation applications.

Discovery of novel materials and their refinement for a specific separation process is, at its heart, an optimization problem. Any optimization requires knowledge of targets and set-points. These targets (selectivity, capacity, *etc.*) will need to be more clearly defined than at present, and there exists considerable impetus to define standardized tests and metrics to assess the performance of candidate structures. This will ensure that the scientific community has not only a common goal to achieve, but a readily available measure of progress towards that target.

Inverse design and the computational prediction of new structures could open completely new avenues for discovery of carbon capture materials. The excitement of these "high risk, high gain" approaches lies in their potential to move the scientific community beyond continued study of perturbations of known materials, towards a "disruptive" technology capable of leading to dramatically different suggestions for materials, synthesis techniques and processing conditions, to answer the looming carbon capture problem.

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