From *SIAM News*, Volume 44, Number 8, October 2011

ICIAM 2011

Empty Space and New Materials: Computational Tools for Porous Materials

By Maciej Haranczyk, Chris Rycroft, and James Sethian

Crystalline porous materials are some of the most important synthetic products ever made. Assembled into periodic 3D networks from building blocks, they can be as simple as tetrahedral SiO_4 blocks, in the case of all silicious zeolites, or as complex as a set of alternating metal ions and multi-ring organic molecules, in the case of metal organic framework materials (MOFs).

Imagine such a material from "inside the void." From that perspective, the surface of the void is decorated by the chemical building blocks, creating a unique environment for various physical and chemical processes. Zeolites, for example, have found wide use—as catalysts in petroleum refining, separation membranes, and water softeners. One indication of the importance of zeolites can be seen in their commercial impact: roughly $350 billion per year. Metal organic frameworks, a relatively new family of porous materials, are already generating interest for their potential use in gas separation or storage.

The search for new materials to meet new challenges is ongoing. Roughly 1400 zeolite materials with various chemical compositions have been synthesized so far, corresponding to 190 types of framework topologies (see Figure 1); awaiting investigation are millions of potential new zeolites that have been generated and stored in databases (a list can be found at www.hypotheticalzeolites.net). While thousands of new MOFs have been synthesized in the last decade, large databases of hypothetical MOFs are now being compiled.

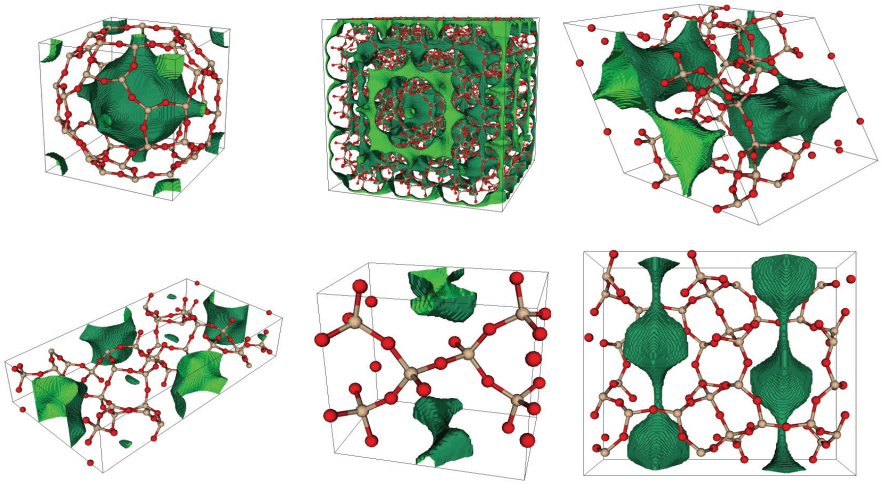

Figure 1. *Examples of periodic unit cells of zeolites, with oxygen and silica atoms shown in red and tan, respectively. Isosurfaces (green) represent the boundary of void spaces accessible to a probe molecule, with lighter green denoting the inside of pores.*

Even armed with large databases of new and possibly breakthrough materials on the one hand, and computational modeling techniques allowing in silico prediction of a material's properties on the other, researchers don't have an easy job discovering new materials. Screening new materials requires investigating millions of structures, which simply cannot be done by hand. Because of the complexity of material structures, each structure, and more importantly, its void space, must be analyzed in detail before expensive computational characterization is performed. Locating accessible regions, computing paths for probes through new materials, and determining inaccessible pockets (see Figure 2) are key to accurate follow-up Monte Carlo and molecular dynamics simulations. Sealing off those pockets must be done in preprocessing; otherwise, the calculations may produce inaccurate or even wrong results.

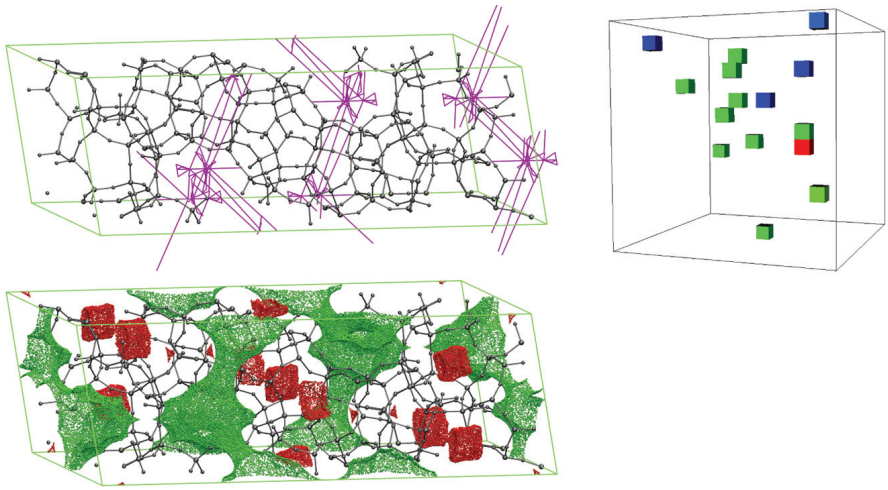

Figure 2. *Top left, periodic unit cell of DDR zeolite with a probe-accessible Voronoi network (magenta). Bottom left, points obtained in Monte Carlo sampling of the surface area based on information about the underlying Voronoi network. The green points correspond to probe-accessible surfaces, the red points to probe-inaccessible regions. Right, 3D hologram representing accessible void space of DDR. The axes correspond to bins characterizing each edge of the network, the colors to numbers of edges of each type.*

What is needed are automatic tools for material analysis that bypass human visual analysis. At UC Berkeley and Lawrence Berkeley National Laboratory, we (a chemist and two applied mathematicians) have been building a suite of such computational tools. We have used these tools to perform high-throughput analysis of void space, and to determine accessibility of new materials to guest molecules and probes, along with energy-permitting pathways through the materials; techniques for analyzing, comparing, and grouping materials have also been produced. The tools capitalize on a host of state-of-the-art advances in mathematics, computational algorithms, and hardware and software breakthroughs in high-performance com-

puting, in particular parallel processing on multicore CPUs and GPUs.

With these computational tools, the large sets of porous materials in the space of possibilities are first pruned automatically. The resulting vastly reduced candidate data set is then pipelined into more sophisticated molecular dynamics simulations.

In one step of this initial pruning, structures with pores too tiny to be practical are removed. Geometric algorithms, such as Voronoi decomposition, are used to identify, for a given set of a material's atoms, a simple graph representation of the void space, the Voronoi network. This network is then analyzed with Dijkstra-like graph algorithms to obtain information about geometric constraints restricting the diffusion of guest species inside a material (Figure 2). These algorithms are also used both to identify the dimensionality of the channels in a pore system and to perform Monte Carlo integration of the surface area and volume available to guest molecules, as shown in Figure 2. All these parameters, obtained until recently only after extensive visual analysis of pore topology, are now computed in just seconds of CPU time.

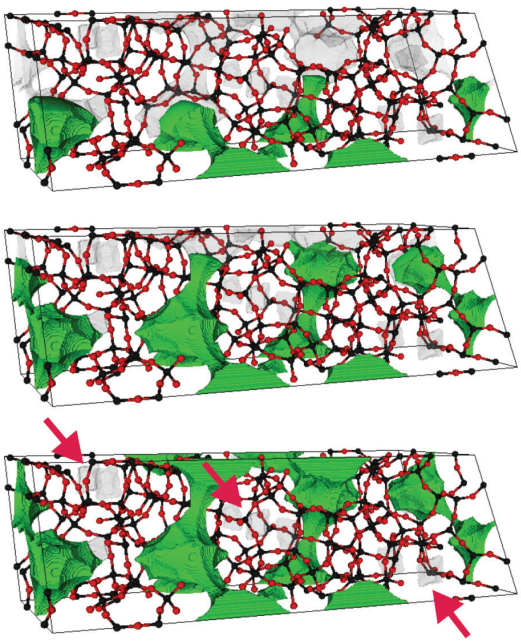

Figure 3. *Snapshots of a propagating front (green) in 3D that explores void channels in the periodic unit cell of DDR zeolite. The red arrows point to pockets that cannot be accessed by the front.*

Preselected structures can then undergo more detailed analysis with PDE-based techniques. Here, goals are to find and to seal off inaccessible regions, as well as to determine accessible pathways. The first step is to find the specific cost of accessing various parts of the void space, which depends on material-specific chemical interactions. Then, realistically shaped, flexible "molecular worms," which rotate at the chemical bonds, are used as path-planning robots; the goal is to find all places that are reachable by these worms. A high-dimensional fast marching method quickly computes the arrival times and pathways within the structure for these robots, segmenting the material into accessible and non-accessible space (Figure 3). The regions determined to be accessible become the domain for molecular simulations executed to predict guest molecule-related properties, such as Henry coefficients and adsorption isotherms.

Finally, when hundreds of thousands of materials have been characterized by molecular simulations and screened, and when tens or hundreds of promising materials have been identified, Voronoi networks representing the void space come into play one more time. This time, each structure is assigned a Voronoi network-based molecular hologram (Figure 2), a histogram-type representation that is then used to find (dis)similarities between identified structures. Visual analysis, saved for the very end and limited to a set of unique, structurally distinct materials, is used to find atomic configurations that lead to the desired properties of a material.

By rethinking and transforming the techniques for use on parallel and high-performance computing architectures, our team, which includes Richard Martin and Thomas Willems, is building a high-throughput computational environment currently being used to plow through large databases of materials. As an example, with researchers at UC Berkeley's Energy Frontier Research Center for Gas Separations, led by Berend Smit, we are working together to discover new materials that can efficiently capture carbon dioxide from flue gases emitted by power plants.

Acknowledgments

This work was sponsored in part by the Advanced Scientific Computing Research and Basic Energy Sciences programs of the U.S. Department of Energy, and by the National Science Foundation's Division of Mathematical Sciences.

For Further Reading

M. Haranczyk and J.A. Sethian, *Automatic structure analysis in high-throughput characterization of porous materials*, J. Chem. Theory and Comput., 6 (2010), 3472–3480.

M. Haranczyk and J.A. Sethian, *Navigating molecular worms inside chemical labyrinths*, Proc. Natl. Acad. Sci. USA, 106 (2009), 21472–21477.

R.L. Martin, B. Smit, and M. Haranczyk, *Addressing challenges of identifying geometrically diverse sets of crystalline porous materials*, J. Chem. Information and Modelling, submitted.

T.F. Willems, C.H. Rycroft, M. Kazi, J.C. Meza, and M. Haranczyk, *Algorithms and tools for high-throughput geometry-based analysis of crystalline porous materials*, Microporous and Mesoporous Materials, in press.

Maciej Haranczyk is a chemist and research scientist in the Computing Sciences Division of the Lawrence Berkeley National Laboratory. Chris Rycroft is a Morrey Assistant Professor in the Mathematics Department at UC Berkeley and a faculty scientist at LBNL. James Sethian is a professor of mathematics at UC Berkeley and head of the Mathematics Department at LBNL.