Mathematical Tools for Discovery of Nanoporous Materials for Energy Applications

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Abstract. Porous materials such as zeolites and metal organic frameworks have been of growing importance as materials for energy-related applications such as CO$_2$ capture, hydrogen and methane storage, and catalysis. The current state-of-the-art molecular simulations allow for accurate \textit{in silico} prediction of materials’ properties but the computational cost of such calculations prohibits their application in the characterisation of very large sets of structures, which would be required to perform brute-force screening. Our work focuses on the development of novel methodologies to efficiently characterize and explore this complex materials space. In particular, we have been developing algorithms and tools for enumeration and characterisation of porous material databases as well as efficient screening approaches. Our methodology represents a ensemble of mathematical methods. We have used Voronoi tessellation-based techniques to enable high-throughput structure characterisation, statistical techniques to perform comparison and screening, and continuous optimisation to design materials. This article outlines our developments in material design.

1. Introduction
Crystalline porous materials have been exploited in industrial applications for many years, for instance as catalysts for oil refinement, water softeners, and membranes for separations. They are also promising candidates for economically-competitive application to emerging energy challenges such as vehicular natural gas storage and carbon dioxide capture. Porous materials exhibit complex networks of internal empty space, which permit the diffusion and adsorption of guest chemical species. The size, shape and connectivity of a material’s pore structure determine the interactions which occur between the guest and the host material, and in turn, its suitability for a particular application.

However, identifying optimal materials for a particular application remains a great challenge. Zeolites, perhaps the most well-known class of porous material, consist of tetrahedral arrangements of silicon, bridged by oxygen atoms; despite their homogeneous chemistry, approximately 200 unique zeolite topologies are known to exist, while over two million hypothetically achievable topologies have been computationally enumerated [1]. Furthermore, new classes of so-called advanced porous materials have emerged in recent years; materials such as metal-organic frameworks (MOFs)[2] or porous polymer networks (PPNs)[3] permit nearly unlimited structural variation through control of both crystal topology and chemistry. On-going efforts to computationally enumerate advanced porous materials have so far resulted in over 100 thousand material designs, and soon next generation efforts
will lead to exceeding the number of predicted zeolite structures. With such a vast search space of possible materials, it is clear that exhaustive synthesis is not a feasible strategy for materials discovery, and so there is a pressing need for computational methods for high-throughput screening and discovery of porous materials.

We have been developing techniques for the characterisation, enumeration, screening and design of porous materials. The core of our approaches involves a computational geometry technique - the Voronoi tessellation [4] - and focus on characterisation of a material’s void space and its properties relevant to chemical applications, e.g. internal surface area. In a parallel effort, we have been developing the capability to construct three-dimensional structure models of advanced porous materials from a set of given molecular building blocks and a corresponding resulting material topology (also referred to as a net; determining how building blocks are connected in three-dimensional space). Our developed capabilities are being combined into higher-level hybrid approaches to perform material discovery and design, e.g. to perform a material’s property optimisation with respect to its building blocks. In the following, we will briefly discuss the developed methodologies and capabilities as well as illustrate their application in the design of a high internal surface area material; in particular, two analogues of PPN materials based on the diamond topology.

2. Methods

2.1 Characterisation of porous materials

The core of our approaches involves the Voronoi tessellation, which is employed to translate structural information (e.g. position of atoms, size and shape of the periodic unit cell) into a periodic graph representation of the spaces between atoms and their connectivity. This graph representation (Voronoi network or Voronoi diagram) can be efficiently analysed to identify probe-accessible regions of void space (with respect to particular probe sizes) and their related properties.

In the Voronoi tessellation (also referred to as the Voronoi decomposition), the space surrounding \( n \) atoms is divided into \( n \) irregular polyhedral cells such that the cell for a given atom comprises of the space that is closer to that atom than any other. Mathematically, if the atoms have positions \( x_i \), for \( i = 1, \ldots, n \) and the Euclidean distance between two positions \( x \) and \( y \) is written as \( d(x,y) \), then the Voronoi cell for atom \( i \) is the space \( x \) that satisfies

\[
    d(x,x_i) < d(x,x_j)
\]

for all \( j \) not equal to \( i \). The Voronoi cells tessellate the space, and each Voronoi cell face is the perpendicular bisector between two neighbouring atoms. Edges of the Voronoi cells are lines that are equidistant from three neighbouring atoms, whereas the vertices of the cells, the Voronoi nodes, are positions equidistant from four neighbouring atoms. Taken together, the Voronoi edges and nodes form a three-dimensional graph that represents the pores and channels. The nodes of the graph are the local maxima of the function \( D(x) = \min \{ d(x,x_i) : i = 1, \ldots, n \} \) that gives the minimum distance from a position \( x \) to an atom, and the edges of the graph are the least restrictive paths from one local maximum to the next. Due to this correspondence, it can be shown that determining the (guest-probe) accessibility of the structure is mathematically equivalent to examining the accessibility of the Voronoi network.

In the context of crystalline porous materials, the volume in question is the periodic structural unit, which comprises multiple atoms. As a consequence of the Voronoi tessellation, the Voronoi network is obtained. Our open source porous materials analysis suite, Zeo++ [5], exploits this graph abstraction of a material's porosity to efficiently calculate restricting pore diameters [5], internal surface areas [5] and other geometric characteristics (e.g. as pore size distributions[6]) of materials in a high-throughput manner. The corresponding algorithms rely on various mathematical methods. For example, Dijkstra-like graph propagation [7] is employed to identify diffusion paths in the periodic structure, and their corresponding restricting pore diameters. Monte Carlo sampling is used to calculate surface area and accessible volume etc.
2.2 Periodic structure assembly
When exploring the space of advanced porous materials, it is important to have the capability to predict the material structure(s) resulting from a set of given building blocks. We have developed an approach for modelling crystalline porous structures that emphasizes realism in terms of symmetry and stability [8]. Our new computational tools are based upon guaranteeing a pre-specified topology, by utilizing topology-specific symmetry operations to position building units in accordance with a particular underlying net (e.g., those provided by the Reticular Chemistry Structure Resource (RCSR) [9], which has assigned to each a three-letter name, e.g. Figure 1). Our structure assembly method has been also implemented in our Zeo++ code.

Figure 1. Illustration of crystal structure assembly. Combination of a square-coordinated building unit (Cu₂ paddlewheel) with a trigonal organic linker results in a three-dimensional periodic structure exhibiting the tbo net.

2.3 Materials Design by Optimisation
The outlined structure assembly and characterisation tools can be combined into a technique for the automated design of advanced porous materials using mathematical optimisation. At each iteration of optimisation, our structure assembly algorithm builds three-dimensional framework models, for which material properties, e.g. surface area and pore volume, can be calculated using algorithms implemented in Zeo++. Based on such properties, the next iteration is executed, and the procedure is continued until convergence.

In our current approach, the organic molecular building units of advanced porous materials are abstracted as geometric shapes (a union of rods and discs described by a set of radii and length parameters, the variables in optimisation, see Figure 2). This abstraction serves to enable optimisation in the continuous space of geometric shapes, rather than the discrete space of chemistry, and can therefore make use of rapid continuous optimisation algorithms. We utilize gradient-based optimisation to automatically tune properties of the material, for example, maximize its internal surface area, an important property in storage and separation applications. Here, for a ligand defined by a set of properties \( p \) (the vector of parameters describing the shape and size of organic ligand), the ligand \( p_{i+1} = p_i + s \nabla g(p_i) \) is built in the optimisation step, where \( g() \) defines the surface area of the assembled material structure, and \( s \) is a scalar. Our approach utilizes a number (typically ten) random start points to mitigate the problem of converging to a local minimum, and is based on a radius/length step size of 0.1 Å. Moreover, the search space is typically constrained to the domain corresponding to parameters observed in experimental structures, and can be further extended to explore the frontiers of the material space. Having identified idealized molecular shapes with respect to a particular property, the real chemistry which most closely fits the shape can be identified, and properties of the resulting system determined.

Our work to date has demonstrated the potential of this strategy with a prototype method implemented for MOF materials [10]. Our prototype work focused on gravimetric surface area as the optimized property [10]. Calculating gravimetric surface area (i.e. surface area per mass of the material) requires defining the “molecular” mass of the abstract structure model, which is predicted via a statistical model requiring the surface area of the building block involved as input. This statistical model is trained using a set of hydrocarbon-backbone dicarboxylic acid molecules, the most common form of organic building block in MOF assembly [10]. In our most recent work, we have also explored optimisation of volumetric surface area [11] (i.e. surface area per volume of material) as well as multiobjective optimisation combining both surface area functions [12]. This initial work was focused
on MOF materials. The following Results section will present an example of automated design of high surface area porous polymer network (PPN) materials based on the diamond (dia) net.

Figure 2. Abstract space-filling molecule constructed from the nine geometric parameters

3. Results
Here, we provide an example of our optimisation-based design technique applied to porous polymer network (PPN) materials, based on linear linkers and tetrahedral cores (adamantane or silicon, i.e. analogues of PPN-3 and PPN-4, see Figure 3)[13]. PPN materials are typically non-crystalline, however recent work has suggested that idealized dia net crystal models can be used to reproduce experimental adsorption isotherms [14].

Figure 3. Schematic connectivity for dia net in PPN materials. The corner building blocks used to synthesize PPN-3 and PPN-4 are also presented.

Accordingly, we have generated optimized linker shapes for these PPN materials within the dia net, with constrained optimisation (limiting the search algorithm to the simplest linker complexity bounds as described in our previous work [11]). The objective function is the product of gravimetric surface area (GSA) and volumetric surface area (VSA), a metric which we refer to as GVSA; optimizing for this objective function leads to framework designs which exhibit the optimal compromise between these two typically competing objectives. Our previous results for the dia net, albeit for MOF materials rather than PPNs, highlighted that the optimal GVSA for this net arises from maximizing GSA at the expense of VSA[12]; this behaviour is also observed here for PPNs, and further exaggerated due to the lighter (non-metal) cores in PPN materials. In order to design real frameworks based on optimal abstract templates, it is necessary to project the final linkers onto real molecules. Projecting these abstract shapes onto the closest real chemistry corresponds to a slight extension of the organic linkers from the shape provided by the optimal template; this projection causes an increase in GSA and a corresponding decrease in VSA (see Table 1). We note that our designed analogues of PPN-3 and PPN-4 exhibit much higher gravimetric surface area than the current record holder material obtained in experiment (NU-110 with GSA of ca. 6700 m$^2$/g) and one obtained by enumeration of possible materials based on a linker library (hmoF-5036495 with GSA of ca. 6700 m$^2$/g). Our GVSA-optimized GSA is a lower bound with respect to the maximum possible GSA.

Table 1. Calculated surface areas for optimal abstract frameworks and corresponding real frameworks generated by projecting onto the closest real chemistry. All descriptors were calculated using the
Zeo++ software package.

|                        | PPN-3 analogue | PPN-4 analogue |
|------------------------|----------------|----------------|
| Volumetric surface area (m$^2$/cm$^3$) | Abstract 1515.92 | Real 1294.86 |
|                        | Abstract 1759.24 | Real 1705.2   |
| Gravimetric surface area (m$^2$/g)           | 8473.64        | 9933.75       |
|                        | 8904.82        | 9993.47       |

4. Conclusions
We have developed algorithms and a software tool (Zeo++) that enable advanced porous material structure assembly and characterisation as well as efficient material design. We used Voronoi tessellation-based techniques to enable high-throughput structure characterisation. They provide the Voronoi network representation of the void space inside a material, which is used to derive material descriptors such as limiting pore diameters, accessible surface area and pore size distributions. We demonstrated how these structure characterisation tools can be combined with structure assembly capabilities to perform material structure optimisation with respect to its properties. This optimisation is performed within the framework of an abstract material model, in which molecular building blocks are represented by geometric objects (i.e. union of rods and disks). A material structure is assembled from these geometric building blocks, and its property is calculated. Then, in an iterative procedure the structure is modified following the gradient of property with respect to the structure parameters describing the building blocks. Multiple starting points are considered to mitigate the local minimum problem. We demonstrated such optimisation-based material design using two analogues of porous polymer network (PPN) material materials.

Acknowledgements
This work was partially supported by CAMERA: The Center for Applied Mathematics for Energy Research Applications at Lawrence Berkeley National Laboratory supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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