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Towards accurate porosity descriptors based on guest-host interactions

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ABSTRACT

For nanoporous materials at the characterization level, geometry-based approaches have become the methods of choice to provide information, often encoded in numerical descriptors, about the pores and the channels of a porous material. Examples of most common descriptors of the latter are pore limiting diameters, accessible surface area and accessible volume. The geometry-based methods exploit hard-sphere approximation for atoms, which (1) reduces costly computations of the interatomic interactions between the probe guest molecule and the porous material framework atoms, (2) effectively exploit applied mathematics methods such as Voronoi decomposition to represent and characterize porosity. In this work, we revisit and quantify the shortcoming of the geometry-based approaches. To do so, we have developed a series of algorithms to calculate pore descriptors such as void fraction, accessible surface area, pore limiting diameters (largest included sphere, and largest free sphere) based on a classical force field model of interactions between the guest and the framework atoms. Our resulting energy-based methods are tested on diverse sets of metal-organic frameworks and zeolite structures and comparisons against results obtained from geometric-based method indicate deviations in the cases for structures with small pore sizes. The method provides both high accuracy and performance making it suitable when screening a large database of materials.

1. Introduction

Nanoporous materials contain intrinsic void spaces, which can be penetrated by guest molecules and exploited in a variety of applications including carbon capture, gas storage, catalysis, and drug delivery [1–4]. Nanoporous materials include several families of materials such as zeolites, metal organic frameworks (MOFs), covalent organic frameworks (COFs), porous polymer networks (PPNs) and related families of materials, which contain virtually unlimited number of possible structures. MOFs, for example, consist of metal atoms and organic linkers that can be linked together in variety of different ways due to a wide selection of possible metals and ligands as well as their compatible topologies. Accordingly, the number of experimentally synthesized MOFs has exceeded 5000 [5], while even greater number of predicted MOF structures in hypothetical MOF database awaits experimental confirmation [6]. Similarly, databases of predicted and synthesized zeolites, COFs and other porous structures have been collected and made available to the community [7–9].

The current state-of-the-art methodologies based on molecular simulations and/or electronic structure calculations allow for prediction of guest-related adsorption and diffusion properties of a porous material [10]. The undisputed workhorse underlying such predictions are classical force fields, which provide models (and parameters) describing the interaction potential between atoms of the material framework and the guest molecules. With proper parameterization based on fitting to either experimental or *ab initio*-predicted data, material properties such as Henry's constants, adsorption isotherms, and diffusion coefficients can be reliably predicted [11–13]. The molecular simulations can also be used in high-throughput manner, exploiting parallel computing architectures, to predict properties and screen very large sets of structures. For example, Wilmer et al. have conducted methane storage screening on over 100,000 hypothetical MOF structures to identify structures with high methane uptake properties [6]. Lin et al. have developed a metric of parasitic energy and screened a large database of zeolites and ZIF structures to identify materials

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best for carbon capture [14]. Kim et al. have screened over 80 000 pure silica zeolite structures for CH_4/CO_2 selective materials [15]. Haldoupis et al. have screened over 250 000 porous materials for various diffusion properties [16]. More recently, Simon et al. have screened the most of the available large material datasets (500k+ structures), referred-to as the Nanoporous Materials Genome, in the context of both methane storage and noble gas separations [17,18].

In typical studies of porous materials, oriented towards either small, e.g. one-to-few, or large sets of materials, there is a need to characterize particular pores or entire porosity of a structure. In the past, there have been many research reports on methods as well as software codes to compute the porosity characteristics [19–22]. These are typically simplified to a number of numerical descriptors such as void fraction, accessible surface area, pore limiting diameters or vectors like pore size distributions. Vast majority of reported methods consider solely the geometry of the framework atoms and the spherical probe. These geometry-based methods assume that (1) atoms are hard spheres of certain, chemistry-determined radii and (2) the porosity corresponds with a region that can be occupied by the probe center without overlapping with any of the framework atoms. Following this definition, porosity descriptors like largest diameter of included sphere and free sphere (Di and Df, respectively), void fraction (VF) and accessible surface area (ASA) have been introduced [19]. Di and Df indicates the largest diameter of the probe that can respectively, occupy or diffuse through the pores. VF corresponds to the volume that can be occupied by the center of a probe with a given radius without overlapping with the framework's atoms. Similarly, ASA integrates the surface that defines the probe-accessible volume in the VF calculation.

The geometry-based methods allow reductions in costly computations of the interatomic interactions between the probe guest molecule and the porous material framework atoms, and effectively exploit applied mathematics methods such as Voronoi decomposition to represent and characterize porosity. Moreover, for certain applications like methane and hydrogen storage, these geometrical properties correlate well with material performances [18,23] and compared to the more computational intensive Monte Carlo or molecular dynamics simulation codes, the geometric-based tools can be used to quickly screen through a very large database of porous materials and be embedded as a part of a scoring function in optimization-based design approaches [24,25]. The geometry-based tools have become the methods of choice when (pre) screening large sets of materials mainly due to their non-prohibitive computational cost. However, the effect of their shortcomings and approximations that comes in particular from reducing any interactions to a binary, nearest neighbour functions, has not yet been systematically investigated.

In this work, we present a series of algorithms to calculate void fraction, surface area, largest included sphere, and the largest free sphere for a given pair of material and guest molecule. Our approach involves a force field model of guest-host interaction, and therefore we refer to it as energy-based approach. These contributions have allowed us to cross-examine the energy-based and the geometrical-based algorithms to provide a better understanding and quantify the errors coming from the shortcoming of the latter approach.

The paper is organized as follows. In Section 2, the energy-based algorithm is explained in detail. In Section 3, simulation results obtained for a selected set of metal-organic framework and zeolite structures are shown for both energy-based and geometric-based methods. In Section 4, a concise summary of the work is presented with possible future work with regards to this topic.

2. Methodology

The scope of our energy-based method focuses on crystalline porous materials. Amorphous materials can be treated as well provided that an assumption about their periodicity on a (large) spatial scale is made. Given the repetitive nature of the crystalline materials, the energy-based method analysis is conducted on a unit cell of the porous material with imposed periodic boundary conditions. On top of the unit cell, a three-dimensional energy grid with uniform spacing ($\Delta = 0.15$ Å) is constructed. The code was constructed such that the user can easily change the grid sizes along all three spatial directions. Each grid point represents the two-body potential energy between a probe molecule placed at the grid point and all of the framework atoms as well as their periodic images within 12.8 Å of cutoff distance. In all of our work, methane and helium probes are used given their simplicity (e.g. these particles can be represented by a single point and long-range electrostatic interaction energies can be omitted) and the Lennard-Jones potential is used to model the potential energy interactions. For the host atom force field parameters, UFF is used for all of the metal organic framework (MOF) atoms [26] and Garcia-Perez et al. force fields are used for zeolites [27]. For the methane probe, the Trappe force field is used as it has been shown to reproduce the vapor-liquid curve as well as predict accurately adsorption isotherm data in various porous materials [28]. Helium force field parameters are taken from Dubbeldam et al. [29].

The energy-based code was written from scratch using C++ and is available upon request. For comparison purposes, we used Zeo++ code, which is a geometric-based code developed by Willems et al. [19], using high accuracy routines of in Ref [30]. Four important properties of porous materials (void fraction, surface area, largest included sphere, and largest free sphere) are obtained using both of the methods as we present the details behind the energy-based method in what is to follow.

2.1. Void fraction

Void fraction measures the fraction of empty space found within the porous material. In general, the void fraction is inversely proportional to the framework density as the presence of framework atoms take up empty volume. In the two extreme cases, a void fraction of one indicates complete absence of framework atoms while a void fraction of zero indicates non-porous materials. In our energy-based methodology, the void fraction is determined from the potential energy values assigned to the energy grid points. After computing the energy grid, an additional binary grid (comprised of 0's and 1's) is constructed where an energy threshold value of $15k_BT$ is used to assign the binary grid values into either accessible (set to 0) or inaccessible (set to 1). $15k_BT$ was chosen as a reasonable criterion that determines accessibility in a typical experimental time-scale [31]. Upon obtaining the binary grid, a flood fill algorithm is conducted to identify regions of 0's that are surrounded by 1's in all spatial directions, thereby identifying and blocking inaccessible regions for a given probe The detail behind the flood fill algorithm is explained elsewhere [31]. Finally, the void fraction is computed from the binary grid as the ratio between the number of 0's and the total number of grid points (i.e. sum of 0's and 1's).

2.2. Surface area

The surface area of porous materials quantifies the amount of material exposed to and available to interact with the penetrating gas/liquid phase. For application purposes, the surface area may correlate well with, for example, gas storage capacity. To compute the surface area using an energy-based method, the previously defined binary grid is re-used. In order to determine the interface