



Analytical representation of micropores for predicting gas adsorption in porous materials

Aaron W. Thornton^{a,*}, Scott A. Furman^a, Kate M. Nairn^a, Anita J. Hill^a, James M. Hill^b, Matthew R. Hill^{a,c}

^aCSIRO Materials Science and Engineering, Locked Bag 33, Clayton Sth MDC, Vic 3169, Australia

^bNanomechanics Group, School of Mathematical Sciences, The University of Adelaide, SA 5005, Australia

^cSchool of Chemistry, University of Melbourne, Vic 3010, Australia

ARTICLE INFO

Article history:

Received 10 November 2011

Received in revised form 3 August 2012

Accepted 3 September 2012

Available online 12 September 2012

Keywords:

Adsorption

Metal–organic framework

Nanotube

Activated carbon

Potential energy

ABSTRACT

A straightforward method for the prediction of the gas storage capabilities of porous materials has been established. The Topologically Integrated Mathematical Thermodynamic Adsorption Model (TIMTAM) combines analytical surface potential energies with classical physisorption thermodynamics in a computationally inexpensive fashion. Experimental and simulated isotherms from leading sorbent candidates such as metal–organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), carbon nanotubes and activated carbons have been used to verify the model. Furthermore, the effect of pore size and shape upon gas storage characteristics is explored using the TIMTAM routine.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

One of the challenges of the 21st century is the generation, storage and delivery of energy in an affordable, renewable and clean fashion [1,2]. The ability to efficiently capture, store and release gases plays an important role in addressing such issues, for example: carbon capture and storage (CCS) for clean coal, petroleum and natural gas combustion [3–5]; methane capture and storage for climate control or safe energy transport [6,7], and hydrogen capture and storage from photolytic water splitting or coal gasification for clean combustion or fuel cell technologies [1]. Porous materials are poised to meet such challenges.

The leading candidates for efficient high capacity gas storage porous materials are metal–organic frameworks (MOFs) [8–11], zeolitic imidazolate frameworks (ZIFs) [12–14], nanotubes [15–17], and graphenic carbons [18–22], which can each undergo physisorption, with capacity closely related to surface area. The usage of such adsorbents depends strongly on key factors such as the capacity, operating temperature, cyclability and kinetics of operation. Within a porous gas adsorbent, the nature of the pores is integral to addressing these issues, with pore shape, size, concentration and surface chemistry all important to the overall performance.

Experimental materials discovery has led to substantial improvements in gas storage performance. However, the formulation of improved guidelines for further development of new materials could greatly speed this process. Whilst detailed, atomic level resolution modeling can elucidate the fundamental atomic interactions, a model that focuses on the overall impact of pore topology on overall performance is pertinent. Furthermore, a quick, accurate, yet accessible model would strengthen the feedback loop between experimentalists and modelers.

Modeling techniques for addressing physisorption range in complexity, accuracy and utility. Firstly there are fundamental equations such as the Langmuir single-layer model [23] and the Brunauer, Emmett and Teller (BET) multi-layer model [24] that have simplicity, such that anyone can calculate adsorption properties without the need for extensive computational or modeling expertise. Then, on a more complex level, there are the simulation (or computational) techniques such as Molecular Dynamics (MD) [25–30], Monte Carlo (MC) [16,30–34] and those based on ab initio principles [35–41] or mean-field density functional theories [42,43]. Each of these techniques offer useful functions that have significant impact on the field of materials science and more specifically on the current demand for high performing membranes and adsorbents [44]. The simple equations offer quick estimates of surface area and heat of adsorption from experimental adsorption isotherms, while the computationally-expensive simulation techniques offer in-depth detail and prediction of all aspects of adsorption within specific atomic structures. A tool that is missing

* Corresponding author. Tel.: +61 3 9545 8018; fax: +61 3 9545 2837.

E-mail address: aaron.thornton@csiro.au (A.W. Thornton).

for the porous materials community is a simple predictive model that can speedily estimate gas uptakes based on obtainable details such as pore size, shape and composition. Therefore we present a technique that exists on the middle ground – it is as straightforward as the BET type models and as predictive as the simulation techniques. As such it can be readily applied by those without extensive modeling experience. We envisage that this technique will also be utilized for computational screening of large databases of potential adsorbents where detailed simulation techniques are not suitable.

By exploiting thermodynamic and kinetic principles we develop a model that can be used to investigate the gas adsorption phenomenon and which encompasses the main characteristics found by statistical simulation studies. Essential input factors for the model include temperature, pressure, and pore geometry (which is used to derive the potential energy landscape, free volume and surface area). For complex atomic structures, algorithms for calculating potential energy, free volume and surface area are readily available [45–48]. For structures with simple pore geometries that can be approximated by spheres, cylinders or slits, we provide analytical formulations which are used throughout this study. These formulations are ideal as they do not rely on specific atom positions for which computationally expensive methods are needed to calculate the potential energy at each point within the structure. Therefore, by approximating the topology, integrating the potential energy within the cavity and incorporating thermodynamic theory we establish the Topologically Integrated Mathematical Thermodynamic Adsorption Model (TIMTAM). The major advantage of our TIMTAM approach is that it provides researchers with analytical formulae that are computationally instantaneous, and therefore many distinct scenarios can be rapidly investigated to accelerate material design [11]. The primary function of the model will be the simulation of adsorption isotherms from estimates of pore volume, size and shape.

The following section outlines the basic theory and formulations for the model. Experimental and simulation results are then used to validate the model, followed by an investigation into the effect that pore shapes have on adsorption. This approach has already been used to investigate the performance of a new class of adsorbents, MOFs impregnated with nanostructures [11]. The model successfully described the uptake within existing MOFs and predicted an enhanced hydrogen and methane uptake within MOFs infused with fullerenes and decorated fullerenes. Here we fully present the model in its complete form, demonstrating its ability to model gas uptake in a range of adsorbents such as MOFs, ZIFs, nanotubes and activated carbons, and direct the reader to a graphical user interface, Adsorb IT, that we have developed to demonstrate the speed, versatility, usability and accuracy of the TIMTAM approach.

2. Theory and mathematical formulation

The interactions between a gas molecule and a surface, arising from van der Waals forces, are well described by the Lennard-Jones (L-J) potential energy function. This potential is known in this context as the potential energy for adsorption, found by integrating the atom–atom L-J function over the surface. Here we assume a continuous surface and formulate the potential energy within cavities that can be represented as analytical geometric shapes. For conventional Monte Carlo algorithms, the potential energy is calculated numerically where the surface is treated as discrete atoms to produce a potential map [45,47,48]. However, since generating the potential map is the most time-consuming element of a Monte-Carlo algorithm, it is advantageous to approximate the geometry where possible. Here the available analytical

formulations for the potential energy within three different cavity shapes are given below and we refer the reader to [49,50] for further details.

Slit-shaped cavity:

$$PE_{\text{slit}}(\rho) = \eta(-AH_{\text{slit}}[4] + BH_{\text{slit}}[10]),$$

$$H_{\text{slit}}[n] = \frac{2\pi}{n} \left(\frac{1}{((d/2) - \rho)^n} + \frac{1}{((d/2) + \rho)^n} \right) \quad (1)$$

Cylindrical cavity:

$$PE_{\text{cyl}}(\rho) = \eta(-AH_{\text{cyl}}[3] + BH_{\text{cyl}}[6]),$$

$$H_{\text{cyl}}[n] = \frac{2\pi^2 d^2}{(d)^{2n} (2n-2)!} \sum_{j=0}^{\infty} \left(\frac{\rho^j (2n+2j-2)!}{(2d)^j j! (n+j-1)!} \right)^2 \quad (2)$$

Spherical cavity:

$$PE_{\text{sph}}(\rho) = \eta(-AH_{\text{sph}}[6] + BH_{\text{sph}}[12]),$$

$$H_{\text{sph}}[n] = \frac{\pi d}{\rho(2-n)} \left(\frac{1}{(\rho + (d/2))^{n-2}} - \frac{1}{(\rho - (d/2))^{n-2}} \right) \quad (3)$$

ρ is the distance of the gas molecule from the cavity center, d represents the cavity dimension (distance between surface nuclei) and η is the atomic surface density of the cavity wall. A and B are the attractive and repulsive constants, respectively, defined as $A = 4\varepsilon\sigma^6$ and $B = 4\varepsilon\sigma^{12}$ (σ is the kinetic diameter and ε is the well depth for interacting pairs of atoms). Potential energy maps are shown within each cavity shape in Fig. 1. The potential minimum is deepest within cavities with higher curvature where the gas is closer to more surface atoms. Note that this potential is independent of both temperature and pressure. The kinetic energy of the gas, as a result of the specified temperature, relative to the size of the potential energy for adsorption, determines the probability that surface adsorption of a gas molecule will occur [51].

According to kinetic theory, the average translational kinetic energy per molecule KE_{gas} in an ideal gas is equal to $3k_B T/2$ where k_B is the Boltzmann constant and T is the temperature. Usually the values for the kinetic energy of a gas molecule KE_{gas} and the potential energy for adsorption PE_{surface} are similar and hence there exists a continuous mixture of adsorbed and bulk phases rather than the discrete monolayer adsorption as assumed by the Langmuir treatment [23]. Generally speaking, if $KE_{\text{gas}} < PE_{\text{surface}}$ then surface adsorption occurs. Following this, the probability of adsorption at a distance ρ from the cavity center can be approximated as

$$P_{\text{ad}}(\rho) = 1 - \exp\left(\frac{-|PE(\rho)|}{KE_{\text{gas}}}\right), \quad (4)$$

where $\exp(-|PE|/KE_{\text{gas}})$ is the probability that $KE_{\text{gas}} > PE_{\text{surface}}$, i.e. the probability that a gas molecule is in the bulk phase. Note this criterion is of similar form to the acceptance probability used in MC simulations, though in this case we are not calculating the acceptance of a certain particle but rather determining the phase likely to exist at this position.

The total free volume V_f within a cavity is defined here as the volume for which the potential energy is less than zero. In other words, the boundaries for this free volume are located where the potential energy for adsorption is zero at a distance ρ_0 from the center of the cavity, indicated in Fig. 1. Alternatively, temperature dependent boundaries could be chosen at which the potential energy is equal to the average kinetic energy, which gives a more accurate free volume but is found not to significantly affect the total uptake. Here the former definition is used. By integrating the probability function in Eq. (4) over the total free volume we determine the volume free for adsorption V_{ad} as follows,

Download English Version:

<https://daneshyari.com/en/article/73752>

Download Persian Version:

<https://daneshyari.com/article/73752>

[Daneshyari.com](https://daneshyari.com)