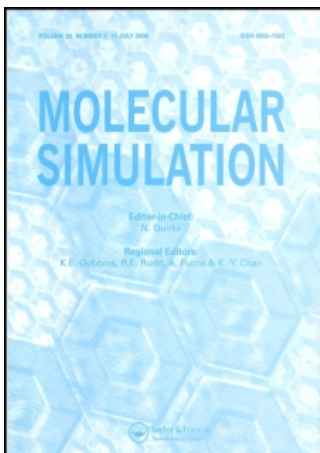


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T. Roussel^a; J. Jagiello^b; R. J. -M. Pellenq^a; M. Thommes^b; C. Bichara^a

^a Centre de Recherche sur la Matière Condensée et Nanosciences - CNRS, Marseille Cedex 9, France

^b Quantachrome Instruments, Boynton Beach, FL, USA

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Testing the feasibility of using the density functional theory route for pore size distribution calculations of ordered microporous carbons

T. ROUSSEL[†], J. JAGIELLO^{‡*}, R. J.-M. PELLENQ[†], M. THOMMES[‡] and C. BICHARA[†]

[†]Centre de Recherche sur la Matière Condensée et Nanosciences—CNRS, Campus de Luminy, 13288 Marseille Cedex 9, France

[‡]Quantachrome Instruments, 1900 Corporate Drive, Boynton Beach, FL 33426, USA

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The pore size distribution (PSD) characterization of microporous carbon materials is traditionally obtained from the analysis of N₂ adsorption isotherms at 77 K. In this work, we aim at testing the feasibility of using the density functional theory (DFT) route for PSD calculations of interconnected carbon pore structures. The first step of this study was to generate using an atomistic simulation approach, an ordered porous carbon material with well-defined porosity using NaY zeolite as a templating matrix. For this purpose, we used the grand canonical Monte-Carlo (GCMC) technique in which the carbon–carbon interactions were described within the frame of a newly developed tight binding approach and the carbon–zeolite interactions assumed to be characteristic of physisorption. We calculated the PSD of such a carbon porous material. At a second stage, we calculated nitrogen adsorption isotherms at different temperatures. These data were subsequently used as inputs for DFT calculation to obtain the PSD. Comparisons between DFT–PSD and MC–PSD are made. In particular, we show that with an appropriate wall thickness of two graphene layers, the PSD obtained from DFT calculation agrees well with that from direct analysis of the simulated structure.

Keywords: Pore size distribution; Density functional theory; Grand canonical Monte-Carlo technique; Carbon–carbon interactions

1. Introduction

It is experimentally important to understand the relationships between the pore size distribution (PSD) and adsorption properties of porous materials among which there are many carbonaceous materials. In this paper, we aim at testing the reliability of the density functional theory (DFT) route for PSD calculations of interconnected carbon pore structures. This approach relies on using adsorption isotherm data of simple fluids such as nitrogen or argon and is routinely employed in the characterization procedure of porous materials. For a given set of adsorbate–adsorbate and adsorbate–substrate interaction potentials and for a given pore geometry (slit or cylinder), DFT describes well the thermodynamics of a confined fluid. When applied to real material, the idea is to fit the experimental adsorption data and find the PSD using a set of DFT isotherms; each isotherm of the set

corresponding to a given pore size. There are obvious outcomes of such an approach. First, it considers the porous material as a set of independent and unconnected pores. Second, one must specify pore geometry. As in all inverse problems, there is a question about the uniqueness of the solution. To obtain a stable and meaningful solution we apply the regularization procedure in our PSD calculations.

Over the last decade, new form of carbon have become available among which are the replica of zeolite porosity. The basic idea is the deposition of an element such as carbon from its vapour phase inside the porosity of such crystalline materials (that have a narrow PSD) to obtain a collection of (carbon) nanostructures after matrix removal (using acid leaching for instance). The zeolitic crystalline matrix gives to the carbon replica its high degree of order making these new carbon porous materials good candidates for testing adsorption-based characterization

*Corresponding author. Email: jacek.jagiello@quantachrome.com

methods including PSD calculations. Experimental results for carbon adsorption in zeolites were first attempted by Wang *et al.* [1]. These authors describe a route to ultra-small single wall carbon nanotubes (SWNTs) using the porosity of zeolite AlPO₄-5 made of parallel channels of 7.3 Å in diameter and studied with the same method proposed in this paper [2]. Selenium and carbon adsorption was also carried out in the porosity of faujasite [3,4]; a zeolite that has a porous network made of cages of 10 Å in diameter connected to each other through 7 Å large windows.

This paper is organized as it follows. We first present the numerical synthesis of the ordered carbon material. We then present the results of a series of grand canonical Monte-Carlo (GCMC) simulations of N₂ adsorption in the porosity of this 3D interconnected carbon structure at various temperatures. These data are subsequently used as inputs for DFT calculation to obtain the carbon replica PSD. The DFT-based PSD is then compared to that obtained from the direct analysis of the carbon replica porosity using the Gelb–Gubbins method [5].

2. Computational methods

2.1 Generating the carbon porous material

The carbon adsorption in the porous framework of faujasite zeolite (assumed to be purely siliceous) was performed using a GCMC method at 1000 K. The adsorbate–adsorbate (C–C) interactions are described in a tight binding approximation (TB) that is a parameterized version of the Hückel theory. We use a minimal s, p_x, p_y and p_z atomic orbital basis set and a Slater Koster parameterization to build the Hamiltonian matrix describing the carbon–carbon interaction. To avoid the time consuming diagonalization of this matrix, we use the recursion method to calculate the local density of electronic states on each atom. We restrict the continued fraction expansion at the fourth moment's level [6]. The adsorbate–zeolite interactions were calculated with the PN–TrAZ potential function as originally reported for adsorption of rare gases and nitrogen in silicalite-1 zeolite [7]. The PN–TrAZ potential function is based on the usual partition of the adsorption intermolecular energy restricted to two body terms only. The transferability of this model allowed to generate various nanostructures from different zeolitic hosts (AlPO₄-5, silicalite and faujasite [8]) in good agreement with experimental studies. After zeolite removal, we checked the stability of the carbon replica and compared with experimental results [9].

2.2 Simulating nitrogen adsorption

To simulate the adsorption of N₂ in the faujasite replica, we used the standard GCMC method with Lennard–Jones

(LJ) potential functions to describe the N₂–N₂ and N₂–C interactions, ($\sigma_{\text{N}_2-\text{C}} = 3.609 \text{ \AA}$, $\varepsilon_{\text{N}_2-\text{C}} = 100.4 \text{ K}$; $\sigma_{\text{C}-\text{C}} = 3.400 \text{ \AA}$, $\varepsilon_{\text{C}-\text{C}} = 28.0 \text{ K}$; the cross-parameters being obtained with the usual Lorentz–Berthelot rules). We calculated the N₂ adsorption isotherms at 77, 87 and 100. To calculate the saturated pressure P_0 of the LJ fluid at different temperatures, we used the state equation given by Kofke [10].

2.3 DFT route for pore size distribution

In this work, we calculate the model N₂ isotherms following the implementation of Tarazona's [11] non-local DFT (NLDFT) described by Lastoskie *et al.* [12]. We assume the slit pore model for carbon pores with three special cases regarding the pore wall thickness [13]:

1. Classical case: both walls are infinitely thick, Steele potential [14].
2. Model 2G: double graphene layer walls.
3. Model 1G: single graphene layer walls.

In the NLDFT calculations of the model isotherms the same LJ parameters were used as in the GCMC simulations of the N₂ adsorption isotherms for the faujasite replica.

The calculation of the carbon PSD is based on its fundamental relationship with the measured adsorption isotherm, V , given in the form of the following adsorption integral equation:

$$V(p) = \int_{\alpha}^{\beta} \rho(p, w) f(w) dw \quad (1)$$

where $\rho(p, w)$ is the kernel which represents the set of model (NLDFT) adsorption isotherms given in terms of the adsorbate density calculated for model pores as a function of pore width, w , and the equilibrium pressure, p . In this approach, the pores of different sizes are considered independent. The PSD to be determined is represented as a differential pore volume distribution, $f(w)$. Mathematically, equation (1) is a Fredholm linear integral equation of the first kind. Due to its ill-posed character, solving this equation presents certain numerical difficulties and requires special treatment. To obtain stable and physically feasible results, the numerical algorithm, SAIEUS [15], is used. This algorithm utilizes the regularization procedure and imposes non-negativity constraints on the solution. A more detailed description of the method is given elsewhere [16].

2.4 The Gelb–Gubbins analysis for pore size distribution

We determine the geometric properties of the Y-zeolite carbon replica using a Monte-Carlo integrations related to those developed for previous stereological studies [17,18].

This method consists of test points randomly placed in the simulation box, and if an adsorbate particle placed at a test point overlaps with the pore material (that is inside the accessible surface), the point is accumulated. The porosity is just the number of misses divided by the total number of insertions. We use the LJ parameters (used before to calculate N_2 adsorption isotherms) to determine the accessible surface. This method insures that we calculate the “real porosity” of the nanostructures.

3. Results and discussion

Carbon adsorption in faujasite at 1000 K leads to the formation of a 3D connected porous carbon structure that is the (negative) replica of the original zeolite cavity network (figure 1). The resulting structure is stable upon matrix removal (it does not collapsed in any way but locally rearranges). It is interesting to note that this structure closely resembles to those predicted by Terrones *et al.* [19,20] and is close to Schwarz minimal surface. It presents a narrow PSD (see below) with a simple pore topology made of spherical pores tetrahedrally interconnected. The density of this replica is around 0.9 g/cc , and the walls are rather thin. Figure 2 shows N_2 simulated adsorption isotherms at 77 K. The shape of this isotherm is in a good agreement with recent experimental results [21,22].

Taking the simulated isotherms as “experimental” data we try to invert the problem and find the underlying PSD associated with these data. First, we solve equation (1) for the isotherm simulated at 77 K using three DFT kernels obtained for the three pore models. Fits of the three models are shown in figure 2 and the resulting differential and cumulative PSD are shown in figure 3. It is clear that the best fit is obtained for single layer pore wall model (1 G), however, the PSD obtained for this model is not in

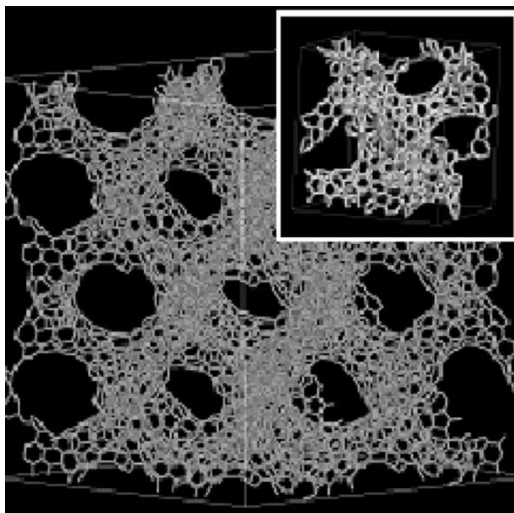


Figure 1. Carbon replica of faujasite zeolite 1000 K (inset) and the replicated at 125 times to show the porosity of the carbon replica.

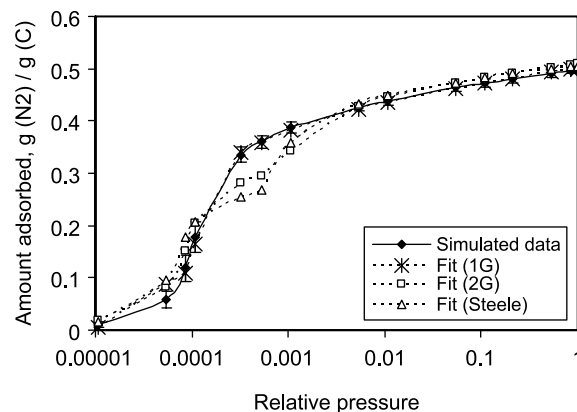


Figure 2. Simulated N_2 adsorption isotherm at 77 K compared with DFT fits obtained using different pore models.

good agreement with the underlying “exact” PSD data. The best agreement between the DFT based PSD and the “exact” data is achieved with the double layer (2 G) pore wall model. We performed more extensive calculations for this model by fitting equation (1) simultaneously to all three simulated isotherms. Taking into account uncertainty (error bars) of the simulated isotherms, the fit may be considered acceptable (figure 4). At the same time the differential and cumulative PSDs calculated from this fit are in a fairly good agreement with the “exact” data (figure 5). Using total pore volume of 0.57 cc/g obtained from this analysis and assuming the skeleton density of the carbon replica to be equal to the density of graphite (2.2 g/cc), we obtain 0.97 g/cc for the average density of

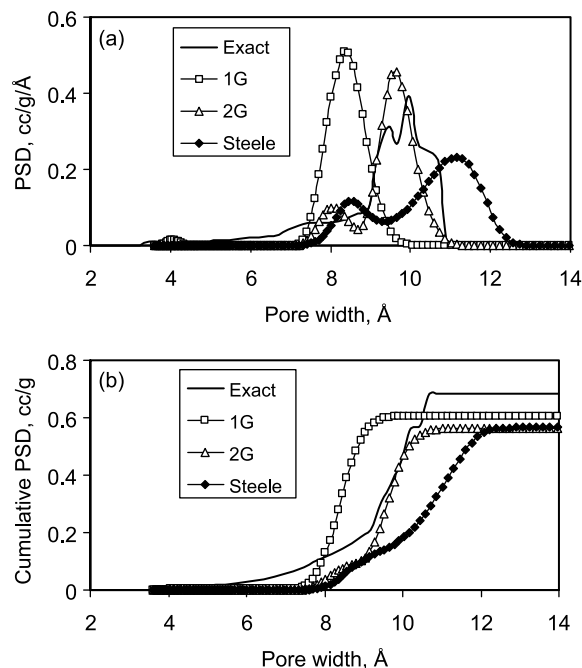


Figure 3. Exact differential (a) and cumulative (b) PSDs calculated using Gelb–Gubbins method compared with DFT–PSDs calculated from the N_2 adsorption isotherm at 77 K using different pore models.

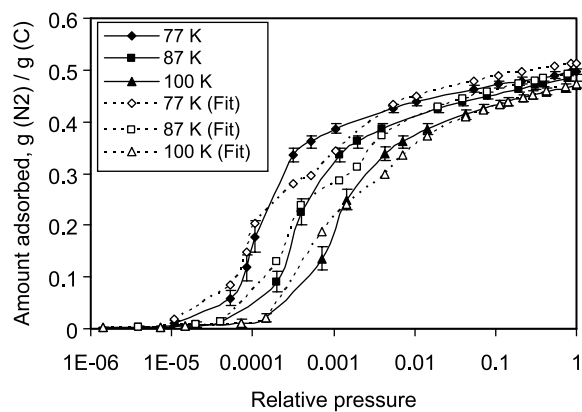


Figure 4. Simulated N_2 adsorption isotherms at 77, 87, and 100 K compared with simultaneous DFT fit obtained using model of pore walls consisting of two graphite sheets (2G).

the carbon replica. This value is not far from the replica density of 0.9 g/cc estimated based on its structure.

Based on this PSD analysis we find that the goodness of fit of the model to the experimental data is not the most important criterion for selecting the appropriate model to describe the carbon pore structure. Example with the simple single layer pore wall model demonstrates that despite the excellent fit, this model fails to accurately describe the carbon PSD. It means that even if we considered some more sophisticated models such as pores with heterogeneous wall thickness [23] or curved pore geometry we would still have the same problem of choice of the most appropriate model. More systematic study of various carbon structures would be necessary to provide

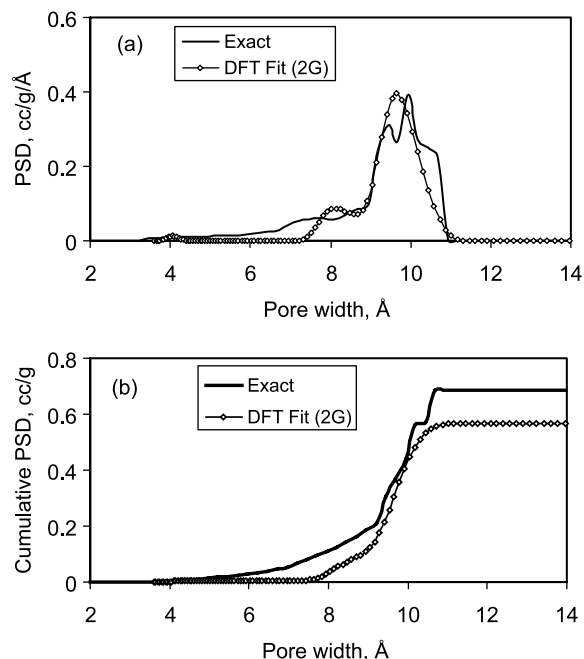


Figure 5. Exact differential (a) and cumulative (b) PSDs compared with DFT-PSDs calculated by simultaneous fit to three N_2 adsorption isotherms using the 2G pore model.

some guidance on extracting maximum information about the carbon structure from adsorption data. On the other hand, we realize that even though we use the slit pore models which do not resemble the actual structure of the carbon replica, we obtain reasonably representative information about this structure in terms of average pore size and material density.

4. Conclusion

Based on the analysis of adsorption data simulated for the carbon replica, we may conclude that application of simplified carbon models may provide reasonable representation of the carbon PSD even though the assumed pore model does not fully agree with its actual structure. On the other hand, since the PSD results are strongly model dependent, additional information about the plausible carbon structure would be useful to improve the results of the carbon PSD calculation.

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