

On the influence of heterogeneity of graphene sheets in the determination of the pore size distribution of activated carbons

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Abstract We model carbon-based microporous materials, such as activated carbons, taking into account surface defects in the form of geometrical rugosity in the inner surface of each graphitic slit pore. The used model is a simplified variation of the randomly etched graphite (REG) pore model (Seaton et al., *Langmuir* 13:1199–1204, 1997).

When subcritical Ar or N₂ is used as probe-gas to simulate the adsorption process in slit pores assembled with ideally perfect graphene walls, the resulting pore size distribution (PSD) rather consistently shows a relatively low population of pores around 12–13 Å. This feature is supposed to be an artifact introduced by the perfect graphene sheets modeling assumptions.

In this study, we particularly examine to which extent the gap of the PSD around 12–13 Å is linked to the perfect graphene sheet model and the effects of surface rugosity in the determination of the PSD. Adsorption isotherms of nitrogen at 77 K and local density distributions are studied simultaneously in the simulation. We found that, by mixing a complete series of heterogeneous pores with 25% of repulsive sites, a noticeable improvement in the fitting between the theoretical and the experimental isotherms was achieved and the PSD gap was eliminated. The mixed model with 25% of repulsive sites provided a more realistic estimate of the internal structure of microporous carbons.

Keywords Pore size distribution · Slit geometry · Heterogeneity · Monte Carlo simulation

1 Introduction

Nanoporous materials, with pores sizes of several molecular diameters currently find numerous applications in modern technologies as adsorbents, catalysts, and host systems. Their engineering properties are determined primarily by their ability to specifically adsorb certain species from bulk fluid phases. The practical problem of predicting the adsorption properties of active carbons, zeolites, pillared clays, mesoporous molecular sieves, and many other traditional and newly synthesized adsorbents gave rise to several theoretical models capable of constructing adsorption isotherms in model pores (Neimark and Ravikovitch 1997).

Most of the studies on adsorption in the literature are limited to well-defined surfaces, such as crystalline surfaces of graphitized thermal carbon black (GTCB). Unfortunately, real surfaces are far from that ideal situation, and assuming a perfect surface to study adsorption in pores could lead to serious errors in the determination of adsorption isotherms (Do and Do 2006). Several authors have been trying to introduce defects in an explicit way in their simulations, e.g., edge sites (Seaton et al. 1997), pore wall heterogeneity with variable number of layers (Nguyen and Bhatia 2004) randomly oriented crystallites (Segarra and Glandt 1994), rumpled graphite surfaces (Bakaev 1995), pores of finite length (Wongkoblap et al. 2005), rough amorphous carbon surfaces (Neimark et al. 2009) and reverse Monte Carlo carbon reconstruction (Thomson and Gubbins 2000). More recent works have also included heterogeneity in the geometric shape of the pores (Azevedo et al. 2010).

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Recently, Lucena et al. (2010) applied the Seaton model (Seaton et al. 1997) to test the potential of an explicit randomly etched model in a Grand Canonical Monte Carlo Simulation (GCMC) scheme to overcome the S-shape fitting of the theoretical isotherm and the observed absence of pores around 12–13 Å. They also showed that the already identified minimum close to that pore size range can be eliminated with the introduction of a few etched pores. This minimum removal is followed by a considerable improvement of the fitting between the theoretical (from the calculated PSD) and the experimental isotherms.

In the present study, we assume that rough and perfect graphene sheets co-exist in real activated carbons. We obtain the PSD from a continuous mixed kernel (50% perfect slit pores and 50% with heterogeneity) of isotherms. Since in the previous etched model, only six etched isotherms of two pores widths were used to obtain the mixed kernel, we wish to investigate the effect of introducing a complete series of heterogeneous pores. Finally, the kernel is applied to a standard active carbon fiber sample (P15) in order to compare our results with those of the previous work (Lucena et al. 2010).

2 Surface heterogeneity model

In order to simulate the effects of a realistic partially crystalline surface structure, we proposed a variant of the randomly etched graphite-REG model. To account for surface heterogeneity of the adsorbent, we roughened the fluid-solid energy landscape by placing additional repulsive sites randomly distributed over the surface. In our model (Fig. 1), we introduce surface heterogeneity by random and irreversible adsorption of spherical particles on the surface of the pores at different coverage θ . These particles interact with the adsorbate by means of a rigid sphere potential. The REG structure could also be considered to be due to carbon deposition, which is one of the steps involved in carbon molecular sieves production.

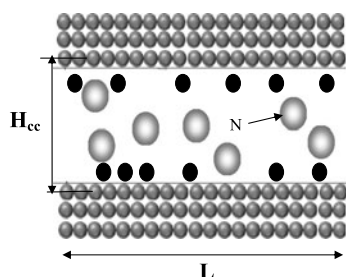


Fig. 1 Schematic diagram of a slit pore with heterogeneous particles pictured in *black*

3 Grand canonical Monte Carlo simulation

The adsorption of N₂ in slit-like micropores has been investigated by Grand Canonical Monte Carlo simulations because it allows a direct calculation of the phase equilibrium between a gas phase and an adsorbed phase. The implementation of this simulation method is well established see, for example (Nicholson and Parsonage 1982; Steele 1974).

The interaction between adsorbate molecules is modeled using the truncated Lennard-Jones potential.

$$U_{gg}(r) = -4\varepsilon_{gg} \left[\left(\frac{\sigma_{gg}}{r} \right)^6 - \left(\frac{\sigma_{gg}}{r} \right)^{12} \right] \quad (1)$$

where ε_{gg} and σ_{gg} are the energetic and geometrical parameters of the LJ potential and r is the molecular separation. Each wall of the model graphitic slit pore was represented by a series of stacked planes of LJ atoms. The interaction energy between a fluid particle and a single pore wall at a distance z (measured between the centers of the fluid atom and of the atoms in the outer layer of the solid) was described by the Steele's 10-4-3 potential (Steele 1974).

$$U_{gs-STEEL}(z) = 2\pi\varepsilon_{gs}\rho_C\sigma_{gs}^2\Delta \left\{ \frac{2}{5} \left(\frac{\sigma_{gs}}{z} \right)^{10} + \left(\frac{\sigma_{gs}}{z} \right)^4 - \frac{\sigma_{gs}^4}{3\Delta(z+0.61\Delta)^3} \right\} \quad (2)$$

where Δ is the separation between layers in graphite (0.335 nm), ρ_C is the density of carbon atoms per unit volume of graphite (114 nm⁻³), z is the distance from the site of a fluid molecule to the nuclei of the carbon atoms in the surface graphitic plane, ε_{gs} and σ_{gs} are the LJ parameters for the interaction between an adsorbate molecule (gas) and a graphite carbon atom (solid). The cross LJ parameters are determined using the standard Lorentz-Berthelot combining rules (arithmetic mean for collision diameter and geometric mean for well depth). The values of the parameters included in the interaction potentials ((1) and (2)) are given in Table 1 (Ravikovitch et al. 2000).

Three types of attempts with equal probability are performed randomly in each step of the GCMC simulation

Table 1 Parameters used in the GCMC for the LJ

Molecule	σ_{gg} (nm) ^a	ε_{gg}/k_B (K) ^a	σ_{gs} (nm) ^a	ε_{gs}/k_B (K) ^a
N ₂	0.3615	101.5	0.3494	53.22
Carbon	0.343	28.0	–	–

^aRavikovitch et al. (2000)

^bBoltzman constant: $k_B = 1.380/650424 \times 10^{-23}$ (J/K)

(Frenkel and Smit 1996; Allen and Tildesley 1987): displacement, adsorption and desorption. Transition probabilities for each Monte Carlo attempt are given by the usual Metropolis rules. The lateral dimensions of the cell for the slit geometry were taken as $L = 10.3$ nm and periodic boundary conditions were used in these directions. The cut-off distance, beyond which the potential is neglected, is set to be $5\sigma_{gg}$. Equilibrium was generally achieved after 2×10^7 MC attempts, after which mean values were taken over the following 2×10^7 MC attempts for configurations spaced by 10^3 MC attempts, in order to ensure statistical independence. The volume of the simulation cell is given by $L \times L \times H$, where L is the length and H is the width.

4 Determination of accessible volume for perfect and heterogeneous pores

The accessible pore volume for a perfect slit pore is defined as the space available to the center of an adsorbate molecule where the solid-fluid potential is negative (Do and Do 2005). So if z_0 is the distance at which the solid-fluid potential is zero, the volume space available to the fluid molecule is

$$V = (H_{cc} - 2z_0 + \sigma_{gg})A \quad (3)$$

where $A = L \times L$, H_{cc} is the physical width of the pore, which is defined as the distance from the plane passing through the centers of all carbon atoms of the outermost layer of one wall to the corresponding plane of the opposite wall. In this way, the effective accessible width for the adsorbate molecule in the slit pore is given by:

$$H_{eff} = H_{cc} - 2z_0 + \sigma_{gg} \quad (4)$$

In the case of the heterogeneous slit pore we should subtract the volume occupied by the heterogeneity from the accessible volume corresponding to the perfect slit pore. Then the accessible volume for pores with heterogeneity will be

$$V = (H_{cc} - 2z_0 + \sigma_{gg})A - V_{hm} \quad (5)$$

where V_{hm} is the volume due to heterogeneity.

5 Pore size distributions

Pore size distributions for perfect, heterogeneous and mixed slit pores have been calculated with kernels containing pore sizes between 4 and 52 Å for N_2 . The theoretical adsorption isotherm, θ^{theor} , can be expressed as a superposition of isotherms corresponding to each pore size (H_j), pressure P and temperature T , called “local isotherms,” θ_L , each one

with a contribution corresponding to the pore size distribution, $f(H_j)$:

$$\theta_i^{theor} = \sum_{j=1}^m \theta_L(H_j^*, P_i, T) f(H_j^*) \delta H_j \quad (6)$$

The pore size distribution is then derived solving (6) numerically via a fast non-negative least square algorithm in combination with a method to stabilize the result, incorporating additional constraints that are based on the smoothness of the PSD. This method, called regularization, has been described in detail in several works (Wilson 1992; Szombathely et al. 1992; Merz 1980; Whaba 1977). In this work, we used the procedure proposed by Davies et al. (1999) and by Davies and Seaton (1998).

6 Results and discussion

In Fig. 2, GCMC simulated adsorption isotherms for N_2 at 77 K are shown for some selected sizes, for perfect (a) and heterogeneous (b) slit pores. Isotherms in Fig. 2b correspond to a proportion of 25% heterogeneity, measured as the percentage of atoms, which are similar to carbon, that are deposited on the top layers. For small pores, we see that the adsorption isotherm has a stepped behavior when the pore is perfect (0% heterogeneity) and takes a smoother behavior when the amount of defects is increased. This is simply due to the irregular packing in the case of heterogeneous pores, compared to a much more ordered layering in the case of perfect slit pores (Fig. 3a).

To rationalize the behavior of the adsorption isotherms and the effect of molecular interaction, we show in Fig. 3b the local density distributions at different values of heterogeneity for 10 Å pores. The local distribution in the perfect slit pore distinctly shows narrow peaks, suggesting that adsorbed layers are parallel and reside at fixed distances from the surface. On the other hand, in the slit pore with heterogeneity, the peaks tend to decrease as heterogeneity increases, indicating that layers are less distinct, especially in the layer that is close to positions with defect particles at the surface.

In Fig. 4, we show the PSD calculated from the application of kernel A (31 perfect slit pores or 30 parameters of pore size distribution) and, in the inset, we also plotted the PSD using 44 parameters. We can see that, when the number of isotherms increases, the resolution is higher, mainly in the range between 4 and 20 Å. In both cases, a gap around 10 Å is observed. In the same Fig. 4, we show the fits of the experimental isotherm of sample P15 for 30 and 44 parameters (inset). It is clear that, in both fitting curves, the S-shaped behavior around $P/P_0 = 0.001$ is noticeable. We decided to work with 30 parameters so that our results can

Fig. 2 Selected Monte Carlo isotherms of N₂ at 77 K. (a) Kernel A: 31 perfect slit pores. (b) Kernel C: 31 Heterogeneous slit pores (25%)

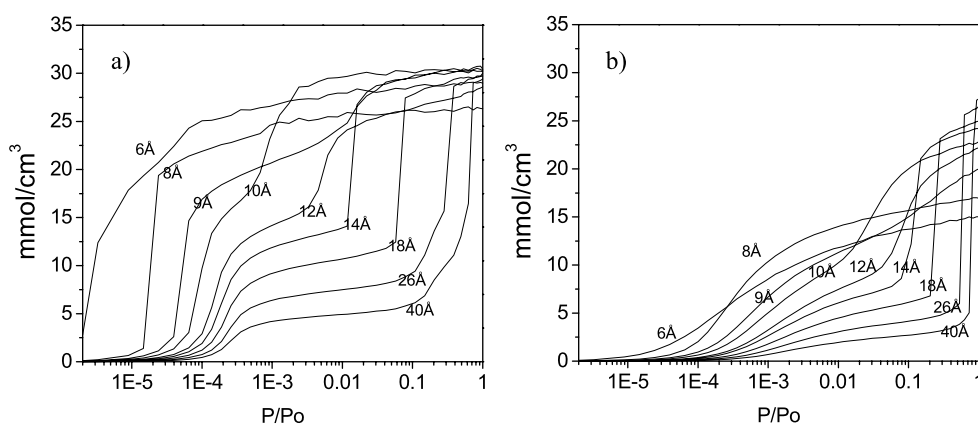


Fig. 3 (a) Snapshots from nitrogen adsorption simulations in a 10 Å perfect slit pore (top) and with 25% of heterogeneity (bottom). (b) Plot of local density distribution versus distance in a 10.8 Å pore with 0%, 10% and 25% of heterogeneity for relative pressures of 0.0621. In this last figure, the distance is measured from the tangent plane to the carbon atoms in the pore wall

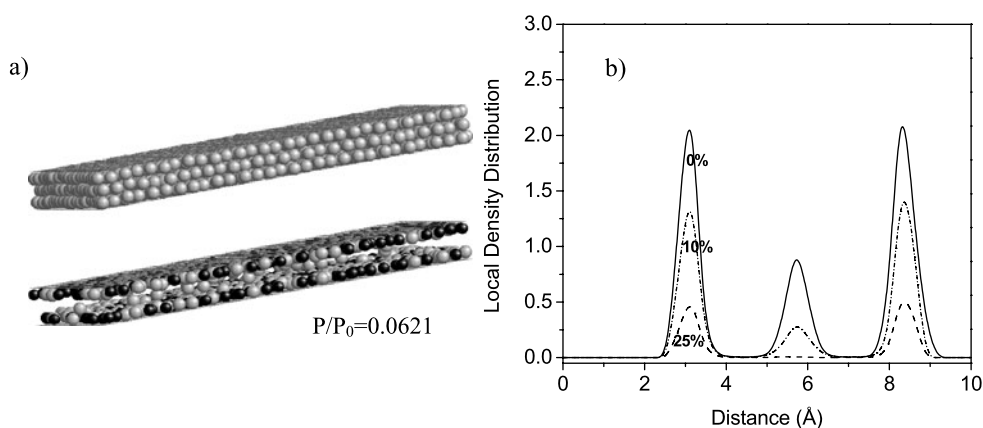
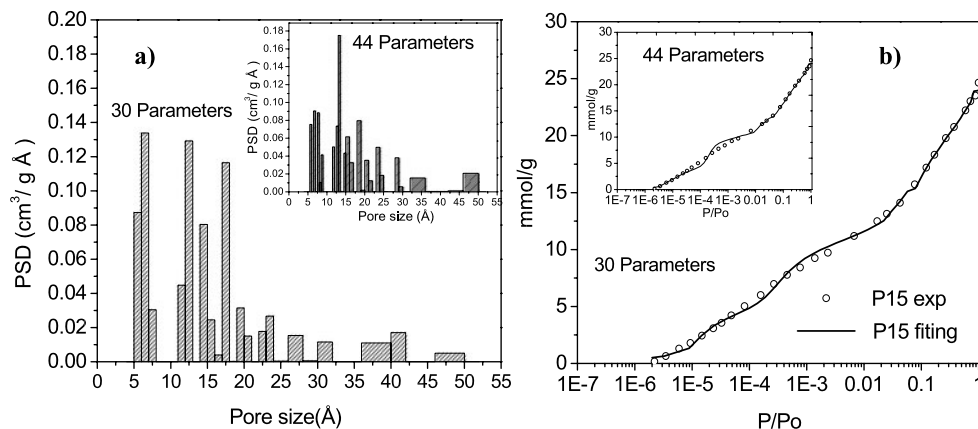


Fig. 4 (a) PSD of P15 carbon fiber calculated from kernel A of N₂ isotherms at 77 K using GCMC, in the inset the PSD obtained utilizing 44 parameters. (b) Fit of experimental isotherm of sample P15. Experimental isotherm (points). Theoretical fit (solid line)



be compared with those of the etched model (Lucena et al. 2010).

In addition to kernel A, we calculated two extra kernels, B and C. Kernel B includes 31 isotherms with heterogeneity of 10% for each pore size, while kernel C includes the same number of isotherms but the heterogeneity is 25%. The PSDs and the fits using the two kernels are presented in Fig. 5. For kernel B (a), the PSD is similar to that calculated with kernel A (perfect slit pores). In fact, the fit of the experimental isotherm of sample P15 is a little better, but the gap is still present. The PSDs calculated with kernel C

(b) visibly do not reproduce the main characteristics found previously, although the error in the fit is similar.

We calculated two additional kernels, D and E, to test the effects of mixing perfect and heterogeneous pores in the material characterization. Kernel D was obtained by using 50% of the parameters corresponding to kernel A (perfect slit pore) plus 50% of the parameters corresponding to kernel B (10% of heterogeneity). For kernel E, we combined in the same proportions kernels A and C (25% of heterogeneity). The PSDs calculated from kernels D and E are called total PSDs to distinguish them from the slit PSDs (those cal-

Fig. 5 (a) PSD of P15 carbon fiber calculated from kernel B. (b) Utilizing the Kernel C

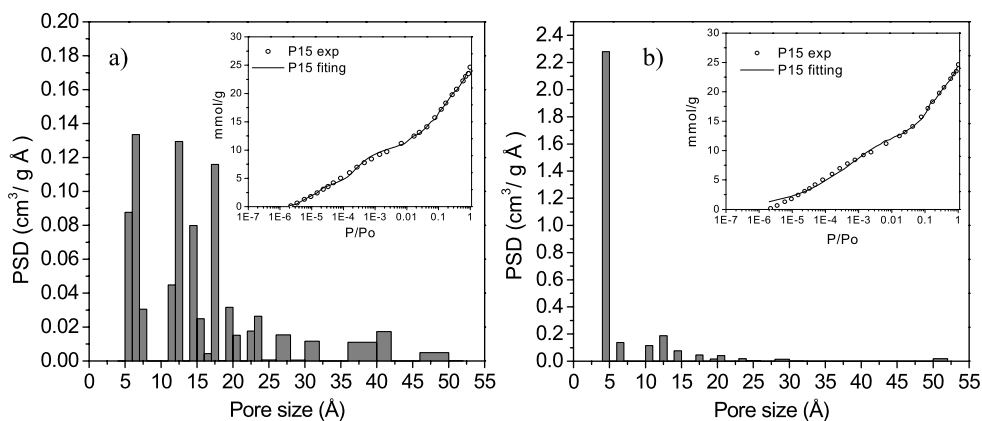
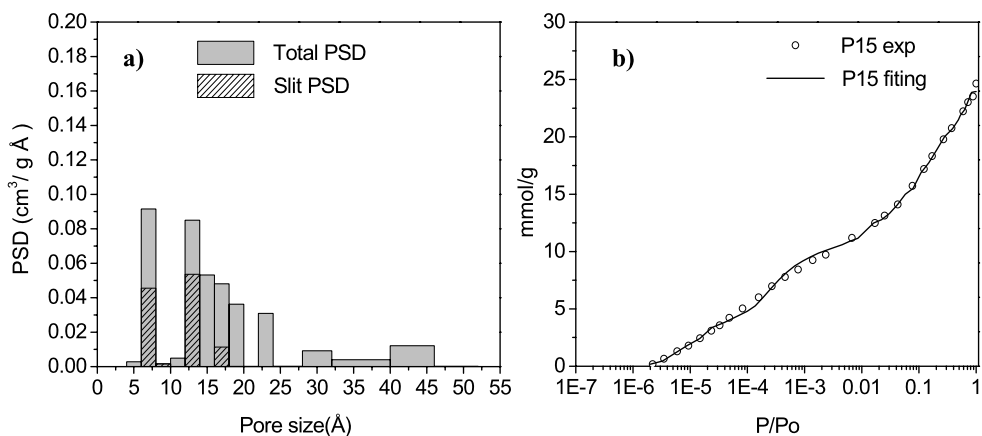


Fig. 6 (a) PSD of P15 carbon fiber calculated from kernel D of N₂ isotherms at 77 K using GCMC. (b) Fit of experimental isotherm of sample P15. Experimental isotherm (points). Theoretical fit (solid line)



culated from kernel A). In Fig. 6, the results for kernel D are presented, where the total PSD is similar to the slit PSD, with the gap near 10 Å. The fit still shows the S shape, which means that 10% of heterogeneity is not enough to avoid the ordered layering in the adsorbate. Finally, the PSD obtained for kernel E are shown in Fig. 7a, indicating the contributions due to perfect slit pores and to pores with 25% of heterogeneity. For the first time, we can observe that the gap has disappeared. The deconvolution algorithm found a solution for the total PSD that seems to better represent the P15 activated carbon structure than the kernels A, B, C or D. This solution does not show spikes in the PSD and, from this point of view, it is more plausible than that obtained with the addition of only a few randomly etched pores (Lucena et al. 2010), as may be seen in Fig. 7b. Figure 7c shows the fits of the kernel E model and those of the etched model as compared to the experimental P15 isotherm. In both cases, there is a very good agreement with the experimental data.

Table 2 presents the calculated textural properties of the samples, such as porosity and specific surface area, calculated from simulated data of the different models and compared to the values obtained by standard methods like Dubinin-Radushchevich and BET. We observe that all of the proposed heterogeneous models yield greater values of sur-

Table 2 Surface area and total pore volume calculated from semi-empirical models and from Monte Carlo simulation

	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)
Slit pore Geom.	1548	0.90
Our model –25%	1781	0.98
Our model –10%	1294	0.85
Etched model	–	0.83
BET	1545	–
DR	–	0.76

face area and total pore volume than the values calculated using the standard methods.

7 Conclusions

The analysis of the adsorption isotherms of a standard activated carbon fiber (P15), by using the methodology developed in the present study, suggests that heterogeneity due to chemical and geometrical imperfections of the graphene walls is a promising method to obtain realistic PSDs. We have showed that the already identified gap within the pore

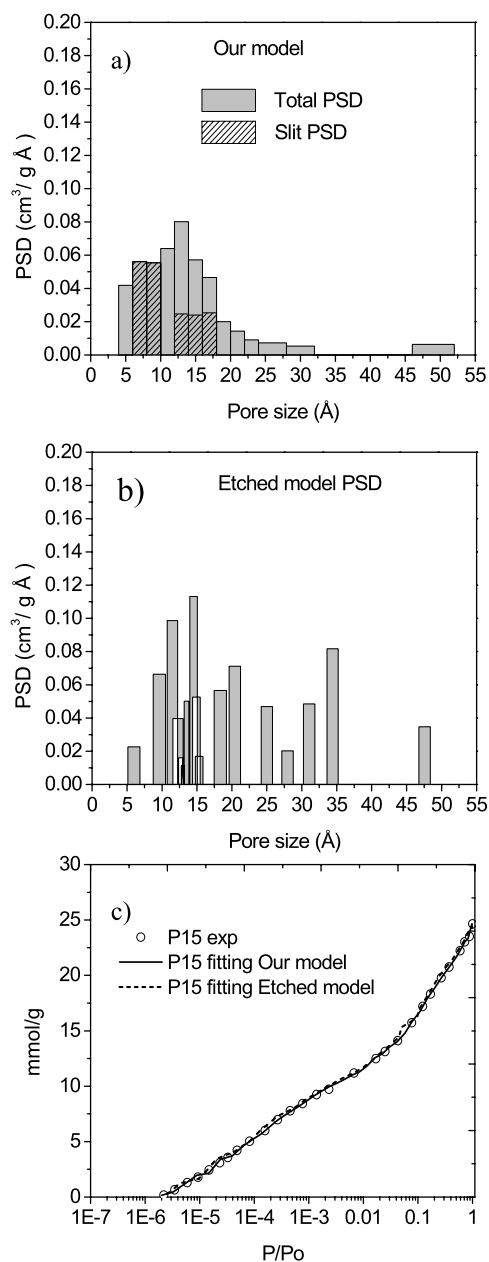


Fig. 7 PSD of P15 carbon fiber calculated for N_2 isotherms at 77 K using GCMC. (a) Calculated from kernel E using our model. (b) Calculated by Lucena et al. using a mixed model with few etched pores (Etched model). (c) Fit of experimental isotherm of sample P15. Experimental isotherm (points). Theoretical fit our model (solid line) and theoretical fit Etched model (short dash)

size range of 12–13 Å can be eliminated by using a mixed isotherms kernel with perfect pores and heterogeneous pores with 25% of repulsive sites randomly distributed over the surface. This mixed model provided a more realistic estimate of the internal structure of the microporous activated carbon under study.

The agreement between the simulated and experimental data is a positive step for further application of this general model to study adsorption in porous solids.

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