

How realistic is the pore size distribution calculated from adsorption isotherms if activated carbon is composed of fullerene-like fragments?[†]

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A plausible model for the structure of non-graphitizing carbon is one which consists of curved, fullerene-like fragments grouped together in a random arrangement. Although this model was proposed several years ago, there have been no attempts to calculate the properties of such a structure. Here, we determine the density, pore size distribution and adsorption properties of a model porous carbon constructed from fullerene-like elements. Using the method proposed recently by Bhattacharya and Gubbins (BG), which was tested in this study for ideal and defective carbon slits, the pore size distributions (PSDs) of the initial model and two related carbon models are calculated. The obtained PSD curves show that two structures are micro-mesoporous (with different ratio of micro/mesopores) and the third is strictly microporous. Using the grand canonical Monte Carlo (GCMC) method, adsorption isotherms of Ar (87 K) are simulated for all the structures. Finally PSD curves are calculated using the Horvath–Kawazoe, non-local density functional theory (NLDFE), Nguyen and Do, and Barrett–Joyner–Halenda (BJH) approaches, and compared with those predicted by the BG method. This is the first study in which different methods of calculation of PSDs for carbons from adsorption data can be really verified, since absolute (*i.e.* true) PSDs are obtained using the BG method. This is also the first study reporting the results of computer simulations of adsorption on fullerene-like carbon models.

1. Introduction and the aim of the study

Activated carbons are fascinating materials with applications in many different areas of technology including as adsorbents, catalysts and supports. Two major factors determine their applicability in the adsorption field, namely porosity and the chemical composition of the surface layer.¹ It is perhaps surprising that the detailed microstructure of these carbons is still unknown. Recently developed methods applying the reverse Monte Carlo (RMC) technique led to very interesting results in this field, the most important conclusion of which is that the results predicted for the ideal slit-like model of carbon

pores are far from reality.^{1–6} Biggs *et al.*^{7,8} and Do *et al.*^{9–11} drew similar conclusions from theoretical studies of the adsorption on their proposed disordered and significantly heterogeneous modelled carbonaceous adsorbents. The results published recently by Coasne *et al.*¹² are interesting and important, showing that the filling pressure for the assembly of slit pores is much lower than that for disordered porous carbon. This raises questions about the reliability of the pore size distribution (PSD) curves obtained from adsorption measurements *via* typical adsorption apparatus connected with, for example, the density functional theory (DFT) software where the local isotherms are simulated for ideal carbon slits. Incidentally, this PSD usually has two peaks regardless of the origin of the carbon material.^{13–17}

Several years ago a model of non-graphitizing carbon which incorporated fullerene-related elements was proposed by Harris *et al.*^{18–21} Although this model is quite widely known, there have been no attempts to calculate the properties of such a structure. This model was based on detailed studies of typical non-graphitizing microporous carbons using high-resolution transmission electron microscopy (HRTEM).^{18–21} These studies showed that carbons heated to high temperatures (up to 2800 °C) often contained fullerene-related structures including closed nanoparticles and saddle-points. On the basis of these findings, and of observations of the “fresh” carbons, a new model was put forward in which the structure consists of discrete fragments of curved carbon sheets in which pentagons and heptagons are dispersed randomly throughout networks of hexagons. An illustration of this model is given in Fig. 1.

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[†] Electronic supplementary information (ESI) available: The rotating HC2 structure (Movie S1); the animations of Ar adsorption (87 K) in the HO structure seen in the whole box (Movie S2a) and inside the box (Movie S2b); the animations of Ar adsorption (87 K) in the HC1 structure seen in the whole box (Movie S3a) and inside the box (Movie S3b); and the animations of Ar adsorption (87 K) in the HC2 structure seen in the whole box (Movie S4a) and inside the box (Movie S4b). See DOI: 10.1039/b710552e

(It should be noted that all animations and graphics collected in Fig. 1, 2, 4, and 7 were created using the VMD program.)²² Some of the individual fragments are shown in Fig. 1(i), while the complete (2-D) structure is shown in Fig. 1(ii). This fullerene-like model explains many properties of so called “hard” synthetic activated carbons, especially their porosity and resistance to graphitization. The presence of fullerene-like structures has been supported by both experimental^{23–28} and theoretical^{23,24,29,30} studies.

Therefore, the evidence for fullerene-like structures in “hard” carbons is growing. However, there is still the problem of constructing a simulation box for such a model which will mimic the adsorption properties of real carbon samples. This requires the evaluation of a simulation method (analogous to RMC) taking into account not only the presence of those fragments in the carbon structure, but also their mutual arrangement and percentage contents (moreover some of the structures can be also multi-walled). This problem, and the comparison of simulated and experimental adsorption isotherms (and enthalpy), will be reported in the future. In the current study we focus only on the calculation of the PSD curves for hypothetical carbon structures composed of fullerene-related fragments. Since real “hard” carbons contain these structures, it is interesting to perform the type of experiment proposed in this study, *i.e.* to assume for a moment that

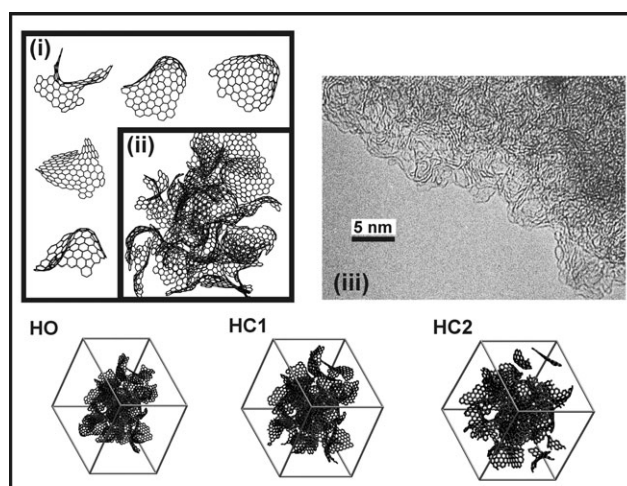


Fig. 1 Model of non-graphitizing carbon based on fullerene-like elements: (i) the individual fragments; (ii) structure constructed from fragments (2-D); (iii) typical HRTEM results for synthetic activated carbon A obtained from poly(furfuryl alcohol).^{16,57–61} Also, the (3-D) models of the structures of studied synthetic “hard” carbons: HO—the original (micro-mesoporous) structure postulated from HRTEM results; HC1—micro-mesoporous structure cut from the structure HO; HC2—the internal (microporous) box cut from the structure HO.

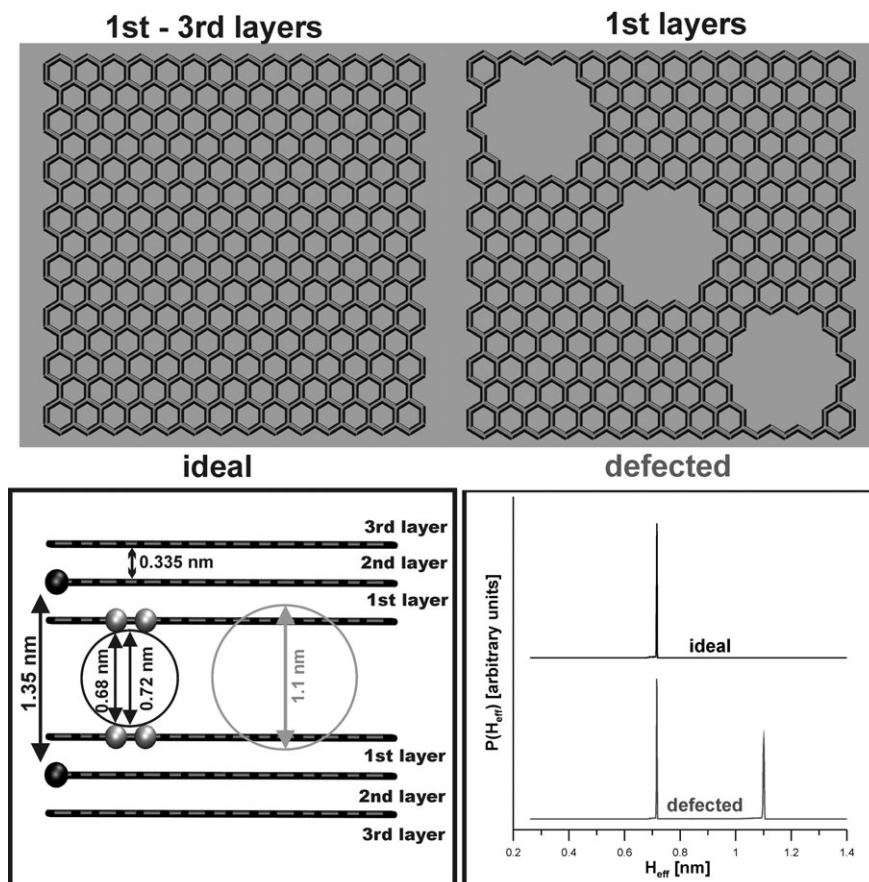


Fig. 2 The slit-like graphitic pore formed from the walls containing three ideal (top left) and two ideal and one defected (top right) graphite layers. The ideal of the BG method (bottom left) and the distribution of probability curves, $P(H_{\text{eff}})$, for the slit-like ideal and defected pores calculated from the method of Bhattacharya and Gubbins (bottom right).³²

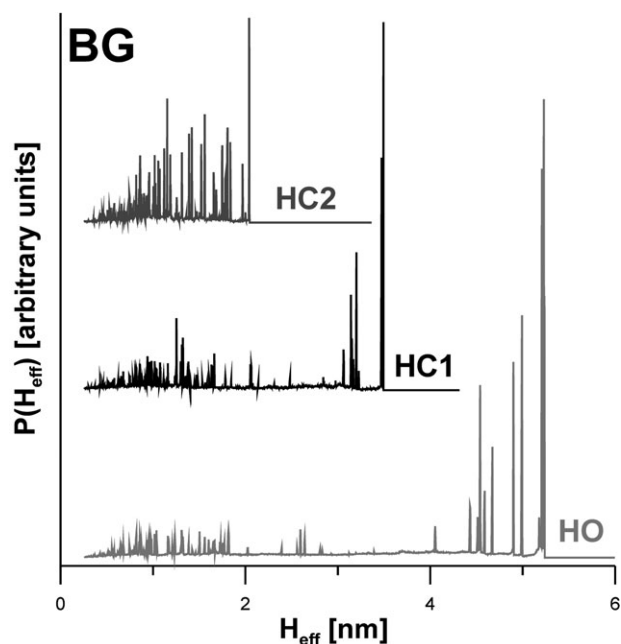


Fig. 3 The PSDs from BG method for all studied structures.

the model of Harris *et al.*^{18–21} is realistic, and take a look at what happens if we apply typical methods of carbon porosity calculation. It should be pointed out that the purpose of this study is not to criticise the typical and widely-applied methods of porosity determination. It is well known that they were developed on the basis of an ideal slit-like model of carbon pores proposed by Everett and Powl³¹ and we are sure that they are very sophisticated. These methods are based on the measurements of (for example) Ar or N₂ adsorption and fitting the global adsorption isotherm equation to experimental data, applying (usually) the non-local density functional theory (NLDFT) local isotherms. Sometimes (for mesopores) the relations between the pore filling pressure and pore diameter can be also used (see below). Therefore we assume that the initial structure (proposed from the analysis of many HRTEM micrographs) is very close to that observed in non-

graphitizing carbons. Next, by some geometric manipulations, different pore structures are created, namely microporous and micro-mesoporous. The “experimental” isotherms (Ar, $T = 87$ K) for those structures are obtained by the grand canonical Monte Carlo (GCMC) simulation method, and the PSDs are calculated using the most popular and standard approaches (as applied in the sophisticated adsorption apparatus, for example ASAP type, Micromeritics, USA) assuming slit-like porosity. Of course, it is desirable to verify the reality of the obtained PSDs by an independent approach, and in this field a new and important possibility is offered by the method proposed recently by Bhattacharya and Gubbins (BG).³² They reported a new technique of fast computation of PSD of model materials, from a knowledge of the molecular coordinates. The PSD is defined as the statistical distribution of the radius of the largest sphere that can be fitted inside a pore of a given point. Since the geometric coordinates of carbon atoms in the simulation boxes are known, the BG method is applied as the reference method of the true (absolute) PSD calculation. To our knowledge, this is the first study in which different methods of calculation of PSDs for carbons from adsorption data can be really verified since using the BG method absolute (*i.e.* true) PSDs are obtained. This is also the first study reporting the results of computer simulations of adsorption on fullerene-like carbon models.

2. HRTEM studies

Samples (“hard” carbon from poly(furfuryl alcohol)) were prepared for transmission electron microscopy by grinding gently and depositing on “lacey” carbon support films. The microscope employed was a JEOL 2010, with a point resolution of 0.19 nm, operated at 200 kV. Images were recorded photographically.

3. Calculation details

The density of carbon structures

The density of the carbon structures was determined in the following way. The volume was calculated based on Monte

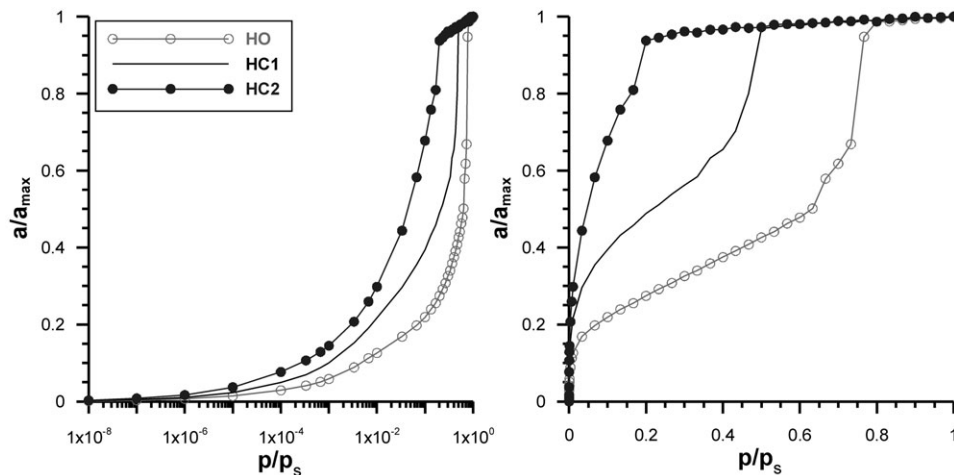


Fig. 4 Ar adsorption isotherms (87 K) simulated by the GCMC method for the studied structures.

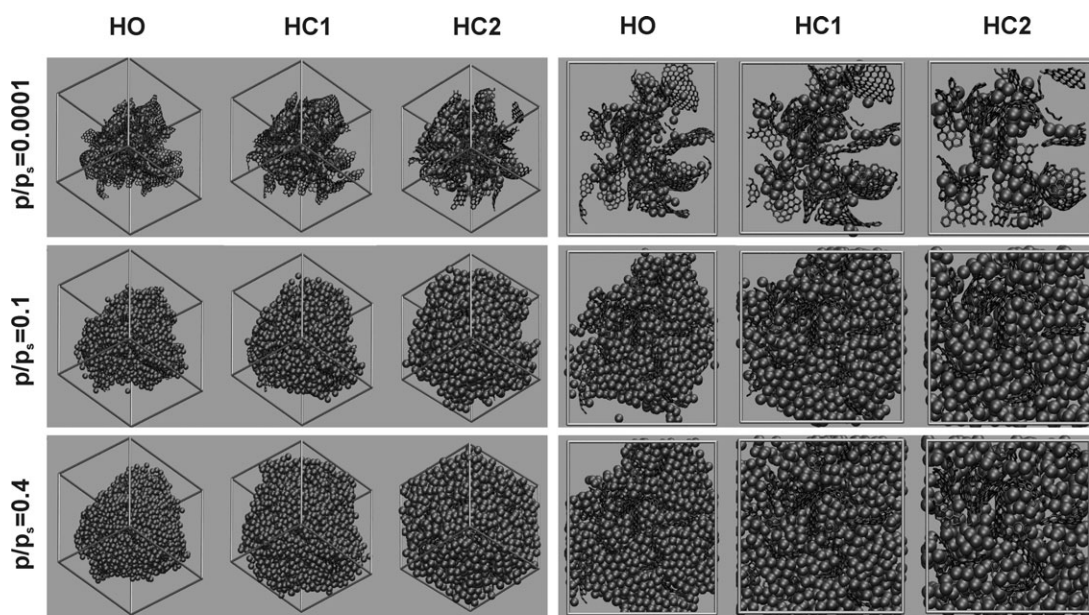


Fig. 5 Selected snapshots of equilibrium configurations from GCMC isotherms generated for HO, HC1, and HC2 for the following values of the relative pressure: $p/p_s = 0.0001$, 0.1 , and 0.4 . Left panels show the whole simulation boxes, right panels the snapshots seen parallel to the surface dividing the boxes into two rectangular prisms.

Carlo integration. For the randomly chosen points inside the simulation box (we selected 1×10^6 points as a sufficient number. However, the convergence usually occurs after a few tens of thousands of iterations) the potential of interactions of

Ar with the carbon structure (U_{tot}) at each point was calculated. The criterion for deciding whether a chosen point is inside the carbon structure was $U_{\text{tot}} > U_{\text{sf}}$ (0.17 nm) (where U_{tot} is the total potential energy of solid–fluid interactions,

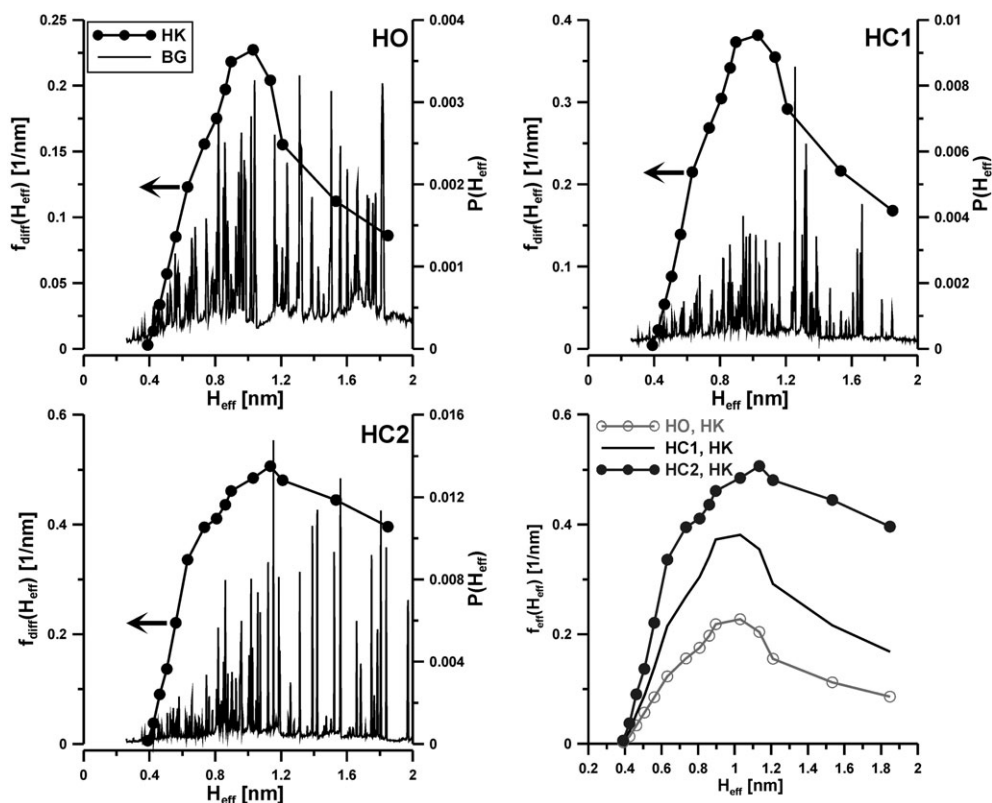


Fig. 6 PSD curves for the studied carbon structures from BG and HK methods.

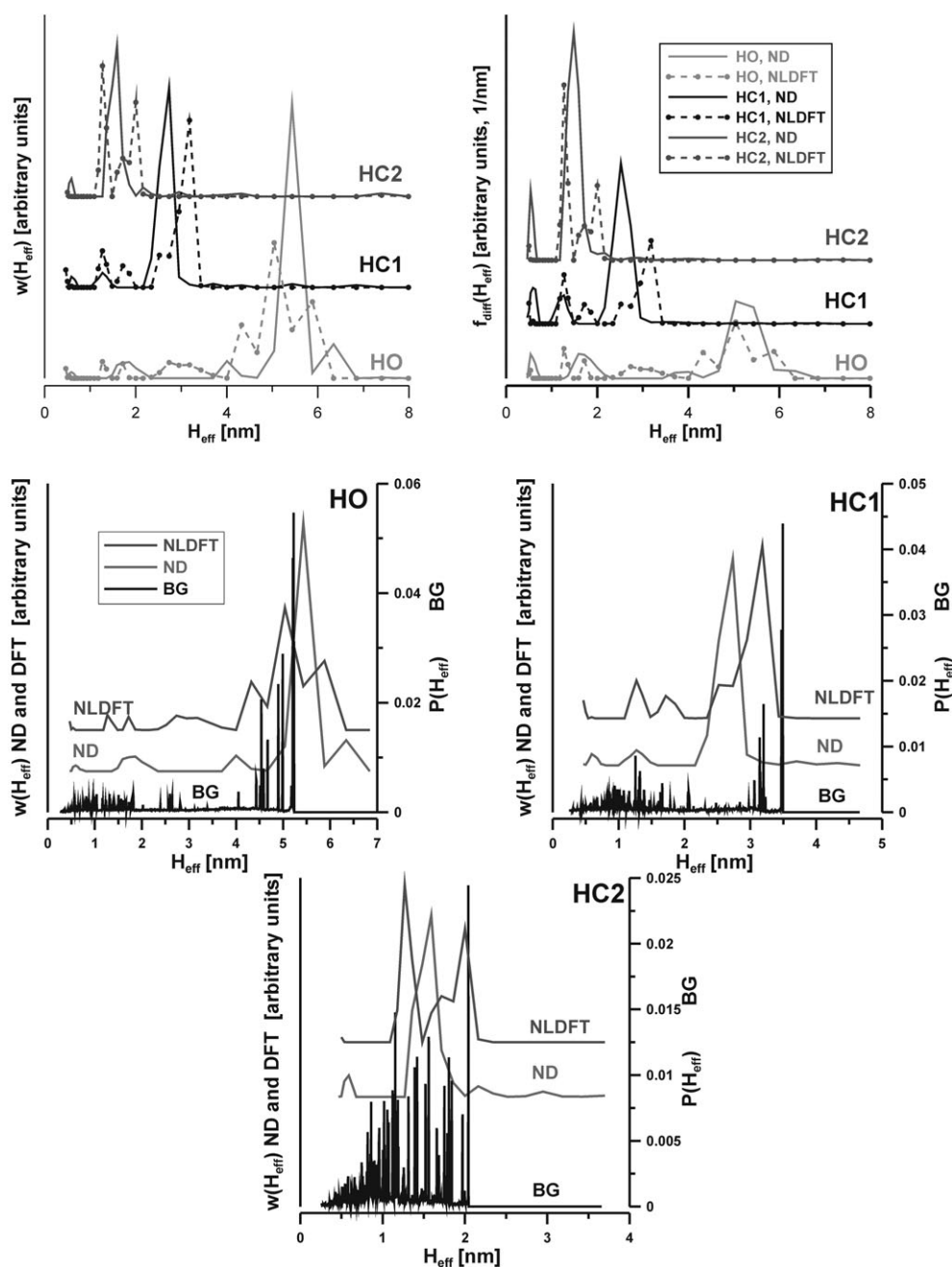


Fig. 7 The differential PSDs ($f_{\text{diff}}(H_{\text{eff}})$) and the distributions of weights ($w(H_{\text{eff}})$) curves for the studied carbon structures calculated from simulated Ar isotherms (Fig. 5) from NLDFT and ND methods, and the comparison with the distribution of probability ($P(H_{\text{eff}})$) from the BG method.

and U_{sf} (0.17 nm) is this energy calculated at the distance 0.17 nm, which is the assumed carbon atom radius). Empty space corresponds to $U_{\text{tot}} \leq U_{\text{sf}}$ (0.17 nm).

4. Simulation details

The energy of intermolecular interactions between atoms x and y (where x and/or y denote Ar (fluid (f)) or C (solid (s)) atoms) were modeled by the classical Lennard-Jones

potential:³³

$$U_{xy}(r_{xy}) = 4\epsilon_{xy} \left[\left(\frac{\sigma_{xy}}{r_{xy}} \right)^{12} - \left(\frac{\sigma_{xy}}{r_{xy}} \right)^6 \right] \quad (1)$$

with the following values of the parameters: $\sigma_{\text{ff}} = 0.34$ nm, $\epsilon_{\text{ff}}/k_{\text{B}} = 120.0$ K, $\sigma_{\text{sf}} = 0.34$ nm, $\epsilon_{\text{sf}}/k_{\text{B}} = 58.0$ K.³⁴ The potential cut-off was chosen at $r_{\text{cut,xy}} = 5\sigma_{xy}$. All isotherms were simulated for a temperature of $T = 87$ K. Periodic boundary conditions were applied in all three directions. The probabilities of the change of state of the systems *via*

Table 1 The volumes and densities of studied carbon structures

Structure	Volume of carbon structure/nm ³	<i>d</i> /g cm ⁻³
Original structure (HO)	42.5	2.24
Cut from inside (HC1)	37.5	2.20
Cut from inside (HC2)	24.7	2.18

displacement, creation and/or annihilation of the adsorbate atom were the same (equal to 1/3). The dimensions of the simulation boxes, together with the number of carbon atoms forming the studied structures, are given in Table 2. For each adsorption point, 25×10^6 iterations were performed during the equilibration and then 25×10^6 further iterations for the equilibrium, which were then used for the calculation of the averages (one iteration = an attempt to change the state of the system by displacement, creation or annihilation).

5. Pore size distributions of carbons from simulated isotherms

Since the major aim of this study is the comparison of PSDs calculated from the BG method with those obtained from simulated isotherms, we used typical widely-applied methods of carbon porosity calculation. The simplest method for calculation of the PSD of micropores applied in this study is the Horvath–Kawazoe (HK) condensation-approximation type method,^{35,36} with parameters characteristic for the carbon–Ar system.³⁷ The next two methods studied are: the NLDFT^{38–44} and the method proposed by Nguyen and Do (ND).^{13,15,45–51} The latter is a relatively simple approach, faster than the NLDFT, and leads to exactly the same PSDs (as was shown for many porous materials having different structures and origin—see Fig. 3 and the results published by Kowalczyk and coworkers¹⁶). The basis of 82 ND or NLDFT local isotherms was generated in the current study for the same effective width range (from 0.465 to 233.9 nm, *i.e.* micro-, meso-, and macropores), as in the DFT software (DFT PLUS, ASAP 2010, Micromeritics).

It is widely accepted that capillary condensation in macropores larger than *ca.* 100 nm does not occur. However, the results of PSD calculations performed in this study vanish for pores larger than *ca.* 8 nm. Therefore, local isotherms with pore diameters larger than 8 nm do not contribute to the PSD curves. The supplementary details and the values of the parameters for ND^{47,52} and NLDFT^{39–42} models can be found elsewhere. Finally, the PSDs were calculated using the adsorption stochastic algorithm (known as ASA)^{15,45,46} to solve the unstable linear Fredholm integral equation of the first kind.

The Barrett–Joyner–Halenda (BJH) method,⁵³ with or without the respective corrections, was used for the calculation of the PSDs of mesopores. The calculations of the distribution of mesopores from the BJH method were based on the assumption of the capillary condensation phenomenon, the mechanism of which follows the classical Kelvin approach. Two approaches were applied in this study. The diameters of the pores were calculated by applying the classical equation in which it was assumed that desorption takes place from the meniscus having cylindrical and/or spherical shapes. The

parameters were taken from the paper written by Kruk and Jaroniec.⁵⁴ We also introduced the correction term (0.438 nm) suggested by them.⁵⁴ This correction term was estimated from the analysis of Ar adsorption data on MCM-41 materials.^{54,55} The volume of the adsorbate in the monolayer was calculated from the standard Ar adsorption isotherm measured at 87 K on a non-graphitizing carbon black Cabot BP280.⁵⁶

6. Results and discussion

6.1 HRTEM results and construction of carbon models

Fig. 1(iii) shows an HRTEM micrograph of synthetic activated carbon obtained for the purpose of this study. This sample (named carbon A) was synthesised in the 1980s from poly(furfuryl alcohol).^{16,57–61} One can see the curved fullerene-like fragments. Similar micrographs were published for other synthetic carbons,^{1,21,23,28,62,63} and the structure of all these non-graphitizable carbons appears to be very similar. From previous studies as well as the HRTEM results presented in this study, the initial simulation box was constructed (Fig. 1—the HO structure) with the most probable arrangement of carbon fragments (as observed in real samples). Next, based on a numerical analysis, the density of such a carbon model structure was calculated. This density 2.24 g cm⁻³ (Table 1) is practically the same as observed from experiment for typical non-graphitizable carbons by true density measurements (reported densities for the series of synthetic carbons from poly(furfuryl alcohol) were in the range: 2.38–2.3 g cm⁻³).⁶⁴

To obtain carbon models having different structures from the initial one, we cut out a box from the HO structure (Fig. 1—this structure is called HC1—see Table 1). Finally the third box (see Fig. 1—HC2) was obtained by cutting out an internal fragment from the initial structure. Movie S1 (in the ESI)† shows the arrangement and the mutual contributions of carbon fragments in the HC2 structure. The number of carbon atoms in the three considered models, and some “technical” details of the GCMC simulations are given in Table 2.

6.2 Test of the Bhattacharya–Gubbins (BG) method

Bhattacharya and Gubbins³² tested their method for a series of model structures with known pore diameters (for example SBA-15 and MCF). In the current study we test the validity of the approach proposed by Bhattacharya and Gubbins by generating two model structures having graphitic slit-like pores (Fig. 2). The first of them contains 2784 carbon atoms arranged in the pore wall consisting three ideal graphite layers (the distance between them is 0.335 nm—Fig. 2). The pore

Table 2 The properties of simulation boxes studied

Structure	Number of C atoms in the box	<i>L</i> _{box,x} /nm	<i>L</i> _{box,y} /nm	<i>L</i> _{box,z} /nm
Original structure (HO)	4766	6.4	7.1	7.8
Cut from inside (HC1)	4145	5.5	5.8	6.3
Cut from inside (HC2)	2704	4.57	4.59	4.59

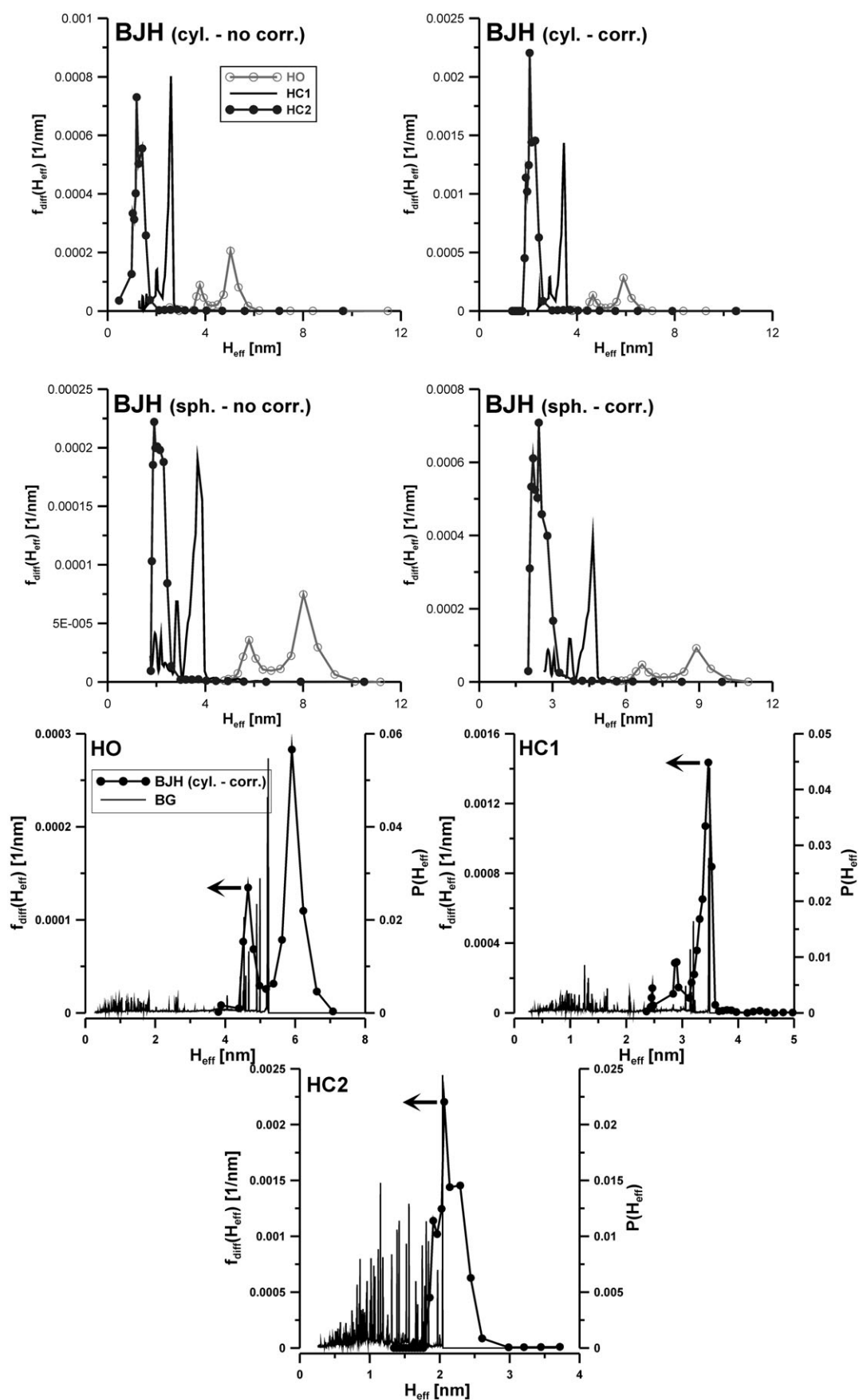


Fig. 8 PSD curves for the studied carbon structures from the BJH method (upper figures, with correction and without correction, for cylindrical and/or spherical shapes), and the comparison of the BG and BJH methods (BJH for a cylindrical meniscus with correction term).

effective width is equal to exactly 0.68 nm. Next, defects were introduced into the same pore by removing 144 atoms (firstly from inner layers only) and the pattern shown in Fig. 2 was formed (finally 2640 atoms were used in the defected structure). Thus, the effective pore diameters should be equal to 0.68 and 1.35 nm for the defected slit-like structure. Since periodic boundary conditions were applied during the simulations, we applied them also in the code using the BG method.

The PSD of the ideal graphite slit-like pore structure obtained from the BG method shows the occurrence of the peak located at 0.72 nm (Fig. 2). A small difference is caused by the detection (by the BG method) of some “pores” located inside benzene rings forming the graphite walls. For the defected graphite pore the first peak occurs exactly at the same pore width as for the ideal graphite slit, and the second peak (related to the spaces inside walls) occurs at 1.1 nm. In this case, the second pore width should be equal to 1.35 nm, and the difference is caused by the diameter of the hole formed inside the graphitic layers. Since it is too small, the testing sphere can not reach the bottom of the pore (this is shown schematically in Fig. 2). Generally, the BG method works very well and taking into account the previous results published by Bhattacharya and Gubbins³² and the results from the current paper, can be successfully applied as the reference method.

6.3 Absolute PSDs for studied carbon structures

The distribution of probability $P(H_{\text{eff}})$ curves for the initial carbon structure (HO) shows the presence of a micro-mesoporous system of pores (Fig. 3). The PSD of HC1 is in fact similar to HO but, as was expected, the ratio of micropores to mesopores increases. Finally, the HC2 structure is strictly microporous.

6.4 PSDs for simulated adsorption isotherms and comparison with the true distributions

Adsorption isotherms for Ar (87 K) obtained from GCMC simulations are shown in Fig. 4. As was expected, the development of mesoporosity (from HC2 structure to HO) leads to a conversion of simulated adsorption isotherms from type I of the IUPAC classification to type IV *i.e.* the shape changes from one typical for microporous solids to one typical for mesoporous ones. Fig. 5 shows selected snapshots (for the following values of the relative pressure, $p/p_s = 0.0001, 0.1,$ and 0.4) from the GCMC simulations and Movies S2a–S4b in the ESI† show animations of the adsorption process in all three considered structures seen in the whole box (Movies a) and inside the box (Movies b).

The simplest method of microporosity characterization is the HK method. Since this was developed only to describe microporosity, in this study we limit the results from this method to a discussion of PSDs from the micropore range. The HK method shows the presence of distributed microporosity for all structures, with a strongly marked maximum at 1 nm (Fig. 6). The development of microporosity is observed from the HO structure to HC2. It is also interesting that the average micropore diameter is recovered relatively well. This is probably caused by the quasi-Gaussian PSDs of micropores in the studied systems, since the HK method

usually leads to a single peak in the PSD covering the whole range of micropore diameters. The problem of the correctness of the HK method was studied recently for ideal carbon slits^{45,60,65–69} and needs further studies for disordered structures (which do not have quasi-Gaussian microporosity) as reported in this paper.

Differential PSD curves ($f_{\text{diff}}(H_{\text{eff}})$) calculated from the ND and NLDFT methods are shown in Fig. 7. We show here also the distribution of weights of local isotherms ($w(H_{\text{eff}})$) contributing to the global adsorption isotherm equation. One can notice relatively good compatibility between ND and NLDFT as expected.^{15,16} In fact both methods show that the HC2 structure is the most microporous, the HC1 structure contains some amount of mesopores and the HO structure is micro-mesoporous. It seems that NLDFT gives slightly better results than the ND method. For instance, the true PSD for HC1 has a large spike about 3.5 nm; the NLDFT PSD peak is much closer to this spike. The same is observed for HC2. The most important finding is the detection of a bimodal microporous structure for all three carbon models. This is usually observed on the PSDs of real microporous carbons calculated from DFT (ND) software connected with sorption apparatus. In fact from Fig. 7 one can observe that the BG method in the range of microporosity shows quasi-Gaussian PSD curves. Therefore, the slit-like model of micropores and the neglecting of pore connectivity lead to an absence of pores around *ca.* 1 nm on the PSD curve. Both methods show the presence of mesopores, and the diameters of that type of pore are recovered relatively well, especially for the HO structure. Fig. 8 shows the results from the BJH method. Here the assumption of a cylindrical meniscus and the correction proposed by Kruk and others^{54,55} leads to the most reasonable results. As one can see from Fig. 8, the PSDs in the range of mesopores for the HO and HC1 structures are reasonable, while for HC2 structure the corrected BJH method can detect even the widest micropores. In the case of the HO structure, mesopores are created in the corners of the simulation box. Therefore the shape of the meniscus is probably not spherical or cylindrical but should be approximated in a different way.

7. Conclusions

In this study we have attempted to calculate the properties of a non-graphitizing carbon with a structure constructed from fullerene-like elements, *i.e.* small fragments of curved sp^2 carbon sheets containing non-hexagonal rings. We first calculated the density of the proposed model and found reasonable values, compared to experimental ones, suggesting that the model is a realistic one. Next, using the method proposed by Bhattacharya and Gubbins,³² we calculated the pore size distributions of the initial model and two related carbon models. Then, using the GCMC method, adsorption isotherms of Ar (87 K) were simulated for all the structures. The shapes of the Ar isotherms simulated using the new carbon models corresponded very well with the pore diameters detected by the BG method. Pore size distribution curves were then calculated using the Horvath–Kawazoe, NLDFT, Nguyen and Do, and BJH approaches. It was found that the HK model led to the most reliable PSDs in the range of micropores, assuming a

fullerene-like carbon structure. The assumption of a slit-like pore shape and the failure to take pore connectivity into account are the two major effects leading to bi-modal PSDs of real activated carbons (the range of mesoporosity is reproduced well). The corrected BJH method with the assumption of a cylindrical meniscus shape recovers relatively well the porosity in the range of mesopores.

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