

Can carbon surface oxidation shift the pore size distribution curve calculated from Ar, N₂ and CO₂ adsorption isotherms? Simulation results for a realistic carbon model

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Condens. Matter 21 315005

(<http://iopscience.iop.org/0953-8984/21/31/315005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 20:41

Please note that [terms and conditions apply](#).

Can carbon surface oxidation shift the pore size distribution curve calculated from Ar, N₂ and CO₂ adsorption isotherms? Simulation results for a realistic carbon model

Sylwester Furmaniak¹, Artur P Terzyk^{1,4}, Piotr A Gauden¹,
Peter J F Harris^{2,4} and Piotr Kowalczyk³

¹ Department of Chemistry, Physicochemistry of Carbon Materials Research Group,
N Copernicus University, Gagarin Street 7, 87-100 Toruń, Poland

² Centre for Advanced Microscopy, University of Reading, Whiteknights,
Reading RG6 6AF, UK

³ Applied Physics, RMIT University, GPO Box 2476V, Victoria 3001, Australia

E-mail: aterzyk@chem.uni.torun.pl and p.j.f.harris@rdg.ac.uk

Received 7 May 2009, in final form 8 June 2009

Published 7 July 2009

Online at stacks.iop.org/JPhysCM/21/315005

Abstract

Using the virtual porous carbon model proposed by Harris *et al.*, we study the effect of carbon surface oxidation on the pore size distribution (PSD) curve determined from simulated Ar, N₂ and CO₂ isotherms. It is assumed that surface oxidation is not destructive for the carbon skeleton, and that all pores are accessible for studied molecules (i.e., only the effect of the change of surface chemical composition is studied). The results obtained show two important things, i.e., oxidation of the carbon surface very slightly changes the absolute porosity (calculated from the geometric method of Bhattacharya and Gubbins (BG)); however, PSD curves calculated from simulated isotherms are to a greater or lesser extent affected by the presence of surface oxides. The most reliable results are obtained from Ar adsorption data. Not only is adsorption of this adsorbate practically independent from the presence of surface oxides, but, more importantly, for this molecule one can apply the slit-like model of pores as the first approach to recover the average pore diameter of a real carbon structure. For nitrogen, the effect of carbon surface chemical composition is observed due to the quadrupole moment of this molecule, and this effect shifts the PSD curves compared to Ar. The largest differences are seen for CO₂, and it is clearly demonstrated that the PSD curves obtained from adsorption isotherms of this molecule contain artificial peaks and the average pore diameter is strongly influenced by the presence of electrostatic adsorbate–adsorbate as well as adsorbate–adsorbent interactions.

 Supplementary data are available from stacks.iop.org/JPhysCM/21/315005

(Some figures in this article are in colour only in the electronic version)

1. Introduction and the aims of the study

⁴ Authors to whom any correspondence should be addressed. <http://www.chem.uni.torun.pl/~aterzyk/>, <http://www.personal.rdg.ac.uk/~scscharip/pjfhhome.htm>.

The problem of determination of the pore size distribution (PSD) curve of adsorbents, especially of porous carbons, is extremely important since the PSD determines adsorption

properties. The second factor influencing these properties is the chemical composition of the surface. The PSD curve plays a crucial role in adsorption of non-polar, while the chemical composition of the surface in adsorption of polar, compounds. Moreover, the latter strongly determines the mechanism of adsorption from aqueous solutions, where the porosity is not as important as during adsorption from the gaseous phase [1]. IUPAC recommended the application of Ar adsorption measurements for determination of the PSD curve, since this molecule, being non-polar, is not too 'sensitive' to the chemical composition of the surface. On the other hand, due to practical reasons, nitrogen adsorption isotherm determination (at the boiling point i.e. 77 K) is also the standard tool applied to determination of the PSD curve. Some authors also postulate using CO₂ measurements at ambient temperature as a fast and standard method of determination of the structural parameters of carbons [2]. This postulate is based mainly on experimental findings [3] showing that some pores can be inaccessible for nitrogen due to diffusion restriction. In fact, simulation results of Sweatman and Quirke [4] showed that nitrogen is diffusionally limited in microporous carbons, and that pore connectivity can significantly affect the adsorption of nitrogen at 77 K in carbons. This has important consequences for characterization studies of microporous carbons that employ nitrogen at this temperature. The authors also claimed that measurements of nitrogen adsorption above 90 K and CO₂ above 260 K (but below their respective bulk critical temperatures and up to their respective saturation pressures) will provide more accurate characterization of carbon porosity.

There are many different approaches to porosity characterization; however, it has not been claimed yet, to what extent the application of the three standard molecules (Ar, N₂ and CO₂) can shift the PSD curve for a realistic carbon model, i.e. to what extent the changes in porosity are in fact the changes in porosity and not only the 'apparent' changes caused by the presence of surface groups being able to interact via so called specific interactions. For example, there are many literature reports showing the application of CO₂ for characterization of porosity of chemically modified carbons. After oxidation of carbon, different oxygen surface functionalities are created. The measurement of the adsorption isotherm on such oxidized materials leads to the PSD curve. The PSD curve of the oxidized sample is often compared with the PSD of the initial one (i.e. before surface modification). But the question arises as to what extent the observed shifts on the PSD curve are due to the changes in porosity and to what extent they are due to the change in the nature of the interactions between an adsorbent and adsorbate (note that we still base this only on an isotherm being the balance between enthalpy and entropy). It seems that many researchers have forgotten the results of some experimental findings showing the strong influence of polarity of having a quadrupole moment carbon dioxide molecule on adsorption properties of modified chemically carbons. For example, Meredith and Park [5] studied adsorption of nitrogen and carbon dioxide on metal impregnated carbons and found a strong influence of polarity of CO₂ on adsorption isotherms. The next important paper showing the influence of

carbon surface chemical composition on CO₂ adsorption was published by Park and Kim [6]. They studied the behaviour of carbon modified with HCl and NaOH and their results show small changes in nitrogen adsorption isotherms (leading to similar pore volumes and BET surface areas for virgin and modified adsorbents), however remarkable changes on adsorption isotherms of ammonia and CO₂. Also recently, Samios *et al* [7], when studying the applicability of GCMC local isotherms of CO₂ simulated for carbon slit-like pores to description of experimental data, concluded that the presence of polar sites in the carbon sample considerably affects the calculated optimal PSD, especially at low temperatures. Such polar sites on the internal carbon surface lead to enhanced adsorption, which is more pronounced at low temperature and is interpreted in the PSD analysis as due to extra micropores. They noticed that caution should therefore be exercised when applying the method for the determination of micropore size distribution, and if the existence of polar sites is suspected the use of a non-polar adsorbate (e.g. Ar) may provide a more reliable picture of the micropore structure. Also Tenney and Lastoskie [8], who studied the influence of oxygen on CO₂ adsorption isotherms for different coal models, stated that the electrostatic adsorbate-adsorbent interactions significantly influenced adsorption onto coal-like model surfaces. Increasing the surface density of oxygen containing functional groups generally increased CO₂ adsorption and lowered the pore filling pressure. However, exceptions were noted, and in some cases outwardly small differences between surfaces resulted in very different isotherms. For the coal-like model pores with explicit charge interactions simulated in their study, low-pressure CO₂ uptake was significantly enhanced, and the excess adsorption at the saturation pressure was slightly increased, relative to CO₂ adsorption in comparably sized graphite slit pores. Recently Scherdel and Reichenauer [9], while comparing the structural data for the series of carbons from sucrose obtained from SAXS results with those calculated from adsorption isotherms of Ar, N₂ and CO₂, noticed the differences between porosity parameters from SAXS and from adsorption, especially for CO₂, concluding that sorption of this molecule includes 'unspecified effects' affecting the results. In their interesting study the authors did not characterize the chemical composition of the studied carbons; therefore, it can be suspected that (as will be shown below) some 'artificial' results obtained from CO₂ data can be caused by the specific interactions of this molecule with surface oxides.

To find to what extent the oxidation of carbon can change the absolute porosity (assuming that the oxidation is not destructive for the carbon skeleton) and to what extent this oxidation changes the adsorption isotherms (and the PSDs calculated from those isotherms) of all the above mentioned adsorbates, it is necessary to perform the simulation experiment, since the laboratory experiment is impossible (we do not know the method of determination of the absolute PSD curve for real carbons). This is also possible since one can use the virtual porous carbons [10–16] and among them the realistic carbon model proposed by Harris *et al* [17–19]. The application of the method described by Bhattacharya and Gubbins [20] allows determination of the absolute pore size distribution of carbon before and after chemical modification.

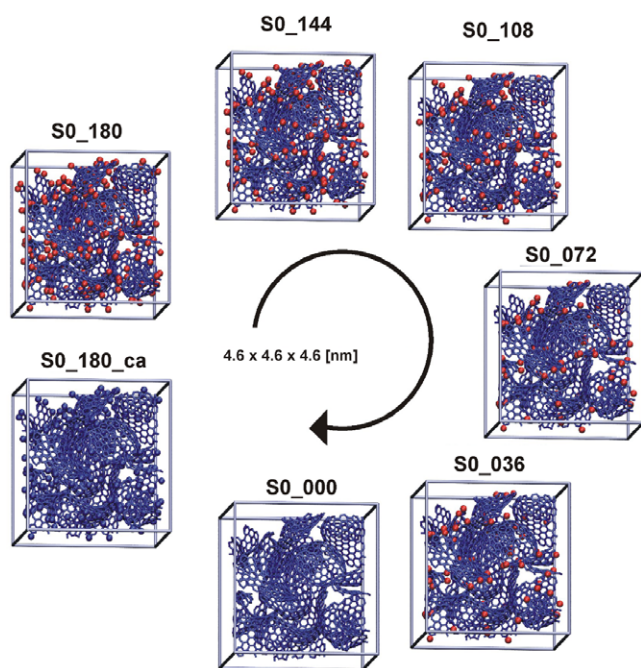


Figure 1. Schematic representation of studied simulation boxes—oxygen atoms are marked in red (spheres). The number by the symbol of the system denotes the number of surface carbonyl groups. For the structure S0_180_ca carbon atoms are introduced in the place of carbonyl oxygen atoms and this structure is called ‘carbon analogue’ (ca).

2. The method

2.1. Virtual oxidation

Two important assumptions are made. First, as mentioned above, we assume that after modification of the carbon surface the carbon skeleton remains unchanged, i.e. the modification procedure does not remove carbon from the skeleton (it can be obtained in a real experiment if the modification conditions are not drastic). The second assumption is that carbon oxygen functionalities (modelled in this study as surface carbonyls) are attached to the most reactive atoms located on the edges of the structure. This is in fact observed in many experiments, as was mentioned by Marsh and Rodriguez-Reinoso [21]. This location of surface groups also makes it possible to explain the experimental changes in adsorption isotherms determined for adsorption of non-electrolytes from aqueous solutions [1]. As the starting structure imitating the real carbon the structure called previously S0 was chosen [14]. This structure, proposed by Harris on the basis of HRTEM measurements, contains 2704 carbon atoms placed in the box having dimensions 4.6 nm × 4.6 nm × 4.6 nm (see figure 1; note that periodic boundary conditions were used in all three directions). To generate the oxidized carbon structures the program was developed. This program starts by detecting carbon atoms having a valence equal to two, i.e. being the most reactive and acting as the potential centres for bonding oxygen atoms. The attachment of oxygen (called ‘virtual oxidation’) is performed in such a way that the oxygen atom and the carbon atom attaching this oxygen (and two nearest

Table 1. The characteristics of simulation boxes.

Box label	The number of carbonyl groups	O/C ^a	{O} ^b (%)	Average pore diameter calculated from the BG method $d_{\text{eff,av}}$ (nm)
S0_180	180	0.0666	8.15	1.057
S0_144	144	0.0533	6.63	1.063
S0_108	108	0.0399	5.06	1.080
S0_072	72	0.0266	3.43	1.096
S0_036	36	0.0133	1.74	1.117
S0_000	0	0	0	1.122
S0_180_ca	0	—	—	1.048

^a The ratio of the number of oxygen/carbon atoms.

^b The mass % of oxygen in the sample mass.

neighbours of this carbon atom) lie in the same plane, and the axis of the carbon–oxygen bond is determined by the secant of the C–C–C angle (to the middle C atom the oxygen atom from the carbonyl group is attached). This oxygen atom is placed in such a way that the length of the carbon–oxygen bond is equal to 0.1233 nm [22] and that there are no overlaps between this atom and the remaining fragments of the structure. The maximum number of surface carbonyl groups which may be introduced in the studied structure is around 180 (see table 1). This number of oxygen atoms leads to a realistic (i.e. as observed in experiment) mass content of oxygen. Therefore, the starting structure of these 180 randomly introduced carbonyl groups was chosen (S0_180) and subsequent structures were generated by the random removal of 20% of the carbonyls from the starting model. In this way six different structures were obtained, starting from one almost totally saturated with carbonyls and finishing on the initial S0 without oxygen (S0_000). Each simulation box has the same dimensions as the original one and contains the same number of carbon atoms (figure 1 and table 1 show applied notation and other characteristics of the boxes).

To determine to what extent the surface chemical composition of carbon, and to what extent the porosity, determine the simulated adsorption isotherms for the structure containing the largest number of carbonyls (S0_180) the ‘carbon analogue’ (S0_180_ca) was created, where in a dummy way the oxygen atoms were replaced by carbon atoms located in the same places (the analogue contains 2884 carbon atoms).

2.2. Determination of the absolute PSD curve

To determine the absolute (geometric) PSD curve the procedure proposed by Bhattacharya and Gubbins [20] was applied [14–16]. In this method a uniform grid of points is generated in the simulation box (for studied structures 100 × 100 × 100) and for each such point (located in a pore) the largest sphere containing this point (and situated in the pore) is found. The diameter of this sphere is equal to the diameter of the pore and the collection of histograms of the diameters of pores for each such a point of the grid makes it possible to plot the histogram of the pore diameters (related to the PSD curve). The program works in an iterative way. For each node of the grid located in the structure of carbon, the centre of the testing sphere is placed randomly (at the start the coordinates

of the node are assumed as the centre of the sphere; the diameter of the sphere is limited by the distance to the nearest fragment of carbon structure). Each displacement of the centre of the sphere (the sphere must contain the test point) leading to a rise in the diameter is accepted and the next attempts of displacement are made. The program stops calculations for a given point when after 1000 subsequent iterations a sphere with a larger diameter is not found. We assumed that the radii of C and O are equal to 0.17 and 0.15 nm, respectively.

2.3. Molecular simulations

Adsorption of Ar (at 87 K), N₂ (at 77.3 K) and CO₂ (at 298 K) was studied. A typical GCMC method was applied [23]. In the case of Ar creation, translation and annihilation of atoms were applied as the methods of changing the state of the system (with the probabilities 1/3). In the case of N₂ and CO₂, where the molecules are modelled as multiple centres, additionally rotation is applied as the method of changing the state of the system (the probability of the change of state by rotation and displacement is equal to 1/6, by creation and annihilation to 1/3). In the case of these two molecules the displacement is connected with the change in the angular position. For each adsorption point 25×10^6 iterations were performed during the equilibration, and next 25×10^6 equilibrium ones, applied for the calculation of the averages (one iteration = an attempt to change the state of the system by displacement, creation or annihilation).

Argon atoms were modelled as the Lennard-Jones centres, nitrogen and carbon dioxide molecules were modelled as three centre models of the TraPPE types [24]. A truncated LJ potential was applied. Generally the energy of interactions between a pair of molecules at a distance r (for the case of N₂ and CO₂ this energy depends also on the angular position) can be written as

$$U(r) = \sum_{i=1}^N \sum_{j=1}^N U_{\text{LJ}}^{ij}(r_{ij}) + U_{\text{electr}}(r) \quad (1)$$

where N denotes the number of LJ centres (for Ar $N = 1$, for N₂ $N = 2$, for CO₂ $N = 3$), $U_{\text{LJ}}^{ij}(r_{ij})$ is the energy of dispersion interactions between a pair of centres i and j being placed at the distance r_{ij} , and calculated from the truncated LJ potential:

$$U_{\text{LJ}}^{ij}(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] & r_{ij} < r_{\text{cut},ij} \\ 0 & r_{ij} \geq r_{\text{cut},ij} \end{cases} \quad (2)$$

where σ_{ij} and ϵ_{ij} are the collision diameter and the well depth of the potential energy for interactions between i and j . The second term in equation (1) ($U_{\text{electr}}(r)$) is the energy of electrostatic interactions between a pair of molecules, which can be written as

$$U_{\text{electr}}(r) = \begin{cases} \frac{1}{4\pi\epsilon_0} \sum_{i=1}^M \sum_{j=1}^M \frac{q_i q_j}{r_{ij}} & r < r_{\text{cut,C}} \\ 0 & r \geq r_{\text{cut,C}} \end{cases} \quad (3)$$

where M is the number of point charges in the molecule (for Ar $M = 0$, for N₂ and CO₂ $M = 3$), q_i and q_j denote the values of the charges of the centres, and ϵ_0 ($8.8543 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$) is the dielectric permittivity of free space. We use the cut-offs for electrostatic interactions for the whole molecules [25], and if the centres of mass of two molecules are located at the distance smaller than $r_{\text{cut,C}}$ the sum of the energy of interactions between all pairs of charges occurring in the molecules is calculated, otherwise the electrostatic interactions are neglected. The cut-off for electrostatic interactions ($r_{\text{cut,C}}$) was assumed at 1.5 nm (the length of the box is equal to 4.6 nm). At this distance the energy of interactions of a pair of molecules is negligibly small (the energy of electrostatic interactions for studied molecules (having quadrupole moments) decreases proportionally to the fifth power of the distance [26]).

The interactions between studied molecules and the structure of the adsorbent can be written as

$$U_{\text{sf}} = \sum_{i=1}^{N_C} \sum_{j=1}^N U_{\text{LJ}}^{ij}(r_{ij}) + \sum_{i=1}^{N_K} \sum_{j=1}^2 \sum_{k=1}^M U_{\text{LJ}}^{jk}(r_{ijk}) + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N_K} \sum_{j=1}^2 \sum_{k=1}^M \frac{q_j q_k}{r_{ijk}} \quad (4)$$

where N_C is the number of carbon atoms non-bonded with oxygen and N_K is the number of carbonyl groups. For the last two terms the second summation (with respect to j) denotes the sum with respect to the atoms of the carbonyl group ($j = 1 - \text{C atom}$, $j = 2 - \text{O atom}$). For all LJ interactions the cut-offs were placed at $r_{\text{cut},ij} = 5\sigma_{ij}$. Table 2 shows the values of the parameters applied (we used the Lorentz–Berthelot mixing rules).

3. Results

Figure 2 shows the simulation results for all three adsorbates. It is seen that for Ar adsorption the changes in the chemical composition of carbon very slightly influence the adsorption isotherms, and only small differences are observed (they occur especially at low pressures). So in this case, since electrostatic interactions are absent, those differences reflect small changes in porosity caused by the virtual oxidation process. For nitrogen and carbon dioxide one can observe the rise in adsorption with the number of surface oxygen groups. Therefore, based only on N₂ and CO₂ adsorption data, one can conclude that the oxidation of the carbon surface changes the porosity of the carbon since adsorption isotherms are different, and this effect will of course change the position of the PSD curves since they are calculated from isotherms. To explain this effect in detail one can study the results from figure 3 where we show the comparison between isotherms simulated for initial carbon (S0_000—no surface oxides present), carbon with maximum number of surface oxygen groups (S0_180) and for carbon analogues (S0_180_ca) where (as mentioned above) oxygen carbonyl groups were replaced by carbon atoms. The results from this figure clearly demonstrate that the changes in adsorption isotherms after virtual oxidation are due to the electrostatic interactions between nitrogen and carbon dioxide

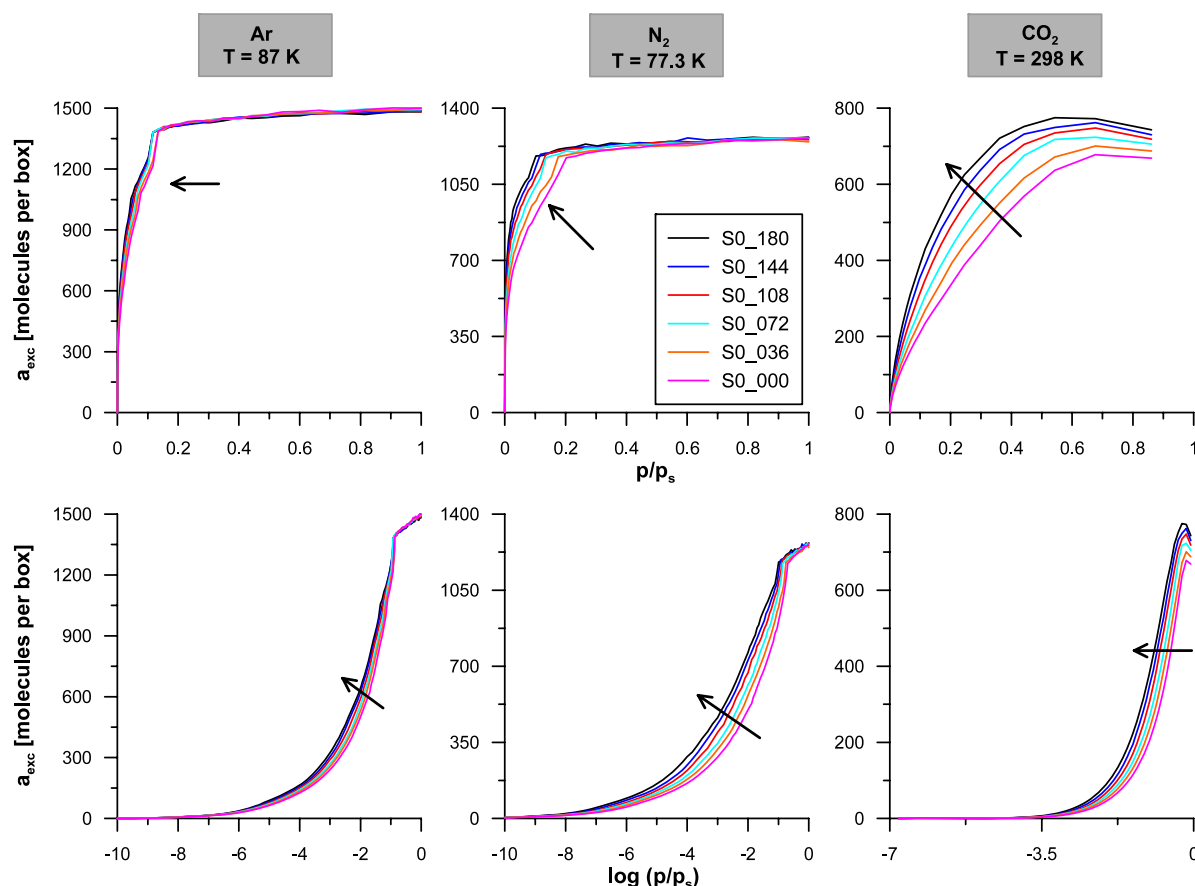


Figure 2. The plots of simulated adsorption isotherms (the arrow shows the direction from structure S0_000 up to S0_180).

Table 2. The values of LJ parameters and point charges located on the centres of studied systems.

Molecule	Geometric parameters	Centre	ε/k_B (K)	σ (nm)	q (e)	Reference
Ar	—	—	119.8	0.3405	—	[27]
N ₂	$l_{NN} = 0.110$ nm	N	36.0	0.3310	−0.482	[24]
		COM ^a	0.0	0.0000	+0.964	
CO ₂	$l_{CO} = 0.116$ nm	C	27.0	0.2800	+0.700	[24]
		O	79.0	0.3050	−0.350	
Adsorbent	$l_{CO} = 0.1233$ nm	C ^b	28.0	0.3400	—	[22]
		C ^c	28.0	0.3400	+0.500	
		O	105.8	0.2960	−0.500	

^a Centre of mass.

^b Non-carbonyl group atom of C.

^c Carbonyl group C atom.

and surface carbonyl groups (i.e. the influence of surface chemistry) and not by the changes in porosity after oxidation. Of course electrostatic interactions influence the plots of the isosteric enthalpy of adsorption (figure 4), being especially affected for N₂ and CO₂. This is the most important result for further discussion. Therefore, the influence of surface oxides is drastic, while in fact the porosity practically remains unchanged. These shifts of adsorption isotherms will lead to differences in the PSDs (but in practice the porosity is the same). The confirmation of this can be obtained if one compares the absolute PSD curves from the BG method, shown in figure 5. We observe here that the introduction of surface

carbonyl groups practically does not change the porosity (very small changes are observed for pores located around 2 nm—and they appear on Ar isotherms shown in figure 2).

To test what influence will be observed on the PSD one can use the standard procedure applied in a typical experiment, namely one can calculate the PSD curves using the typical and widely applied methods from adsorption apparatus software. To do this we can for a moment treat the simulation results as experimental ones (of course we are in a comfortable situation since we exactly know the structure of carbon, the absolute pore size distribution and the number and type of introduced surface groups). Therefore, first of all we used the Nguyen

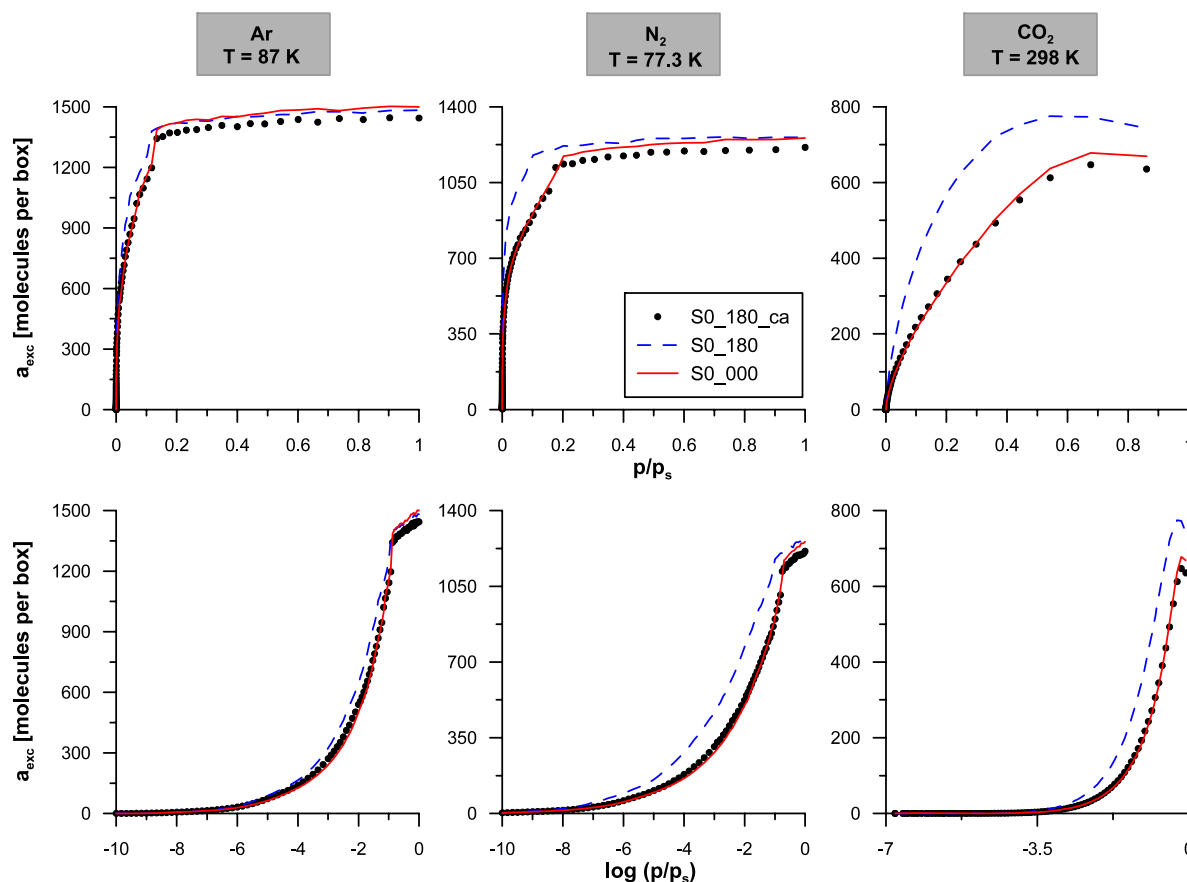


Figure 3. The comparison of adsorption isotherms simulated for carbon analogue (S0_180_ca) with those for carbon having the maximum number of surface oxygen groups (S0_180) and having no groups (S0_000).

and Do approach [28, 29] (leading to exactly the same PSDs as from the DFT software—this has been proved for many different carbons [30]) for the calculation of the PSDs from Ar and N₂ isotherms. The results shown in figure 6 confirm the presence of almost the same PSDs for all samples if they are calculated from Ar adsorption data and larger differences if the adsorption isotherms of N₂ are taken for calculations. It is seen that for the same structure the rise in oxidation shifts the nitrogen PSD to larger pore diameters. Moreover, this effect occurs even in the case of carbon without surface oxides. In this figure we also show the PSDs calculated from CO₂ local isotherms obtained using the GCMC for the series of slit-like pores (in this case we obtain very similar isotherms as published by Samios *et al* [7]) together with the (proposed previously) KAROLINA algorithm [31–33]. In the range of so called primary micropore filling the illusion appears that CO₂ detects slightly smaller pores than Ar; however, for larger pores we observe total failure of the applicability of CO₂, leading to appearance of artificial porosity even for carbon without surface oxygen groups. This puts into question the applicability of CO₂ for determination of pore size distributions of carbons (even without surface chemical groups). The results for cumulative PSDs are shown in figure S1 (available at stacks.iop.org/JPhysCM/21/315005). To check the influence of the adsorbate type as well as the virtual oxidation on the PSDs on a global scale in figure 7 we compare

the average pore diameters calculated from the whole PSD with those from the BG method (the latter are the true values). For unmodified carbon (S0_000) the deviation can be attributed to differences between adsorption mechanisms in slit-like pores and in the studied virtual carbon model. One can observe that for this carbon Ar leads to the closest value to the true one. Therefore, it can be concluded that determination of porosity by measurement of the Ar adsorption isotherm has another important advantage, i.e. low sensitivity to the deviation of pores from slit-like shape. On the other hand, due to the presence of electrostatic interactions, N₂ and especially CO₂ adsorption data can overestimate pore diameters drastically. The differences for non-oxidized and slightly oxidized carbons increase with the rise in the value of quadrupole moments of adsorbates (experimental values of quadrupole moments for N₂ and CO₂ show that for the former molecule it is half [34] or even one-third that of the latter [26]). It may seem strange that the differences in average pore diameters calculated from BG and from PSDs become smaller with the rise in the content of surface oxides. This is due to the compensation of two opposite effects i.e. the overestimation of porosity for unoxidized structure and the shift in the condensation pressure in pores containing surface oxygen groups.

Finally, to show how the surface carbonyl groups affect the adsorption mechanism we analysed molecules interacting with surface groups (i.e. adsorbed at a distance not larger than

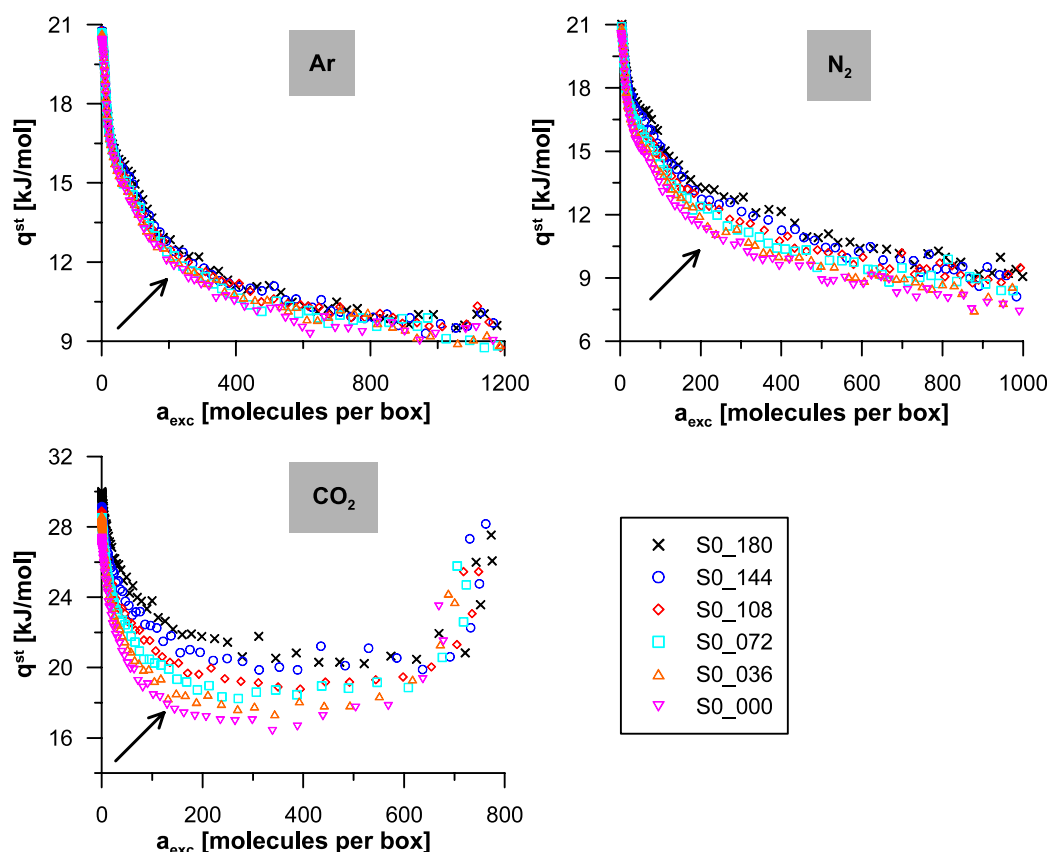


Figure 4. The plots of the isosteric enthalpy of adsorption for the systems from figure 2.

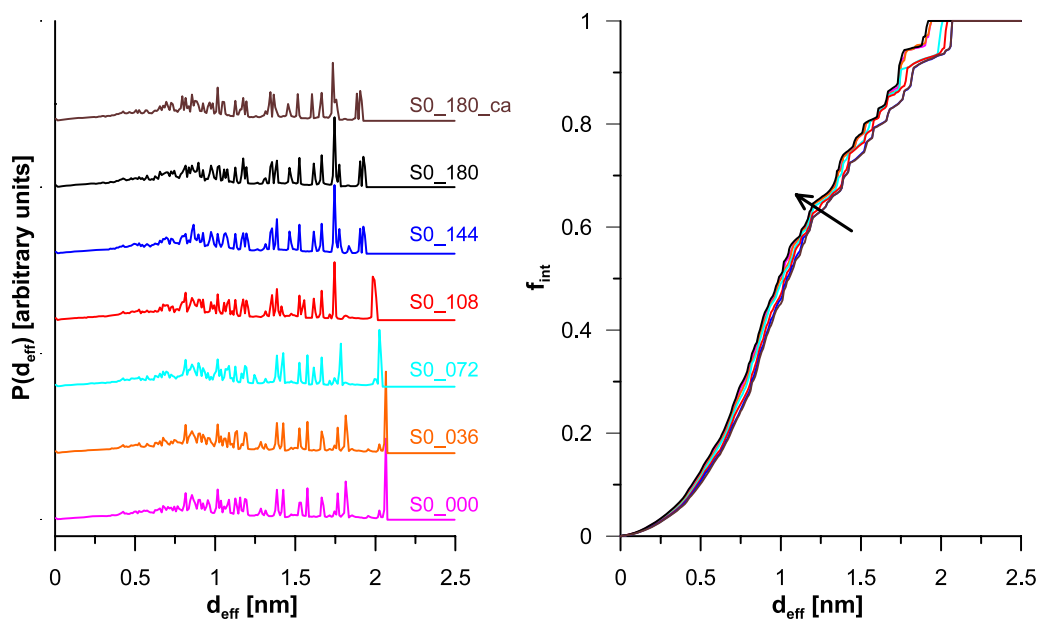


Figure 5. The histograms of pore diameters obtained from the BG method (left). Right, the integral distributions (the arrow shows the direction from structure S0_000 up to S0_180).

the collision diameter). A similar procedure was also used for the structures where those groups are not present (i.e. S0_000 and S0_180_ca), and here we marked the molecules adsorbed in the same space as determined by carbonyl groups in the structure S0_180 (see movies 1–3 from supplementary data available at stacks.iop.org/JPhysCM/21/315005. All snapshots

and movies attached to supplementary data were created using the VMD program [35, 36]). Figure 8 shows the comparison of the number of molecules adsorbed in this space for all these structures. As one can observe, the number of those molecules drastically increases from Ar up to CO₂ with the rise in surface polarity and this is consistent with the results from

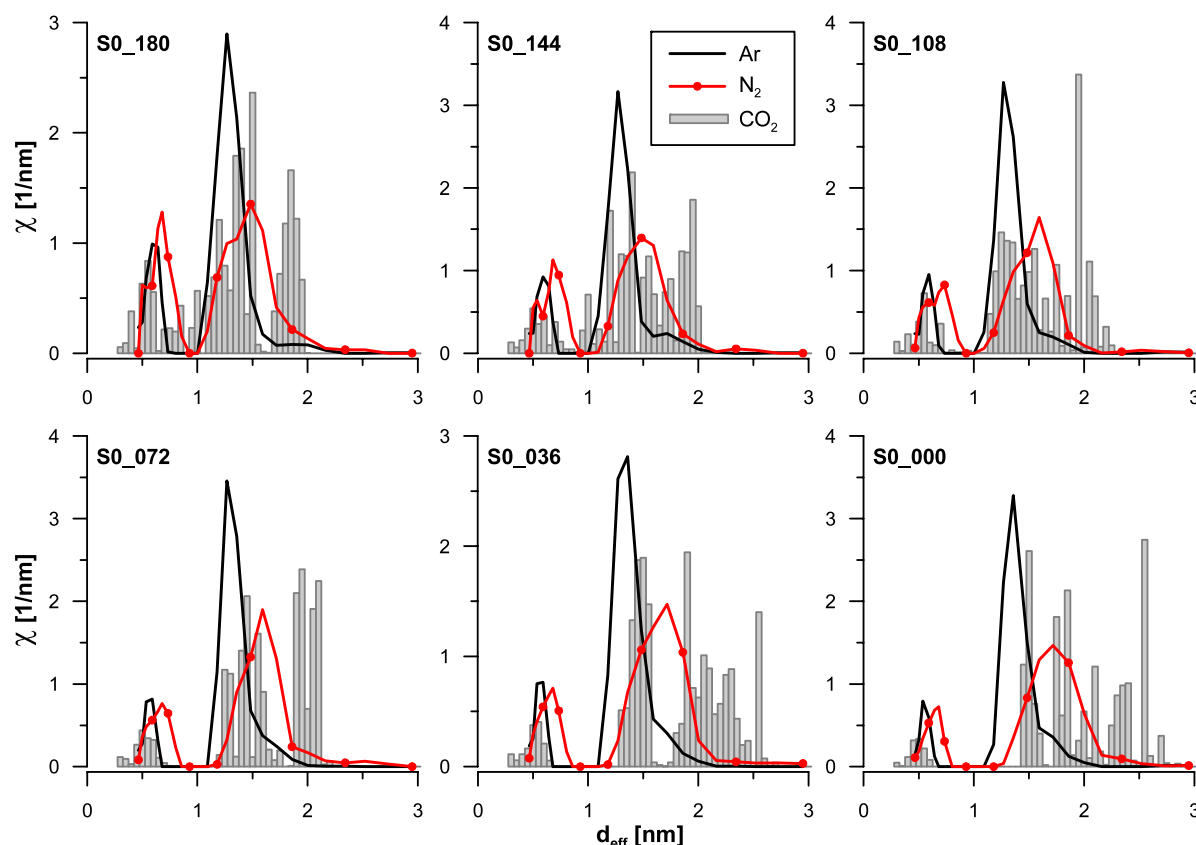


Figure 6. The comparison of the PSDs obtained from simulated isotherms described by the local isotherms generated for the slit-like pores (Ar and N₂—ND method, CO₂—local isotherms were calculated by GCMC and fitted to the global isotherm using the KAROLINA algorithm.)

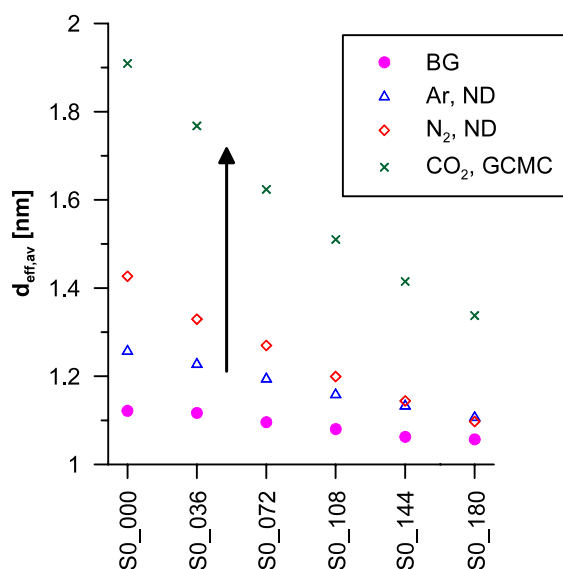


Figure 7. The comparison of the average micropore diameters obtained from the BG method with those calculated using the PSDs from figure 5. The arrow shows the rise in the value of quadrupole moments of studied molecules.

figures 2 and 3. Also interesting is that the interactions with surface carbonyls is present even at relatively low pressures. These results explain the anomalous shifts of PSDs towards

smaller diameters for CO₂ (first peak in figure 6) in the primary micropore filling range, and detection of false porosity for larger micropores.

4. Conclusions

The most important conclusions from this study are as follows. Mild oxidation of the carbon structure, if non-destructive for the carbon skeleton, practically does not change absolute carbon porosity in a drastic way. For carbon without surface oxides we observe systematic shifts of the pore size distributions towards larger diameters with the rise in the value of quadrupole moments of studied molecules. Moreover, for CO₂ some artificial peaks on the PSD are seen, especially in the range of larger pores. This effect is strongly pronounced after introduction of surface oxygen groups. Our results also show that Ar is a ‘safe’ molecule for determination of PSD and the average pore diameter of activated carbons. Moreover, for this molecule the approach of the porosity of real carbon by the system of slit-like pores can be applied as a rough approximation, and the values of approximate average pore diameters can be calculated even for carbons having large numbers of surface oxides. In contrast, the results of PSD calculation from CO₂ adsorption isotherms are questionable even for carbons without surface oxygen groups. Since in the current paper only one carbon structure was studied, we

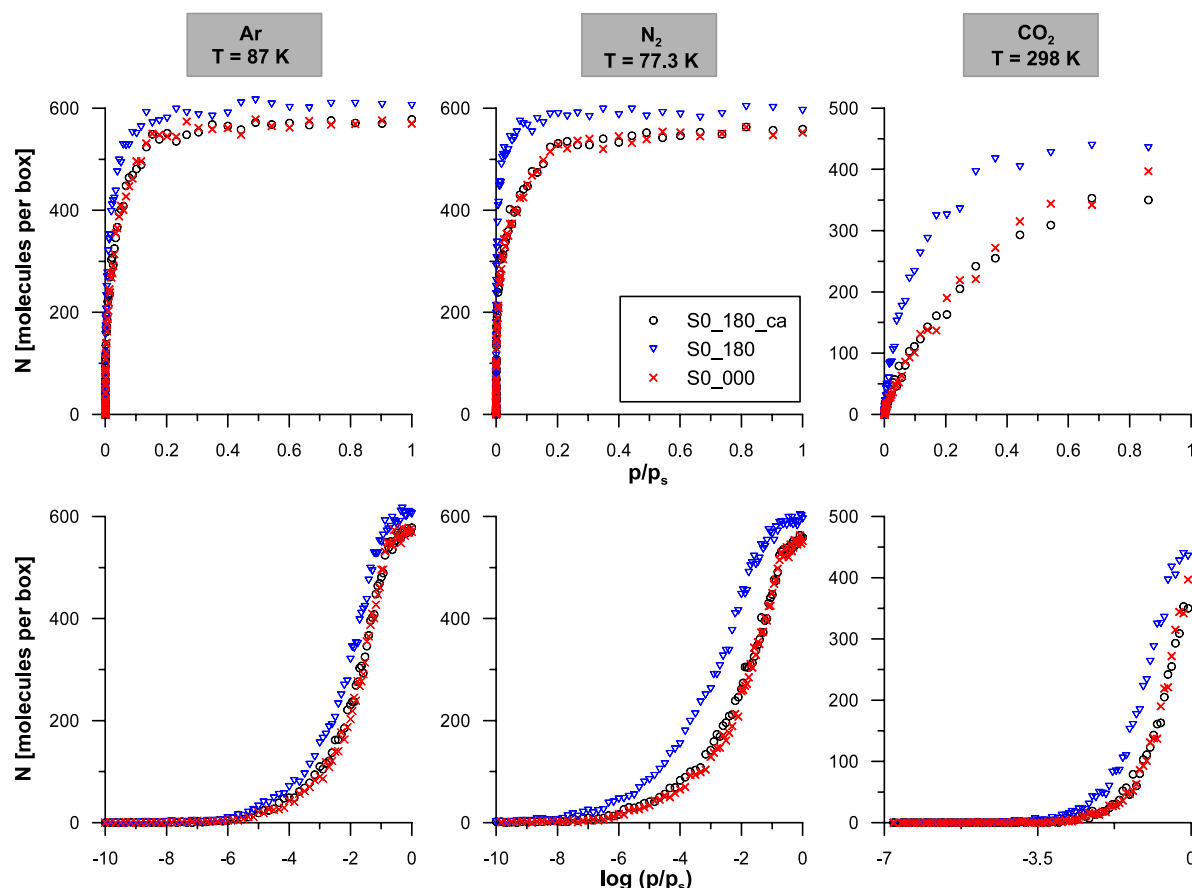


Figure 8. The number of molecules interacting with surface oxygen groups (if present) or adsorbed in the space where these interactions would occur if the groups were present (unoxidized carbons).

plan to perform additional simulations for more microporous carbons and to check how the introduction of different surface groups influences the results of micropore volumes and pore diameters calculated from Dubinin's type analysis. Some molecular dynamics simulations of CO₂ diffusion in studied VPC structures could also be interesting. This will be the subject of our future studies.

Acknowledgments

The authors acknowledge the use of the computer cluster at Poznań Supercomputing and Networking Center and the Information and Communication Technology Center of the Nicolaus Copernicus University (Toruń, Poland). The project was supported by grants N204 009934 (2008–2010, APT and SF) and N N204 288634 (2008–2010, PAG). SF gratefully acknowledges the financial support from the Foundation for Polish Science.

References

- [1] Terzyk A P 2004 *J. Colloid Interface Sci.* **275** 9
- [2] Lozano-Castello D, Cazorla-Amoros D and Linares-Solano A 2004 *Carbon* **42** 1233
- [3] Cazorla-Amoros D, Alcaniz-Monge J and Linares-Solano A 1996 *Langmuir* **12** 2820
- [4] Sweatman M B and Quirke N 2000 *Langmuir* **17** 5011
- [5] Meredith J M and Park C A 1967 *J. Chem. Eng. Data* **12** 259
- [6] Park S J and Kim K D 1999 *J. Colloid Interface Sci.* **212** 186
- [7] Samios S, Stubos A K, Papadopoulos G K, Kanellopoulos N K and Rigas F 2002 *J. Colloid Interface Sci.* **224** 272
- [8] Tenney C M and Lastoskie C M 2006 *Environ. Prog.* **25** 343
- [9] Scherdel C and Reichenauer G 2009 *Carbon* **47** 1102
- [10] Biggs M J, Buts A and Williamson D 2004 *Langmuir* **20** 5786
- [11] Biggs M J, Buts A and Williamson D 2004 *Langmuir* **20** 7123
- [12] Biggs M J and Buts A 2006 *Mol. Simul.* **32** 579
- [13] Cai Q, Buts A, Biggs M J and Seaton N A 2007 *Langmuir* **23** 8430
- [14] Terzyk A P, Furmaniak S, Gauden P A, Harris P J F, Włoch J and Kowalczyk P 2007 *J. Phys.: Condens. Matter* **19** 406208
- [15] Terzyk A P, Furmaniak S, Harris P J F, Gauden P A, Włoch J, Kowalczyk P and Rychlicki G 2007 *Phys. Chem. Chem. Phys.* **9** 5919
- [16] Terzyk A P, Furmaniak S, Gauden P A, Harris P J F and Włoch J 2008 *J. Phys.: Condens. Matter* **20** 385212
- [17] Harris P J F and Tsang S C 1997 *Phil. Mag. A* **76** 667
- [18] Harris P J F 1997 *Int. Mater. Rev.* **42** 206
- [19] Harris P J F, Liu Z and Suenaga K 2008 *J. Phys.: Condens. Matter* **20** 362201
- [20] Bhattacharya S and Gubbins K E 2006 *Langmuir* **22** 7726
- [21] Marsh H and Rodriguez-Reinoso F 2006 *Activated Carbon* (Amsterdam: Elsevier)
- [22] Jorge M, Schumacher C and Seaton N A 2002 *Langmuir* **18** 9296
- [23] Frenkel D and Smit B 1996 *Understanding Molecular Simulation* (San Diego, CA: Academic)
- [24] Potoff J J and Siepmann J I 2001 *AIChE J.* **47** 1676

- [25] Ungerer P, Tavitian B and Boutin A 2005 *Applications of Molecular Simulation in the Oil and Gas Industry* (Paris: Edition Technip)
- [26] Gray C G and Gubbins K E 1984 *Theory of Molecular Fluids* vol 1 (Oxford: Clarendon)
- [27] Do D D and Do H D 2005 *Fluid Phase Equilib.* **236** 169
- [28] Nguyen C and Do D D 1999 *Langmuir* **15** 3608
- [29] Gauden P A, Terzyk A P, Rychlicki G, Kowalczyk P, Ćwiertnia M S and Garbacz K 2004 *J. Colloid Interface Sci.* **273** 39
- [30] Kowalczyk P, Terzyk A P, Gauden P A, Leboda R, Szmechtig-Gauden E, Rychlicki G, Ryu Z and Rong H 2003 *Carbon* **41** 1113
- [31] Furmaniak S, Terzyk A P, Gauden P A, Lota K, Frąckowiak E, Béguin F and Kowalczyk P 2008 *J. Colloid Interface Sci.* **317** 442
- [32] Furmaniak S, Terzyk A P, Gauden P A and Jaroniec M 2008 *Microporous. Mesoporous. Mater.* **116** 665
- [33] Bałys M R, Czepirski L, Furmaniak S, Terzyk A P and Gauden P A 2009 *Proc. 8th Int. Symp. COPS* p 240
- [34] Hirschfelder J O, Curtis C F and Bird R B 1954 *Molecular Theory of Gases and Liquids* (New York: Wiley)
- [35] Humphrey W, Dalke A and Schulten K 1996 *J. Mol. Graph.* **14** 33
- [36] <http://www.ks.uiuc.edu/Research/vmd/>