

Carbon slit pore model incorporating surface energetical heterogeneity and geometrical corrugation

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Abstract In our recent paper (Jagiello and Olivier, Carbon 55:70–80, 2013) we considered introducing energetical heterogeneity (EH) and geometrical corrugation (GC) to the pore walls of the standard carbon slit pore model. We treated these two effects independently and we found that each of them provides significant improvement to the carbon model. The present work is a continuation of the previous one, as we include both effects in one comprehensive model. The existing standard slit pore model widely used for the characterization of activated carbons assumes graphite-like energetically uniform pore walls. As a result of this assumption adsorption isotherms calculated by the non-local density functional theory (NLDFT) do not fit accurately the experimental N₂ data measured for real activated carbons. Assuming a graphene-based structure for activated carbons and using a two-dimensional-NLDFT treatment of the fluid density in the pores we present energetically heterogeneous and geometrically corrugated (EH–GC) surface model for carbon pores. Some parameters of the model were obtained by fitting the model to the reference adsorption data for non-graphitized carbon black. For testing, we applied the new model to the pore size analysis of porous carbons that had given poor results when analyzed using the standard slit pore model. We obtained an excellent fit of the new model to the experimental data and we found that the typical artifacts of the standard model were eliminated.

Keywords Characterization of porous carbons · Pore size distribution · Non-local density functional theory · Modification of the standard carbon slit pore model

1 Introduction

In the first application (Seaton et al. 1989) of a molecular model for the characterization of the pore size distribution (PSD) of activated carbons, the carbon pores were modeled as slits between infinitely extended graphitic walls. Due to its simplicity, the slit pore model has become the standard in the development of methods for the characterization of carbon PSD. The solid–fluid interaction potential in this model was described by the closed form formula (Steele 1973). Various approaches for calculating densities of fluids adsorbed in such pores have been employed. Application of molecular models was initiated using density functional theory (DFT) in its local version (Evans and Tarazona 1984) this approach was then refined by using more advanced fluid theories such as non-local DFT (NLDFT) (Tarazona 1985, 1987; Lastoskie et al. 1993; Olivier et al. 1994) and the fundamental measure theory (Rosenfeld 1989) as well as grand canonical Monte Carlo simulations (GCMC) (Samios et al. 1997; López-Ramón et al. 1997; Ravikovitch et al. 2000; Konstantakou et al. 2006).

A typical procedure for the determination of the PSD of porous carbons from adsorption data consists of two parts: calculating a kernel that is a series of model adsorption isotherms for a series of pore widths and then fitting this kernel to the experimental data. Weights associated with the model isotherms obtained from the fitting procedure represent the calculated PSD. The most commonly used kernels for the characterization of porous carbons were

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kernels calculated using NLDFT for N₂ at 77 K and Ar at 87 K assuming standard slit pore model. Over time, however, two artifacts have become apparent in the PSD calculation results: the sharp minimum in the PSD plot at about 10 Å, and the typical S-shaped deviation between the theoretical and experimental isotherms occurring in the case of nitrogen data near 10⁻⁴ *p/p*₀.

A broad discussion by several authors (Olivier 1998; Jagiello and Tolles 1998; Ravikovitch et al. 2001; Nguyen and Bhatia 2004; Ustinov et al. 2006; Neimark et al. 2009; Lueking et al. 2009) pointed out that the source of these artifacts is in the assumed energetical homogeneity of the carbon pores. Theoretical adsorption isotherms calculated for such ideal pores are not able to fit accurately the experimental data for real carbons. Several modifications to the standard slit pore model have been proposed to introduce some form of energetical heterogeneity (EH) to the pore space of the model. Since the solid–fluid interaction potential depends on the geometrical structure, the EH was introduced via variable pore wall thickness (Ravikovitch et al. 2001; Nguyen and Bhatia 2004).

Finite pore models represent another modification of the carbon pore geometry that introduces energy heterogeneity due to the reduced interaction potential near the pore edge. The effects of finite sizes have been studied using theoretical and molecular simulation methods (Marini Bettolo Marconi and Van Swol 1989; Sarkisov and Monson 2001; Wongkoblap and Do 2006; Siderius and Gelb 2009). In this category, we have discussed finite slit pore geometries such as channels and pores confined between parallel graphene discs and strips (Jagiello and Olivier 2009; Jagiello et al. 2011).

A different carbon structure was assumed in the models developed by Ustinov et al. (2006) and Neimark et al. (2009). These two models differ in details and theoretical treatment but essentially, they both treat carbon as an amorphous solid with variable density near the surface.

In our recent paper (Jagiello and Olivier 2013) we provided a more detailed review of modifications proposed to improve the standard slit pore model and we also presented modifications that introduce surface EH and geometrical corrugation (GC) to the model pore walls. We treated these two effects independently and we found that each of them provides significant improvement to the carbon model. The present work is a natural extension of the previous one, as we include both effects in one comprehensive model. We assume graphene-based carbon structure and use the two-dimensional (2D)-NLDFT calculations to study the combined effects of surface curvature and EH on adsorption on open carbon surfaces and in the model carbon pores. The long-standing concept of a graphene-based structure of activated carbons has been recently strongly confirmed by the new scanning transmission electron microscopy (STEM) study (Guo et al. 2012). The atomic-resolution images

presented in this study show that the nanoporous carbons consist of curved, defective graphene sheets. The analysis of a large number of images led the authors of this study to the conclusion that the carbon building blocks are mostly composed by the hexagonal carbon lattice.

2 Results and discussion

2.1 Energetically heterogeneous and geometrically corrugated (EH–GC) surface model

In addition to the geometrical effects discussed in the introduction, the surface EH of real carbons may be due to several factors such as chemical composition, impurities, and surface chemical groups. The “chemical” influence on the surface EH was first modeled using DFT by adding a periodic function to the solid–fluid–solid interaction potential in the direction parallel to the pore wall (Röcken et al. 1998; Huerta et al. 2000).

For clarity, in our recent paper (Jagiello and Olivier 2013) we discussed the effects of surface EH and GC separately. Here however, we consider these two effects jointly, which is more realistic for modeling real activated carbons.

The EH–GC model that we present in this work is a modification of the standard slit pore model with uniform pores still commonly used to describe pore structure of porous carbons. The solid–fluid interaction potential ϕ_{sf} for a gas molecule interacting with an infinite uniform graphitic slab is usually described by the Steele potential (1973) that is a sum of two components

$$\phi_{sf}(z) = \phi_1(z) + \phi_\infty(z), \quad (1)$$

where z is the distance from the centers of surface atoms in graphite, ϕ_1 is the potential of interaction with the surface graphitic layer and ϕ_∞ represents the sum of interactions with all other layers of graphite. Practically, the surface layer contributes about 87 % and the first three layers contribute 99 % to the value of ϕ_{sf} at the potential minimum. For the energetically uniform surface these potentials can be expressed in the following closed forms:

$$\phi_1(z) = A \left[\frac{2}{5} \left(\frac{\sigma_{sf}}{z} \right)^{10} - \left(\frac{\sigma_{sf}}{z} \right)^4 \right], \quad (2)$$

$$\phi_\infty(z) = - \frac{A \sigma_{sf}^4}{3\Delta(z + 0.61\Delta)^3}. \quad (3)$$

The composite parameter A is given by

$$A = 2\pi\sigma_{sf}^2\varepsilon_{sf}\rho_s\Delta, \quad (4)$$

where ε_{sf} and σ_{sf} are the Lennard-Jones (LJ) solid–fluid interaction parameters, ρ_s and Δ are the density and

interlayer distance of graphite. The total external potential of interaction between a molecule and the slit pore V_{ext} , also called the wall potential, is written as

$$V_{ext}(z) = \phi_{sf}\left(\frac{1}{2}H + z\right) + \phi_{sf}\left(\frac{1}{2}H - z\right), \tag{5}$$

where H is the pore width measured between the centers of atoms composing the surface planes of the opposite walls.

In our modified pore model, we describe the pore wall potential in two dimensions, $V_{ext}(x, z)$. This potential varies in the x and z directions but is independent of the y direction. The 2D description of the system allows considering spatial non-uniformity of surfaces.

The effective surface EH can be a combined effect of several factors including variation of the energy parameter ϵ_{sf} and surface density ρ_s . To account for this heterogeneity we introduce a function $F(x)$ that describes the variation of the energy of surface sites. For convenience in applying periodic boundary conditions, we express this function as a trigonometric series

$$F(x) = \sum_{k=1}^n \beta_k \sin(2\pi kx/\lambda), \tag{6}$$

where β_k are the adjustable parameters and λ defines the periodicity.

Curvature of graphenes is another source of EH of porous carbons. Since early studies of Franklin (1951) it has been understood that carbon structure consists of more or less curved graphene layers and recent studies using high resolution electron transmission microscopy (HRTEM) (Pre et al. 2013) and STEM (Guo et al. 2012) confirmed this concept and showed (Pre et al. 2013) that there is a certain degree of parallelism between curved layers.

Here we describe the corrugation of graphene sheets by a simple sine curve

$$t(x) = \alpha \sin(2\pi x/\lambda), \tag{7}$$

where α is the amplitude of corrugation.

For simplicity, the variation of surface energy and corrugation are introduced in our model only to the surface layer and the potential ϕ_1 is calculated by integration of the LJ potential in two steps. First, analytical integration over the y variable yields the following integral of one variable that can be easily evaluated by numerical integration

$$\phi_1(x, z) = A \int F(x) \left[\frac{63}{512} \left(\frac{\sigma_{sf}}{q}\right)^{11/2} - \frac{3}{16} \left(\frac{\sigma_{sf}}{q}\right)^{5/2} \right] g dx', \tag{8}$$

where

$$q = (z + t(x'))^2 + (x - x')^2, \tag{9}$$

$$g = \sqrt{1 + (dt/dx')^2}. \tag{10}$$

Function g in Eq. (8) appears because the integration is performed over the curved surface. The full solid–fluid interaction potential for the EH–GC surface is obtained by modification of Eq. (1)

$$\phi_{sf}(x, z) = \phi_1(x, z) + \phi_\infty(z + \alpha), \tag{11}$$

where ϕ_∞ is shifted by α to avoid geometrical overlapping of the two components of ϕ_{sf} . For consistency with the Steele potential, ϕ_∞ is calculated by Eq. (3) but conceptually it can be viewed as a background potential exerted by the adjacent carbon structure whose exact form is unknown.

The total external potential for the carbon pore is defined by Eq. (5). This form of the external potential with ϕ_{sf} given by Eq. (11) may be regarded as a description of the model of adsorption in energetically heterogeneous and geometrically corrugated (EH–GC) carbon pores. We use this model to study the effects of the pore heterogeneity on nitrogen adsorption at 77 K. We apply the implementation of Tarazona’s NLDFT (1985, 1987) described by Lastoskie et al. (1993) to calculate equilibrium fluid densities and theoretical isotherms of adsorption in the pores and on the open surface of carbons. We use values of the LJ interaction parameters that were previously reported (Jagiello et al. 2011) and that are very similar to those used by other authors (Lastoskie et al. 1993; Ravikovitch et al. 2000). In the calculations, periodic boundary conditions were applied in the x direction.

The most appropriate surface model for analyzing the PSD of a given activated carbon would be the model that accurately describes adsorption on the open surface of the pore walls of that carbon. Currently, however, such data are not available, so we follow other studies (Ustinov et al. 2006; Neimark et al. 2009) where the experimental data for non-graphitized carbon black BP 280 (Kruk et al. 1997) were treated as a reference of N₂ adsorption on the a non-porous heterogeneous surface. In our recent paper (Jagiello and Olivier 2013) we found that using the GC surface model with $\alpha = 0.4$ and $\lambda = 5.0$ as corrugation parameters it was possible to obtain relatively good agreement with the reference data and that the calculated isotherm did not show any layering transitions. In contrast, the EH surface model did not eliminate the layering transitions associated with the formation of the second and higher layers. Here, we assume $\alpha = 0.45$ and $\lambda = 6.0$ which represent slightly smaller relative amplitude of surface corrugation ($\alpha/\lambda = 0.075$) than in the case of the previous study and we attempt to fit the reference data with our EH–GC surface model in the relative pressure range from 10^{-6} to 0.1. A reasonably good fit (Fig. 1) by the least squares method was obtained with the following parameters: $\beta_1 = 0.065$ and $\beta_2 = 0.565$.

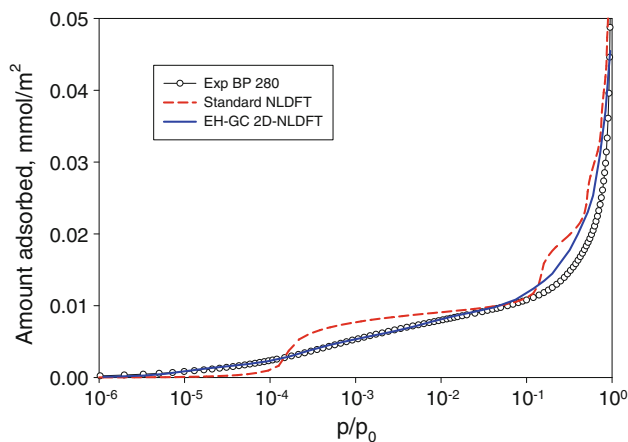


Fig. 1 Comparison of the N_2 adsorption isotherms calculated using standard NLDFT model, the new EH-GC surface model and the reference experimental data for BP 280

In Fig. 1 we also included the standard NLDFT model isotherm to show the dramatic difference in shape and values between that isotherm and the BP 280 data. In contrast, the isotherm based on the EH-GC model is in a good agreement with the reference data in the relative pressure range up to about 0.1 p/p_0 and it does not exhibit any visible layering transitions.

Figure 2 illustrates the effects of surface EH and corrugation on the external potential calculated for the open surface. We can clearly observe local variations of this potential influenced by these two factors. As expected, concave areas of the surface generate lower values the potential i.e. stronger interactions with adsorbed molecules than the convex areas.

The total external potential V_{ext} of a pore with the EH-GC surface is given by Eq. (5) where ϕ_{sf} is calculated using Eq. (11). We choose the configuration of the opposite pore walls to be “in phase”. In such configuration, the pore width H defined as the distance measured between the centers of the surface carbon atoms of the opposite walls is

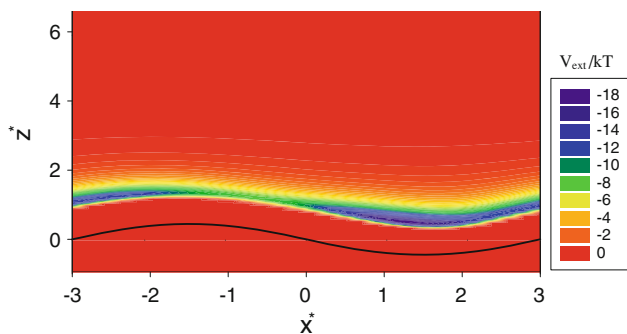


Fig. 2 Effect of the surface curvature and energy site distribution on the external potential. *Black solid line* shows the location of the surface graphene. The reduced coordinates are used in this figure: $x^* = x/\sigma_{ff}$, $z^* = z/\sigma_{ff}$

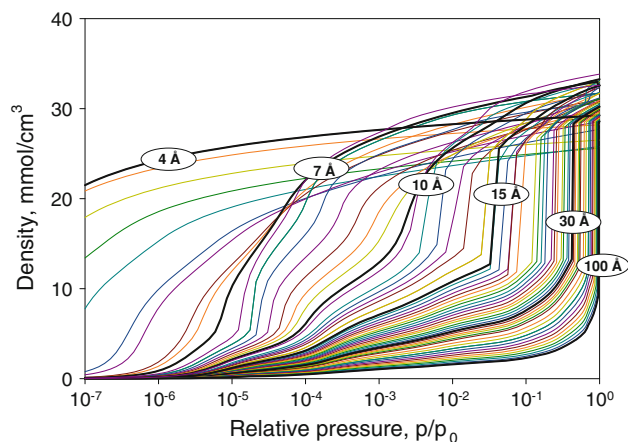


Fig. 3 Selected 2D-NLDFT isotherms for N_2 adsorption at 77.3 K calculated for the carbon slit pore model with surface EH and GC

constant for a given pore. The N_2 adsorption isotherms selected from the kernel calculated for this model are shown in Fig. 3. The isotherms are expressed in terms of the average fluid densities calculated per effective pore volume. Pore size in our approach is defined as the effective pore width (Everett and Powl 1976) $w = H - 3.4 \text{ \AA}$. Labels attached to isotherms calculated for several pores show values of their pore sizes. In accordance with the isotherm calculated for the open heterogeneous surface (Fig. 1) the isotherms of this kernel do not exhibit any layering transitions. As discussed in the introduction, this should improve the PSD analysis of the N_2 isotherms measured for porous carbons.

It is interesting to investigate the relationship between the kernel isotherms and the isotherm calculated for the open surface. In Fig. 4 we compare three isotherms for pores larger than 15 Å in size expressed in terms of the amount adsorbed per surface area of the pore with the

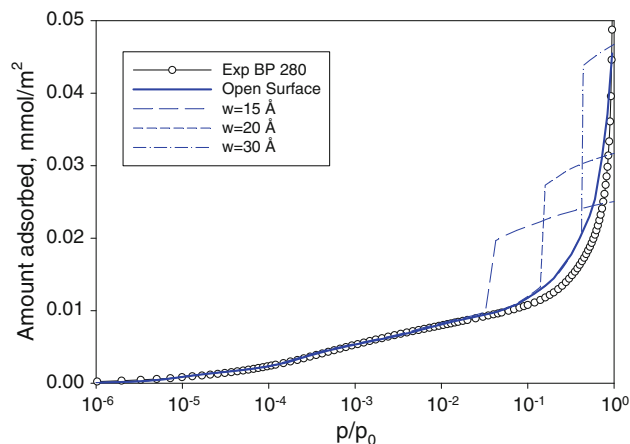


Fig. 4 Selected 2D-NLDFT isotherms for N_2 adsorption calculated for carbon slit pores and open surface compared with experimental data for BP 280

curve that was obtained by fitting the reference data. The kernel isotherms follow exactly the calculated surface isotherm up to the point of condensation in a given pore. This demonstrates that the reference used in the kernel development imprints its signature in the part of the kernel data related to the larger pores.

To better envision the impact of heterogeneity and corrugation on the calculated adsorption isotherms we show how the pores are being filled during adsorption for an example pore of width $H = 27 \text{ \AA}$. We calculated density profiles at increasing pressures for nitrogen at 77.3 K in that pore. The calculated cross-sectional contours of the local N_2 densities are shown in Fig. 5. As expected, the fluid densities near the walls are strongly affected by the EH and curvature of the walls, especially at low relative pressures. It is clear that the densities in the first and second layer increase with pressure faster in the areas where wall potential is stronger and slower in the areas of weaker potential. As a result, the increase of the average fluid density in the pores with EH–GC surfaces is more gradual than in a homogeneous pore where a whole layer is completed at the same pressure causing the layering transition effect. Moreover, fluid layers in the pores with EH–GC surfaces are completely disrupted at higher pressures, which is mostly due to the GC that has a stronger influence on the molecular order of the confined fluid than the EH alone. Similar effects were demonstrated in the GCMC

study (Kuchta et al. 2008) of methane adsorption in cylindrical pores with heterogeneous walls.

To test the new model we use N_2 adsorption isotherms measured on porous carbons PC58 and -76 derived from poly(ethylene terephthalate) precursor with different degrees of burn-off and analyzed elsewhere (Jagiello et al. 2007). We choose these data, because their PSD analysis with the standard NLDFT model showed significant artifacts. These data were also analyzed in our most recent paper and thus this allows for gaining a perspective on similarity and differences between different models. We evaluate the PSDs for the two carbons using our new EH–GC kernels and perform calculation using the numerical algorithm SAIEUS (Jagiello 1994) which solves the adsorption integral equation utilizing splines and a regularization procedure.

The results of the PSD analysis obtained using the new and standard models are compared in Figs. 6 and 7. Part (a) of each of these figures compares the goodness of fit to the experimental data by the new and standard models. The important improvement of the new model is elimination of the significant S-shaped deviations of the fit from the data produced by the standard model. The standard deviations of fit calculated in the whole range of data with the new model are reduced by more than 60 % from their values for the standard model. In the pressure range between 10^{-5} and $10^{-2} p/p_0$ this deviation reduction is 80 %. Comparing

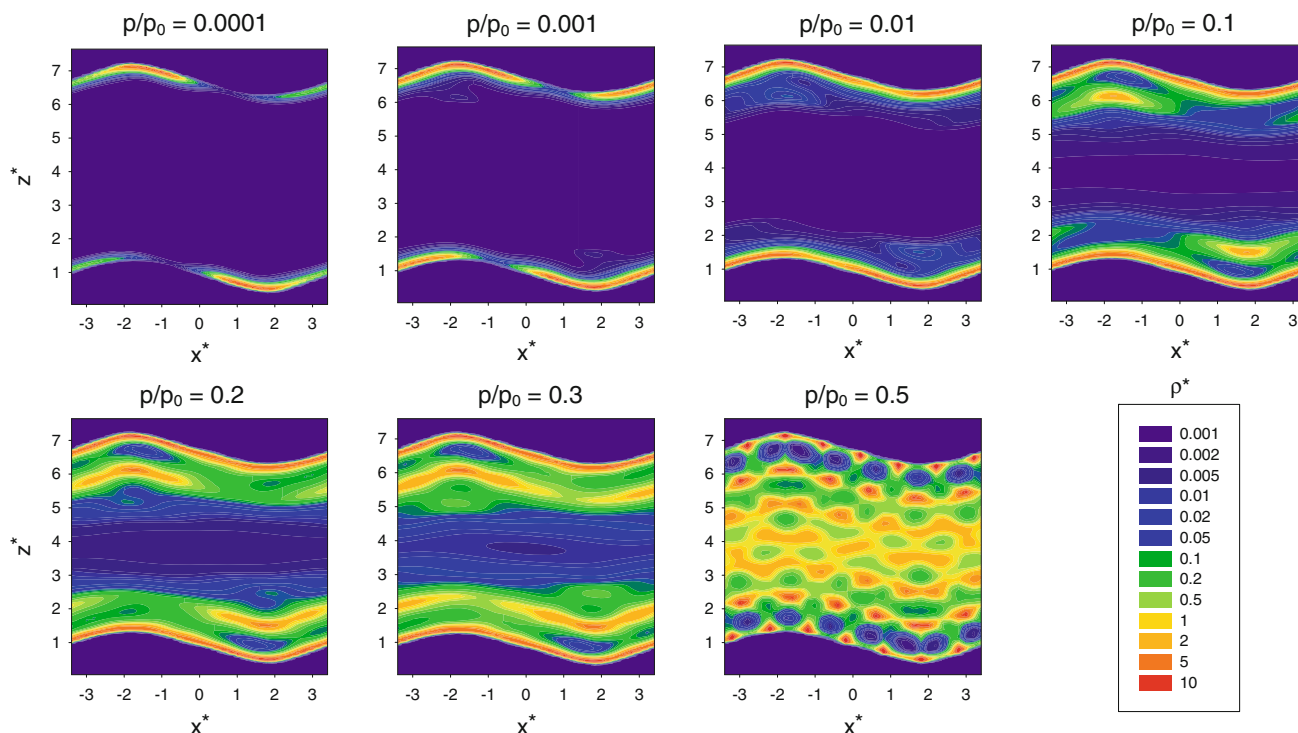


Fig. 5 Calculated cross-sectional contours of the local N_2 densities at 77 K at increasing relative pressures in the pores with the EH–GC surfaces. The reduced variables are used in this figure: $x^* = x/\sigma_{ff}$, $z^* = z/\sigma_{ff}$ and $\rho^* = \rho\sigma_{ff}^3$

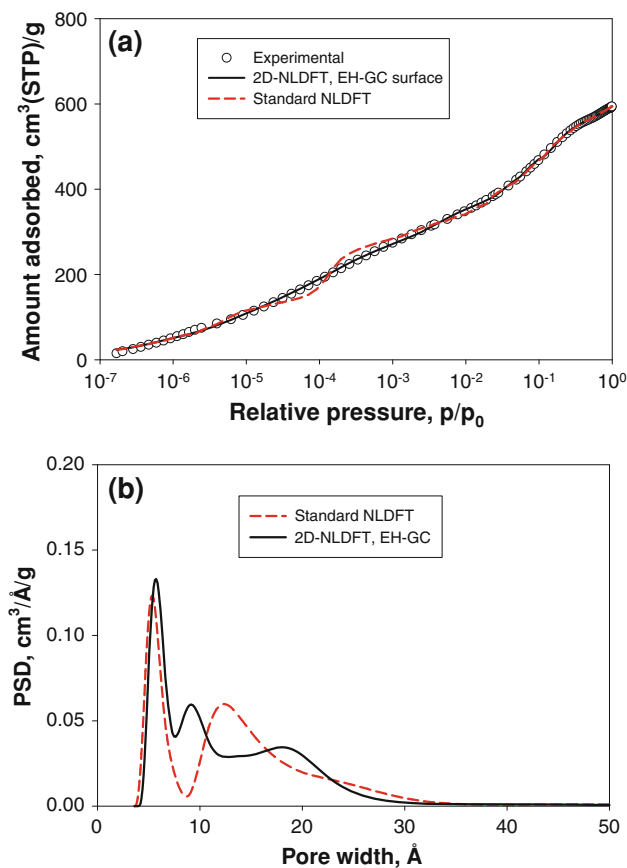


Fig. 6 Pore structure analysis of PC58 carbon sample by the standard and new models. **a** Goodness of fit of N_2 experimental isotherms by theoretical kernels. **b** Calculated PSDs

PSDs calculated using the new EH–GC and the standard models (Figs. 6, 7, part b) the following observations could be made: (i) Both PSDs cover the same pore size range. (ii) Both contain the first peak (for the smallest pore sizes) at the same position. This may be explained by the fact that the position of this peak corresponds to the pressure range that is below the first layering transition of the standard kernel. (iii) The PSD curves for the standard model show deep minima near 10 Å which are the signatures of the artifacts discussed in the introduction. (iv) The curves for the new model show minor maxima in this range.

There is an overall similarity between the results calculated using the EH–GC model and the models presented in our recent paper (Jagiello and Olivier 2013). This is important from the viewpoint of extracting meaningful PSD of a porous carbon. Considering the differences in the assumptions of these models and differences in the fluid density profiles during pore filling, it would be logical to expect a model dependent diversity between the calculated PSDs. Apparently; however, even though the local density profiles are different, the theoretical isotherms that represent averaged densities are similar for these models. It

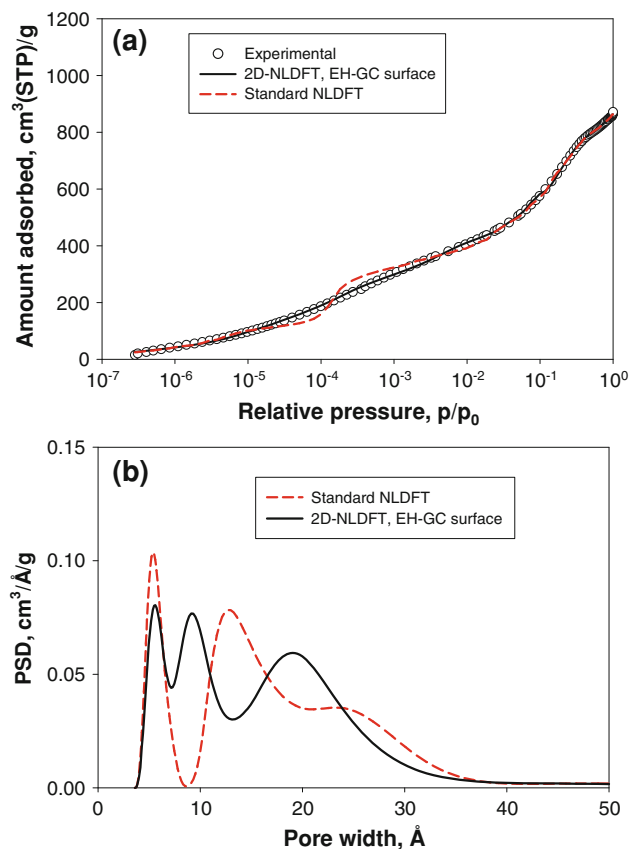


Fig. 7 Pore structure analysis of PC76 carbon sample by the standard and new models. **a** Goodness of fit of N_2 experimental isotherms by theoretical kernels. **b** Calculated PSDs

follows that the new models are able to provide a robust characterization of carbon porosity.

3 Conclusions

It was demonstrated in this work that modification of the standard slit pore model by introducing EH and GC to the surface of pore walls could significantly improve carbon pore structure analysis from gas adsorption data. The modifications we consider are supported by the overall knowledge of the structure of carbon materials and specifically on the findings of the most recent studies of activated carbons using HRTEM and STEM.

The important improvement of the new model is elimination of the artifacts produced by the standard slit pore model. In tests, the calculated standard deviations of the fit with the new model were reduced by more than 60 % from their values for the standard model. It was found interesting that the PSDs calculated using the EH–GC model and the models (EH and GC) presented in our recent paper show an overall similarity, which may suggest that these models capture the essential feature of the analyzed activated

carbons which is a non-uniform solid–fluid interaction potential. This common factor of our models makes them relatively robust for PSD characterization.

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