

# IMPROVED DFT METHODS FOR MICROPORE SIZE CHARACTERIZATION OF ACTIVATED CARBONS: ROLE OF PORE WALL HETEROGENEITY

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## Introduction

The density functional theory (DFT) based method for the calculation of pore size distribution (PSD) of activated carbons from nitrogen adsorption isotherms has become a standard characterization procedure in recent years [1-4]. The data obtained by this method provide detailed representation of the carbon porosity in the range of micro and mesopores. However, in spite of overall reliability of this characterization method, two unexplained, persistently occurring features of the results have been observed. First, the plots of the fitted isotherms often show S-shaped deviations from the experimental isotherms in the relative pressure range between 0.00001 and 0.01. Second, the differential PSDs for various carbons often show sharp minima at 10 and 20 Å [3-5]. The occurrence of the minima at the same positions for different carbons seems to be a model-related artifact [5]. These two usually observed features indicate that the theoretical model is not fully accurate in its description of the actual nitrogen adsorption on activated carbons. The theoretical isotherms usually utilized in PSD calculations are based on the nonlocal DFT for the model of slit shape pores with infinitely thick walls [1-5]. Such a model, although adopted in the standard software [2] of commercial gas porosimetry instruments, does not seem to be fully justified for the description of actual activated carbons. The purpose of this study is to investigate the possibility of improvement of existing methods and to gain better insight on the accuracy of the theoretical models.

## Experimental

Nitrogen adsorption isotherms were measured at 77 K using a Coulter Omnisorp 100 instrument for four representative Westvaco carbons. Two samples (WV-A 1100 and BAX 1500) are commercial phosphoric acid activated wood based carbons. The other two samples are wood based KOH activated developmental carbons obtained using different KOH to carbon ratios. One of these is discussed in this abstract.

## Theory and Method

### The Slit Shape Pore Model

In the present work, four special cases of the slit pore model are considered with regard to the pore wall thickness. The pore wall is regarded as a graphite crystallite consisting of  $n$  infinite parallel plane layers. The following cases are considered:

1. Model  $n_{\infty}$ : Classical case; both walls are infinitely thick ( $n=\infty$ ).
2. Model  $n_2$ : Double layer walls ( $n=2$ ).
3. Model  $n_1$ : Single layer walls ( $n=1$ ).
4. Model  $n_{\infty/1}$ : Mixed walls model; one wall (left) is infinitely thick and the other (right) consists of a single layer ( $n_L=\infty$ ;  $n_R=1$ ).

The potential of interaction between a gas molecule and a pore,  $u_{\text{pore}}$ , depends on the width of the slit and the thickness of pore walls. This potential is given as a sum of potentials of gas-solid interactions with single walls

$$u_{\text{pore}}(z) = u_{\text{wall1}}(z) + u_{\text{wall2}}(x-z) \quad (1)$$

where  $z$  is the distance of the molecule from the surface atoms nuclei of one of the pore walls that are separated by the distance  $x$ . The potential of interaction of a molecule with the wall is then given by the sum of its interaction potentials with each plane,

$$u_{\text{wall}}(z) = \sum_{j=1}^n u_{\text{plane}}(z, j) \quad (2)$$

The latter potential is derived by integrating of the gas molecule-carbon atom Lennard-Jones (LJ) interaction potential over the plane, which leads to the following expression:

$$u_{\text{plane}}(z, j) = 2pr_s e_{gs} s_{gs}^2 \left[ \frac{2}{5} \left( \frac{s_{gs}}{z+(j-1)d} \right)^{10} - \left( \frac{s_{gs}}{z+(j-1)d} \right)^4 \right] \quad (3)$$

where  $\rho_s$  and  $d$  are the density of graphite and the separation distance of its lattice planes,  $\epsilon_{gs}$  and  $\sigma_{gs}$  are the LJ potential parameters for interactions between a gas molecule and a carbon atom in the graphite lattice.

### Calculation of the Theoretical Model Isotherms

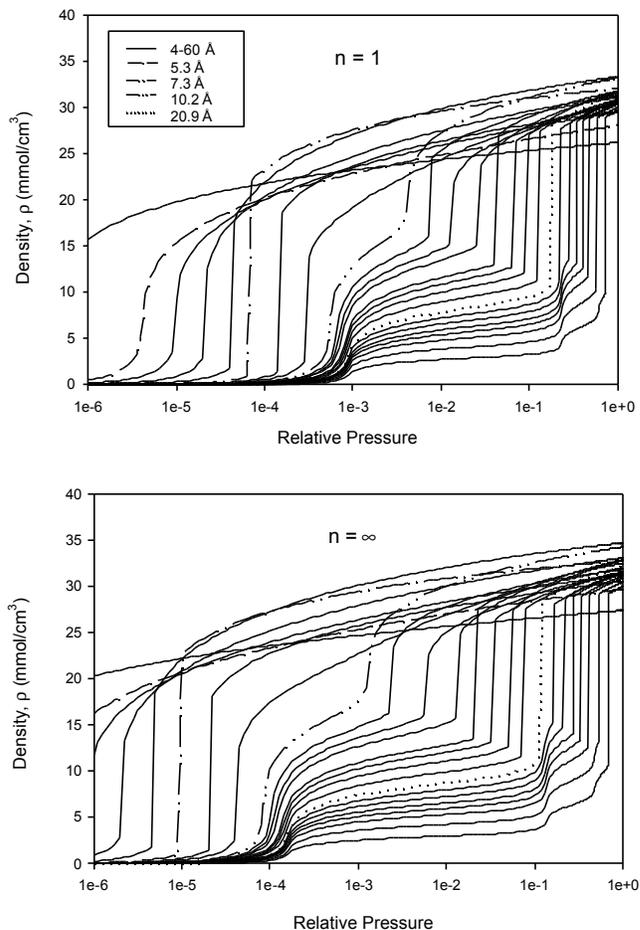
The isotherms for the four pore models were calculated using the non local DFT of Tarazona [6]. Details of the calculation method and the parameters used are reported elsewhere [4, 7]. The isotherm data are given for 112 pore sizes in the range of 3-350 Å and at 218 pressure points in the relative pressure range of  $10^{-7}$  - 1.0. Selected isotherms for models  $n_1$  and  $n_\infty$  are plotted in Figure 1. A general similarity in shapes is observed between the isotherms calculated for both models for the corresponding pore sizes. However, due to a deeper potential well for the  $n_\infty$  model, the steps on the isotherm are shifted to lower pressures compared to those for the  $n_1$  model. The sequence of isotherms (Figure 2) for symmetrical pore models is consistent with the strengths of  $u_{\text{pore}}$  interaction potentials. The isotherms for the mixed wall model,  $n_{\infty/1}$ , (Figure 2) are mostly located between the corresponding isotherms for models  $n_1$  and  $n_2$ . However, for the larger pores at low pressures, these isotherms are located between those for models  $n_2$  and  $n_\infty$ . This is because in such conditions adsorption first takes place near the infinitely thick wall where the  $u_{\text{pore}}$  potential is dominated by interactions with this wall.

### Calculation Method of the Carbon PSD Using DFT Data.

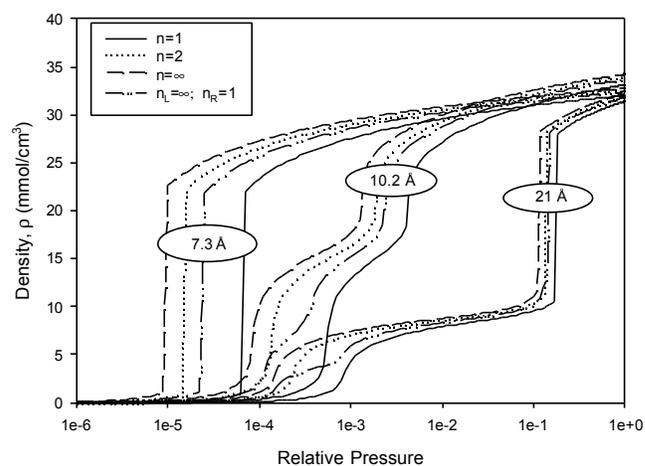
The calculation of the carbon PSD is based on its fundamental relationship with the measured adsorption isotherm,  $V$ , given in the form of the following adsorption integral equation:

$$V(p) = \int_{\alpha}^{\beta} \rho(p, w) f(w) dw \quad (4)$$

where  $\rho(p, w)$  is the model adsorption isotherm given in terms of the adsorbate density calculated for model pores as a function of pore width,  $w$ , and the equilibrium pressure,  $p$ . The PSD to be determined is represented as a differential pore volume distribution,  $f(w)$ . The lower limit of the integration range,  $\alpha$ , is determined by the accessibility of pores for a given adsorbate. The theoretical upper limit is  $\beta = \infty$ ; in practice, however, only limited number of model isotherms are calculated, and thus some finite value for  $\beta$  is assumed.



**Figure 1.** Selected NLDFT isotherms of  $N_2$  at 77 K for the single layer (top) and infinitely thick (bottom) pore wall models.



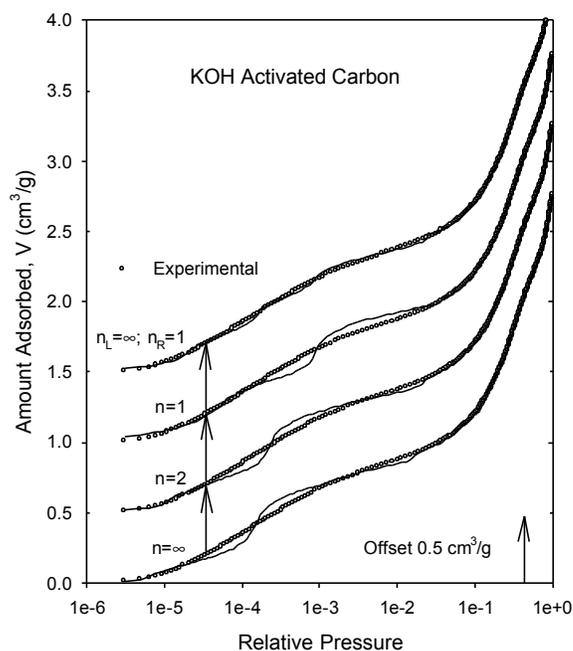
**Figure 2.** Effect of the assumed pore wall model on the calculated NLDFT adsorption isotherms of  $N_2$  at 77 K.

Mathematically, Equation 4 is a Fredholm linear integral equation of the first kind. Due to its ill-posed character, solving this equation presents certain numerical difficulties and requires special treatment. To obtain stable and physically feasible results, the numerical algorithm, SAIEUS [8], was adopted. This algorithm utilizes the regularization procedure and imposes nonnegativity constraints on the solution. A more detailed description of the method is given elsewhere [3, 8]. Since the model isotherms  $\rho(p, w)$  are given as an array of values calculated for the finite number of pressures and pore sizes, to evaluate integrals in Equation 4, appropriate interpolations are performed in two steps. First, the values of  $\rho$  are obtained from all theoretical DFT isotherms for all experimental pressures,  $p_i$ . Then, the  $\rho$  values are evaluated at each of these pressures for all pore sizes used in the integration procedure. If the combination of pore types is assumed, then the interpolations are performed for individual models, and the resulting values are combined in the assumed proportion.

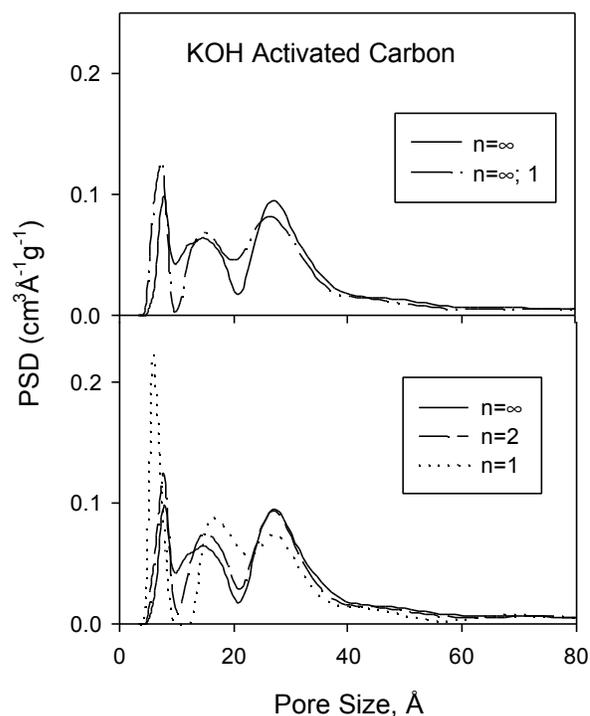
## Results and Discussion

Results of the application of different models to the analysis of the experimental data are given in Figures 3 and 4. Substantial improvement of the fit to the experimental isotherms is obtained for the mixed wall model. The symmetrical pore models show S-shaped deviations, which systematically shift to higher relative pressures as the thickness of the pore wall decreases. Pronounced minima in the PSDs are retained for all models. The following general features are observed in the comparison of the PSDs calculated for different pore models:

1. The distributions are shifted to smaller pores as the pore wall thickness decreases, which is consistent with the earlier discussion about the shift of model isotherms.
2. As a consequence of this trend, the surface areas are higher for the models with thinner walls (Figure 4). Surface areas for the  $n_1$  model become unrealistically high for the KOH- activated carbons.
3. Only micropore volumes are affected by the wall model, while the total pore volume is not sensitive.
4. Except for the  $n_1$  model, the results for the other models are relatively similar.
5. The minima at 10 and 20 Å exist for all the considered models.



**Figure 3.** Nonlocal DFT fitting of  $N_2$  experimental adsorption isotherm using different pore wall models.



**Figure 4.** Nonlocal DFT pore size distributions calculated using different pore wall models.

Thus, the major effect of the mixed pore wall model is the improved fit to the experimental data (Figure 3) without significant change in the general trimodal shape of calculated PSD (Figure 4). The latter result points out the relative robustness of the DFT method.

The mixed pore wall model introduces an additional heterogeneity. However, it does not seem to be enough to reduce the minima on the PSD curves at 10 and 20 Å. A low population of pores around 6 and 10 Å, calculated with the DFT model for Ar at 87 K, has been noted earlier by Olivier [5], who recognized this as a model induced artifact, and put forward an explanation which relates this artifact to the packing effects exhibited by the parallel rigid pore wall model.

In our recent study [4] we argued that these artificial minima are primarily due to the homogeneous nature of the model. One of the characteristic features of the low-temperature adsorption isotherms in the homogeneous model is a sharp monolayer formation, which occurs at approximately the same relative pressure in most of the pores. Indeed, Figure 1 shows that, starting from pores which can accommodate more than one layer of molecules, the monolayer forms at the relative pressure of ca.  $10^{-4}$ . Similarly, the second layer in pores that can accommodate 4 or more layers forms at the relative pressure of ca. 0.1, etc. These pressures coincide with the pore filling steps in ca. 10 and 20 Å pores, respectively. In the mixed pore wall model the monolayer formation splits into two steps, however the general picture remains largely the same (Figure 2). Most of the activated carbon adsorbents are highly heterogeneous, and their adsorption isotherms are relatively smooth, and do not exhibit very sharp inflections, which would clearly indicate the filling of a dominant group of pores. In this challenging situation, the PSD calculation algorithm tends to distribute the pores relatively uniformly. However, the fitting procedure will diminish the contribution of 10 and 20 Å range pores in the PSD because there already exists a significant proportion of the theoretical isotherms with the multilayer formation steps at the same pressures at which pore filling occurs in 10 and 20 Å pores. This compensation effect is a purely mathematical artifact. Its origin lies in the inadequate representation of the structure and adsorption isotherms of activated carbons in the DFT models. This does not exclude a possibility of a significant dilation of the activated carbon structure during adsorption, which would smear out all the packing effects seen in the parallel wall model [5]. This indicates that the search for better models and methods for adsorption characterization of activated carbons is topical [9, 10].

## Conclusions

We considered several improved models for the wall thickness in activated carbons. Agreement between the experimental adsorption isotherms and the theoretical model improves when a nonuniform or combined pore wall structure is assumed. The calculated pore volumes are moderately sensitive to the assumed pore wall model. The calculated surface areas are higher for the pore models with thinner walls. The surface areas calculated for the pore model with single layers are unrealistically high for some of KOH activated carbons. For example, surface areas calculated for the carbon with pore size distributions shown in Figure 4 are 3200 and 2600 m<sup>2</sup>/g for single layer and mixed wall models respectively. The former value is higher than the theoretical surface area of a single graphite sheet. Nevertheless, except for this single layer model, the pore structure parameters of activated carbons obtained with the other models are quite similar, which points toward robustness of the DFT method for practical applications. Discrimination between the models based solely on an analysis of nitrogen adsorption data is not sufficient to determine the specific pore model that is appropriate for a given carbon. Additional data obtained from independent sources, such as XRD, may be useful to improve structural description of activated carbons.

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