

## Critical Discussion of Simple Adsorption Methods Used to Evaluate the Micropore Size Distribution

MICHAL KRUK AND MIETEK JARONIEC

*Separation and Surface Science Center, Department of Chemistry, Kent State University, Kent, OH 44242*

JERZY CHOMA

*Institute of Chemistry, WAT, 01489 Warsaw, Poland*

*Received May 17, 1996; Revised September 6, 1996; Accepted September 22, 1996*

**Abstract.** The well-known simple adsorption methods used to evaluate the micropore size distribution from low pressure adsorption isotherms were examined by employing model isotherms for slit-like graphite micropores obtained from nonlocal density functional theory. It was shown that in the range of pore sizes from about 0.4 to 0.9 nm, the Horvath-Kawazoe (HK) method satisfactorily reproduces the shape of the micropore size distribution, but the pore sizes are underestimated. In the case of micropores wider than 0.9 nm, the method fails as the formation of the monolayer on the pore walls produces a peak corresponding to 0.6 nm micropores on the HK pore size distribution. Therefore, the HK method indicates the presence of microporosity even for nonporous samples. The Dubinin-Astakhov adsorption isotherms were also examined and it was shown that their application to represent local adsorption isotherms for homogeneous pores is questionable. However, the adsorption potential distributions seem to be promising for micropore analysis.

**Keywords:** carbons, porous structure, Horvath-Kawazoe method, Dubinin-Astakhov equation, gas adsorption

### Introduction

Porous materials such as carbon blacks, active carbons, zeolites and silica gels, are widely applied in many areas of modern science and technology such as mixture separation, removal of trace impurities, catalysis, fuel storage (Bansal et al., 1988; Bergna, 1994; Bonneviot and Kaliaguine, 1995; Jansen et al., 1994; Vansant et al., 1995). The usefulness of porous materials often results from their remarkable adsorption properties. These in turn depend on the surface properties (i.e., the structure of surface layers, the presence of heteroatoms, functional groups and surface irregularities) and porous structure properties (such as the geometry of pores and their connectivity) (Jaroniec and Madey, 1988). A considerable effort has recently been made in order to design new materials of well-defined porosity, leading to adsorbents exhibiting regular

array of micropores (Bonneviot and Kaliaguine, 1995; Jansen et al., 1994) as well as mesopores (Kresge et al., 1992). However, the most popular porous materials such as active carbons and silica gels, possess much less regular porous structures. In both cases, there arises the need to develop simple and unambiguous methods for characterization of these porous solids. Adsorption (especially nitrogen adsorption) proved to be a fast and convenient characterization technique, which allows to obtain the pore size distribution (PSD) as well as the specific surface area and the adsorption energy distribution for samples under study (Jaroniec, 1996). The pore size distribution within the range from about 7.5 nm (Lastoskie et al., 1993a) to about 100 nm can be obtained by using either the Kelvin equation or its modifications to relate the pressure of the capillary condensation in pores to their size. For smaller pores (widths below 7.5 nm), the Kelvin equation is

not applicable, since the pore filling process is significantly influenced by attractive potential of pore walls, especially in the case of micropores (pore widths below 2 nm). Information about the presence of fine pores is crucial for understanding adsorption and catalytic properties of many porous solids, and therefore numerous characterization methods were developed to obtain micropore size distributions.

Many researchers have used approaches based on empirical Dubinin-Radushkevich (DR) and Dubinin-Astakhov (DA) equations (Dubinin, 1975). The latter adsorption equations were used to represent the local adsorption isotherms in the integral equation for the total amount adsorbed. However, the comparison of the DA or DR equations with isotherms calculated on the basis of computer simulations or nonlocal density functional theory (Lastoskie et al., 1993a and 1993b; Olivier, 1995) strongly suggests that the DR and DA equations represent adsorption in pores of significant geometrical and/or surface heterogeneity. Therefore, the use of these equations to represent local adsorption isotherms in homogeneous pores is questionable. This subject will be discussed later in the current paper.

Another simple method to obtain the pore size distribution in the micropore range is based on the Horvath-Kawazoe (HK) procedure and its modifications (Horvath and Kawazoe, 1983; Cheng and Yang, 1994). The Horvath-Kawazoe method has been widely applied to characterize various microporous solids (see Cheng and Yang, 1994 and references therein). However, the quantitative analysis of the resulting PSDs was rather difficult because of lack of both microporous solids of well-defined and simple geometries and reliable model adsorption isotherms for such systems. The latter data can now be obtained from non-local density functional theory and computer simulations. Recently, Kaminsky et al. (1994) tested the validity of the Horvath-Kawazoe method for cylindrical pores using model theoretical isotherms and found moderate agreement between the assumed and calculated HK PSDs. It was shown that the HK method not only gives somewhat incorrect values of pore sizes but also predicts the polymodal PSDs for monodisperse systems.

The most promising, but unfortunately the most complicated and model-dependent methods for evaluating microporosity, are based on advanced computational techniques such as nonlocal density functional theory (DFT) and computer simulations, which provide reliable local isotherms for pores of well-defined geometry (Lastoskie et al., 1993a, 1993b; Olivier, 1995).

The essence of these methods is to invert the integral equation for the total adsorbed amount with respect to the pore size distribution. The approach developed by Lastoskie et al. (1993a) requires an arbitrarily assumed form of the PSD to be calculated. Olivier et al. (1994) developed a numerical program based on the regularization method (Szombathely et al., 1992) in which no restrictions are imposed on the form of the PSD. Both methods mentioned above are quite involved so it would be desirable to find out if simpler methods of micropore analysis can lead to reasonable results. The current paper is intended to assess the validity of the Horvath-Kawazoe method. The problem of application of the DR and DA adsorption equations in calculations of micropore size distributions will also be addressed.

## Methods

### Theoretical Approach

Horvath and Kawazoe (1983) introduced a simple method for calculation of the micropore size distribution from a single adsorption isotherm. Later, Jaroniec et al. (1996) developed an equivalent procedure based on the adsorption potential distribution. Now that second approach will briefly be outlined, because it is used in the current work.

Under the assumption of the condensation approximation (CA), the pore volume distribution  $J(x) \equiv \frac{dV}{dx}$  (where  $x$  is a pore width and  $V$  is the amount adsorbed expressed in  $\text{cm}^3$  of liquid adsorbate per gram of the adsorbent) can be related to the adsorption potential distribution through the following equation:

$$J(x) \equiv \frac{dV}{dx} = \left( \frac{dV}{dA} \right) \left( \frac{dA}{dx} \right) = -X(A) \left( \frac{dA}{dx} \right) \quad (1)$$

The adsorption potential  $A$  is equal to the change in the Gibbs free energy of adsorption with the minus sign:  $A = -\Delta G = RT \ln(p_0/p)$ . The pore size  $x$  is defined as a distance between the walls of the pore rather than the distance between the centers of atoms, which form first layers of the opposite pore walls. The differential adsorption potential distribution function  $X(A)$  is defined as:

$$X(A) = -\frac{dV(A)}{dA} \quad (2)$$

On the basis of Eq. (1), the pore volume distribution  $J(x)$  can be calculated by multiplying the adsorption

potential distribution by the negative derivative of the adsorption potential with respect to the pore width:  $-\frac{dA}{dx}$ . Therefore, the latter quantity needs to be obtained for a specified pore size range and pore geometry. In the case of slit-like micropores, the derivative of the adsorption potential  $A$  with respect to the pore width  $x$  can be found from the following relation between  $A$  and  $x$  (Horvath and Kawazoe, 1983):

$$A = \frac{C_1}{x - d_a} \left( \frac{C_3}{(x + \delta)^9} - \frac{C_2}{(x + \delta)^3} + C_4 \right) \quad (3)$$

where constants  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are characteristic for a given adsorbent-adsorbate system (Horvath and Kawazoe, 1983; Cheng and Yang, 1994; Choma et al., 1994; Jaroniec et al., 1996). The symbol  $d_a$  stands for the diameter of the adsorbate molecule and  $\delta$  is equal to  $\frac{d_A - d_a}{2}$ , where  $d_A$  is the diameter of the adsorbent atom. After differentiation of Eq. (3) with respect to the pore width  $x$ , the following expression is obtained:

$$\begin{aligned} \frac{dA}{dx} = & \frac{C_1}{x - d_a} \left( \frac{3C_2}{(x + \delta)^4} - \frac{9C_3}{(x + \delta)^{10}} \right) \\ & - \frac{C_1}{(x - d_a)^2} \left( \frac{C_3}{(x + \delta)^9} - \frac{C_2}{(x + \delta)^3} + C_4 \right) \end{aligned} \quad (4)$$

The values of the constants in Eq. (4) for nitrogen adsorption in slit-like carbonaceous micropores at 77.5 K are the following:  $C_1 = 39.6003 \text{ kJ} \cdot \text{nm/mol}$ ,  $C_2 = 1.8942 \cdot 10^{-3} \text{ nm}^3$ ,  $C_3 = 2.7048 \cdot 10^{-7} \text{ nm}^9$ ,  $C_4 = 0.05012$ ,  $d_a = 0.30 \text{ nm}$ ,  $d_A = 0.34 \text{ nm}$  and  $\delta = 0.02 \text{ nm}$  (Horvath and Kawazoe, 1983; Choma et al., 1994). The adsorption isotherm data allow to obtain the differential adsorption potential distribution  $X(A)$ , which after multiplying by the expression from Eq. (4) and changing the sign, leads to the pore volume distribution  $J(x)$ .

The model adsorption isotherms were calculated from nonlocal density functional theory (Olivier, 1995). A proper correction was introduced to the method in order to reproduce the adsorption behavior on nonporous and highly homogeneous Sterling FT-G(2700) graphite. The isotherms obtained by Olivier (1995) are in a very good agreement with previously reported nonlocal density functional theory results of L stoskie et al. (1993a; 1993b). The latter authors and others (Chmiel et al., 1994) compared their DFT calculations with Monte Carlo simulations and found no considerable differences between adsorption isotherms

predicted by both methods. Hence, the model isotherms employed can be regarded as an accurate description of adsorption in homogeneous pores. It needs to be remarked that real porous adsorbents exhibit more or less pronounced surface heterogeneity, which is expected to broaden the regions of phase transitions in pores. It was shown that energetic heterogeneity of pore walls may change first-order capillary condensation transitions into continuous pore filling (Karykowski et al., 1994).

### Adsorption Measurements

Adsorption isotherms were measured using ASAP 2010 volumetric adsorption equipment from Micromeritics, Norcross, GA. Before adsorption measurements, the samples were degassed under vacuum at 473 K. Adsorption isotherms were measured in relative pressure range from  $10^{-6}$  to 1. Standard characterization of the samples studied involved calculation of the specific surface area  $S_{\text{BET}}$  (the standard BET method), the external surface area  $S_{\text{ex}}$  and the micropore volume  $V_{\text{mi}}$  (t-plot) and the total pore volume  $V_t$  (obtained from the amount adsorbed at a relative pressure about 0.975). A more detailed description of the adsorbents and the experimental methods used in the current study can be found elsewhere (Jaroniec et al., 1996; Kruk et al., 1996).

The adsorbents studied in the current work are listed in Table 1. BP 280 and BP 800 carbon blacks were provided by Cabot Corporation, Special Blacks Division, Billerica, MA. Sterling FT-G was obtained from Laboratory of the Government Chemist, Queens Road, Teddington, Middx, UK. Carbopack B was provided by Supelco, Bellefonte, PA. Darco and ROW active carbons were obtained from Norit Co., Amersfoort, The Netherlands.

Table 1. The BET specific surface area  $S_{\text{BET}}$ , the external surface area  $S_{\text{ex}}$ , the micropore volume  $V_{\text{mi}}$  and the total pore volume  $V_t$  for the adsorbents studied.

Adsorbent	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{ex}}$ (m <sup>2</sup> /g)	$V_{\text{mi}}$ (cm <sup>3</sup> /g)	$V_t$ (cm <sup>3</sup> /g)
Cabot BP 280	41	36	—	0.10
Cabot BP 800	242	195	0.02	0.68
Sterling FT-G	11	10	—	0.03
Carbopack B	88	95	—	0.41
Darco	485	190	0.13	0.51
ROW	940	156	0.38	0.62

## Results and Discussion

Selected model adsorption isotherms calculated using the nonlocal density functional theory (Olivier, 1995) are shown in Fig. 1. For pore widths  $x$  equal to 0.536 nm and 0.733 nm, the isotherm curves exhibit one more or less steep step associated with the volume filling of the micropore. In the case of 0.929 nm pores, the presence of two broad steps can be noticed. The step at relative pressures between  $10^{-5}$  and  $10^{-4}$  results from the formation of the monolayer on the pore walls and the other one corresponds to the condensation of the adsorbate confined between these monolayers. The same behavior is observed for pores of the diameter equal to 1.09 nm, 1.48 nm and 2 nm. It can be noticed that the condensation approximation (CA) (which assumes the degree of pore filling  $\Theta = 0$  for pressures below the characteristic condensation pressure  $p_c$  and  $\Theta = 1$  for  $p > p_c$ ) is not likely to give a reasonable description of the micropore filling, at least for the pore

widths greater than 0.9 nm, as for those pores at least two steps reflecting the monolayer formation and the condensation inside the pore, can be observed. Notice that for pores wider than 0.9 nm, the step associated with the formation of the monolayer appears at relative pressures about  $10^{-4}$  and undergoes only a slight shift towards higher pressures as the pore size increases.

Shown in Fig. 2 are distributions of the adsorption potential  $X(A)$  for the model pores. They were calculated using the degree of the pore filling instead of the adsorbed amount (see Eq. (2)), because the former quantity is easily available from the computational data. As it can be expected from the shape of the adsorption isotherms, the  $X(A)$  distributions for the model pores exhibit one peak for micropores of  $x < 0.9$  nm and two peaks for micropores of  $x > 0.9$  nm. In the first case, the position of the peak is related to the pore size (see Fig. 3). In the second case, the peak at higher values of the adsorption potential (about 6 kJ/mol) corresponds to the formation of the

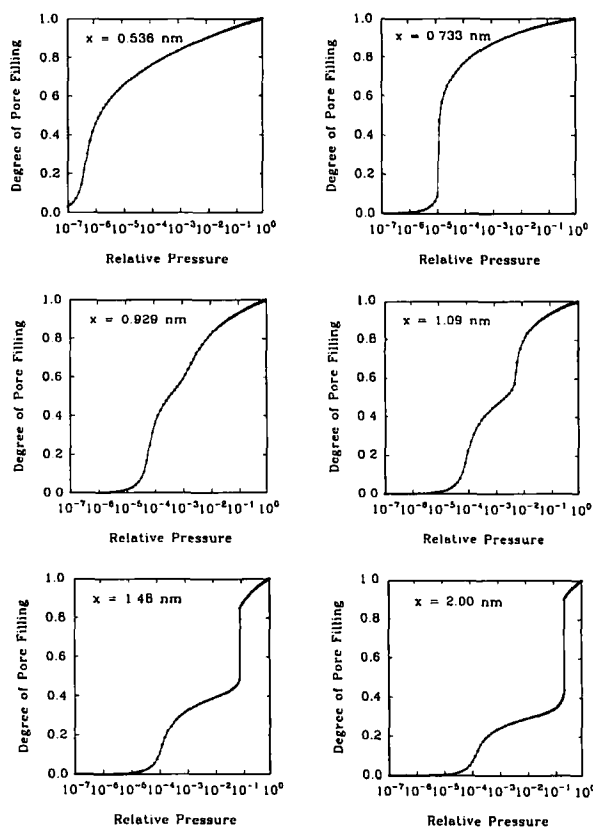


Figure 1. Adsorption isotherms for graphite slit-like homogeneous micropores calculated from the nonlocal density functional theory.

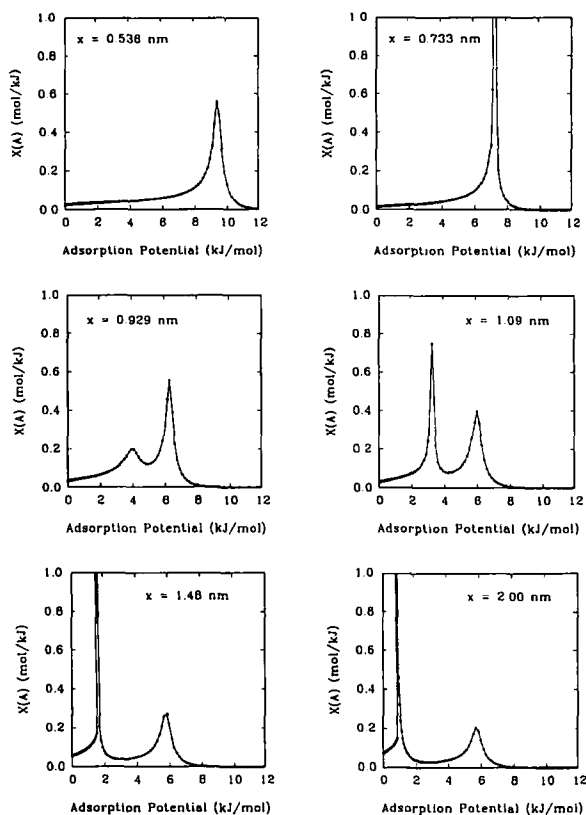


Figure 2. Distributions of the adsorption potential for the model isotherms.

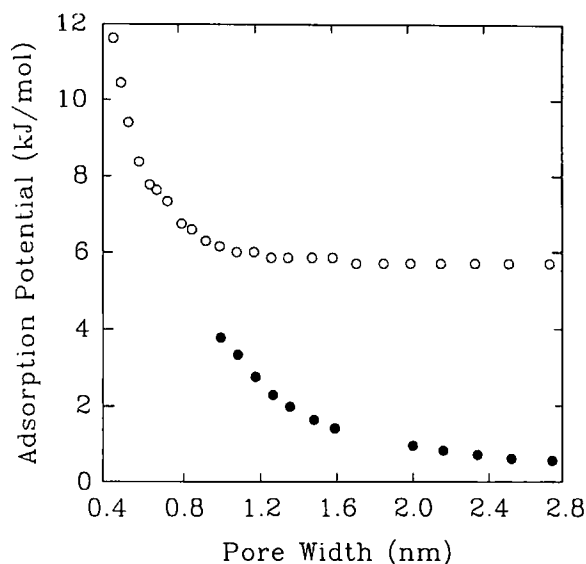


Figure 3. The adsorption potential ( $A$ ) of the maxima on the adsorption potential distributions plotted as a function of the pore width. Hollow circles indicate  $A$  for peaks arising from the condensation inside the pore ( $x < 0.9$  nm) and the monolayer formation ( $x > 0.9$  nm). Filled circles show  $A$  for the condensation of the adsorbate confined between already formed adsorbate film on the pore walls.

first adsorbate layer on the pore walls. The second peak, which appears at lower values of the adsorption potential, results from the condensation of the adsorbate inside the pore and can be used to assess the pore size (see Fig. 3). This problem will be discussed later. It needs to be remarked that the presence of the surface heterogeneity is expected to broaden the peaks on the adsorption potential distributions and probably shift them to some extent. Moreover, the data described above are relevant for nitrogen adsorption in graphite slit-like pores at 77.35 K. For many other adsorbent-adsorbate systems or other temperatures, considerably different behaviors can be expected. However, it needs to be kept in mind that nitrogen adsorption at 77.35 K is a standard and most widely applied method to obtain information about surface and structural properties of porous solids. In the case of argon adsorption at 87.3 K, which is another frequently used method, adsorption isotherms for homogeneous graphite pores calculated from the DFT (Olivier, 1995) have similar shapes as those for nitrogen. The agreement is obviously qualitative and for example the pressure ranges of phase transitions, such as monolayer buildup or the capillary condensation, are different. But still many conclusions drawn for nitrogen adsorption should be valid, when

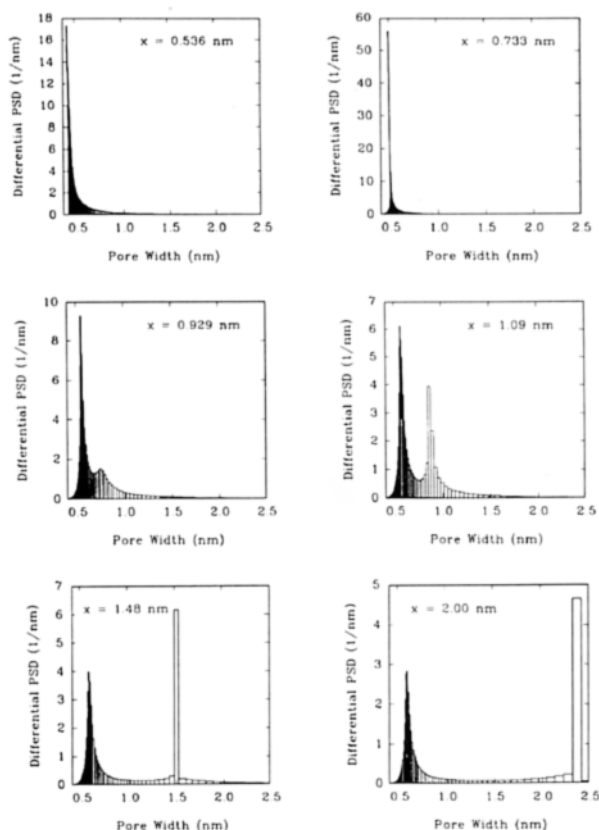


Figure 4. Horvath-Kawazoe micropore size distributions calculated from the adsorption isotherms for model pores.

argon adsorption data at 87.3 K are applied to evaluate PSDs by the Horvath-Kawazoe method.

The Horvath-Kawazoe pore size distributions obtained from the model adsorption isotherms for homogeneous slit-like pores are shown in Fig. 4. In the case of small micropores (widths below 0.9 nm), one sharp peak is obtained, which indicates that the Horvath-Kawazoe method can be used to calculate PSDs for pores of the width up to 0.9 nm. However, the size of pores in that range is underestimated. These results suggest that the relation between the adsorption potential and the pore size requires corrections in order to obtain a correct estimation of the pore size from the HK method. The correction mentioned above can be made with the help of computer simulation or DFT results.

The Horvath-Kawazoe PSDs obtained for micropores wider than 0.9 nm exhibit two peaks. One of them indicates the presence of pores of the width about 0.6 nm, but actually results from the monolayer

formation on the surface. It was mentioned before that for pore widths greater than 1 nm, the pressure, for which the first adsorbate layer is formed on the pore walls, does not change much with the increase of the pore size. These results suggest that even for completely nonporous samples, the Horvath-Kawazoe method is likely to show the presence of a certain amount of micropores about 0.6 nm. The second peak, which appeared on the pore size distributions is associated with the condensation of the adsorbate inside the pore. Its position changes significantly with the change in the pore width of model isotherms. For the pore size of 1.48 nm, the peak position on the PSDs agrees well with the size of the model pore. However, for smaller pores, the second peak obtained from the Horvath-Kawazoe method lies below the actual pore size (i.e., the pore size is underestimated), whereas for pores wider than 1.5 nm, the pore size is overestimated. Once again, one can try to find an improved relation between the adsorption potential and the pore width, which will allow for the correct estimation of pore sizes.

In order to provide further test of the Horvath-Kawazoe method, composite adsorption isotherms were obtained from selected pairs of model isotherms. In the case of all composite isotherms, the weighting factors were 0.5 for smaller pores and 0.5 for bigger ones. The mixed isotherms are shown in Fig. 5. The isotherm for two small micropores (0.536 nm and

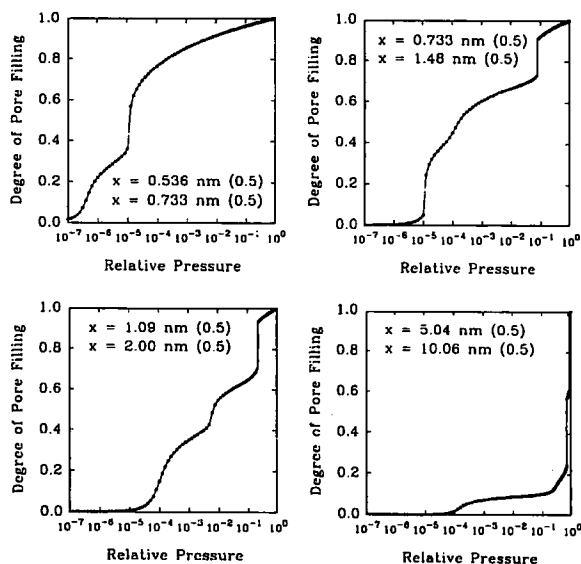


Figure 5. Composite isotherms obtained from two isotherms for homogeneous slit-like pores.

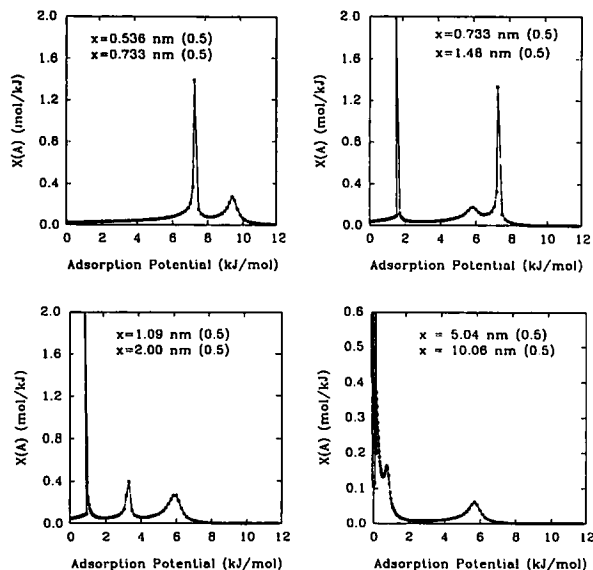


Figure 6. Distributions of the adsorption isotherms for the composite isotherms shown in Fig. 4.

0.733 nm) exhibits two steps, which both correspond to the adsorption potential values above 6 kJ/mol (see Fig. 6). Two other composite isotherms (0.733 nm and 1.48 nm; 1.09 nm and 2.00) feature three steps. In the case of the mixed isotherm obtained for pores wider than 0.9 nm, both single isotherms exhibit two steps (see Fig. 1). But as it was mentioned above, the step corresponding to the monolayer formation shifts only slightly with an increase of the pore size. Therefore, only one step can be observed on the isotherm at a relative pressure range below  $10^{-3}$ . This step corresponds to the adsorption potential of about 6 kJ/mol.

The Horvath-Kawazoe pore size distribution functions for composite isotherms are shown in Fig. 7. In the pore size range below 0.9 nm, the bimodal distribution of pore sizes is reproduced reasonably well. But for wider pores, the interpretation of the PSDs is obscured by the presence of the peak, which results from the monolayer buildup. On the PSD obtained from the 0.733 nm and 1.48 nm composite isotherm, the latter peak related to 1.48 nm pores almost coalesces with the peak corresponding to the presence of 0.733 nm micropores. In the case of the 1.09 nm and 2.00 nm mixed isotherms, the PSD artificially shows the presence of significant amount of 0.6 nm micropores. Another problem results from the fact that distance between peaks corresponding to the pores of given sizes is greater than the actual difference in pore sizes. For

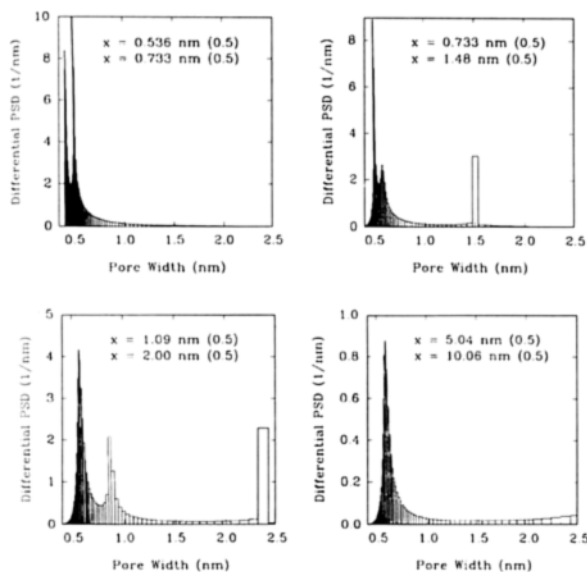


Figure 7. Horvath-Kawazoe micropore size distributions calculated from composite isotherms shown in Fig. 4.

example, the difference in pore sizes between 1.09 nm and 2.00 nm pores is 0.91 nm, but the distance between two corresponding maxima on the PSD is about 1.5 nm. Therefore, the Horvath-Kawazoe method is expected to broaden the pore size distribution peaks. Experimental adsorption studies provide further support for the results presented above.

For illustrative purposes, several carbonaceous materials of variable surface and porous properties were chosen. Sterling FT-G is a nonporous adsorbent of high surface homogeneity. Carpack B has a much higher surface area in comparison to Sterling, but still similar surface properties. BP 280 is a low surface area carbon black and serves as an example of a rather nonporous adsorbent with a heterogeneous surface. BP 800 exhibits similar surface properties as BP 280, but possesses a small fraction of micropores. Darco and ROW are considerably microporous. The adsorption isotherms for these adsorbents are shown in Fig. 8. Sterling FT-G, Carpack B and BP 280 exhibit small adsorption in the low pressure range and then a steep increase in gas uptake is observed for pressures close to the saturation pressure. BP 800 exhibits noticeable, but still rather low adsorption in the low pressure region and a hysteresis loop (difficult to notice on the logarithmic scale) in the capillary condensation pressure region. Darco and ROW adsorb considerable amount of nitrogen at relative pressures as low as  $10^{-5}$ , which

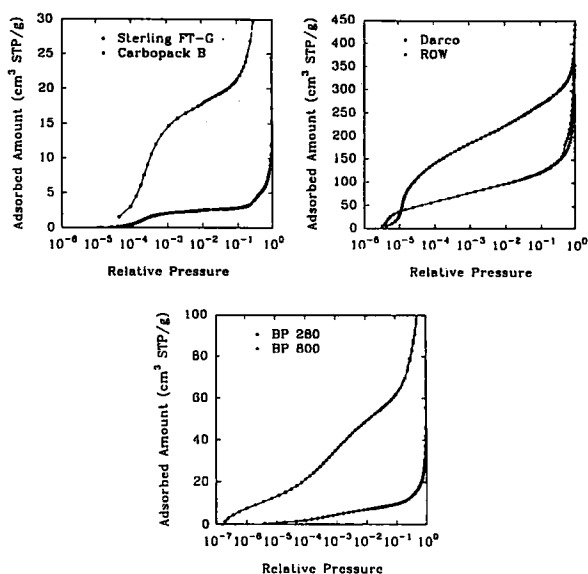


Figure 8. Experimental adsorption isotherms for homogeneous nonporous (Sterling FT-G, Carpack B), heterogeneous nonporous (BP 280), porous (BP 800) and highly microporous (Darco, ROW) adsorbents.

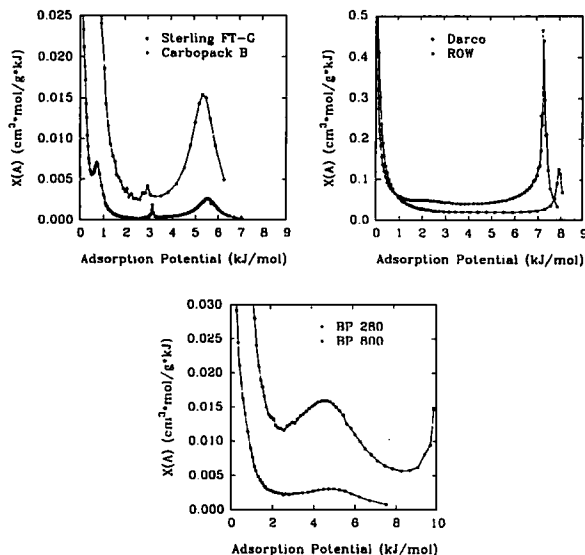


Figure 9. The distributions of the adsorption potential for selected adsorbents (see caption to Fig. 8).

indicates their high microporosity. The isotherm on Darco features a hysteresis loop in the higher pressure region. The differences in the adsorption properties of these carbonaceous samples can be seen very clearly on their distributions of the adsorption potential (Fig. 9). Both Sterling FT-G and Carpack B

exhibit a well-pronounced peak at about 5.5 kJ/mol, which corresponds to the formation of a monolayer of the adsorbate on the adsorbent surface. For low values of the adsorption potential  $A$ , the adsorption potential distribution  $X(A)$  rises abruptly at 1–1.5 kJ/mol due to the multilayer formation and possibly the capillary condensation in mesopores. The adsorption potential distributions for Darco and ROW exhibit sharp peaks for  $A = 8$  kJ/mol and  $A = 7.2$  kJ/mol, respectively. Based on Fig. 3, the size of pores in these samples can be estimated as 0.7–0.8 nm. The  $X(A)$  distributions are rather flat and featureless for  $A$  from about 1.5 to 6.5 kJ/mol, but then they increase for  $A$  close to zero, which indicates either multilayer formation on the surface or capillary condensation in mesopores and possibly small macropores. There is no peak at  $A$  about 5.5 kJ/mol, which would be expected to appear as a fraction of larger pores is present in the samples. Before a possible explanation will be put forward, the distributions of the adsorption potential for BP 280 and BP 800 need to be examined. BP 280 is essentially nonporous, similarly to Sterling FT-G and Carbopack B, but differs in surface properties, as its distribution of the adsorption potential shows no sharp maximum. The peak, which represents the monolayer formation, is very broad and its maximum lies at about 5 kJ/mol. The differences in adsorption behavior between the compared nonporous samples can be attributed to surface heterogeneity and/or slightly different structure of surface layers for BP 280. Notice, that BP 800 (as well as several other Black Pearl carbon blacks not mentioned in the current study) exhibits the same shape of the  $X(A)$  in the range from 2 to 7 kJ/mol, as a nonporous BP 280. The difference can be seen on the distribution at higher adsorption potentials. Namely,  $X(A)$  for BP 800 increases for the values of  $A$  about 9 kJ/mol and reaches its local maximum close to 10 kJ/mol, which indicates noticeable amount of very narrow micropores. The use of Fig. 3 or the comparison with  $X(A)$  for the model isotherms allows to estimate the width of the latter pores as about 0.5 nm.

The broad and diffuse nature of the monolayer formation peak, which is present on the  $X(A)$  curve for the BP samples at about 5 kJ/mol, suggests that similar broadening due to heterogeneity effects might be the case for the  $X(A)$  curves for microporous Darco and ROW samples. Therefore, there is no noticeable maxima on their distributions of the adsorption potential at the  $A$  value about 5–5.5 kJ/mol.

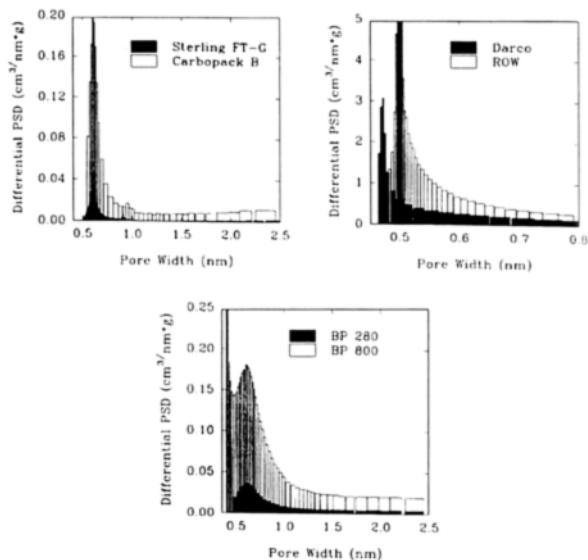


Figure 10. Horvath-Kawazoe pore size distributions for selected adsorbents (see caption to Fig. 8).

At this point, the Horvath-Kawazoe pore size distributions will be examined (Fig. 10). In all cases, HK PSDs show the presence of micropores of the size below 0.7 nm. As it was shown before, the HK method relates the increase in adsorbed amount resulting from the monolayer formation to the presence of nonexistent micropores of the widths about 0.6 nm. This effect can be seen very clearly for Sterling FT-G, Carbopack B and BP 280. The area of the 0.6 nm peak corresponds to the volume of the nonexistent pores (or the liquid adsorbate confined in them). The latter volume can be converted into the volume of the gas adsorbate at the standard temperature and pressure and appears to be roughly equivalent to the BET monolayer capacity, which once again proves an artificial nature of the peak. Because of the low surface area of the nonporous samples, the area of their 0.6 nm peak is small, which allows to easily distinguish them from microporous samples, as the latter usually exhibit much higher adsorption capacities (see Fig. 10).

In the case of the microporous samples, sharp peaks can be noticed on HK PSDs. But as it was mentioned before, the pore sizes assessed by the HK method are expected to be inaccurate (underestimated in the case of Darco and ROW). One faces even more difficult problems trying to examine the microporosity of BP 800, for which the peak, which indicates the presence of the actual microporosity, overlaps with the peak resulting



from the monolayer formation. Therefore, the assessment of microporosity for carbonaceous materials by means of the Horvath-Kawazoe method appears to be quite difficult. If the sample is essentially microporous with the pore sizes below about 0.8 nm, the application of the method is possible, but parameters used in the method need to be adjusted. Recent advances in modeling of adsorption in porous media, such as applications of nonlocal density functional theory and computer simulations can be used in order to correct the parameters mentioned above. For samples exhibiting considerable mesopore or macropore surface area (for which the course of adsorption, at least until the monolayer is formed, is similar to that for a nonporous adsorbent) the application of the HK method is rather difficult. That problem was discussed above, when the composite model isotherms and the experimental data were examined.

As it was shown, in many cases the examination of adsorption potential distributions  $X(A)$  provides a valuable insight into surface and porous properties of the samples. That is evident, when the presence of microporosity needs to be assessed. The peaks on  $X(A)$  function, which correspond to micropores, are much better separated than the peaks on the HK pore size distributions. The relation between maxima on the  $X(A)$  functions and the pore size can be obtained from the DFT or computer simulation. The application of the adsorption potential distributions to evaluate microporosity from the experimental data appears to be promising, especially as the quantity  $X(A)$  is model independent and can be used to calculate the differential enthalpy and the differential entropy of adsorption (Jaroniec, 1987). The problem of elucidating information about microporosity from adsorption potential distributions will be a subject of our further studies.

Some comments need to be made regarding methods of micropore analysis based on the Dubinin-Radushkevich (DR) or the Dubinin-Astakhov (DA) equation. The latter isotherms were expected to represent adsorption in homogeneous micropores. In Fig. 11 shown are DA adsorption isotherms, which are described by the following equation:

$$\Theta = \exp \left[ - \left( \frac{A}{E} \right)^n \right] \quad (5)$$

where  $E$  and  $n$  are constants.

The comparison of the DA equation with the model isotherms for graphite slit-like pores leads to the

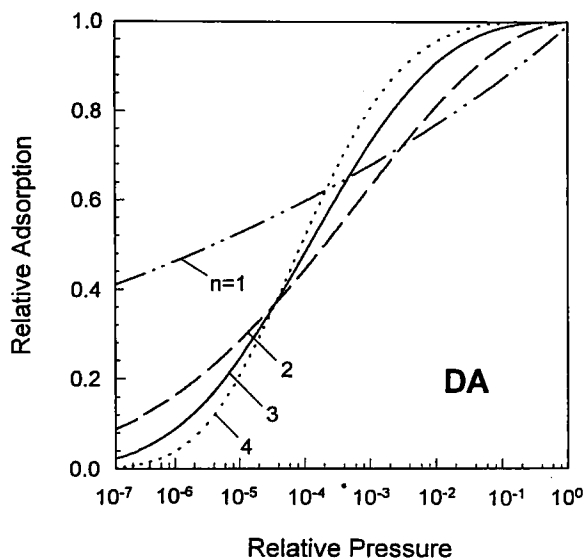


Figure 11. Dubinin-Astakhov adsorption isotherms. The parameters in the DA equations were:  $E = 35$  kJ/mol for  $n = 1$  and  $E = 20$  kJ/mol for  $n = 2, 3$  and  $4$ .

conclusion that none of them can be adequately represented by the DA equation. The latter equation predicts a rather gradual increase in the adsorbed amount. This increase is spread over several orders of magnitude of the relative pressure. That is not the case for adsorption in actual monodisperse homogeneous pores, which is predicted to exhibit a quite steep increase, for instance at pressures of the monolayer formation or condensation inside a given pore. The gradual rather than stepwise pore filling predicted by the DA equation results in the distributions of the adsorption potential (Fig. 12), which have one extremely broad peak (for  $n = 2, 3$  and  $4$ ). Such distributions do not have any counterpart among the model distributions shown in Fig. 2, which exhibit one or two rather narrow peaks. It can be concluded that the DA equation may possibly represent adsorption in the system of considerable surface and/or structural heterogeneity. Therefore, the use of the DA equation as a local adsorption isotherm in the integral equation for the total amount adsorbed is questionable and requires further studies.

Finally, it needs to be remarked that the accuracy of low pressure adsorption measurements is essential for any method of micropore analysis to provide meaningful results. The problems associated with low pressure adsorption measurements were recently discussed by Bereznitski et al. (1997).

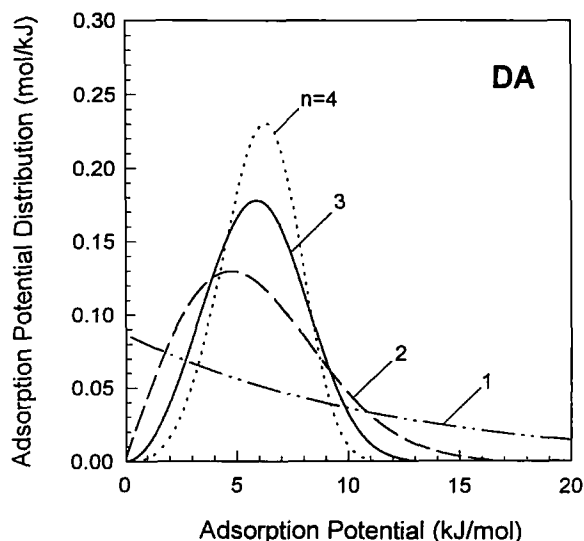


Figure 12. The distributions of the adsorption potential for DA equation with several different values of the exponent  $n$ .

## Conclusions

The Horvath-Kawazoe method was examined against model adsorption isotherms obtained from the nonlocal density functional theory for homogeneous slit-like graphite pores. It was shown that the HK method qualitatively reproduces the shape of PSDs in the 0.4–0.9 nm pore size range, but the pore sizes are underestimated. In the case of pores wider than 0.9 nm, HK PSDs for monodisperse model isotherms exhibit two peaks. The one, which appears at about 0.6 nm, corresponds to the monolayer formation on the pore walls and is not an indication of actual microporosity. The second peak arises from the condensation of the adsorbate between already formed adsorbate layers on the pore walls, and in principle can be used to estimate the pore size. For pores of the width above 1 nm, the relative pressures for the monolayer buildup do not change appreciably with the pore size increase, so the HK method shows the presence of 0.6 nm micropores for mesoporous, macroporous and nonporous samples. The conclusions of our model studies were confirmed by relevant experimental data.

The Dubinin-Astakhov equation was also examined. It was shown that it does not provide a satisfactory representation of adsorption in homogeneous microporous systems. Therefore, its application to calculate micropore size distributions is questionable and requires further studies.

The distribution of the adsorption potential appeared to be useful in micropore analysis. It is a model independent quantity, related to thermodynamic functions, such as the differential enthalpy and the differential entropy of adsorption. Hence, further studies are intended in the direction of the application of the adsorption potential distribution in micropore analysis.

## Nomenclature

- $A$  Adsorption potential (kJ/mol)
- $C_1$  Constant in Eq. 3 and 4 (kJ \* nm/mol)
- $C_2$  Constant in Eq. 3 and 4 (nm<sup>3</sup>)
- $C_3$  Constant in Eq. 3 and 4 (nm<sup>9</sup>)
- $C_4$  Constant in Eq. 3 and 4 ( )
- $d_a$  Adsorbate molecule diameter (nm)
- $d_A$  Adsorbent atom diameter (nm)
- $\Delta G$  Change in the Gibbs free energy (kJ/mol)
- $J$  Pore size distribution (cm<sup>3</sup>/(g \* nm))
- $R$  The universal gas constant = 8.31431 (J/(mol \* K))
- $T$  Absolute temperature (K)
- $V$  Amount adsorbed expressed in cm<sup>3</sup> of liquid adsorbate per 1 g of the adsorbent  
= 0.0015468 \* amount adsorbed expressed in cm<sup>3</sup> STP/g (cm<sup>3</sup>/g)
- $x$  Pore width (nm)
- $X$  Differential adsorption potential distribution (cm<sup>3</sup> \* mol/(g \* kJ))
- $\delta$  Constant defined as  $\frac{d_A - d_a}{2}$  (nm)
- $p$  Pressure (Pa)
- $p_0$  Saturated pressure = 760 torr = 101325 Pa (Pa)
- $p_c$  Condensation pressure (Pa)
- $\Theta$  Degree of pore filling ( )
- $S_{\text{BET}}$  BET specific surface area (m<sup>2</sup>/g)
- $S_{\text{ex}}$  External surface area obtained from  $t$ -plot method (m<sup>2</sup>/g)
- $V_{\text{mi}}$  Micropore volume obtained from  $t$ -plot method (cm<sup>3</sup>/g)
- $V_t$  Total pore volume (cm<sup>3</sup>/g)
- $E$  Characteristic energy in the Dubinin-Astakhov equation (kJ/mol)
- $n$  Exponent in the Dubinin-Astakhov equation ( )

## Acknowledgments

The authors want to express their thanks to Dr. J.P. Olivier for providing nonlocal density functional isotherm data. Cabot Corporation (Special Blacks

Division, Billerica, MA), Supelco (Bellefonte, PA) and Norit Co. (Amersfoort, the Netherlands) are gratefully acknowledged for providing carbon samples.

## References

- Advanced Zeolite Science and Applications*, J.C. Jansen, M. Stocker, H.G. Karge and J. Weitkamp (Eds.), Studies in Surface Science and Catalysis, 85, Elsevier, Amsterdam and New York, 1994.
- Bansal, R.C., J.-B. Donnet, and F. Stoeckli, *Active Carbon*, Marcel Dekker, Inc., New York and Basel, 1988.
- Berezniński, Y., M. Jaroniec, and K.P. Gadkaree, "Influence of Analysis Conditions on Low Pressure Adsorption Measurements and its Consequences in Characterization of Energetic and Structural Heterogeneity of Microporous Carbons," *Adsorption* (1997), (in press).
- Characterization and Modification of the Silica Surface*, E.F. Vansant, P. Van der Voort, and K.C. Vrancken (Eds.), Elsevier, Amsterdam, 1995.
- Cheng, L.S. and R.T. Yang, "Improved Horvath-Kawazoe Equations Including Spherical Pore Models for Calculating Micropore Size Distribution," *Chem. Eng. Sci.*, **49**, 2599–2609 (1994).
- Chmiel, G., L. Lajtar, S. Sokolowski, and A. Patrykiewicz, "Adsorption in Energetically Heterogeneous Slit-like Pores: Comparison of Density Functional Theory and Computer Simulations," *J. Chem. Soc. Faraday Trans.*, **90**, 1153–1156 (1994).
- Choma, J., M. Jaroniec, and J. Klinik, "Micropore Size Distribution Functions for Active Carbons Calculated from Low Temperature Nitrogen Adsorption," *Karbo-Energochemia-Ekologia*, **10**, 258 (1994).
- Dubinin, M.M., "Physical Adsorption of Gases and Vapors in Micropores," *Progress Surface Membrane Sci.*, **9**, 1–69 (1975).
- Horvath, G. and K. Kawazoe, "Method for Calculation of Effective Pore Size Distribution in Molecular Sieve Carbon," *J. Chem. Eng. Japan*, **16**, 470–475 (1983).
- Jaroniec, M., "Thermodynamics of Gas Adsorption on Heterogeneous Microporous Solids," *Langmuir*, **3**, 795–799 (1987).
- Jaroniec, M., "Characterization of Nanoporous Materials," *Access to Nanoporous Materials*, T.J. Pinnavaia and M. Thorpe (Eds.), pp. 255–272, Plenum Press, New York, 1996.
- Jaroniec, M. and R. Madey, *Physical Adsorption on Heterogeneous Surfaces*, Elsevier, Amsterdam, 1988.
- Jaroniec, M., K.P. Gadkaree, and J. Choma, "Relation Between Adsorption Potential Distribution and Pore Volume Distribution for Microporous Carbons," *Colloids and Surfaces*, **118**, 203–210 (1996).
- Kaminsky, R.D., E. Maglara, and W.C. Connor, "A Direct Assessment of Mean-Field Methods of Determining Pore Size Distributions of Porous Media from Adsorption Isotherm Data," *Langmuir*, **10**, 1556–1565 (1994).
- Karykowski, K., W. Rzyśko, A. Patrykiewicz, and S. Sokolowski, "Grand Canonical Ensemble Monte Carlo Simulations of Adsorption in Energetically Heterogeneous Slit-like Pores," *Thin Solid Films*, **249**, 236–240 (1994).
- Kresge, C.T., M.E. Leonowicz, W.J. Roth, J.C. Vartuli, and J.S. Beck, "Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism," *Nature*, **359**, 710–712 (1992).
- Kruk, M., M. Jaroniec, and Y. Berezniński, "Adsorption Study of Porous Structure Development in Carbon Blacks," accepted to *J. Col. Surf. Sci.*, (1996).
- Lastoskie, C., K.E. Gubbins, and N. Quirke, "Pore Size Distribution Analysis of Microporous Carbons: A Density Functional Theory Approach," *J. Phys. Chem.*, **97**, 4786–4796 (1993a).
- Lastoskie, C., K.E. Gubbins, and N. Quirke, "Pore Size Heterogeneity and the Carbon Slit Pore: A Density Functional Theory Model," *Langmuir*, **9**, 3693–3702 (1993b).
- Olivier, J.P., "Modeling Physical Adsorption on Porous and Nonporous Solids Using Density Functional Theory," *J. Porous Mater.*, **2**, 9–17 (1995).
- Olivier, J.P., W.B. Conklin, and M.v. Szombathely, "Determination of Pore Size Distribution from Density Functional Theory: A Comparison of Nitrogen and Argon Results," *Stud. Surf. Sci. Catal.*, **87**, 81–89 (1994).
- Szombathely, M., M. Brauer, and M. Jaroniec, "The Solution of the Adsorption Integral Equations by Means of the Regularization Method," *J. Comput. Chem.*, **13**, 17–32 (1992).
- The Colloid Chemistry of Silica*, H.E. Bergna (Ed.), Amer. Chem. Soc., Washington, D.C., (1994).
- Zeolites: A Refined Tool for Designing Catalytic Sites*, L. Bonnevot and S. Kaliaguine (Eds.), Studies in Surface Science and Catalysis, 97, Elsevier, New York, 1995.