

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228585094>

The Application of a CONTIN Package for the Evaluation of Micropore Size Distribution Functions

ARTICLE *in* LANGMUIR · JULY 2002

Impact Factor: 4.46 · DOI: 10.1021/la011555q

CITATIONS

25

READS

11

3 AUTHORS, INCLUDING:



Piotr A Gauden

Nicolaus Copernicus University

224 PUBLICATIONS 1,942 CITATIONS

SEE PROFILE

The Application of a CONTIN Package for the Evaluation of Micropore Size Distribution Functions

Piotr Kowalczyk,[†] Artur P. Terzyk,^{*,‡} and Piotr A. Gauden[‡]

Department of Respiratory Protection, Military Institute of Chemistry and Radiometry, gen. Chruściel Avenue 105, 00-910 Warsaw, Poland, and Physicochemistry of Carbon Materials Research Group, Department of Chemistry, N. Copernicus University, Gagarin St. 7, 87-100 Toruń, Poland

Received October 15, 2001. In Final Form: April 16, 2002

This paper consists of three main parts. In the first part, the new model isotherm equations for adsorption on heterogeneous microporous solids are presented, using different (and never before utilized) pore-size distribution functions. In the second part, freshly developed adsorption isotherms are applied to check the power of the CONTIN algorithm. Finally, in the third part, the micropore-size distributions (MPSD) of two strictly microporous activated carbons (of synthetic origin) are calculated on the basis of different adsorption models and numerical methods of solving the global adsorption isotherm equation. The following methods are put to use: the recently developed gamma-type adsorption isotherm (GTAI) equation, applied for the first time in adsorption studies, the modified Galerkin method, CONTIN, and, finally, the density functional theory. The usefulness of CONTIN and the similarities between the results of the applied methods are discussed. The influence of the heterogeneity parameter (n) of the Dubinin–Astakhov equation as well as the relation between characteristic adsorption energy and pore diameter on the shape and position of the MPSD is considered. Some remarks on the optimization process of fitting GTAI to experimental data are also given.

I. Introduction

It is generally accepted that the surfaces of solids are energetically and structurally heterogeneous to a greater or lesser extent.^{1–3} They are usually both geometrically (i.e., fine pores of different size and shapes, surface irregularities) and chemically (various surface groups, impurities) nonuniform. Among the adsorbents used in industry, activated carbons are the most complex and also the most versatile due to their extremely high surface area and pore volume.⁴ It is well-known that sorption properties of porous materials depend mainly on the quantity of the smallest pores called micropores.^{1–4} These pores are, in carbons, slit-shaped, and their sizes are smaller than 2 nm.^{5,6} Several of the most common techniques of modeling of vapor adsorption onto microporous materials are based on the Dubinin's theory of micropore filling (TOMF).^{3–5,7–10} The potential adsorption theory, originally proposed by Polanyi and developed by

Dubinin and co-workers, is classified as the "thermodynamic" approach since it is based on the phenomenological thermodynamics.^{3,10} The well-known Dubinin–Radushkevich (DR) adsorption isotherm equation was initially used for description of adsorption of vapors in homogeneous activated carbons⁸

$$\Theta = \exp \left[- \left(\frac{A}{\beta E_0} \right)^2 \right] \quad (1)$$

where Θ is the degree of micropore filling, $A = RT \ln(p_0/p)$ is the differential free enthalpy of adsorption, β is the similarity coefficient, and E_0 is the characteristic energy of adsorption. Later, this equation was found useful for the description of adsorption on a variety of adsorbents (for example, silicas, zeolites, and other materials) especially at low pore fillings.^{5,10–12}

As many authors reported, the DR equation has not adequately described the experimental adsorption data on carbons, especially in the cases of high burnoff.^{13,14} To overcome this difficulty, many authors applied the three-parameter Dubinin–Astakhov (DA) equation in the form^{3,5,10,14}

$$\Theta = \exp \left[- \left(\frac{A}{\beta E_0} \right)^n \right] \quad (2)$$

where n is the empirical heterogeneity parameter. It can be used as a macroscopic measure of the sharpness of the micropore size distribution. For solids having a relatively

* To whom correspondence should be addressed. E-mail: aterzyk@chem.uni.torun.pl.

[†] Military Institute of Chemistry and Radiometry.

[‡] N. Copernicus University.

(1) Rudziński, W.; Everett, D. H. *Adsorption of Gases on Heterogeneous Surfaces*; Academic Press: New York, 1992.

(2) Rudziński, W.; Steele, W. A.; Zgrablich, G. Eds. *Equilibria and Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces*; Elsevier: Amsterdam, 1997.

(3) Wojsz, R. *Characteristics of the Structural and Energetic Heterogeneity of Microporous Carbon Adsorbents Regarding the Adsorption of Polar Substances*; UMK: Toruń, 1989 (in Polish).

(4) Jankowska, H.; Świątkowski, A.; Choma, J. *Active Carbon*; Ellis Horwood: New York, 1991.

(5) Do, D. D. *Adsorption Analysis: Equilibria and Kinetics*; Imperial College Press: London, 1998.

(6) (a) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: London, 1982. (b) Kruk, M.; Jaroniec, M.; Gadkaree, K. P. *Langmuir* **1999**, *15*, 1442.

(7) Dubinin, M. M. In *Progress in Membrane and Surface Science*; Cadenhead, D. A., Ed.; Academic Press: New York, 1975; Vol. 9, p 1.

(8) Dubinin, M. M.; Radushkevich, L. V. *Dokl. Akad. Nauk SSSR* **1947**, *55*, 327.

(9) Dubinin, M. M.; Stoeckli, F. *J. Colloid Interface Sci.* **1980**, *75*, 34.

(10) Dubinin, M. M. *Adsorption and Porosity*, WAT: Warsaw, 1975 (In Polish).

(11) Lebeda, R.; Turov, V. V.; Charnas, B.; Skubiszewska-Zięba, J.; Gun'ko, V. M. *J. Colloid Interface Sci.* **2000**, *223*, 112.

(12) Lebeda, R.; Marciniak, M.; Gun'ko, V. M.; Grzegorzczak, W.; Malygin, A. A.; Malkov, A. A. *Colloids Surf., A* **2000**, *167*, 275.

(13) Marsh, H.; Rand, B. *J. Colloid Interface Sci.* **1970**, *33*, 101.

(14) Trznadel, B. J.; Ziętek, S.; Świątkowski, A. *Adsorpt. Sci. Technol.* **1999**, *17*, 11.

narrow micropore size distribution curve, the DA equation with n equal to 3 describes experimental data well. Therefore, if the parameter n of a system deviates from 3 (usually smaller than 3), that system is said to be heterogeneous or has a wide micropore size distribution. A typical value of n for strongly activated carbons is between 1.2 and 1.8.¹⁰

Dubinin and Izotova proposed an alternative equation (DI) describing the adsorption isotherm on a heterogeneous and microporous solid¹⁵

$$\Theta = \exp\left[-\left(\frac{A}{\beta E_{01}}\right)^{n_1}\right] + \exp\left[-\left(\frac{A}{\beta E_{02}}\right)^{n_2}\right] \quad (3)$$

The DI equation suggests a biporous structure of micropores. Two independent regions of a micropore system are characterized by the DA or DR equation. This approach is one of the simplest approaches dealing with nonhomogeneous solids. It is obvious that real heterogeneous solids are usually composed of several independent regions of micropores. Thus, obviously eq 3 can be extended as

$$\Theta = \exp\left[-\left(\frac{A}{\beta E_{01}}\right)^{n_1}\right] + \exp\left[-\left(\frac{A}{\beta E_{02}}\right)^{n_2}\right] + \dots + \exp\left[-\left(\frac{A}{\beta E_{0M}}\right)^{n_M}\right] = \sum_{i=1}^M \exp\left[-\left(\frac{A}{\beta E_{0i}}\right)^{n_i}\right] \quad (4)$$

where M is the number of independent microporous regions. Consequently, when M tends to infinity, the patchwise character of topography of micropores is observed (i.e., the sum in eq 4 can be replaced by a continuous spectrum). In other words, micropores are grouped together into patches, which could be considered as independent adsorption subsystems, forming the systems analogous to so-called "homotactic" surfaces.^{1-5,9}

For such more complex microporous systems, Stoeckli proposed a general form of global adsorption isotherm (GAI) equation assuming the DR (eq 1) or DA (eq 2) equation as a kernel⁹

$$\Theta = \int_{\Omega(B)} \exp[-By] f(B) dB = \int_{\Omega(B)} \left[\sum_{t=0}^{\infty} \frac{(-By)^t}{t!} \right] f(B) dB \quad (5)$$

where $B = 1/E_0^n$ is a structural parameter, $y = (A/\beta)^n$, $f(B)$ is an unknown distribution function of B , and $\Omega(B)$ is the integration range. Strictly speaking, the range of integration should reflect the properties of a microporous system, i.e., the proper limit range should be between B_{\min} and B_{\max} .^{3,16-23,30} Different authors in their studies extend the integration range beyond this limit.^{9,24-28} In such cases simple adsorption isotherm equations can be obtained by applying the Laplace transform or other simple invert techniques. However, as mentioned by Cerofolini and Re²⁸

and clearly shown in numerical research by Wojsz,³ as well as by Gauden and Terzyk,²⁹⁻³² the extending of the integration range of eq 5 to unphysical values is questionable and can lead to incorrect results. Supporting this idea in the current paper, $\Omega(B)$ is strictly connected with the properties of a microporous system. Another problem is the correctness of the assumed local isotherm equation. As pointed out by Gregg and Sing and others,⁶ the mechanism of adsorption in micropores changes with the diameter of slits; i.e., it can be divided into two main stages. Primary micropore filling takes place in pores, which can accommodate not more than two layers of adsorbed molecules, and secondary micropore filling in wider micropores.⁶ Some theoretical studies suggest that Dubinin's theory sufficiently represents only the primary process. Moreover, some authors are of the opinion that the DA equation does not represent adequately the adsorption process in a homogeneous microporous structure (and it cannot be used as a local adsorption isotherm in the GAI equation), but the experimental results presented recently³³ do not confirm this view. It was shown that the DA equation fits successfully the experimental results of nitrogen and benzene adsorption on the series of microporous films with almost homogeneous microporosity (pore size distributions were determined using the density functional theory (DFT)). On the other hand, recent experimental studies reported by Stoeckli and co-workers³⁴ showed that if one assumes that the porosity consists mainly of locally slit-shaped micropores, model isotherms can be obtained by computer simulations and used to assess the pore size distribution (PSD) on the basis of experimental isotherms. In their study,³⁴ CO isotherms have been measured on well-characterized microporous carbons with average micropore widths between 0.65 and 1.5 nm and analyzed with model isotherms obtained with standard Monte Carlo simulations. The resulting PSDs are in good agreement with those obtained from a modified Dubinin equation, from liquid probes of molecular dimensions between 0.4 and 1.5 nm, from scanning tunneling microscopy (STM), and from modeling based on CH₄ adsorption at 308 K.³⁴

On the other hand we want to point out that the results obtained from computer simulations of adsorption in microporous carbons should be treated with caution. There is no doubt that real adsorbents possess a very complicated porous structure and the assumption of slitlike geometry of pores in carbons is simplification. Computer simulations simplify the structure of carbons and usually neglect pore connectivity. It is well-known that a model of the structure of microporous carbon does not exist that can successfully explain all measured experimentally physical and chemi-

- (15) Izotova, T. I.; Dubinin M. M. *Zh. Fiz. Khim.* **1965**, *39*, 2769.
 (16) Terzyk, A. P.; Gauden, P. A.; Rychlicki, G.; Wojsz, R. *Carbon* **1998**, *36*, 1703 (*Carbon* **1999**, *37*, 539).
 (17) Wang, K.; Do, D. D. *Langmuir* **1997**, *13*, 6226.
 (18) McEnaney, B.; Mays, T. J.; Causton, P. D. *Langmuir* **1987**, *3*, 695.
 (19) Terzyk, A. P.; Gauden, P. A.; Rychlicki, G.; Wojsz, R. *Colloids Surf., A* **1999**, *152*, 293.
 (20) Kaneko, K. *J. Membr. Sci.* **1994**, *6*, 59.
 (21) Do, D. D.; Wang, K. *Langmuir* **1999**, *14*, 7271.
 (22) Jaroniec, M.; Kruk, M.; Olivier, J. *Surf. Sci.* **1995**, *342*, L1127.
 (23) Jagiello, J.; Schwarz, J. A. *J. Colloid Interface Sci.* **1992**, *154*, 225.

- (24) Jaroniec, M.; Madey, R. *Physical Adsorption on Heterogeneous Solids*; Elsevier: Amsterdam, 1988.
 (25) Carrott, P. J. M.; Carrott, M. M. L. R. *Carbon* **1996**, *34*, 647.
 (26) Jagiello, J.; Schwarz, J. A. *Langmuir* **1993**, *9*, 2513.
 (27) Hu, X.; Do, D. D. *Langmuir* **1994**, *10*, 3296.
 (28) Cerofolini, G. F.; Re, N. *Riv. Nuovo Cimento Soc. Ital. Fis.* **1993**, *16*, 1.
 (29) Gauden, P. A. Theoretical Description of the Structural and Energetic Heterogeneity of Carbonaceous Materials (Thesis), UMK: Toruń, 2001 (in Polish).
 (30) (a) Gauden, P. A.; Terzyk, A. P. *J. Colloid Interface Sci.* **2000**, *227*, 482. (b) Gauden, P. A.; Terzyk, A. P.; Rychlicki, G.; Kowalczyk, P. *J. Colloid Interface Sci.* **2001**, *244*, 439.
 (31) Terzyk, A. P.; Gauden, P. A.; Rychlicki, G.; Wojsz, R. *Langmuir* **1999**, *15*, 285.
 (32) Gauden, P. A.; Terzyk, A. P.; Rychlicki, G. *Carbon* **2001**, *39*, 267.
 (33) Terzyk, A. P.; Gauden, P. A.; Zawadzki, J.; Rychlicki, G.; Wiśniewski, M.; Kowalczyk, P. *J. Colloid Interface Sci.* **2001**, *243*, 183.
 (34) Stoeckli, F.; Guillot, A.; Slassi, A. M.; Hugli-Cleary, D. *Carbon* **2002**, *40*, 383.

cal features of this material.³⁵ This was pointed out by Fitzer, Iwashita, and Inagaki³⁵ and recently by Pesin and Baitinger.³⁶ They stated that an extreme complexity of electronic structure and atomic arrangement of carbon is a firmly established fact. This is the main reason for the absence of a unique and commonly adopted carbon structural model nowadays. The most frequently used ones for data interpretations are those introduced by Jenkins and Kawamura and by Oberlin.³⁵ Unfortunately these models are entirely contradictory to one another. According to the first one, synthetic active carbon is a conglomerate of randomly twisted and highly anisotropic graphite-like fibrils whose width gradually increases due to high-temperature annealing. In contrast, the second model postulates the existence of practically spite isometric, but heavily crumpled, graphite-like sheets; heat treatment regularly reduces these layer distortions.³⁵ All these simplifications as well as different irregularities obtained on PSDs calculated from the DFT model led Jagiello and Tolles to the statement that the pore model used in the DFT calculations does not adequately represent actual activated carbons.³⁷ Thus further refinements of the model are desired in order to better described the complex structure of activated carbons. Summing up the methods of PSD determination from analytical equations based on Dubinin's theory as well as from computer simulations requires a solid experimental verification.

Thus it can be concluded that some experimental results support Stoeckli's concept⁹—he was the first to propose to apply Dubinin's equations as kernels in GAI (eq 5).

The physical meaning of $f(B)$ implies the properties of non-negativity and normalization,²⁸ thus

$$\forall B: f(B) \geq 0 \quad (6)$$

$$\int_{\Omega(B)} f(B) dB = 1 \quad (7)$$

It has been shown previously that the classical numerical invert of eq 5 leads to the unstable form of $f(B)$, and for this reason, specially projected numerical procedures must be adopted.^{24,28}

Obviously, from the practical point of view, the micropore size distribution (MPSD) is more applicable than $f(B)$. For this reason, many investigators started seeking a relation between the parameter of micropore structure (mainly micropore half-width x) and B . Up to the present, several empirical relations between the structural parameter and the micropore half-width have been proposed.^{9,38–45} It is also important that the relations of this type can be developed based on theoretical considerations.^{16,29,33,46–49} Dubinin postulated the most widespread

relation, defined by the formula⁹

$$x^n = BC^n \quad (8)$$

For the adsorption of nitrogen on activated carbons Bhatia and Shethna⁵⁰ assumed $C = 11.4$. With the $f(B)$ function known, the micropore size distribution can be obtained using the following transformations

$$f(x) = f(B) \frac{dB}{dx} \quad (9)$$

The current paper consists of three parts. In the first part (based on eqs 5–7), the new model isotherm equations for adsorption on heterogeneous microporous solids are presented. In the second part, developed adsorption isotherm equations are used to check the power of the CONTIN algorithm.^{51–55} Finally, in the third part, MPSDs of two strictly microporous activated carbons (of synthetic origin) are calculated based on different adsorption models and numerical methods of solving the global adsorption isotherm equation. The following equations and procedures are adjusted: the gamma-type adsorption isotherm equation (GTAI),^{30,48,56} applied for the first time in adsorption studies, the modified Galerkin method (MGM),⁵⁷ the Horvath and Kawazoe model (HK),⁵⁸ CONTIN,^{51–55} the density functional theory (DFT),⁵⁹ and the theory of micropore filling (TOMF).^{3–5,7–10,15,29,48} The usefulness of CONTIN as well as the similarities between the results of the methods are discussed. The influence of the heterogeneity parameter (n) of the Dubinin–Astakhov equation as well as the relation between characteristic adsorption energy and pore diameter on the shape and position of the MPSD is considered. Some remarks on the optimization process of fitting GTAI to experimental data are also given.

II. The New Isotherm Equations for Adsorption on Heterogeneous Microporous Solids

As it was mentioned by Rudziński et al.,⁶⁰ really existing heterogeneous solids can be characterized by a pretty complicated form of MPSD, with a number of local minima and maxima. However, to a certain degree of accuracy, the real MPSD curve can be (for practical purposes) approximated by some “smoothed” functions and their shape is described by a small number of parameters. Certainly, when the proposed model of the MPSD does

- (35) (a) Fitzer, E. *Contemp. Topics in Polym. Sci.* **1984**, 5, 101. (b) Iwashita, N. Intercalation Reactions into Graphite Followed by Potential and Their Application to Battery (Thesis), Hokkaido University, 1992. (c) Iwashita, N.; Inagaki M. *Carbon* **1993**, 31, 1107. (d) Inagaki, M. *Tanso* **1985**, 122, 114.
- (36) Pesin, L. A.; Baitinger, E. M. *Carbon* **2002**, 295.
- (37) Jagiello, J.; Tolles, D. In *Fundamental of Adsorption*; Meunier E. F., Ed.; Elsevier: Paris, 1998; p 629.
- (38) McEnaney, B. *Carbon* **1987**, 25, 69.
- (39) McEnaney, B.; Mays, T. J. In COPS II Conference. Alicante, 1990.
- (40) Stoeckli, H. F. *Carbon* **1990**, 28, 1.
- (41) Stoeckli, H. F.; Huguenin, D.; Laederach, A. *Carbon* **1994**, 32, 1359.
- (42) Stoeckli, H. F.; Ballerini, L.; De Bernardi, A. *Carbon* **1989**, 27, 501.
- (43) Choma, J.; Jaroniec, M. *Karbo-Energochemia-Ekologia* **1997**, 11, 368 (in Polish).
- (44) Ohkubo, T.; Iiyama, T.; Nishikawa, K.; Suzuki, T.; Kaneko, K. *J. Phys. Chem.* **1999**, 103, 1859.
- (45) Stoeckli, H. F.; Morel, D. *Chimia* **1980**, 34, 502.

- (46) Chen, S. G.; Yang, R. T. *Langmuir* **1994**, 10, 4244.
- (47) (a) Terzyk, A. P.; Gauden, P. A. *Colloids Surf., A* **2001**, 177, 57. (b) Terzyk, A. P.; Kowalczyk P. Gauden P. A. Rychlicki G., Ziętek S. *Colloids Surf., A* **2002**, 201, 17.
- (48) Gauden, P. A.; Terzyk, A. P. *Theory of Adsorption in Micropores of Carbonaceous Materials*; WICHIR: Warsaw, in press (in Polish).
- (49) Chen, S. G.; Yang R. T. *J. Colloid Interface Sci.* **1996**, 177, 298.
- (50) Bhatia, S. K.; Shethna, H. K. *Langmuir* **1994**, 10, 3230.
- (51) Provencher, S. W. *Comput. Phys. Commun.* **1982**, 27, 213.
- (52) Provencher, S. W. *Comput. Phys. Commun.* **1982**, 27, 229.
- (53) Gun'ko, V. M.; Lebeda, R.; Marciniak, M.; Grzegorzczak, W.; Skubiszewska-Zięba, J.; Malygin, A. A.; Malkov, A. A. *Langmuir* **2000**, 16, 3227.
- (54) Puziy, A. M.; Matynia, T.; Gawdzik, B.; Poddubnaya, O. I. *Langmuir* **1999**, 15, 6016.
- (55) Gun'ko, V. M.; Do, D. D. *Colloids Surf., A* **2001**, 193, 71.
- (56) Kowalczyk, P.; Terzyk, A. P.; Gauden, P. A. *J. Colloid Interface Sci.* **2001**, 243, 300.
- (57) Gerald, C. F. *Applied Numerical Analysis*; Addison-Wesley: California, 1977.
- (58) (a) Horvath, G. *Colloids Surf., A* **1998**, 141, 295. (b) Horvath, G.; Kawazoe, K., *J. Chem. Engn. Jpn.* **1983**, 16, 6.
- (59) Oliver, J. P. *J. Porous Mater.* **1995**, 2, 9.
- (60) Rudziński, W. In *Physical Adsorption: Experiment, Theory and Application*; Fraissard, J., Conner, C. W., Eds.; Kluwer Academic Publishers: Dordrecht, 1996; p 181.

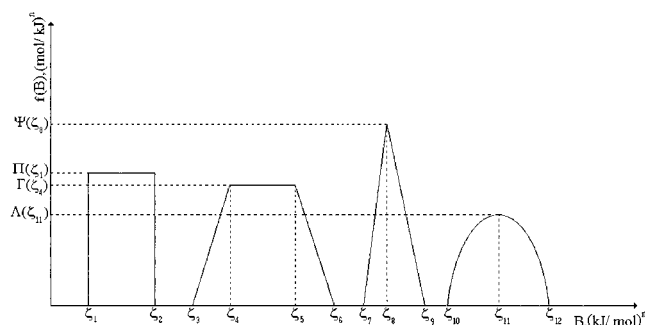


Figure 1. The shapes of model functions (uniform, trapezoidal, triangular, and parabolic) used for the representation of the $f(B)$ distribution.

not describe the equilibrium data well, a series of “smoothed” functions should be introduced.⁶⁰

Developed in this section, new adsorption isotherm equations (assuming different common shapes of the distribution function $f(B)$) can be used in investigations on the stability of advanced numerical algorithms intended for the evaluation of MPSD from the adsorption data.⁶¹ Assuming simple functions (uniform, triangular, parabolic, trapezoidal, and others) for representation of $f(B)$ 14 analytical formulas of the new adsorption isotherms (describing heterogeneous system of micropores) are developed. Since most of them have a complicated mathematical form, we are presenting in Supporting Information (see pages S1–S4 of the Supporting Information) the analytical solutions only for the uniform, triangle, parabolic, and trapezoidal forms of $f(B)$ (the schematic representation of these functions (ζ_i , the parameters determining the shape of $f(B)$), and the notations are given in Figure 1).

III. Adsorption Method (GTAI) and Numerical Algorithms (MGM, CONTIN, and DFT)

1. Gamma-Type Adsorption Isotherm (GTAI)

Equation. Recovering MPSD from experimental data belongs to the most difficult problems in adsorption science. In practice, optimization methods are very popular since they offer an opportunity to obtain the stable physical form of MPSD.^{1,18,28} These methods are based on the choice of an analytical form for MPSD (containing some parameters subsequently determined by the best fitting of the calculated global isotherm, through a simple numerical integration, to the experimental data). Thus, it is obvious that the choice of MPSD form is very important.

Gauden and Terzyk^{30,48} have recently solved eq 5 assuming DA equation as the kernel of the integral adsorption equation, MPSD as the gamma-type distribution, and physical boundaries of a micropore system. The following (gamma-type) adsorption isotherm equation (GTAI) was obtained

$$\Theta = \left(\frac{A^n}{\beta^n \rho} + 1 \right)^{-(\nu+1)} \left[\gamma \left(\nu + 1, \left(\frac{A^n}{\beta^n} + \rho \right) \zeta x_{\max}^n \right) - \gamma \left(\nu + 1, \left(\frac{A^n}{\beta^n} + \rho \right) \zeta x_{\min}^n \right) \right] \left[\gamma \left(\nu + 1, \zeta \rho x_{\max}^n \right) - \gamma \left(\nu + 1, \zeta \rho x_{\min}^n \right) \right] \quad (10)$$

(61) Rudziński, W.; Borowiecki, T.; Panczyk, T.; Dominko, A. *Adv. Colloid Interface Sci.* **2000**, *84*, 1.

where γ is the incomplete gamma function⁶² or in an integrated form:^{56,63}

$$\Theta = \frac{\left(\frac{A^n}{\beta^n \rho} + 1 \right)^{-(\nu+1)} \int_{\left(\frac{A^n}{\beta^n} + \rho \right) \zeta x_{\min}^n}^{\left(\frac{A^n}{\beta^n} + \rho \right) \zeta x_{\max}^n} \exp[-t] t^\nu dt}{\int_{\rho \zeta x_{\min}^n}^{\rho \zeta x_{\max}^n} \exp[-t] t^\nu dt} \quad (11)$$

for $x_{\min} \leq x \leq x_{\max}$, where ν and ρ are the gamma-type distribution function parameters, x_{\min} and x_{\max} are the lower and upper limits of a micropore system, respectively, and ζ relates E_0 to micropore dimension x by the following equation³⁰

$$\zeta = E_0^{-n} x^{-n} \quad (12)$$

On the basis of the eq 5, the parameters of MPSD can be evaluated using the following formula of the well-known gamma-type function^{5,18,24,29,30,48,64}

$$f(x) = \chi x^{\nu(\nu+1)-1} \exp(-\rho \zeta x^n) \quad (13)$$

where the normalization factor is defined by^{30,48}

$$\chi = \frac{n(\rho \zeta)^{\nu+1}}{\gamma(\nu+1, \zeta \rho x_{\max}^n) - \gamma(\nu+1, \zeta \rho x_{\min}^n)} \quad (14)$$

for $x_{\min} \leq x \leq x_{\max}$.

The proposed GTAI equation is very promising because the assumed gamma-type distribution function generates different shapes (for example, increase to infinity, exponential, fractal, asymmetrical bell-shaped, constant, and others).^{30,48,65} This equation can be used for the description of one-peak distribution functions and (in some cases) multippeak distributions.

2. Modified Galerkin (MGM) Method. In the current study we want also to apply the modified Galerkin method, which, to our knowledge, has not been applied yet for the evaluation of heterogeneity of microporous solids. This method is based on the Galerkin theorem.^{57,66} Namely, the unknown function $f(B)$ is approximated at first by the linear combination of simple functions. Obviously, the shapes of chosen functions are strictly connected to the examined physical problem. For approximation of adsorption integral equations, the series of triangles, trapezoids, uniforms, and parabolas appears to be a good choice.⁶⁰ Thus, $f(B)$ now is defined by

$$f(B) = \sum_{i=1}^N a_i \psi_i(B) \quad (15)$$

where the chosen functions $\psi_i(B)$ form a base with Hilbert space. Now the classical Gauss minimization least-squares procedure leads to the system of linear equalizations

(62) Press: W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in Fortran*; Cambridge University Press: Cambridge, 1992.

(63) Kowalczyk, P.; Terzyk, A. P.; Gauden, P. A.; Ziętek, S. *Proceedings of the Conference: Evolutionary Algorithms and Global Optimisation*; Jastrzębia Góra, 2001.

(64) Sircar, S. J. *Colloid Interface Sci.* **1984**, *98*, 306.

(65) Bronsztejn, I. N.; Siemiendajew, K. A. *Mathematics—the Encyclopaedic Handbook*; PWN: Warszawa, 1986 (in Polish).

(66) Bhatia, S. K.; Chakraborty, D. *AIChE J.* **1992**, *38*, 868.

$$Q(a_i) = \left\| \sum_{j=1}^M \left[\int_{\Omega(B)} \exp(-By_j) \sum_{i=1}^N a_i \psi_i(B) dB - \Theta(p_j) \right] \right\|^2 \quad (16)$$

Plenty of solution methods of the system of linear equalizations have been presented up until now.⁶³ In the computer program applied in this study, the Gauss–Jordan method was utilized. Considering our numerical experiments, we suggest a small number of base functions ($M = 2$ or 3). This is caused by the fact that although a greater number of base functions describes the measured adsorption isotherm better, the unphysical values of $f(B)$ can be generated simultaneously (the negative values of distribution functions). Thus, a small number of base functions is a good compromise between the data fitting and the smoothing requirement.

3. CONTIN Package. Developed by Provencher, CONTIN is a package for solving noisy linear integral equations of the first kind and system of (possibly ill-conditioned) linear algebraic equations.⁶⁷ This program is often applied for solving the integral equations of the first kind for effectively continuous distributions of diffusion coefficients, molecular weights, relaxation times, electron densities, adsorption energy distributions, pore size distributions, etc.^{51–55} Solving eq 5 is generally an ill-posed problem.^{1,28} This means that, even for an arbitrarily small (but nonzero) noise level in Θ , there still exists a large (typically infinite) set of solutions, $f(B)$, that all fit the Θ in eq 5 within the noise level. In CONTIN the classical functional of the following form

$$\text{VAR} = \sum_{i=1}^L \left\| \Theta_i - \int_{B_{\min}}^{B_{\max}} \exp(-By_i) f(B) dB \right\|^2 = \text{minimum} \quad (17)$$

where L , a number of isotherm points, is replaced by the functional proposed by Provencher⁶⁷

$$\text{VAR} = \sum_{i=1}^L \left\| \Theta_i - \int_{B_{\min}}^{B_{\max}} \exp(-By_i) f(B) dB \right\|^2 + \alpha \|f''(B)\|^2 = \text{minimum} \quad (18)$$

where α is a regularization parameter determined in CONTIN using a Bayesian approach.⁵¹ We want to point out here that there are no assumptions about the shape and the sign of $f(B)$ in the CONTIN package; however, applying natural condition of no negativity of $f(B)$ at any B , one can obtain stable solution possessing physical meaning.

4. DFT Method. Pore size distributions (PSDs) were calculated using the DFT software from Micromeritics (Norcross, GA).⁶⁸ A local mean field DFT was first used by Seaton et al.⁶⁹ and Lastoskie et al.⁷⁰ improved this method using a nonlocal mean field DFT. Some authors suggest this method as the more quantitatively accurate approach to determine the MPD and small mesopore structures.

IV. Results and Discussion

Developed new adsorption isotherm equations (see Supporting Information, pages S1–S4, eqs S.1–S.31) are

(67) Provencher, S. W. *CONTIN Users Manual (Version 2)*; Max-Planck-Institut für Biophysikalische Chemie: Göttingen, 1984.

(68) Webb, P. A.; Orr, C. *Analytical Methods in Fine Particles Technology*; Micromeritics Instrument Corp.: Norcross, GA, 1997.

(69) Seaton, N. A.; Walton, J. P. R. B.; Quirke, N. *Carbon* **1989**, *27*, 853.

(70) Lastoskie, C.; Gubbins, K. E.; Quirke, N. *J. Phys. Chem.* **1993**, *97*, 4786.

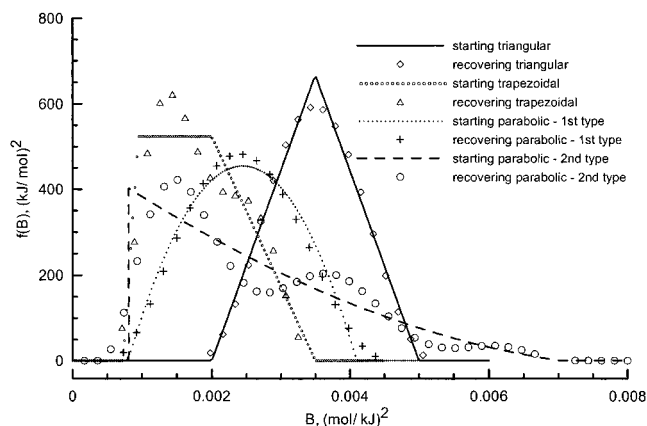


Figure 2. The recovering results (points obtained using CONTIN package) of starting triangular, trapezoidal, and parabolic forms of $f(B)$ function (lines).

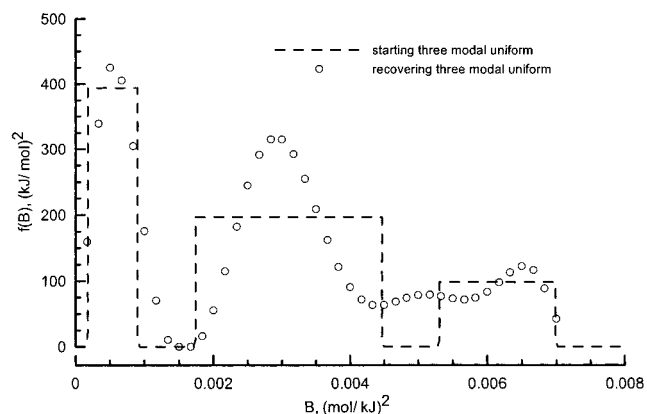


Figure 3. The recovering results (points obtained using CONTIN package) of starting three modal uniform $f(B)$ function (lines).

used to check the power of the CONTIN algorithm. Considering the results we want to underline that to test the power of the CONTIN package, some nontrivial continuous and discontinuous functions were applied. Nevertheless, the shape of the considered $f(B)$ and the MPD are very well reproduced without any assumptions concerning the shape of the examined functions (see Figures 2, 3, and S1–S6 (Supporting Information)). Furthermore, that package copes very well with the functions consisting of more than one peak (despite the discontinuous character of some examined functions) (see Figures 3 and S4–S6 (Supporting Information)). Additionally, CONTIN clearly smoothes unphysical bounds of some examined functions (for instance discontinuous uniform distributions). Finally, these functions have more realistic shapes because in practice many physical processes lead to similar bell-shaped distribution functions. It should be noticed that used by us models can successfully approximate the Gaussian or similar distributions. Summing up, CONTIN is a very powerful package and it can be successfully applied for predicting the pore-size distribution of microporous systems.

To examine the results of CONTIN and to compare them with other MPDs, the nitrogen adsorption data determined at 77.5 K for two strictly microporous activated carbons (of synthetic origin) were applied. The properties of studied solids were described previously.^{29,48,71–75}

(71) Rychlicki, G. *Role of Carbon Surface Chemistry in Adsorption and Catalytic Processes*; UMK: Toruń, 1985 (in Polish).

(72) Rychlicki, G.; Terzyk, A. P. *Adsorpt. Sci. Technol.* **1998**, *16*, 641.

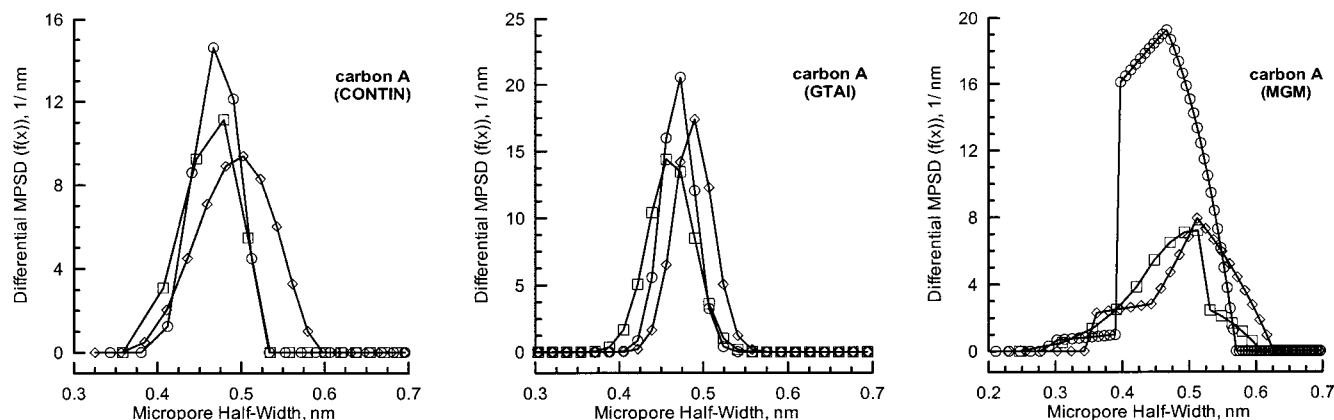


Figure 4. MPD of activated carbon (carbon A, the data for carbon B are shown in Supporting Information, Figure S7) obtained using CONTIN, GTAI, and MGM for different values of the heterogeneity parameter of DA equation ($n = 2$, diamonds; $n = 2.535$, circles; $n = 3$, squares).

Figures 4 and S7 (Supporting Information) show the MPDs for carbon A and B obtained using CONTIN for different values of an empirical parameter of the DA equation (n of DA equation was fixed in this case (as well as in the case of GTAI and MGM) as constant starting parameter in the CONTIN program; the values of n were taken as equal to 2 and 3 and the third value was taken from the best fitting of the DA equation to the nitrogen isotherm data^{48,75}). That means that we are assuming different forms of the kernel in eq 5 and different models of adsorption in homogeneous patches of the considered adsorbents. The obtained results indicate that the influence of the DA heterogeneity parameter on the position as well as on the shape of the MPD is not large. Moreover, this parameter affects the MPDs of the considered activated carbons in a different nonregular way.

In the same figures (Figures 4 and S7 (Supporting Information)), one can see the MPD of the examined carbons obtained using GTAI. The primary advantage of GTAI is that it is conceptually and computationally simple, contrary to CONTIN. In this case, similarly to CONTIN, the Gaussian forms of MPD are obtained. Additionally, the obtained MPD cover similar ranges of pore half-widths as CONTIN results. Here also the heterogeneity parameter of the DA equation influences insignificantly the shape and position of the peaks. We want to pay attention to the procedure of the fitting of GTAI to the measured adsorption isotherms. In the current study a special hybrid system consisting of random search, genetic algorithm, and simulated annealing was projected. It is commonly known that such methods, as opposed to classical gradient and none gradient ones, are resistant to local extremes of the considered functions topography. That property is clearly shown in Figures 5 and S8 (Supporting Information). Ten independent runs of the constructed program lead to very similar shapes and positions of MPDs.

MGM algorithms detect the similar position of MPDs as CONTIN and GTAI methods do (Figures 4 and S7 (Supporting Information)). The shape of the MPD of the considered activated carbons is similar to a deformed trapezoidal function. It is not surprising since for the construction of MPD of the studied carbons the bitrapezoidal model of $f(B)$ was applied. It is very important from a practical point of view that this method can be

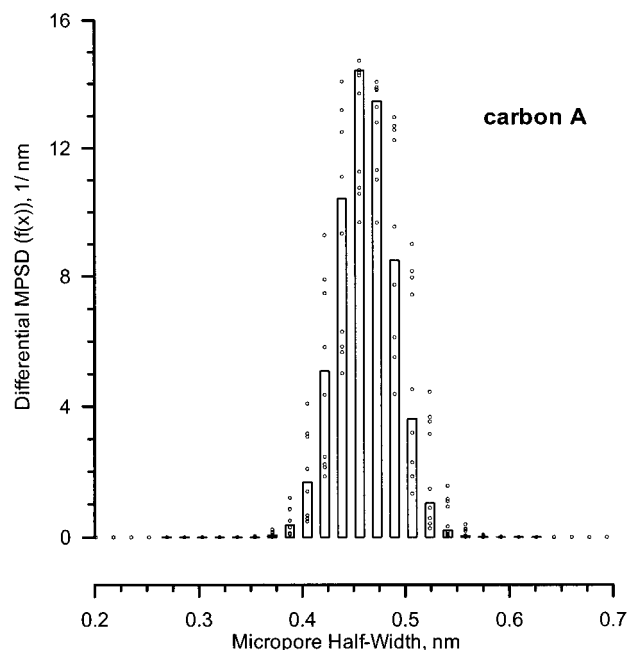


Figure 5. The results of the fitting of the GTAI equation (eq 10 or 11) to the adsorption isotherm on activated carbon A: bars, the best fitting values of $f(x)$; dots, arbitrarily chosen results of the other fitting procedures (the program was started 10 times). The hybrid algorithm was applied consisting of the random search method and the simple genetic algorithm.

successfully applied because it always gives stable results. And here also the obtained curves of MPDs of carbon A and B are similar.

Contrary to the method mentioned above, the Horvath and Kawazoe⁵⁸ (HK) method suggests an exponentially decreasing form of the MPD curves (see Figure 6). DFT results suggest strictly microporous structure of both carbons (Figure 6). Moreover, the MPD of carbon B (oxidized) is imperceptibly shifted to a smaller value of micropore half-widths. The shapes of MPD of the both mentioned activated carbons differ not simultaneously, although the MPD of carbon B is smoother. It can be noticed that the HK method approximates DFT results reasonably well. A similar situation was observed for recent studies of strictly microporous homogeneous carbon films.³³ The comparison of all studies in this paper with DFT leads to the conclusion that obtained PSDs (for the relation proposed by Bhatia and Shethna⁵⁰—see eq 8) are narrower than these calculated by DFT software, and they are shifted to larger values of pore half-widths.

(73) Terzyk, A. P.; Rychlicki, G. *Adsorpt. Sci. Technol.* **1999**, *17*, 323.

(74) Terzyk, A. P.; Rychlicki, G. *J. Therm. Anal.* **1999**, *55*, 1011.

(75) Gauden, P. A.; Terzyk, A. P.; Kowalczyk, P.; Rychlicki, G. Submitted.

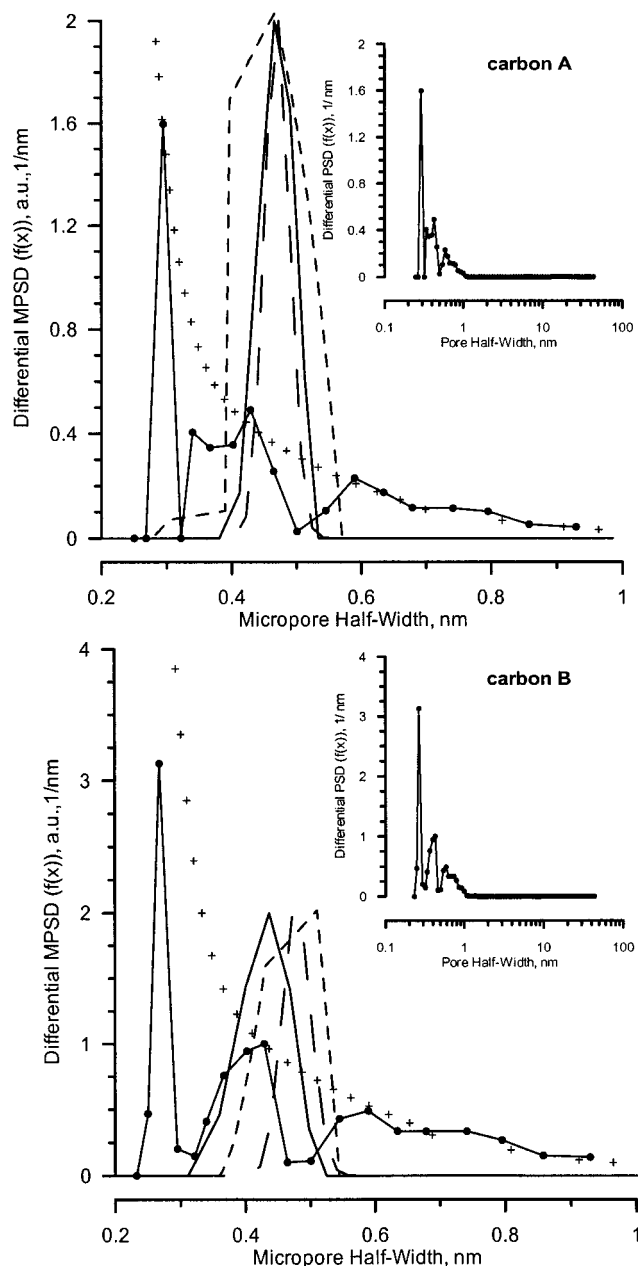


Figure 6. Pore size distributions of activated carbons A and B obtained using the DFT method (closed circles). The comparison of MPD of activated carbons (A and B) obtained using the HK method (crosses), CONTIN (solid line), GTAI (short dashed line), and MGM (long dashed line) for the same value of the heterogeneity parameter of DA equation, $n = 2.535$ (carbon A) and/or $n = 2.386$ (carbon B).

Finally, we decided to check the influence of the relationship between E_0 and x on obtained results. Obviously, this influence will be similar for PSDs calculated by different methods. Because this paper deals mainly with the CONTIN procedure, the peaks recovered by this package for both carbons were chosen (for intermediate n values). It is known that eq 8 is empirical; however some relations of this type were also developed theoretically.^{16,47,48,75} It is hard to state which one relation leads to reliable results. It is possible that recent progress in the synthesis of structurally ordered carbons will provide some answer to this question in the near future. Our fresh studies³³ on microporous carbons with almost homogeneous microporosity lead to some interesting results. Studied in the mentioned paper³³ carbon films

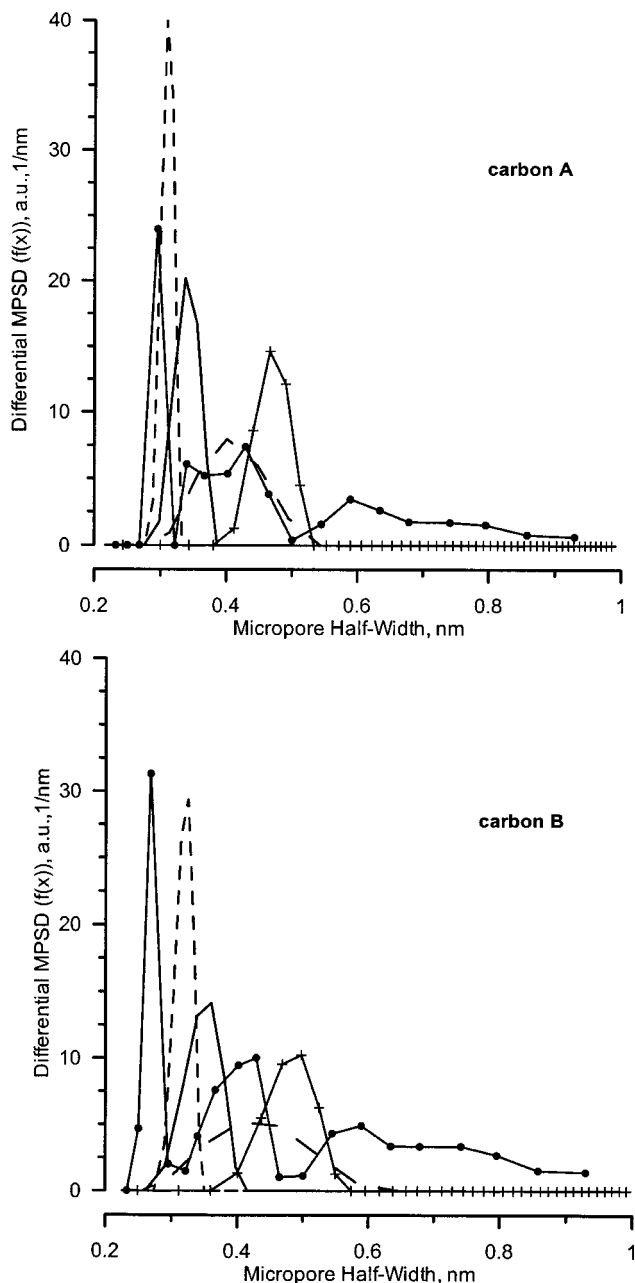


Figure 7. The comparison of MPD of activated carbons (A and B) obtained using the DFT method (closed circles) and CONTIN (the same value of the heterogeneity parameter of DA equation, $n = 2.535$ (carbon A) and/or $n = 2.386$ (carbon B)) based on eq 9 and $C = 11.4$ (crosses), eq 19 (solid line), eq 20 (long dashed line), and eq 21 (short dashed line).

possessed ca. 90% of the pores with almost the same diameter (sharp and very narrow peak on DFT pore size distribution around 0.6 nm was observed). Homogeneity of the pore structure was confirmed independently by calorimetric study of benzene adsorption. The adsorption data of nitrogen and benzene allowed checking the validity of these empirical relationships, and the results were compared with those obtained from the DFT method.³³ Thus despite the equation proposed by Bhatia and Shethna,⁵⁰ we choose in this paper only the relations leading to similar results as obtained from DFT and calorimetric analysis, i.e., Stoeckli's^{41,42}

$$2x = 16.5/E_0 \quad (19)$$

$$2x = \left(\frac{30}{E_0}\right) + \left(\frac{5705}{E_0^3}\right) + 0.028E_0 - 1.5 \quad (20)$$

and developed recently^{16,47,48,75}

$$\frac{2x}{d_A} = \left(\frac{a_{1(\text{mic})}n}{b_{1(\text{mic})} + n}\right) \left(\frac{a_{2(\text{mic})}n}{b_{2(\text{mic})} + n}\right)^{E_0} E_0^{(a_{3(\text{mic})}n/(b_{3(\text{mic})} + n))} \quad (21)$$

where d_A is the diameter of an adsorbed molecule (0.3 nm for nitrogen): $a_{1(\text{mic})} = 24.1672$; $b_{1(\text{mic})} = 2.2709$; $a_{2(\text{mic})} = 0.9960$; $b_{2(\text{mic})} = -1.29 \times 10^{-2}$; $a_{3(\text{mic})} = -0.8586$; $b_{3(\text{mic})} = 1.2266$.

The results are shown in Figure 7. The widest distribution is obtained for one of the relations proposed by Stoeckli.⁴¹ The equation of Bhatia and Shethna⁵⁰ leads to the largest pore diameters. On the other hand, for the new relationship^{16,47,48,75} the peak is narrow and shifted to smaller values of pore diameters. Thus, presented results, together with the results obtained recently³³ lead to the conclusion, that for the primary micropore filling process the DA equation can be used as a local isotherm in GAI. The first peak of DFT PSD (responsible for primary micropore filling process) is reasonably approximated by studying in this paper the procedure for the relationships between E_0 and x given by eqs 19 and 21. Thus one can notice that the influence of the relationship between E_0 and x on obtained results is substantial and cannot be neglected.

V. Conclusions

Considering the obtained results, we want to underline that the CONTIN package is a very powerful tool and it can be successfully applied for inverting of the ill-posed adsorption Fredholm integral equations with DA or DR kernel. As shown in the presented studies, CONTIN recovers continuous and especially discontinuous (one, two, and three modal) forms of $f(B)$ (and MPSPD) very well. Some methods of solving for eq 5 (CONTIN, GTAI, and

MGM) suggest similar forms of MPSPD (one peak, similar to a Gaussian bell) for studied activated carbons and indicate that the main portion of micropores lies between 0.4 and 0.6 nm of half-width. The heterogeneity parameter of the DA equation influences imperceptibly the position and shape of MPSPD for the considered activated carbons. It is interesting that the DFT results are reasonably approximated by the HK method. The MPSPD curves obtained on the basis of Dubinin's TOMF (and the relation proposed by Bhatia and Shethna) are shifted to greater sizes of micropore half-width, compared to DFT and HK methods. Summing up, it is clear that different physical assumptions of considered methods lead to different positions and shapes of MPSPD; however, the numerical procedures of solving for eq 5 lead to similar results despite the ill-posed nature of the examined Fredholm integral adsorption equation of the first kind. The comparison with DFT results allows checking of the applicability of the studies in this paper as well as confirms the validity of the DA equation and eqs 19 and 21 for the representation of the primary micropore filling process. The influence of the relationship between the characteristic energy of adsorption of DA equation and the pore half-width on obtained results is substantial and cannot be neglected. This problem needs further study, and the results will be reported in near future.

Acknowledgment. Authors gratefully acknowledge Professor V. M. Gun'ko (Institute of Surface Chemistry, Kiev) for his useful comments and suggestions concerning the application of the CONTIN package.

Supporting Information Available: Analytical solutions for the uniform, triangle, parabolic, and trapezoidal forms of $f(B)$, recovering results of $f(x)$ and $f(B)$ functions, MPSPDs of activated carbon using CONTIN, GTAI, and MGM, and results of fitting the GTAI equation to the adsorption isotherm on activated carbon B. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA011555Q