

LETTER TO THE EDITOR

The Comparative Analysis of the Properties of Two Micropore-Size Distribution Functions: The Pfeifer–Avnir Function and the Gamma-Type One

The comparative analysis of two micropore-size distribution functions (MSD), i.e., the gamma-type function and the fractal (proposed by Pfeifer and Avnir) one are presented. Theoretical studies performed for different models of the geometrical heterogeneity of microporous solids (characterized by the various intervals of the values of the slit-like half-width and the pore fractal dimension) show that the structural parameters of these MSDs are correlated. In other words, the gamma-type function can be simplified to the Pfeifer and Avnir one under some rigorously mathematical assumptions.

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1. INTRODUCTION AND THEORETICAL

One of the most important problems concerning the description of an adsorbent (carbonaceous solids, especially) is determining geometric and energetic heterogeneity (1, 2). The measurements of physical adsorption are widely used for investigating the texture of porous carbons. The adsorption properties are connected with the presence of a reasonable amount of micropores (1–3). Therefore, those measurements provide a useful “fingerprint” of the microstructure and are essential if the carbonaceous material is used as an adsorbent (1–6). The theoretical description of the overall adsorption process is strongly affected by the micropore-size distribution functions (MSDs). The MSD appears to be especially useful and gives information about a porous solid while characterizing the structural heterogeneity of the adsorbent. There are some methods, proposed in the literature (7–13), which allow evaluating the pore distributions, but unfortunately, although those methods are very useful, all of them have limitations and none of them can be accepted in general (14). It is obvious that the models have their own specific assumptions connected with the description of the porous structure of investigated systems, which affects the obtained results.

In the case of mesoporous carbons, a term “surface” is accepted. On the other hand, for some strictly microporous carbonaceous materials this statement is hard to establish. For those adsorbents, it is better to use “the micropore volume” than “the surface” for describing the degree of microporosity (15). The fractal equivalents of BET (16) or FHH (17) adsorption isotherms were developed some years ago. These isotherms can be applied only for an approximate description of the influence of an adsorbent heterogeneity on adsorption in a microporous system. On the other hand, for microporous systems the theory of volume filling of micropores is accepted to be valid.

According to the theory of adsorption in heterogeneous systems, the “global” (“overall”) adsorption isotherm (GAI) can be written as (7)

$$\Theta = \int_{x_{\min}}^{x_{\max}} \theta_L J(x) dx, \quad [1]$$

where θ_L is the local adsorption isotherm and $J(x)$ is the pore size distribution function that characterizes the geometric heterogeneity of an investigated solid (x is the half-width of the slit).

In the case of the theory of micropore volume filling, θ_L can be represented by the Dubinin–Astakhov equation (DA) (18)

$$\theta_{DA} = \exp[-\mu x^n A^n], \quad [2]$$

where $A = RT \ln(p_s/p)$ is the adsorption potential defined as a change in the Gibb’s free energy taken with a minus sign; R is the universal gas constant; T is the temperature; p and p_s denote the equilibrium pressure and saturation vapor pressure, respectively; μ is the constant equal to $(\beta\kappa)^{-n} (=c/\beta^n)$, where β is the similarity coefficient and κ is the characteristic constant for a defined adsorbate/adsorbent pair in the micropore region (19, 20). Therefore, the structural parameter c is equal to κ^{-n} (21). The value of this characteristic constant for benzene vapor on activated carbon is about 12 kJ nm mol⁻¹ (19, 20).

In previous papers (22–25), the first solutions of the overall adsorption isotherm equations using the Laplace transform and the incomplete gamma function were presented; it was based on the theory of volume filling of micropores formed by Dubinin and co-workers. The Dubinin–Radushkevich (DR) adsorption equation and/or the Dubinin–Astakhov (DA) one were used as a local isotherm in connection with the pore size distribution proposed by Pfeifer and Avnir (26, 27). Substituting the Dubinin–Astakhov equation (DA) (18) (Eq. [2]) and the Pfeifer–Avnir MSD function (26, 27) (χ_{PA} corresponds to the interval of normalized integration, (x_{\min}, x_{\max})),

$$J(x)_{PA} = \chi_{PA} x^{2-D} = \frac{3-D}{x_{\max}^{3-D} - x_{\min}^{3-D}} x^{2-D}, \quad [3]$$

into Eq. [1] and calculating, in the same region of the half-width of the slit (x_{\min}, x_{\max}), gives the following expression for the adsorption isotherm on fractal solids (22–25, 28–31):

$$\theta_{FRDA} = \frac{3-D}{n(x_{\max}^{3-D} - x_{\min}^{3-D})} (\mu A^n)^{(D-3)/n} \left[\gamma\left(\frac{3-D}{n}, x_{\min}^n \mu A^n\right) - \gamma\left(\frac{3-D}{n}, x_{\max}^n \mu A^n\right) \right]. \quad [4]$$

Here, D is the pore fractal dimension (accepted values of this parameter are $2 \leq D < 3$ (14, 25–27, 31)) and γ is the incomplete gamma function. This equation allows evaluating the pore fractal dimension (22–25, 28–35). The overall adsorption isotherm should be integrated in this case in the micropore region

(x_{\min} , x_{\max}), where x_{\min} and x_{\max} are the lower and upper limit of fine pores in which adsorption occurs by a micropore filling mechanism (25, 31, 36). The main properties of both fractal equivalents (FRDR and FRDA) (22, 23) together with the application for describing the experimental data of adsorption and of adsorption heat and entropy were shown previously (24, 28). A general conclusion is that (for some studied carbons) adsorption proceeds by a micropore filling mechanism, and not only the adsorption value but also the process energetics can be correctly described by the fractal analogues of DR and DA equations as well as by the corresponding enthalpy (and entropy) formulas (25, 28, 31). Although different shapes of MSD functions have been proposed for microporous carbons, some experimental findings show that the monotonically decreasing ones (i.e., generating shapes similar to those of the Pfeifer–Avnir equation) are possible (for example: DFT method, Terzyk *et al.* (37); the enthalpies of immersion, Kraehenbuehl *et al.* (38); and the STM analysis, Stoeckli (39)). Moreover, the adsorption isotherm equation developed on the basis of DA isotherm and Pfeifer–Avnir MSD was found to be very useful for characterizing the heterogeneity of some carbonaceous materials (22–25, 28–35).

The starting micropore size distribution function $y(t)$ (where the variable t denotes the slit-pore half-width x or the structural parameter B) can be written in the two equivalent general forms (36),

$$y(t) = a_{(i)}(t - t_0)^b \exp[d(t - t_0)^e] \quad [5a]$$

and/or

$$y(t) = a_{(i)}t^b \exp[dt^e], \quad [5b]$$

where the parameter $a_{(i)}$ is the factor that fulfils the normalization condition (36, 40), b , d , and e are some parameters of Eqs. [5], and t_0 is the characteristic value of the variable t for this distribution function. Both similar forms of the distribution functions (Eqs. [5a] and [5b]) can generate different plots for different values of the parameters b , d , and e . Furthermore, Eqs. [5] can be reduced under some assumptions to simpler expressions (36, 41), for example; the Rayleigh-type ($b = 1$, $d < 0$, and $e = 2$), the Maxwell–Boltzmann ($b = 0.5$, $d < 0$, and $e = 1$), the Gaussian ($b = 0$, $d < 0$, and $e = 2$), the gamma-type ($e = 1$), and others.

In a previous study we suggested (36) that under some specific conditions the gamma-type and Pfeifer–Avnir MSDs can be equivalent. In the next section, the theoretical tools for finding a strictly mathematical correlation between the fractal dimension and the parameters of the gamma-type function will be outlined.

2. RESULTS AND DISCUSSION

The following form of the gamma-type micropore size distribution function (for an arbitrary value of the parameter n) proposed by Jaroniec and co-workers (21) and generalized by us can be written as

$$J(x)_{\text{GTMon}} = \chi_{\text{GTMon}} x^{n-1} (x^n - x_0^n)^v \exp[-qc(x^n - x_0^n)], \quad [6]$$

where q and v are parameters of the above distribution function, x_0 is the characteristic value of variable x , Γ denotes the gamma function, and χ_{GTMon} is the normalization factor (in Jaroniec and co-workers' case (21) is obtained from the integration of the gamma-type MSD function (Eq. [6]) in the interval of integration from zero to infinity, $\chi_{\text{GTMon}(0,\infty)}$). The MSD function, expressed by Eq. [6], can be compared with the starting and general form, Eq. [5a]. Therefore, from this evaluation the following relationships between the variables and the parameters of those two equations are derived:

$$a_{(i)} = a_{(0,\infty)} = \chi_{\text{GT}(0,\infty)} = n \frac{(qc)^{v+1}}{\Gamma(v+1)} \quad [7a]$$

$$t = x^n \quad [7b]$$

$$t_0 = x_0^n \quad [7c]$$

$$b = v \quad [7d]$$

$$e = 1 \quad [7e]$$

$$d = -cq. \quad [7f]$$

The parameters x and x_0 can be calculated based on the dependence of the pore size x (for slit-like micropores) on the structural parameters (7, 19, 36), for example, the characteristic energy of adsorption:

$$x = \kappa/E_0. \quad [8]$$

The problem of the normalization of the MSD function based on the gamma-type one (Eq. [6] for $x_0 = 0$) was presented previously by Gauden and Terzyk (36). Three cases of the integration range (widely known in the literature) of MSD, characterizing the geometric heterogeneity of a solid, were considered: from zero to infinity, from val_{\min} to infinity, and the finite range (val_{\min} , val_{\max}), where $\text{val}(\equiv B, E_0, \text{and/or } x)$. The second and third cases were chosen due to the boundary setting of an adsorbate–adsorbent system. Moreover, the physical meaning of the gamma-type function parameters (ρ and v) was investigated for the mentioned intervals. Six selected cases of the possible shapes of this distribution function ($J(x)_{\text{GT}}$) were analysed. These cases (presented in Fig. 1) were chosen because, in our opinion, they were the most interesting and acceptable for describing the structural heterogeneity of the microporous activated carbons. Others are presented in Bronsztejn and Siemeindajew's book (42). A general conclusion of our paper (36) was that if adsorption proceeds by a micropore filling mechanism and the structural heterogeneity is described in the finite region (val_{\min} , val_{\max}), for all the cases of the possible values of the MSD functions parameters, the generated isotherms (the gamma-type adsorption isotherm (GTAI)) belong to the first class of the IUPAC classification; i.e., Langmuir-type behavior is observed:

$$\Theta_{\text{GT}(x_{\min}, x_{\max})} = \frac{\left(\frac{A^n}{\beta^n \rho} + 1\right)^{-(v+1)} \left[\gamma\left(v+1, \left(\frac{A^n}{\beta^n} + \rho\right) \zeta x_{\max}^n\right) - \gamma\left(v+1, \left(\frac{A^n}{\beta^n} + \rho\right) \zeta x_{\min}^n\right) \right]}{\left[\gamma\left(v+1, \zeta \rho x_{\max}^n\right) - \gamma\left(v+1, \zeta \rho x_{\min}^n\right) \right]}. \quad [9]$$

For the other cases $\text{val} \in (0, \infty)$,

$$\Theta_{\text{GT}(0,\infty)} = \left(\frac{A^n}{\beta^n \rho} + 1\right)^{-(v+1)}, \quad [10]$$

and $\text{val} \in (\text{val}_{\min}, \infty)$,

$$\Theta_{\text{GT}(x_{\min}, \infty)} = \frac{\left(\frac{A^n}{\beta^n \rho} + 1\right)^{-(v+1)} \left[\Gamma(v+1) - \gamma\left(v+1, \left(\frac{A^n}{\beta^n} + \rho\right) \zeta x_{\min}^n\right) \right]}{\left[\Gamma(v+1) - \gamma\left(v+1, \zeta \rho x_{\min}^n\right) \right]}. \quad [11]$$

some erroneous and ambiguous results were obtained (36).

A new numerical procedure based on the simulated annealing algorithm (SA) is proposed by us (43) for optimizing the parameters of a new recently developed gamma-type adsorption isotherm equation (Eq. [9]) to check the problem of the reconstruction of the gamma-type MSDs for microporous carbonaceous adsorbents. This procedure is verified for some modeled adsorption isotherms assuming arbitrarily chosen shapes of this pore size distribution function (the asymmetrical bell-shaped functions possessing one (Fig. 1-III) or two (Fig. 1-II) points of inflection and decreasing to zero-hyperbolic-like function (Fig. 1-V)). The SA algorithm provides (in a very short time) the values of the optimization parameters that are very close to the global minimum of the fitness function. Then, from a practical point of view the obtained results are satisfactory and the proposed method can be successfully applied for determining the parameters of a microporous structure of activated carbons and their MSDs.

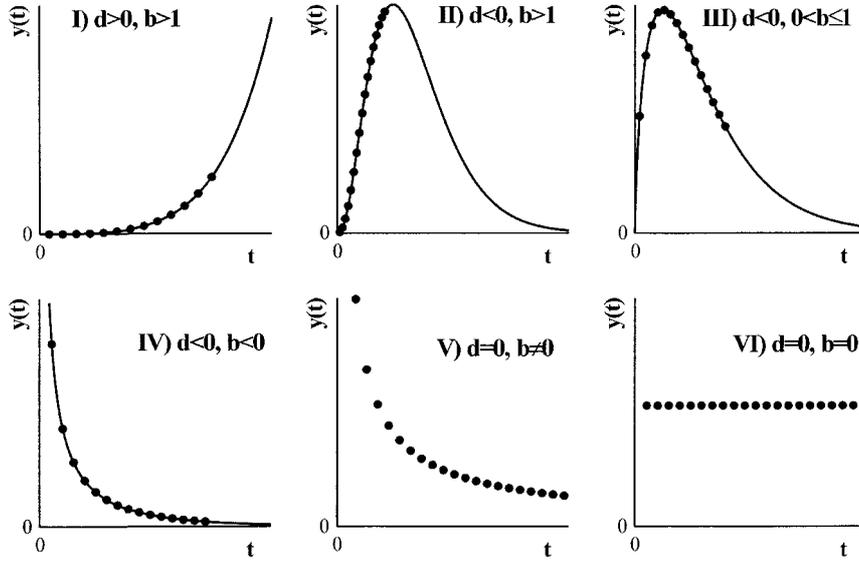


FIG. 1. The possible shapes of the gamma-type distribution function ($e = 1$; Eq. [5b]) (36). The curves are plotted based on the arbitrary values of the parameters d and b . The solid points are attributed to the micropore range (t_{\min}, t_{\max}) but the solid line to $(0, \infty)$. The normalization factors are the following (5): for the cases I–IV are the same for these two intervals of normalization and are equal to $a_{(0, \infty)}$ and for V–VI are equal to $a_{(t_{\min}, t_{\max})}$.

Previously, Gauden and Terzyk (36) suggested the possibility of some connection existing between a gamma-type distribution function (Eq. [5b]; $e = 1$) and the Pfeifer–Avnir one (Eq. [3]). Both distributions can be compared due to the same local adsorption isotherm equation (the DA equation, Eq. [2]) occurring in the GAI (Eq. [1]). At this point, some detailed behavior and properties of this simplification will be analyzed.

First, the equality of the characteristic value (x_0) of the variable x (i.e., the half-width) to zero should be presumed (36). Then, Eq. [6] can be simplified to the following form of the normalized gamma-type micropore size distribution function,

$$J(x)_{\text{GTMon}} = \chi_{\text{GTMon}} x^{n(v+1)-1} \exp[-qcx^n], \quad [12]$$

where the meaning of the parameters of Eq. [12] are described above. The properties of this equation were analyzed by us in great detail previously (36).

It is interesting that only the assumption of the q state being equal to zero or tending to this value leads to the reduction of Eq. [12] to the hyperbolic-like function (36):

$$J(x)_{\text{GTMon}} = \chi_{\text{GTMon}} x^{n(v+1)-1}. \quad [13]$$

On the other hand, the conversion of Eq. [12] into Eq. [13] is justified because c is the structural parameter related to κ , a characteristic constant for a defined adsorbate/adsorbent pair in the micropore region, and therefore, it is always greater than zero ($c = \kappa^{-n}$) and $\kappa > 0$ (19, 20, 36).

To compare $J(x)_{\text{PA}}$ (Eq. [3]) to $J(x)_{\text{GTMon}}$ (Eq. [13]), the normalization factors of these MSDs should be equivalent ($\chi_{\text{PA}} = \chi_{\text{GTMon}} \geq 0$). The values of the pore size distribution function expressed by Eq. [13], for all values of the parameter $\nu \neq -1$, are greater than zero only in the case of the interval of integration from x_{\min} up to x_{\max} and for $\nu < -1$ (x_{\min}, ∞) (36). In contrast to $J(x)_{\text{GTMon}}$, the Pfeifer–Avnir function (Eq. [3]) can be integrated (giving only the positive values of the normalization) in the interval of integration $\Omega_x \in (x_{\min}, x_{\max})$ (25, 31, 36, 44).

The adoption of the assumption $\chi_{\text{PA}} = \chi_{\text{GTMon}} \geq 0$ leads to the statement that the exponents of $J(x)_{\text{PA}}$ (Eq. [3]) and $J(x)_{\text{GTMon}}$ (Eq. [13]) are equal. Then, the

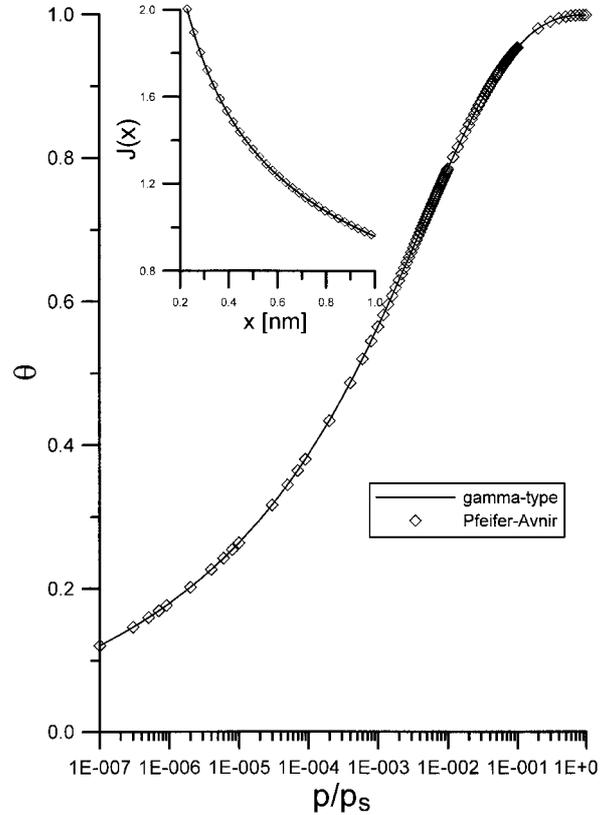


FIG. 2. The comparison of adsorption isotherms and MSDs based on Pfeifer–Avnir pore size distribution (the points) and the gamma-type one (the solid lines). The adsorbate is benzene ($\beta = 1$), temperature is taken as 293 K, the minimal and maximal slit half-widths: $x_{\min} = 0.2295$ and $x_{\max} = 1.0000$ nm, the relative pressure range from 1×10^{-7} to 0.999 p/p_s , $n = 3$, $D = 2.5$, $\nu = -0.83(3)$, and $q = 0$.

pore fractal dimension can be written in the following form:

$$D = 3 - n(v + 1). \quad [14]$$

The accepted values of D are $2 \leq D < 3$ (14, 21–27, 45–51). Based on Eq. [14], the limit values of the parameter ν of the gamma-type function can be derived:

$$\begin{aligned} D = 2 &\Rightarrow \nu = \frac{1-n}{n} \\ D \rightarrow 3 &\Rightarrow \nu \rightarrow -1. \end{aligned} \quad [15]$$

The above two relationships are true for $n > 0$ due to the assumption of identity of the parameter n of the MSD functions (Eqs. [6], [12], and [13]) and the Dubinin–Astakhov isotherm.

As an example, the results of the comparison of adsorption isotherms and MSDs based on Pfeifer–Avnir pore size distribution (the points) and the gamma-type one (the solid lines) are shown in Fig. 2 (the adsorbate is benzene ($\beta = 1$), temperature is taken as 293 K, the minimal and maximal slit half-widths: $x_{\min} = 0.2295$ and $x_{\max} = 1.0000$ nm, the relative pressure range from 1×10^{-7} to 0.999 p/p_s , $n = 3$, $D = 2.5$, $\nu = -0.83(3)$, and $q = 0$). As was expected, excellent agreement is observed.

3. CONCLUSIONS

The comparative analysis of two micropore size distribution functions (MSD), i.e., the gamma-type function and the fractal (proposed by Pfeifer and Avnir) one, is presented and it is proven that the structural parameters of these MSDs are correlated. In other words, the gamma-type function can be simplified to the Pfeifer and Avnir one under some rigorously mathematical assumptions. These results show that the gamma-type function appears to be the most promising one due to the possibility of generating the most common shapes of distributions. The above-presented considerations can be easily spread on other porous systems.

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