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Gas Adsorption on Structurally Heterogeneous Microporous Solids

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Abstract

Isotherm equations for gas adsorption on microporous adsorbents are derived for four distribution functions that characterize the structural heterogeneity of the solids. Since these functions represent the size distributions of micropores, they are physically meaningful for describing gas adsorption on heterogeneous microporous solids. Presentation of relationships between the distribution functions describing either structural or energetic heterogeneity of a solid increases the utility of previous distribution functions for characterization of microporous adsorbents.

INTRODUCTION

One of the most popular isotherm equations in physical adsorption is the Dubinin-Radushkevich (DR) equation (*1*). This equation is widely used to describe adsorption of gases and vapors on microprorous solids [see reviews (*2-4*) and references therein] as well as adsorption from gaseous and liquid phases on heterogeneous solid surfaces [see reviews (*4-7*) and references therein].

For adsorption of a gas on a solid with uniform micropores, the DR isotherm equation may be written as

$$a = a_0 \exp\left[-(B/\beta^2)A^2\right] \qquad (B > 0) \tag{1}$$

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where

$$A = RT \ln (p_0/p) \tag{2}$$

Here, a is the adsorbed amount at the equilibrium pressure p and absolute temperature T, a_0 is the maximum amount adsorbed in the micropores accessible to the adsorbate molecules during the adsorption process, p_0 is the saturation vapor pressure, B is a structural parameter that characterizes a microporous solid, and β is an affinity coefficient that depends on the adsorptive properties only.

Theoretical and experimental studies of Dubinin et al. (*2*, *3*, *8*, *9*) showed that Eq. (1) describes adsorption on solids with a uniform microporous structure. These studies led Izotova and Dubinin (*10*) and Stoeckli (*11*) to generalize Eq. (1) to adsorption on heterogeneous microporous solids. They introduced a distribution function $F(B)$ to characterize heterogeneity of microporous solids. This concept was developed successfully in further papers (*12–22*); in particular, Dubinin (*21*, *22*) proposed a new distribution function of a variable x to describe the structural heterogeneity of microporous solids. The variable x in this function is a characteristic linear dimension of a micropore; e.g., in the case of disk-shaped micropores, x denotes their half-height (*16*). An advantage of this function is that it has a clear physical meaning; it denotes the distribution of the micropore volume with respect to the micropore linear dimension x.

In this paper we describe gas adsorption on heterogeneous microporous solids in terms of a new distribution function $J(x)$; derive analytical isotherm equations for four special cases of $J(x)$; and present the relationships between the distribution functions $J(x)$, $F(B)$, and $X(U)$, where the distribution function $X(U)$ characterizes the adsorbent heterogeneity by means of the adsorption energy U.

THEORY

Theoretical studies coupled with observations of the adsorption of benzene on activated carbon showed (*16*, *21*) that the structural parameter B in Eq. (1) is related to the characteristic dimension x:

$$B = cx^2 \tag{3}$$

where c is the proportionality constant. Using Eq. (3) to replace the parameter B in Eq. (1), we have

$$a = a_0 \exp(-mA^2x^2) \tag{4}$$

where $m = c/\beta^2$. Since Eq. (1) describes local adsorption in micropores of identical shape and dimensions (*10*, *11*), Eq. (4) may also be applied to represent the local adsorption on a solid with uniform micropores since this equation is only an extension of Eq. (1).

Let the structural distribution function $J(x)$ satisfy the following normalization condition:

$$\int_{x_0}^{\infty} J(x)dx = 1 \tag{5}$$

The lower limit x_0 is the dimension characteristic of the smallest micropores. The overall isotherm describing adsorption on a heterogeneous microporous solid characterized by the function $J(x)$ is expressed by the integral equation:

$$a = a_0 \int_{x_0}^{\infty} \exp(-mA^2x^2)J(x)dx \tag{6}$$

Different distributions have been reported in the literature (*23*–*29*) to characterize the heterogeneity of solids without micropores. Four principal distributions are the exponential (*23*), gamma (*24*, *27*, *28*), Rayleigh (*25*, *26*), and Gaussian (*29*) distributions. Dubinin (*21*, *22*) extended the applicability of the Gaussian distribution to describe the structural heterogeneity of solids with micropores. One of the purposes of this paper is to suggest that the other three distributions may be applied to describe the structural heterogeneity of microporous adsorbents in gas adsorption. Here we propose the following general expression to represent a structural distribution function $J(x)$ that is applicable to gas adsorption on heterogeneous microporous solids:

$$J(x) = N(x - x_0)^{\nu} \exp[-q(x - x_0)^{\gamma}] \tag{7}$$

where N is the normalization factor calculated according to Eq. (5), and ν, γ, and q are the parameters characterizing the shape of $J(x)$. The exponential, gamma, Rayleigh, and half-Gaussian distributions are special cases of Eq. (7) as shown in Table 1.

Substituting Eq. (7) into Eq. (6), we obtain a general expression for the overall adsorption isotherm:

$$a = a_0N \int_{x_0}^{\infty} (x - x_0)^{\nu} \exp[-mA^2x^2 - q(x - x_0)^{\gamma}]dx \tag{8}$$

TABLE 1
Special Cases of the Distribution Function $J(x) = N(x - x_0)^\nu \exp[-q(x - x_0)^\gamma]$

Distribution $J(x)$	ν	γ	N
Exponential J^E	0	1	q
Gamma J^Γ	>0	1	$q^{\nu+1}/\Gamma(\nu + 1)$
Rayleigh J^R	1	2	$2q$
Half-Gaussian J^{HG}	0	2	$(q/\pi)^{1/2}$

Introduction of a new variable $y = x - x_0$ into Eq. (8) gives

$$a = a_0 N \exp(-mA^2x_0^2) \int_0^\infty y^\nu \exp(-mA^2y^2 - 2mA^2x_0y - qy^\gamma)dy \tag{9}$$

The integral Eq. (9) may be solved analytically for different sets of parameters ν, γ, and q. For the gamma distribution ($\nu > 0$ and $\gamma = 1$), Eq. (9) gives the following adsorption isotherm:

$$a^\Gamma = a_0^\Gamma q^{\nu+1}(2mA^2)^{-(\nu+1)/2} \exp[-mA^2x_0^2 + (q + 2mA^2x_0)^2/(8mA^2)] \times D_{-(\nu+1)}\left(\frac{q + 2mA^2x_0}{A(2m)^{1/2}}\right) \tag{10}$$

where $D_{-(\nu+1)}$ is the parabolic cylinder function (*30*). The adsorption isotherm corresponding to a simple exponential distribution ($\nu = 0$ and $\gamma = 1$) is easily obtained from Eq. (10):

$$a^E = a_0^E(q/2A)(\pi/m)^{1/2} \exp[-mA^2x_0^2 + (q + 2mA^2x_0)^2/(4mA^2)] \times \left[1 - \Phi\left(\frac{q + 2mA^2x_0}{2Am^{1/2}}\right)\right] \tag{11}$$

where Φ is the probability function (*30*). The solution of Eq. (9) for the Rayleigh distribution ($\nu = 1$ and $\gamma = 2$) is interesting also; in this case,

$$a^R = 2a_0^R q \exp(-mA^2x_0^2)\left\{0.5(q + mA^2)^{-1} - [0.5mA^2x_0/(q + mA^2)] \times [\pi/(q + mA^2)]^{1/2} \exp[m^2A^4x_0^2/(q + mA^2)]\left[1 - \Phi\left(\frac{mA^2x_0}{(q + mA^2)^{1/2}}\right)\right]\right\} \tag{12}$$

The parameter x_0 appearing in Eqs. (10), (11), and (12) is connected with the parameter B_0 by means of Eq. (3). From Ref. *20*, which concerns experimental verification of the overall adsorption isotherms derived by assuming the distribution function $F(B)$, it follows that the parameter B_0 may be approximated by zero for many adsorption systems with microporous solids. When $B_0 = 0, x_0 = 0$; and then Eqs. (10), (11), and (12) reduce to simpler expressions:

$$a^\Gamma = a_0^\Gamma q^{\nu+1}(2mA^2)^{-(\nu+1)/2}\exp(q^2/8mA^2)D_{-(\nu+1)}(q/A\sqrt{2m}) \tag{13}$$

$$a^E = a_0^E q(2A)^{-1}(\pi/m)^{1/2}\exp(q^2/4mA^2)[1 - \Phi(q/2A\sqrt{m})] \tag{14}$$

$$a^R = a_0^R q/(q + mA^2) \tag{15}$$

Equation (15) assumes an especially simple form. This equation relates to the Rayleigh distribution which seems to be appropriate for describing adsorption systems with heterogeneous microporous solids.

The overall adsorption isotherm relating to the Gaussian distribution $J^G(x)$ was obtained previously by Dubinin (*21*, *22*):

$$a^G = a_0^G \frac{1}{2(1 + mA^2/q)^{1/2}} \exp\left(-\frac{m\bar{x}^2A^2}{1 + mA^2/q}\right)\left[1 + \mathrm{erf}\left(\frac{\bar{x}}{q^{-1} + mA^2/q^2}\right)\right] \tag{16}$$

Here $\bar{x}$ is the average value of the characteristic linear dimension x of a micropore. Equation (16) was obtained by integrating an equation analogous to Eq. (6) for a Gaussian distribution with limits from zero to plus infinity. Dubinin (*21*, *22*) used Eq. (16) to describe adsorption of benzene on carbonaceous solids.

Adsorption isotherms corresponding to various $F(B)$ distributions were derived in several papers (*10–20*) by solving the following integral equation, which is analogous to Eq. (6):

$$a = a_0 \int_{B_0}^{\infty} \exp(-BA^2/\beta^2)F(B)dB \tag{17}$$

By comparing Eqs. (6) and (17), we see that $J(x)$ can be obtained from the distribution $F(B)$:

$$J(x) = F(B)(dB/dx), \qquad \text{with } B = B(x) \tag{18}$$

Combination of Eqs. (3) and (18) gives

$$J(x) = 2cxF(B(x)) \tag{19}$$

Equation (19) relates the functions $J(x)$ and $F(B)$. In Table 2 we present three distribution functions $J(x)$ associated with three distribution functions $F(B)$. The isotherms obtained from these three $F(B)$ distributions by integrating Eq. (17) with $B_0 = 0$ are displayed in Column 3 of Table 2.

Equation (19) is useful in interpretation of experimental data; for instance, the overall adsorption isotherm obtained from a (symmetric) Gaussian distribution $F^G(B)$ is associated with an asymmetrical distribution function $J(x)$. Since the distribution function $J(x)$ represents the distribution of the micropore volume with respect to the micropore dimension x, its physical interpretation is clearer and simpler in comparison to that of the function $F(B)$. Through Eq. (3), the variable B indirectly characterizes the micropore dimension; therefore, discussion of the overall adsorption isotherms with respect to the function $J(x)$ is simpler because this distribution function is connected directly with the dimensions of micropores. Thus, the function $J(x)$ is recommended for characterizing heterogeneity of the microporous structure of the solid adsorbents. To illustrate the above considerations, we note first that the adsorption isotherm Eq. (15) corresponds to a Rayleigh distribution $J^R(x)$ (Eq. 7 with $\nu = 1$ and $\gamma = 2$). According to the studies of many authors (see Refs. *31* and *32* and references therein), a Rayleigh-type distribution is a good representation for heterogeneous adsorbents. Earlier, the isotherm Eq. (15) was used successfully to describe adsorption on activated carbons (*31*, *32*). This isotherm was also obtained for the exponential distribution $F^E(B)$:

$$F^E(B) = q^* \exp(-q^*B) \tag{20}$$

TABLE 2
Distribution Functions $J(x)$ Associated with the Distribution Functions $F(B)$ and the Isotherm Equations θ_t Corresponding to These Distributions[a]

Distribution $F(B)$	Distribution $J(x)$	Adsorption isotherm θ_t
$F^E(B) = q^* \exp(-q^*B)$	$J^{FE}(x) = 2qx \exp(-qx^2)$	$\theta_t^{FE} = q^*/(q^* + \alpha)$
$F^\Gamma(B) = Q^*B^\nu \exp(-q^*B)$	$J^{F\Gamma}(x) = 2Qx^{2\nu+1} \exp(-qx^2)$	$\theta_t^{F\Gamma} = q^*/(q^* + \alpha)^{\nu+1}$
$F^R(B) = 2q^*B \exp(-q^*B^2)$	$J^{FR}(x) = 4qcx^3 \exp(-qcx^4)$	$\theta_t^{FR} = [1 - \sqrt{\pi/q^*}(\alpha/2) \times$ $\exp(\alpha^2/4q^*)\ \operatorname{erf}(\alpha/2\sqrt{q^*})]$

[a] $\alpha = (A/\beta)^2$; $q = q^*c$; $Q^* = (q^*)^{\nu+1}/\Gamma(\nu + 1)$; $Q = q^{\nu+1}/\Gamma(\nu + 1)$; $J^R(x) = J^{FE}(x)$.

Although the exponential distribution $F^E(B)$ is less realistic than the Rayleigh one, which generates the isotherm Eq. (15), the distribution $F^E(B)$ corresponds to the Rayleigh distribution $J^R(x)$, which may be obtained from Eqs. (20) and (19):

$$J^R(x) = 2qx \exp(-qx^2) \tag{21}$$

where $q = q^*c$. The above discussion shows that the isotherm Eq. (15) corresponds to the function $J^R(x)$ given by Eq. (21), which is associated with the exponential distribution $F^E(B)$. This result is the reason that the isotherm Eq. (15) is a good representation of many systems with heterogeneous microporous solids. Our analysis of the isotherm Eq. (15) provides a theoretical foundation for the wide applicability of this isotherm for describing gas adsorption on microporous solids.

Now, we consider the relationship between the structural distribution function $J(x)$ and the energy distribution function $X(U)$, which is popular (*4*) for characterizing adsorbent heterogeneity by means of the adsorption energy U. The isotherm Eq. (4) describes single-gas adsorption on homogeneous microporous solids, where the homogeneity is characterized by a Dirac δ-function of the micropore dimension x; however, these so-called homogeneous solids are heterogeneous with respect to the adsorption energy (*19*). Cerofolini (*7*) found that the energy distribution corresponding to Eq. (4) is

$$X_{DR}(U) = 2mx^2(U - U_0) \exp[-mx^2(U - U_0)^2] \qquad (\text{for } U \geqslant U_0) \tag{22}$$

where

$$U - U_0 = A = RT \ln(p_0/p) \tag{23}$$

In Eq. (22), mx^2 determines the shape of the energy distribution $X_{DR}(U)$, and U_0 determines its position on the energy axis. This function is an asymmetric Gaussian distribution widened in the direction of high adsorption energies. The function $X_{DR}(U)$ given by Eq. (22) may be obtained from the isotherm Eq. (4), the relationship given by Eq. (23), and the following approximate expression for $X(U)$:

$$X(U) = -d\theta_t/dU \tag{24}$$

where $\theta_t = a/a_0$. After differentiating Eq. (6) according to Eq. (24), we have

$$X(U) = \int_{x_0}^{\infty} 2mx^2(U - U_0) \exp\left[-mx^2(U - U_0)^2\right] J(x)dx \tag{25}$$

Equation (25) indicates that the physical interpretation of the function $X(U)$, which corresponds to an overall adsorption isotherm derived for a heterogeneous microporous solid, is complex because this function contains $J(x)$ and Eq. (22) for $X_{DR}(U)$. This energy distribution function $X_{DR}(U)$ describes the energetic heterogeneity of micropores that have the same value of the characteristic linear dimension x. The physical interpretation of $X(U)$ given by Eq. (25) is easier for adsorbents characterized by a discrete distribution $J^D(x)$. For a solid with micropores characterized by $x_1, x_2, \ldots, x_s$, the distribution $J^D(x)$ may be expressed as

$$J^D(x) = \sum_{i=1}^{s} g_i \delta(x - x_i) \tag{26}$$

where

$$\delta(x - x_i) = \begin{cases} 0 & \text{for } x \neq x_i \\ 1 & \text{for } x = x_i \end{cases} \tag{27}$$

and

$$\sum_{i=1}^{s} g_i = 1 \tag{28}$$

It is easy to show that Eq. (26) leads to the following expression for $X(U)$:

$$X(U) = \sum_{i=1}^{s} 2g_i mx_i^2(U - U_0) \exp\left[-mx_i^2(U - U_0)^2\right], \qquad \text{for } U \geqslant U_0 \tag{29}$$

where

$$\theta_t = \sum_{i=1}^{s} g_i \exp(-mx_i^2 A^2) \tag{30}$$

Equation (29) shows that the energy distribution $X(U)$ evaluated from adsorption of gases on heterogeneous microporous solids gives global information about the energetic heterogeneity of the adsorbent, which is generated by its microporous structure. In the case of real adsorption systems, the interpretation of $X(U)$ is more difficult because this function also contains information about energetic heterogeneity generated by surface imperfections and various functional groups exposed at this surface.

APPLICATION OF THE ADSORPTION ISOTHERM EQUATIONS

Some equations discussed in this paper (vis., Eqs. 15, 16, and those summarized in Table 2) were applied (*17, 18, 21, 22, 31–34*) for describing gas adsorption on heterogeneous microporous solids. Equations (13) and (14) are more complicated than those presented in Table 2. While they seem less useful for analyzing experimental adsorption isotherms, Eqs. (13) and (14) are presented in this paper for completeness of the analytical solutions of the integral Eq. (9) for all physically realistic micropore distributions. It is noteworthy that this paper presents analytical equations of the micropore distribution $J(x)$, which correspond to the isotherm Eqs. (13)–(15) and equations summarized in Table 2.

Application of the above-mentioned isotherm equations for describing gas adsorption on heterogeneous microporous solids (*21, 31–34*) shows that one of them (viz., the isotherm equation θ_t^{FT} from Table 2) is especially useful for characterizing these solids because of its simplicity and effective approximation. An additional advantage of this isotherm equation is that it relates to the gamma-type micropore distribution, which is physically realistic. Equation (15) is a special case of this isotherm equation.

For illustrative purposes, the benzene adsorption isotherms for two activated carbons NSW and HS43 (*34, 35*) were approximated by the isotherm equation θ_t^{FT} from Table 2. The approximation parameters a_0, q, and ν are given in Table 3. For benzene, the parameter $\beta = 1$ and $c = 6.944 \times 10^{-3}$ (mol/kJ · nm)^2 (*22*). Presented in Fig. 1 is the experi-

TABLE 3

Adsorption Parameters for Benzene on NSW and HS43 Activated Carbons at 293 K Calculated According to the Isotherm Equation θ_t^{FT} from Table 2

Activated carbon adsorbent					
Type	Source	Reference to the isotherm	a_0 (mmol/g)	ν	q (kJ/mol)^2
NSW	Hajnowka, Poland	34	4.93	1.04	793
HS43	Moravske Chemical Co., Czechoslovakia	35	6.85	0.14	151

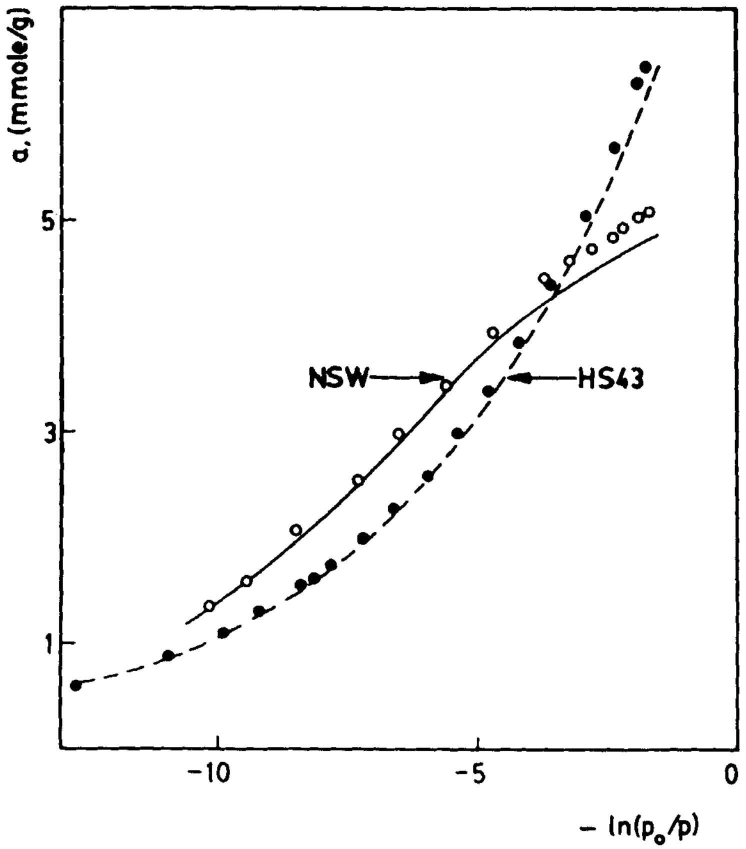

FIG. 1. Experimental dependence of a versus $-\ln(p_0/p)$ for benzene adsorbed on activated carbons NSW (open circles) and HS43 (filled circles). The lines are calculated according to the isotherm equation θ_t^{FT} from Table 2 with parameters from Table 3.

mental dependence of a vs $-\ln(p_0/p)$ for benzene adsorbed on activated carbons NSW (open circles) and HS43 (filled circles) at 293 K. The lines denote a versus $-\ln(p_0/p)$ calculated according to the isotherm equation θ_t^{FT} by using the parameters given in Table 3. It follows from this figure that the above equation gives a good representation of the adsorption isotherms studied.

The micropore distributions $J(x)$ for the systems studied are shown in Fig. 2. Comparison of these micropore distributions shows that the structural heterogeneity of the activated carbon HS43 is greater than that for NSW; moreover, these carbons are characterized by different values

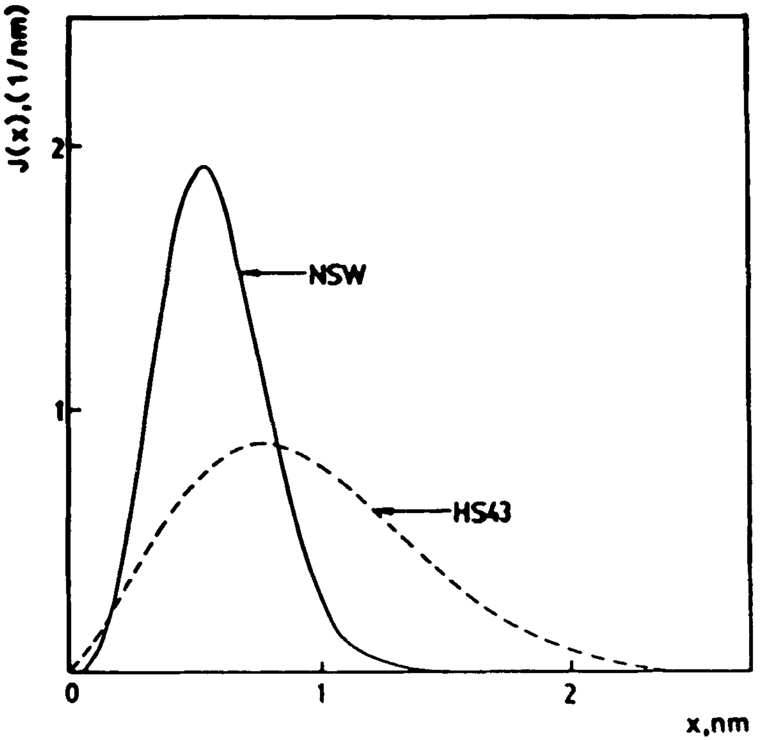

FIG. 2. Micropore distributions for activated carbons NSW (solid line) and HS43 (dashed line) calculated according to the equation for $J^{FT}(x)$ from Table 2 with parameters from Table 3.

of the average micropore dimension x. The micropore distribution reaches a maximum at $x_m = 0.53$ nm for NSW activated carbon and $x_m = 0.78$ nm for HS43 activated carbon.

CONCLUSIONS

In this paper we proposed an expression (viz. Eq. 7) to represent the size distribution of micropores in a solid adsorbent and derived an associated adsorption isotherm (viz. Eq. 9). Four special cases obtained from this general expression are the exponential, gamma, Rayleigh, and half-Gaussian distributions of micropore sizes and associated isotherms. While these four distribution types have been used previously to describe the energetic heterogeneity of solids, we suggest that they may also be used to represent structural heterogeneity of microporous solids. For gas adsorption on microporous solids, the distribution function $J(x)$ of the micropore size x is more physically meaningful than either the distribution function $F(B)$ of a structural parameter B or the distribution function $X(U)$ of the adsorption energy U.

In this paper we related the two previously used distribution functions to the distribution function $J(x)$. These relationships (viz. Eqs. 19 and 25) increase the utility of the two prior distributions because the adsorption isotherms derived for them can be correlated to the $J(x)$ distribution.

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SYMBOLS

A	change of the Gibbs free energy taken with the minus sign (kJ/mol)
a	adsorbed amount (mmol/g)
a_0	maximum amount adsorbed in micropores (mmol/g)
B	structural parameter in the isotherm of Dubinin and Radushkevich $(\mathrm{mol/kJ})^2$
B_0	minimum value of B $(\mathrm{mol/kJ})^2$
c	proportionality constant in Eq. (3) $(\mathrm{mol/kJ \cdot nm})^2$
D	parabolic cylinder function (dimensionless)
F	distribution function of B $(\mathrm{kJ/mol})^2$
g_i	fraction of micropores of the ith type (dimensionless)
J	distribution function of x (1/nm)
J^D	discrete distribution function of x (1/nm)
J^E	exponential distribution function of x (1/nm)
J^{FE}	distribution function of x associated with the exponential distribution function of B (1/nm)
$J^{F\Gamma}$	distribution function of x associated with the gamma distribution function of B (1/nm)
J^{FR}	distribution function of x associated with the Rayleigh distribution function of B (1/nm)
J^G	Gaussian distribution function of x (1/nm)
J^{HG}	half-Gaussian distribution function of x (1/nm)

J^R	Rayleigh distribution function of x (1/nm)
J^Γ	gamma distribution function of x (1/nm)
m	constant defined by Eq. (4) $(\text{mol/kJ} \cdot \text{nm})^2$
N	normalization factor for the distribution function $J(x)$ $(1/\text{nm})^{1+\nu}$
p	equilibrium pressure (mmHg)
p_0	saturation vapor pressure (mmHg)
q	parameter of the distribution function $J(x)$ $(\text{nm})^{-\gamma}$
q^*	parameter defined by Eq. (20) $(\text{kJ/mol})^2$
R	universal gas constant (kJ/°K · mol)
s	number of types of micropores (dimensionless)
T	absolute temperature (°K)
U	adsorption energy (kJ/mol)
U_0	minimum value of U (kJ/mol)
X	distribution function of U (mol/kJ)
X_{DR}	energy distribution function associated with the Dubinin-Radushkevich isotherm (mol/kJ)
x	characteristic linear dimension of a micropore (nm)
x_0	minimum value of x (nm)
$\bar{x}$	average value of x (nm)

Subscript

i	ith type of micropores characterized by x_i

Greek Letters

β	affinity coefficient (dimensionless)
γ	parameter of the distribution function $J(x)$ (dimensionless)
δ	Dirac δ-function of x (1/nm)
ν	parameter of the distribution function $J(x)$ (dimensionless)
Φ	probability function (dimensionless)
θ_t	relative adsorption (dimensionless)

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