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An Isotherm Equation for Adsorption on Fractal Surfaces of Heterogeneous Porous Materials

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Imposing a pore size distribution of a fractal surface on the Dubinin approach for adsorption in porous materials yields the simple isotherm $\theta = K[\ln (p_0/p)]^{D-3}$ in which θ is the relative adsorption, p_0 and p are the saturation and equilibrium pressures, respectively, K is a constant, and D is the fractal dimension of the surface accessible to adsorption. The isotherm has the form of the Frenkel–Halsey–Hill (FHH) equation, and the theoretical range of the exponent $3 - D$ ($2 \leq D < 3$) indeed falls into the range of experimentally observed FHH exponents.

The analysis of data of adsorption and chemisorption on the surfaces of heterogeneous microporous materials has been a key problem in surface science[1] and catalysis.[2] One of the more useful approaches to that problem was proposed by Dubinin.[3] His approach led to the widely used Dubinin–Radushkevich (DR)[4] and Dubinin–Kaganer equations.[5] A conceptual limitation of the Dubinin approach is the assumption of simple underlying surface and pore morphology (see below) for materials such as porous carbons, which actually possess very complex geometries. Numerous studies have suggested that these complex geometries are describable in terms of fractal geometry.[6–9] In particular, it is worthy to mention that extensive studies of carbonaceous materials have revealed fractality of the surface through adsorption studies,[6] through analysis of small-angle X-ray[10,11] and neutron-scattering[12] data, by image analysis,[13] by porosimetry,[14]

and through electrochemical measurements.[11]

These observations motivated us to apply fractal geometry considerations to the Dubinin approach. The result (detailed below) is the very simple adsorption isotherm:

$$\theta = K[\ln (p_0/p)]^{-\nu} \qquad (1)$$

$$\nu = 3 - D \qquad (2)$$

where θ is the relative adsorption, K is a characteristic constant, p_0 and p are the saturation and equilibrium pressures, and D is the fractal dimension of the surface accessible to adsorption. We immediately notice that eq 1 is formally similar to the Frenkel–Halsey–Hill (FHH) equation.[15]

The motivation that led us to this study was shared also by other research groups. Thus, capillary condensation on a fractal surface was studied by Cohen et al.,[16] and the effects of fractality of the surface on the BET isotherm[17] were investigated by Cole et al.,[18] by Fripiat et al.,[19] and by Levitz et al.[20] Although the BET problem was approached differently by these groups, their main conclusion was similar; i.e., at low p/p_0 values (which are usually applied in BET analyses) surface roughness effects are not large. This finding has been of much comfort after 50 years of intensive use of the BET isotherm on all types of irregular surfaces without checking the actual effects of roughness on that isotherm. Our finding (below) predicts high sensitivity of the isotherm to the morphology of microporous solids, even at very low p/p_0 values. Recent attempts to fit experimental data to the modified BET isotherm were not satisfactory,[8] probably because of the known[19] inherent difficulties with the underlying assumptions leading to it, although it was claimed[21] that the data in ref 8 were analyzed incor-

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rectly. In a recent paper,[21] Pfeifer et al. investigated the effects of surface fractality on thick film adsorption, employing a Hill-type approach.[2b] Their main result is that the relationship between the exponent ν in the FHH isotherm (eq 1) and D is given by

$$\nu = (3 - D)/3 \tag{3}$$

This result is briefly discussed below.

Our starting point in the derivation of eq 1 is the Dubinin approach[3] for the description of adsorption on structurally heterogeneous microporous solids:

$$\theta = \int_{x_{min}}^{x_{max}} \exp(-mx^2A^2)J(x)\, dx \tag{4}$$

where

$$A = RT \ln (p_0/p) \tag{5}$$

Here A is the adsorption potential, and RT (defined as usual) and m are constants. We focus our attention on x and $J(x)$, which are the pore size and its distribution function, respectively. Note that $\exp(-mx^2A^2)$ in eq 4 represents the DR isotherm for uniform micropores of size x. The original assumption for eq 4 was that x refers to slit-shaped pores (the half-width of the slit) and that $J(x)$ is a bell-shaped function, e.g., a Gaussian distribution. We now replace this distribution with the pore size distribution of a fractal object.[17,22] We recall that the basic property of a fractal surface is that the number of (spheroidal) molecules, n, necessary to cover it with a monolayer blanket scales with their radius, x, according to

$$n \propto x^{-D} \tag{6}$$

The volume of this blanket therefore scales with width as[17,22]

$$V \propto x^3 x^{-D} = x^{3-D} \tag{7}$$

If V is the pore volume (as is the case for microporous solids in which one or two opposite monolayers fill up the pores), then the pore volume distribution, i.e., the derivative of eq 7, is

$$dV/dx = Cx^{2-D} \tag{8}$$

where C is a proportionality constant.[17,22b] We take this distribution for $J(x)$ and substitute it into eq 4:

$$\theta = \int_{x_{min}}^{x_{max}} Cx^{2-D} \exp(-mx^2A^2)\, dx \quad (\equiv \int_{x_{min}}^{x_{max}} B\, dx) \tag{9}$$

Both x_{min} and x_{max} are experimental bounds. x_{min} is the finest resolution at which fractality prevails; experimentally, it is the size of a (small) adsorptive, e.g., N_2, x_{max} would be either the upper limit of fractality of the object (x_{max} for eq 6) or the upper limit for microporous adsorption behavior. Equation 9 may be rewritten as

$$\theta = \int_0^\infty B\, dx - \int_0^{x_{min}} B\, dx - \int_{x_{max}}^\infty B\, dx \tag{10}$$

Numerical analysis of eq 10 shows[23] that for microporous solids in the region of moderate values of the adsorption potential A (p/p_0 from $\approx$0.05 to the micro-
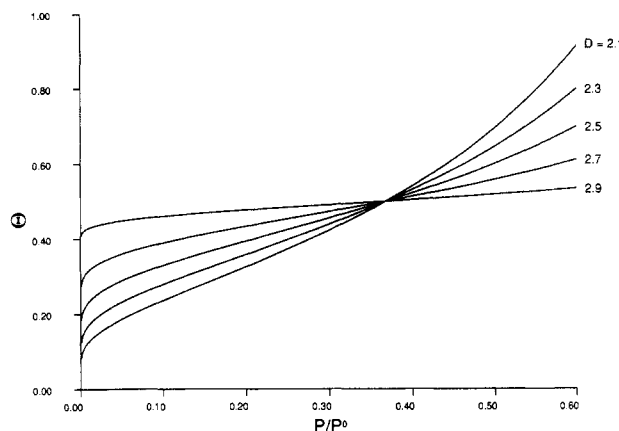

Figure 1. Relative adsorption as a function of partial pressure for surfaces of various degrees of geometric irregularity expressed in terms of D, the fractal dimension of the surface available for adsorption (eq 1; see text).

pore-filling pressures), eq 10 may be approximated by the first integral term. This term can be integrated analytically,[24] giving eq 11 for the adsorption isotherm θ

$$\theta = \frac{1}{2}C\Gamma\left(\frac{3-D}{2}\right)mA^{2-(3-D)/2} \tag{11}$$

(where Γ denotes the Γ function) or (eq 2)

$$\theta = K'A^{-\nu} \tag{12}$$

where, for $2 < D < 3$

$$K' = \frac{1}{2}C\Gamma\left(\frac{3-D}{2}\right)m^{(D-3)/2} \tag{13}$$

The constant K' characterizes both the adsorbent (through D) and the adsorbate (through m^{25}). By resubstituting A with eq 5, one arrives at eq 1, for which

$$K = K'(RT)^{D-3} \tag{14}$$

Figure 1 presents the behavior of the isotherm eq 1 as a function of D. (We are not ready yet to deal with the limits $D = 2$ and $D = 3$ for eq 1: the prefactor C contains the term $D - 2$,[17] and at $D = 3$ the Γ function in eq 13 equals infinity.) As mentioned above, we notice that in contradistinction with the fractal BET isotherm[17,18] eq 1 shows high sensitivity to the D values at low p/p_0 values. Analysis of eq 1 shows that for a given value of K the isotherm curves intersect at one point: $\theta = K$ and $p/p_0 = e^{-1}$. Note that in the derivation of eq 1 from the DR isotherm θ must be ≤ 1 because it is the fraction of micropores filled with an adsorbate at equilibrium pressure p. The conditions $\theta = K$ and $\theta \leq 1$ imply that K values should be smaller than unity. For $K < 1$, the relative adsorption $\theta < 1$ is in the region $p/p_0 < e^{-1} \approx 0.37$; in this region micropore filling occurs. These arguments apply for the full range of D values. The shape of the isotherms changes gradually from type II for the low and intermediate D values to type I for the high D values. From the currently accepted interpretation of these types of shape,[26] this would mean that the low and intermediate D values refer to multilayer adsorption on materials with a relatively low degree of porosity, and the higher D values would be characteristic of microporous solids. The latter can be understood by realizing that for $D \rightarrow$

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3 the distribution function $J(x)$ (eq 8) is steeply decreasing; i.e., the number of micropores with sizes slightly exceeding x_{min} is considerably greater than the number of micropores with sizes slightly smaller than x_{max}. These small micropores are responsible for a rapid rise of the isotherm curve at very low pressures. At higher pressures these micropores are almost filled, and consequently the isotherm curve increases very slowly. Similarly, for intermediate and low D, type II isotherms, the pore size distribution $J(x)$ is less steep; i.e., the wider pores of the microporosity regime become more pronounced, which for multilayer micropore filling requires higher p/p_0 values for the same θ. These trends are seen very nicely in Figure 1. Common to all isotherms is the rapid rise at very low p/p_0 values; this is a reflection of the fact that our derivation emphasizes the existence of microporosity, following the DR approach.

It is obvious that the derivation of eq 1, although based on a semiempirical θ–A relation, contains some idealization of assumptions. For instance, Sing et al. provided evidence[27] to changes in adsorption mechanism with increase in pore size. Also, we do not treat here the expected intimate relation between $A(x)$ and $J(x)$. It is therefore comforting to notice that, despite the approximate picture we chose, the range of experimentally observed ν values (0.35 to close to $1^{15,28-30}$) yields a cor-

responding D range ≈ 2.1 to ≈ 2.7, which is within the expected range of D values for fractal surfaces. Although a direct comparison between D values obtained from eq 1 and D values obtained from other molecule–surface interactions[9] is not at hand yet, we notice that, at least qualitatively, one finds quite often high ν (low D) values for smooth, low-porosity surfaces (e.g., graphite,[30] crystalline compounds[15]) and lower ν values for the more irregular objects (e.g., hydroxylated silica[15]).

We wish to make in conclusion a cautious evaluation of our result. We suggest that the traditional attempts to rationalize experimental ν values in terms of types of interactions[28,29] should have included geometric considerations as well; the agreement between the experimental ν values and the $2 \leq D < 3$ range may thus reflect a physical situation which is more than coincidental.

Finally, we note that if one applies the reported experimental range of ν values to the interpretation of ν given in eq 3, one arrives at D values from close to 0 to 2, i.e., not in the $2 < D < 3$ range of fractal surfaces. It could be that some of the basic difficulties with Hill's thick-layer isotherm[2b] (difficulties which led to the FHH isotherm) may still exist in the deviation of eq 3.

Note Added in Proof. Pfeifer et al. found recently[31] that if surface tension is added to their theory,[21] they obtain the same exponent as ours (eq 2).

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Characterization of a Covalently Bound Phospholipid on a Graphite Substrate by X-ray Photoelectron Spectroscopy and Scanning Tunneling Microscopy

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Received July 24, 1989

A novel method is reported for the covalent binding of a phospholipid to an oxidized graphite substrate using the surface carboxyl functions. The resulting surface is characterized by X-ray photoelectron spectroscopy (XPS), reflectance FTIR, and scanning tunneling microscopy (STM).

Phospholipid monolayer and bilayer membranes find extensive applicability in biomechanistic and biomedical applications.[1-3] However, the two major problems

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associated with such "free-standing" membranes are instability and lack of durability.

Recent experiments on organic and biological matter using scanning tunneling microscopy (STM) indicate the possibility of probing thin organic coatings on solid substrates at a molecular/atomic level.[4-10] Earlier, we conducted an STM study of phospholipid monolayers depos-

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