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Received September 24, 1990. In Final Form: December 11, 1990

It is shown that combination of the Kelvin equation for capillary condensation with a fractal pore distribution on porous materials yields an adsorption isotherm of the form $N/N_m \propto (\ln (p_0/p))^{-(D-3)}$. This isotherm may thus be explained more simply than has previously been thought.

The effects of fractal geometry on adsorption isotherms have been intensively researched in recent years.[1-7] The fractal concept has been used in studies on rough surfaces, microporous solids, and mesoporous (or macroporous) materials. The concept of fractals has proven successful in applying to a wide variety of complex surfaces. The fractal model, when applied to isotherm adsorption, leads to simpler interpretations of experimental data than do traditional ideas based on isolated deviation from planar geometry.

The manner in which adsorption isotherms depend on fractal dimension D of a fractal surface is a currently interesting question. This question may be traced to the Hill isotherm equation in the multilayer adsorption regime[8,9]

$$N \propto N_m[\ln (p_0/p)]^{-\nu} \qquad (1)$$

where N, N_m, p, and p_0 are all defined as usual, and ν is a constant which is equal to 1/3. Halsey obtained a more general equation where the index ν is not necessarily equal to 1/3, and may be somewhere between 1/2 and 1/3. This equation is known as the FHH isotherm equation. However, many observations show that the constant ν can have values between 0 and 1. One explanation for this is based on the assumption that the complex surface of solids has a fractal geometry. Experimentally, the exponent constant ν is taken to be equal to $3 - D$, where D is the fractal dimension of solid surfaces is accessible to adsorption. The theoretical range of D is between 2 and 3.

On the basis of a fractal distribution of roughness, or pores on surfaces, Avnir et al.[1,5] and Pfeifer et al.[2,10,11] developed very interesting theoretical analyses on the isotherm equation. Considering the effect of surface tension to the FHH theory of thick-film adsorption on fractally rough surfaces, Pfeifer et al.[2] qualitatively derived the FHH adsorption isotherm. More quantitatively, Avnir et al.[1,5] imposed a fractal pore size distribution on the traditional DR approach for adsorption in microporous materials. This calculation yielded the isotherm equation

$$N \propto N_m K(D) [\ln (p_0/p)]^{-(3-D)} \qquad (2)$$

where $K(D)$ is a characteristic constant which depends on D. Equation 2 is highly sensitive to micropore filling at low values of p/p_0. It was indicated that eq 2 can be fitted to isotherms on fractal surfaces of heterogeneous porous materials.

The starting point of our derivation is a general integral adsorption isotherm equation of the form

$$N(A) = \int_{x_{min}}^{x_{max}} f(x,A) \, J(x) \, dx \qquad (3)$$

where $N(A)$ is adsorption quantity, A is

$$A = RT \ln (p_0/p) \qquad (4)$$

which is defined as, $-\Delta G$, the negative change of the Gibb's free energy, and x, x_{max}, and x_{min} are the pore size, maximum pore size, and minimum pore size accessible to adsorption respectively. $f(x,A)$ is an adsorbate distribution function that represents the probability of a pore with size x being occupied by an adsorbate molecule in a system with adsorption potential A. $J(x)$ is the pore volume distribution function. By assuming that the pore-size distribution is fractal, $J(x)$ can be written as[1-4]

$$J(x) = bx^{2-D} \qquad (5)$$

where b is a constant. To apply eq 2 to fractal surfaces for adsorption isotherms, the problem is how to choose the adsorbate distribution function $f(x,A)$. In the following discussion, we introduce the Kelvin equation to derive out the adsorbate distribution function. The Kelvin equation can be expressed as[4,12]

$$\ln (p/p_0) = -\frac{2V_m\gamma \cos \phi}{r_m RT} \qquad (6)$$

where r_m is the mean pore radius, ϕ is the contact angle of the adsorbed liquid with the material, γ and V_m are the surface tension and molar volume of adsorbate respectively, R is the universal gas constant, and T is the absolute temperature. The Kelvin equation is usually applied to the adsorption problem by assuming that,[9] along the initial part of the isotherm, the adsorption is restricted to a thin layer on the surface, until capillary condensation commences in the finest pores. With uniform pores, a sudden increase of isothermal adsorption has been found at given pressure p determined by the Kelvin equation. For fractally porous or rough materials, hysteresis may be not observed in the adsorption and desorption cycles, and smooth isotherms will occur.

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In our model, we explain that the adsorption process results in the sequential filling of pores from small size to large, rather than layer by layer surface coverage in the traditional FHH model. The adsorption process can be described by the Kelvin equation. Utilizing the Kelvin equation by taking the mean pore radius, r_m, as the pore size, and further assuming that the contact angle, ϕ, is independent of the size of pores, the adsorbate distribution function $f(x,A)$ can be written into

$$f(x,A) \propto H(cA^{-1} - x) \tag{7}$$

where

$$H(cA^{-1} - x) = \begin{cases} 1 & cA^{-1} > x \\ 0 & cA^{-1} < x \end{cases} \tag{8}$$

and

$$c = 2V_m\gamma \cos \phi \tag{9}$$

Substituting eq 7 to eq 3, if A is small enough, we have

$$N \propto D(3 - D)^{-1}[\ln (p_0/p)]^{-(D-3)} \tag{10}$$

According to early fractal analysis,[13] the monolayer adsorption quantity N_m can be expressed as

$$N_m \propto D(D - 2)^{-1}x_{min}^{2-D} \tag{11}$$

Therefore, the adsorption isotherm of fractally porous materials is

$$N/N_m \propto (D - 2)(3 - D)^{-1}[\ln (p_0/p)]^{-(D-3)} \tag{12}$$

Equation 12 has the form of a fractal FHH isotherm. This simple derivation indicates that the adsorption process of fractally porous materials is dominated by the capillary condensation, which can be described by the Kelvin equation. It is obvious that eq 12 is valid at small values of adsorption potential A, i.e. the traditional multilayer adsorption regime. At large values of adsorption potential A, i.e. at micropore filling range, the Kelvin equation is usually not expected to hold for small pore size.[4,12]

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