

Thermodynamic method for calculating surface fractal dimension

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A new method is proposed for calculating the surface fractal dimension of disordered disperse systems from an experimental adsorption isotherm.

Methods for determining the fractal dimension of disordered disperse systems have recently attracted considerable attention.¹ Porous materials (activated charcoal, xerogels, aerogels, sediment structures, etc.) are characterized by a surface fractal dimension d_{fs} . This quantity is determined theoretically from the proportionality²

$$S(r) \propto r^{2-d_{fs}}, \quad (1)$$

where $S(r)$ is the surface area which would be measured with a gauge of size r . In practice, it is exceedingly difficult to carry out a corresponding experiment. A flawless method from the theoretical standpoint is the method of adsorption probes, which is based on a comparison of adsorption isotherms of various substances in the monolayer region.³ The size range of the molecules of possible adsorbates is extremely narrow (from 0.2 to 1 nm), however, and while high-molecular probes would seem to hold promise, there is the problem of dealing with a change in the conformation of the polymer chain during adsorption.⁴ There is accordingly interest in determining d_{fs} from the adsorption isotherm of a single substance, but over a wide range of the pressure P , up to the saturation vapor pressure P_s , i.e., in the region of polymolecular adsorption and capillary condensation. Several alternative methods for interpreting the experimental adsorption isotherm have been proposed in the literature, and opinion is divided on this matter.^{3–7} These methods all differ in the particular models used

for the structure of the fractal surface and for the mechanism for polymolecular adsorption on this surface.

In the present letter we wish to propose a new method for calculating d_{fs} from an adsorption isotherm. This new method does not lean on any model. It is based on an integral thermodynamic relation between the surface area of the adsorbed film, $S(P)$, and the adsorption isotherm $N(P)$ (Ref. 8):

$$S(P) = (RT/\sigma v_m) \int_N^{N_{max}} \ln(P_s/P) dN, \quad (2)$$

where N_{max} is the adsorption as $P \Rightarrow P_s$, σ and v_m are the surface tension and mole volume of the liquid adsorbate, R is the universal gas constant, and T is the temperature. Equation (2), known as the Kiselev equation, is a balance equation involving the work of adsorption and the work of formation of the interfacial surface. The physical meaning is that the surface of the adsorbate is represented as a surface of constant curvature. The average radius of curvature of the menisci, r_k , is given by Kelvin's equation

$$r_k = 2\sigma v_m / RT \ln(P_s/P). \quad (3)$$

If we all work from this basis, we can interpret the surface area of the adsorbed film in (2) as the surface area of the adsorbent which would be measured by spheres of radius r_k in (3). It follows that d_{fs} can be calculated from the following expression according to our definition of fractal dimensionality in (1) and thermodynamic equation (2):

$$\begin{aligned} d_{fs} &= 2 - \frac{d [\ln S(P)]}{d [\ln r_k(P)]} = 2 + \frac{d [\ln S(P)]}{d [\ln(-\ln P)]} \\ &= 2 + d \left[\ln \int_N^{N_{max}} \ln(P_s/P) dN \right] / d [\ln \ln(P_s/P)] \quad (4) \end{aligned}$$

Equation (4) contains no parameters beyond the experimental absorption isotherm $N(P)$, and we view this circumstance as the basic advantage of this equation over the relations which have been proposed previously³⁻⁷ for determining d_{fs} .

When a thermodynamic method is used to analyze real adsorbents, there is the problem of an adsorption hysteresis in mesopores. In the region of capillary condensation, the adsorption and desorption isotherms generally do not coincide; they instead form a hysteresis loop. The results of a calculation may depend on which branch of the isotherm is used as the starting point for the calculation: the adsorption branch or the desorption branch. Only in the case of ideal fractal surfaces would one expect the two branches to clearly coincide. If there are no clearly defined cooperative effects, preference should apparently be given to the desorption branch, since polymolecular adsorption is manifested to a lesser extent during desorption than during adsorption.⁹ In general, the values of the surface fractal dimension calculated from the adsorption isotherm and the desorption isotherm should be comparable (this assertion is made, of

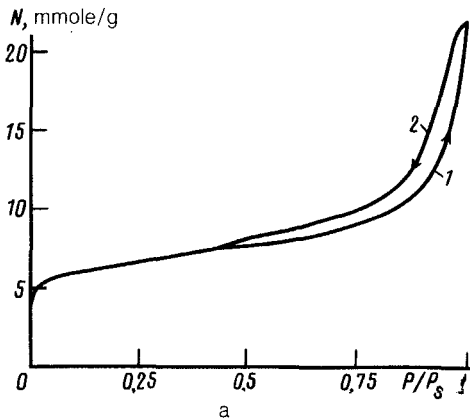
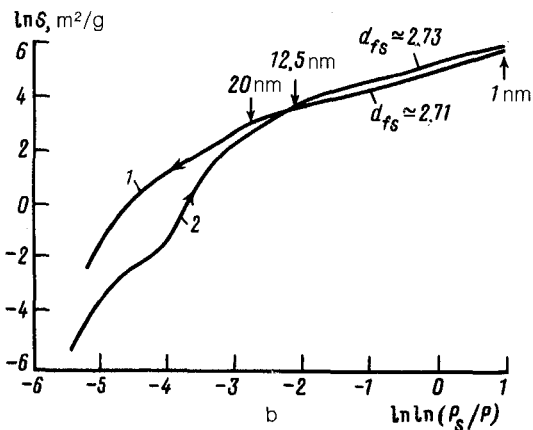


FIG. 1. Calculation of the surface fractal dimension of an activated charcoal sample by a thermodynamic method. *a*—Experimental isotherms of (1) the adsorption and (2) the desorption of nitrogen on (from) activated charcoal;¹⁰ *b*—surface area of the adsorbed film, $S(P)$, from expression (2), versus $\ln(P_s/P)$, in logarithmic coordinates, according to calculations from (1) the adsorption branch and (2) the desorption branch. The arrows show the boundaries of the fractal region.



course, for samples which do indeed demonstrate fractal properties over a sufficiently wide range of scales).

Figure 1 shows the results of a calculation by this thermodynamic method of the surface fractal dimension for an activated charcoal sample on the basis of the experimental adsorption isotherm of nitrogen¹⁰ (Fig. 1a). For this sample one observes a satisfactory correspondence between the values of d_{fs} calculated from the adsorption isotherm and from the desorption isotherm. A linear-regression analysis of the adsorption isotherm for activated charcoal in the coordinates of the thermodynamic method yields $d_{fs} \approx 2.73$ over the range of scales from 1 to 20 nm (Fig. 1b), while an analysis of the desorption isotherm yields $d_{fs} \approx 2.71$ over the range of scales from 1 to 12.5 nm (Fig. 1c).

A similar thermodynamic method could be proposed for calculating the surface fractal dimension from mercury porometry data; that method is also used to determine this dimensionality.¹¹ The analog of the Kiselev equation for impregnation of a non-

wetting fluid is the Rootare-Prenzlow equation¹²

$$S(P) = (I/\sigma \cos \theta) \int_0^V P dV, \quad (5)$$

From this equation one can calculate the area S of the solid-liquid interface as a function of the overpressure P by working from the experimental P dependence of the volume of liquid, V , which has been forced into the sample. The quantity σ in Eq. (5) is the surface tension of the liquid, and θ is the wetting angle. According to the Laplace equation, the pressure P determines the equilibrium average radius of curvature of the menisci of the liquid, $r_l = 2\sigma \cos \theta / P$. Equation (5) thus gives us the surface area of the solid which would be measured by spheres of radius r_l . By analogy with (4), we have

$$d_{fs} = 2 - \frac{d [\ln S(P)]}{d [\ln r_l(P)]} = 2 + \frac{d [\ln S(P)]}{d \ln P} = 2 + d [\ln \int_0^V P dV] / d \ln P. \quad (6)$$

Expression (6) for the surface fractal dimension d_{fs} contains the experimental impregnation curve $V(P)$ alone—without any other parameters.

The nature of this thermodynamic method makes it applicable for analyzing disperse materials characterized by surface fractal dimensions $d_{fs} \geq 2$.

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