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Henry's law of adsorption on a fractal surface

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The problem of adsorption at low coverage N on a fractal surface is addressed. General, but approximate, arguments are presented to show how the fractal dimension D is related to the Henry's-law coefficient of proportionality between N and the pressure. A semiclassical analysis validates this relation at high temperature. An evaluation for a regular fractal surface demonstrates this behavior explicitly. Relation is made to a fractal Brunauer-Emmett-Teller theory of multilayer adsorption.

The concept of fractals represents a paradigm which has remarkably diverse manifestations in the world of physics.[1] The field of adsorption provides a natural application because it involves precisely the phenomenon of covering a surface. Pfeifer, Avnir, and Farin have shown that, indeed, many adsorption systems exhibit fractal behavior.[2,3] That is, adsorbate particles of linear dimension r overlay a surface completely at monolayer coverage

$$N_m = (\gamma/r)^D \quad . \tag{1}$$

Here D is the fractal dimension, nonintegral in general, and γ is a constant which may be determined experimentally by varying r. While a smooth surface satisfies $D = 2$, rough or porous surface geometries exhibit D as large as ~ 3.[2,3] Questions of interest about these observations include (a) whether these values of D coincide with the results of techniques other than adsorption[4-7] (e.g., x-ray scattering) and (b) whether other adsorption phenomena can be used to determine D and hence further characterize the topography. The present work aims at the second goal. We will show how low-coverage thermodynamic data reveal D, in principle. Issues of energetic and geometric nonuniformity are discussed. We hope to stimulate further systematic experiments which characterize the fractal character over a range of adsorbate size.

The quantity of interest is the adsorption isotherm, given by the relation[8]

$$\ln(p\beta/N) = -\left(\frac{\partial \ln Z_N^s}{\partial N}\right)_{T,V,A} \quad , \tag{2}$$

where p is the pressure, $\beta^{-1} = k_B T$, and Z_N^s is the surface configuration integral for N atoms. At low coverage, interactions among adsorbate particles may be neglected, leaving

$$Z_N^s \cong (Z_1^s)^N \quad , \tag{3a}$$

$$Z_1^s = \int_s d\mathbf{r}\, e^{-\beta V(\mathbf{r})} \quad , \tag{3b}$$

$$N/(p\beta) = Z_1^s \quad . \tag{4}$$

The integration domain in Eq. (3b) is the adsorption region, over which $V(\mathbf{r})$, the substrate potential, is non-negligible.

We first evaluate Eq. (4) in three ways, starting with the most heuristic and general, and finishing with the least. Then we relate the result to a multilayer theory which includes interactions. Note that the adsorption volume near the surface Ω_a satisfies

$$\Omega_a \propto r^3 N_m \quad , \tag{5}$$

$$\Omega_a = l^D r^{3-D} \quad , \tag{6}$$

according to Eq. (1). Here l is a length, proportional to γ, which does not depend on the adsorbate. Our estimate of Eq. (3b) is based on the approximation that $V(\mathbf{r}) \simeq \bar{V}$, a constant, within the domain Ω_a. Thus

$$Z_1^s \simeq \Omega_a e^{-\beta\bar{V}} \quad , \tag{7}$$

$$N/(p\beta) \simeq l^D r^{3-D} e^{-\beta\bar{V}} \quad . \tag{8}$$

Equation (8) is the generalization to a fractal surface of Henry's law of proportionality between p and N.[8] In the smooth-surface limit the right-hand side becomes the gas-surface virial coefficient, proportional to the surface area. For a fractal surface, the "area" is ambiguous, or even meaningless. Then, Eq. (8) can be used fruitfully; a measurement of the β dependence of the left-hand side of Eq. (8) for fixed r will yield $\bar{V}$ and the product $l^D r^{3-D}$. If the latter is evaluated for variable r, D can be determined.[9]

We address next an alternative approach to evaluating the adsorption isotherm. Assume that the accessible adsorption volume is partitioned into "sites" having a variable binding energy ε_α. Let N_α be the number of such sites. Then the set of site occupation numbers $\{n_\alpha\}$ may be determined easily if we neglect interactions among the particles, apart from excluding the possibility of multiple occupation of the sites. The result of this analysis is a fractional occupation[10]

$$n_\alpha/N_\alpha = [e^{\beta(\varepsilon_\alpha - \mu)} + 1]^{-1} \quad . \tag{9}$$

That this probability coincides with the Fermi-Dirac distribution is a consequence of the restriction of occupation numbers. From Eq. (9), we obtain the total coverage

$$N = \sum_\alpha N_\alpha / [e^{\beta(\varepsilon_\alpha - \mu)} + 1] \quad .$$

At low coverage, μ is sufficiently small that $\beta(\epsilon_\alpha - \mu) >> 1$ for all sites. Then

$$N \to e^{\beta\mu}\Sigma \quad , \tag{10a}$$

$$\Sigma = \sum_\alpha N_\alpha e^{-\beta\varepsilon_\alpha} \quad . \tag{10b}$$

We may write this in terms of the fractions f_α of the total number of sites N_{sites}:

$$N = e^{\beta\mu} N_{\text{sites}} \sum_\alpha f_\alpha e^{-\beta\varepsilon_\alpha} \ . \tag{11}$$

Equation (11) may be evaluated for any particular distribution of site energies.

It is useful to relate Eq. (11) to the result, Eq. (8), obtained with the continuous space description mentioned above. To do this, we note that a "site" in the semiclassical sense occupies volume λ^3, where

$$\lambda = \hbar(2\pi\beta/m)^{1/2} \tag{12}$$

is the thermal wavelength. Then

$$N_{\text{sites}} = \Omega_a/\lambda^3 \ , \tag{13}$$

$$N = \beta p \, \Omega_a \sum_\alpha f_\alpha e^{-\beta\varepsilon_\alpha} \ , \tag{14}$$

where we have equated the film's chemical potential to that of the vapor; the latter satisfies $\beta\mu = \ln(\beta p \lambda^3)$ for an ideal gas. If we then make the plausible identification

$$\sum_\alpha f_\alpha e^{-\beta\varepsilon_\alpha} = e^{-\beta\bar{V}} \ , \tag{15}$$

Eq. (14) is found to coincide with Eq. (8), and provides an alternative interpretation of the averaging process.

We present next a solution of the problem of adsorption on an explicit, tunable model of a regular fractal surface, generated as follows. Consider a square of side L_0. Subdivide it into b^2 squares of side L_0/b, where b is odd and at least 3. The central square is then depressed a distance L_0/b, creating a cubic depression of that dimension (see Fig. 1). A second iteration applies this procedure to each of the b^2+4 squares. Repetition of this constructs a fractal surface. Its dimension D may be determined by comparing the relative coverages obtainable with particles of size L and L/b, respectively, chosen so that the latter will just manage to fit into a cavity created at a certain level of the preceding iteration. It can come in contact with a factor b^2+4 more faces than the former; thus

$$b^2+4 = \frac{N_m(L/b)}{N_m(L)} = b^D$$

from Eq. (1). This implies that

$$D = \frac{\ln(b^2+4)}{\ln b} \ . \tag{16}$$

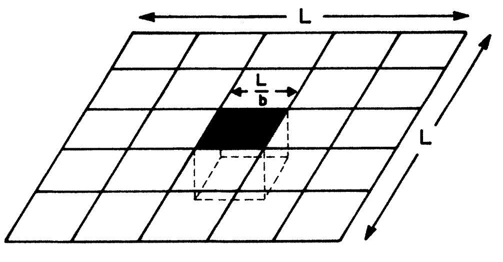

FIG. 1. The result of one step in the generation of the model fractal surface is shown ($b=5$). An initial square ($L \times L$) yields b^2-1 smaller squares in the plane and five square faces of the cubic depression, each L/b on a side.

Adsorption on this surface may now be treated with a variety of assumptions. Here we employ an overly simplistic model in which the adsorbate particle is assumed to gain energy ε from each face in contact with it. Since gas-surface interactions scale with the polarizability,[8,11,12] we assume that ε is proportional to the linear size of the particle, $\varepsilon = r\varepsilon_0$. The evaluation of the partition function reduces then to a geometric problem of finding the total number of sites having a given coordination. Suppose that we have a particle of size $r = L_0/b^n$, where n is the number of iterations necessary to generate the surface to the point where the smallest cavity is of size r. The total number of faces with which the particle may interact is

$$N_f = (b^2+4)^n \ , \tag{17}$$

$$N_f = S_1 + 2S_2 + 3S_3 + 5S_5 \ , \tag{18}$$

where $S_i(r)$ is the number of sites which each have i neighboring faces. Clearly $S_5 = (b^2+4)^{n-1}$. After some calculations (presented in the Appendix) we find the other values

$$S_3 = \frac{4}{(b^2+3)}[(b^2+4)^{n-1} - 1] \ , \tag{19}$$

$$S_2 = \frac{8b[(b^2+4)^{n-1} - b^{n-1}]}{b^2-b+4} - 3S_3 \ . \tag{20}$$

Then the partition function is

$$\Sigma(r) = \sum_{i=1,2,3,5} S_i(r) \exp(-\beta i \varepsilon_0 r) \ . \tag{21}$$

We consider next a particle smaller by a factor 2; denoting its number of sites by $\bar{S}_i$, we find $\bar{S}_5 = 0$ and

$$\bar{S}_3 = \frac{4}{b^2+3}[4(b^2+4)^n - 1] \ , \tag{22}$$

$$\bar{S}_2 = \frac{16b}{b^2-b+4}[(b^2+4)^{n-1} - b^{n-1}] - 3S_3 + 4(b^2+4)^{n-1} \ , \tag{23}$$

$$\bar{S}_1 = 4(b^2+4)^n - 20(b^2+4)^{n-1} + 3S_3 - \frac{32b}{b^2-b+4}[(b^2+4)^{n-1} - b^{n-1}] \ . \tag{24}$$

These expressions allow us to evaluate Σ for particle sizes which are members of either of 2 geometrical series: $r_i = r_0$, br_0, $b^2 r_0$, . . . , . . . , and $r_i' = r_i/2$. The results for Σ are shown in Fig. 2. There we observe that the fractal prediction is obeyed at infinite T; i.e., following Eqs. (10)–(13),

$$\Sigma = N/(p\beta\lambda^3) \ , \tag{25}$$

$$\frac{d \ln\Sigma}{d \ln r} = -D \ . \tag{26}$$

The disagreement with Eq. (8) arises from the absence in this site model of the r^3 factor in Eq. (5). At lower T, the model deviates from this relation owing to preferential adsorption in the strong bonding sites.

Finally, we consider the case of multilayer adsorption, to which we apply the venerable Brunauer-Emmett-Teller (BET) model.[8] This yields the equilibrium number of particles in a pore of radius $R = mr$ as a function of an adsorp-

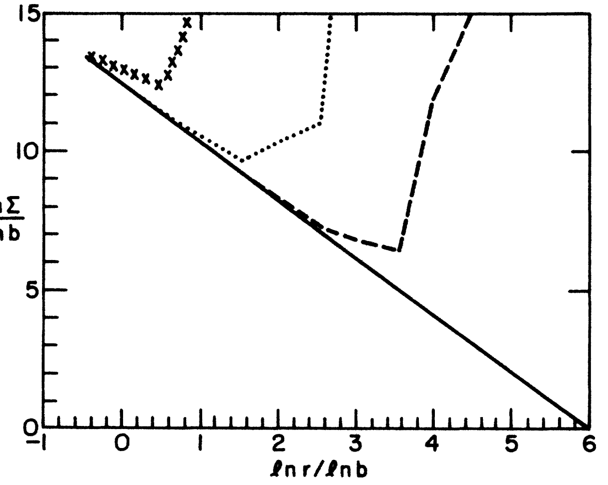

FIG. 2. Computed partition function Σ for adsorption on the model fractal surface ($b=5$, $n=7$), as a function of adsorbate radius r (in units of r_0). Results are shown for the cases $\beta\varepsilon_0=0$ (solid curve), 0.005 (dashes), 0.05 (dots), and 0.5 (×). The solid curve is consistent with Eq. (26), where D is given by Eq. (16).

tion coefficient c and the ratio x of p to the saturated vapor pressure p_0:

$$N_r(R)=N_{\text{sites}}(R)\left(\frac{cx}{1-x}\right)h_m(x)$$
$$=f(N_{\text{sites}}(R),m,x)\ , \tag{27}$$

$$h_m(x)=[1-(m+1)x^m+mx^{m+1}]/[1+(c-1)x-cx^{m+1}]\ .$$

Since pores in a fractal geometry are isotropic (e.g., cube in Fig. 1), the number of possible sites $N_{\text{sites}}(R)=sR^2/r^2$, where s is a geometric factor. It is known that the distribution of pore sizes is $\nu(R)=\nu_0R_{\max}^DR^{-D-1}$, where ν_0 is a constant.[2,13] Then the net coverage is

$$N=\int_r^{R_{\max}}f\left(\frac{sR^2}{r^2},\frac{R}{r},x\right)\nu(R)\,dR\ , \tag{28}$$

$$N=N_{\text{sites}}\frac{cx}{1-x}\frac{g_D(x)}{g_D(0)}\ , \tag{29}$$

$$g_D(x)=\int_1^{R_{\max}/r}m^{1-D}h_m(x)\,dm\ , \tag{30}$$

$$N_{\text{sites}}=\int_r^{R_{\max}}N_{\text{sites}}(R)\nu(R)\,dR\ . \tag{31}$$

Equations (29)–(31) constitute the fractal BET isotherm.[14] For low coverage, Eq. (29) reduces to $N=N_{\text{sites}}cx$. This agrees with the preceding result, Eq. (8), if we replace N_{sites} with N_m and set $c=p_0\beta r^3e^{-\beta\overline{V}}$. The latter correspondence arises from the definition of c as the ratio of a first layer site's partition function to that of bulk saturated vapor.[8] In a cell model this is $(r/d)^3e^{-\beta\overline{V}}$ where d^3, the volume per particle of the vapor, satisfies $d^{-3}\simeq p_0\beta$ (if ideal).

We summarize the results as follows. Low coverage adsorption isotherms are sensitive to the fractal dimension even if the adsorption domain is inhomogeneous. This has been shown to involve a very simple dependence, Eq. (8), at high T. The determination of fractal dimension is straightforward if there exist such data, but is model dependent when the variability of binding energy becomes comparable to T. To our knowledge, there is not yet available systematic data for various adsorbates which can utilize the procedure discussed here; we invite experimentalists to explore this approach.

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APPENDIX

We here derive Eqs. (19), (20), and (22)–(24). To evaluate S_3, note that the first iteration in the fractal construction gives a fivefold coordination site and b^2-1 singlefold coordination sites (these will be denoted 5-sites and 1-sites here). The second iteration converts the 4 corners of the 5-site into 3-sites and creates (b^2+4) new 5-sites. The latter produce $4(b^2+4)$ 3-sites in the next iteration. Repeating the argument throughout the evolution of the fractal yields the number of 3-sites

$$S_3=4\sum_{l=2}^{n}(b^2+4)^{n-l}\ , \tag{A1}$$

which is equivalent to Eq. (19).

The calculation of S_2 is similar. After two iterations, the number of 2-sites is $4(2b-3)$; of these, $(b-2)$ are on each of the four edges bounding the base of the depression made in the first iteration and $(b-1)$ are on each of its 4 side edges. After a third iteration there are (b^2+4) sets of $4(2b-3)$ 2-sites like the original, but the original one becomes $4(2b^2-3)$ sites. When this is repeated at every stage of the process the result is

$$S_2=4\sum_{l=2}^{n}(2b^{l-1}-3)(b^2+4)^{n-l}\ , \tag{A2}$$

which simplifies to give Eq. (20). The number of 1-sites, S_1, is determined from Eqs. (17) and (18) and confirmed by a direct calculation similar to the preceding one.

The numbers $\overline{S}_l$ are calculated as follows. If half-sized particles are considered, each site which contributed to S_1 becomes instead 4 sites contributing to $\overline{S}_1$. Similarly, each site which contributed to S_2 becomes 2 sites in the set $\overline{S}_2$ and 4 in the set $\overline{S}_1$, etc. The equations are

$$\overline{S}_1=4S_1+4S_2+3S_3 \tag{A3}$$

$$\overline{S}_2=2S_2+3S_3+4S_5 \tag{A4}$$

$$\overline{S}_3=S_3+4S_5\ . \tag{A5}$$

Substitution and simplification yields Eqs. (22)–(24).

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[14] For $D=2$, this coincides with the flat surface BET relation to lowest order in x. Deviation otherwise originates from the omission here of the trivial term associated with the external buildup of multilayers when pores are filled; only for $D=2$ does this term dominate.