Adsorption isotherms on fractal substrata

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(Received 18 July 1988)

By means of Monte Carlo simulations, diffusion-limited recombination reactions, followed by desorption and the desorption of single particles from fractal and multifractal substrata, are studied. From all these results, we conjecture that for both processes (a) the dissociative adsorption and associative desorption of diatomic molecules and (b) the nondissociative adsorption and desorption of single particles, the relationship between the particle coverage Θ and the applied pressure p at the steady state (i.e., the adsorption isotherm) may be written, in the limit $\Theta \rightarrow 0$ as $\Theta^{1/2+1/2f}(1-\Theta)^{-1} \propto p^{1/2}$ for (a) and $\Theta(-\ln\Theta)^{1-1/f}(1-\Theta)^{-1} \propto p^{1/2}$ for (b), where f is the site visitation random-walk exponent of the substratum. Classical isotherms are recovered for homogeneous surfaces with $f=1$.

I. INTRODUCTION

It has been established that the surface of most solids on the molecular scale may be regarded as a microscopic fractal structure.[1-10] Furthermore, chemical reactions on fractal media are known to be "anomalous" in the sense that the reaction order depends on the fractal nature of the substrate.[11-20]

The aim of this work is to study the influence of the fractal and multifractal chemical kinetic upon the adsorption isotherms obtained by working with heterogeneous substrata. The study of adsorption isotherms has attracted increasing interest since the beginning of this century. A large number of reviews on this subject can be found in the literature; see, for example, Refs. 21–24. More recently, interest has further increased, due to the study of two-dimensional phase transitions by means of adsorption isotherm measurements.[25,26]

In this work we propose adsorption equilibrium isotherms that are expected to hold, on heterogeneous adsorbents, within the low-coverage regime, and in the absence of lateral interactions. Surface heterogeneity is a consequence of the multiplicity of exposed crystallographic faces, structural defects (such as steps, grain boundaries, vacancies, etc.), the presence of chemisorbed impurities, etc. In order to approach different kinds of heterogeneities, three types of substrata are considered: (a) percolation clusters in two dimensions (geometrical fractal heterogeneities), (b) two-dimensional substrata with multifractal jumping probability distribution (for the definition, see below), and (c) multifractals obtained intersecting, in two dimensions, the substrata of (a) and (b) (combination of geometric and energetic heterogeneities). The structure of the work is the following. The main properties of the employed substrata are briefly reviewed in Sec. II. The theory of desorption reactions from frac-

tals and multifractals is discussed in Sec. III. The Monte Carlo procedure used to simulate the reactions is briefly explained in Sec. IV and the corresponding results are discussed in Sec. V. The adsorption isotherms are derived in Sec. VI. Finally, Sec. VII comprises the discussion of the results and conclusions.

II. SUBSTRATA

The theory of desorption reactions (Sec. III) holds for a great variety of fractal and multifractal substrata. The description of the construction rules and main properties of well-known fractal structures, where the above-mentioned theory works, such as incipient percolation clusters (IPC), diffusion-limited aggregates (DLA), Sierpinski gaskets (SG), etc., are beyond the scope of the present study. The reader is, therefore, referred to review articles; for example, Refs. 27 and 28.

Fractal structures such as IPC, DLA, SG, etc. are characterized by geometrical heterogeneities (holes, branches, loops, etc.) on all scales. For particle diffusion on these media it is assumed that all the sites of the structure have the same time residence probability (μ), i.e.,

$$\mu \sim \exp(-E/kT) , \qquad (1)$$

where E is the activation energy of diffusion, k is the Boltzmann constant, and T the temperature. Therefore, in this sense, the structures are geometrically heterogeneous but energetically homogeneous.

On the other hand, since the study of multifractals has begun very recently,[29-38] let us briefly review the relevant properties. In this work we simulate desorption reactions on multifractals, such as those proposed by Meakin.[32,33] On square lattices of size $L \times L$, with $L=2^n$, these multifractals are constructed as follows. Four normalized probabilities P_i ($i=1, \ldots, 4$) are selected. In the first

generation, these probabilities are randomly assigned to the four quadrants, each of them of linear size $l_1 = L/2$, of the lattice. In the second generation, each quadrant is divided into four smaller quadrants of linear size $l_2 = L/2^2$ [in the mth ($m \leq n$) generation, $l_m = L/2^m$], and the probabilities associated to each quadrant prior to the division are multiplied by P_1, P_2, P_3, and P_4 in random order. After n generations, each A lattice site is associated to a probability (or measure) μ_A of the form $P_1^{S_1} P_2^{S_2} P_3^{S_3} P_4^{S_4}$, with $S_1 + S_2 + S_3 + S_4 = n$. One can assume that

$$\mu_A \sim \exp(-E_A/kT) , \qquad (2)$$

where E_A is the activation energy of diffusion at the A site. Under this assumption and for $n \to \infty$, one has that the obtained structure conforms to a multifractal distribution (MFD) of μ characterized by an infinite set of independent fractal exponents D_q (q real) (for more details, see, for example, Refs. 15, 29–31, 34, and 35). For the MFD used in this work, this set of exponents can be obtained according to

$$\sum_{X=1}^{2^{2m}} \mu_X^q \sim (l_m/L)^{(q-1)D_q} , \qquad (3)$$

where the sum runs over all the quadrants X of linear size l_m, and μ_X is the measure of the Xth quadrant.[15,34,35]

Therefore the MFD is a geometrically homogeneous but energetically heterogeneous substratum. Note that setting $P_1 = P_2 = 1/2(1+Q)$ and $P_3 = P_4 = Q/2(1+Q)$, with $0 < Q < 1$, after n generations, one has a binomial distribution of heterogeneities, which in the limit $n \to \infty$ tends to a Gaussian distribution. Nevertheless, it should be mentioned that in the Gaussian distribution previously employed for the simulation of adsorption and desorption processes on energetically heterogeneous surfaces,[23,39] the sites of different energy are randomly distributed on the surface (i.e., this random distribution does not define a multifractal measure). Let us stress that in the multifractal, it is just the spatial distribution of measures that plays a fundamental role in the physical properties.

Very recently, we have proposed[15] new structures obtained by the intersection, in d dimensions, between a geometric random fractal of dimension D_F and a MFD characterized by an infinite set of D_q dimensions. In this work we have studied recombination reactions on a particular case, called IPC plus MFD, namely, the intersection, in $d = 2$ dimensions, between an IPC on the square lattice and a planar MFD of measures μ_A, as defined above. In the IPC plus MFD model the measure μ'_A associated with a site A is given by

$$\mu'_A = \begin{cases} C\mu_A & \text{if the site } A \text{ belongs to the IPC} \\ 0 & \text{otherwise,} \end{cases} \qquad (4)$$

where C is the normalization constant obtained by demanding $\sum_A \mu'_A = 1$, where the sum runs over all lattice sites. Note that the jumping probabilities of random walkers, as defined by Eq. (18), do not depend on C.

The IPC plus MFD is a multifractal structure charac-

terized by an infinite set of D'_q dimensions given by $D'_q = D_F + D_q - d$ [$d = 2$ and $D_F = \frac{91}{48}$ Ref. (28) for the present example]. More details will be discussed elsewhere.[15] Note that the IPC plus MFD combines both energetic and geometric heterogeneities.

We expect that the study of adsorption and desorption processes on substrata such as those described in the present section would contribute to the understanding of the complex reactions that take place on fractal catalysts. In fact, typical catalysts are composed by fractal clusters of metal[8] distributed on fractal substrata.[4,6]

III. THEORY OF DESORPTION REACTIONS FROM FRACTALS AND MULTIFRACTALS

A. Associative desorption

The theory of recombination reactions (RR's) on fractal[11−13] and multifractal[15,16] surfaces has recently been studied. Let us here briefly review the main arguments. The number of distinct sites (S_N) visited by a random walker after N steps is given by

$$S_N \propto N^f, \quad N \to \infty \qquad (5)$$

where f ($0 \leq f \leq 1$) is the random-walk site visitation exponent. For homogeneous two-dimensional substrata one has $f = 1$ (classical diffusion), while on fractals and multifractals $f < 1$ gives anomalous diffusion. Also for one-dimensional homogeneous substrata $f = \frac{1}{2}$ gives anomalous diffusion.[13,17] For fractal objects, $f = \tilde{d}/2$ if $\tilde{d} < 2$, and $f = 1$ if $\tilde{d} \geq 2$, where $\tilde{d}$ is the spectral dimension related to the density of states for scalar harmonic excitations of the fractal.[40,41] On the other hand, the relation between f and the geometric and/or energetic properties of the MFD's is an interesting open question. Preliminary results allow us to advance that f does not depend on the infinite set of exponents $\{D_q\}$ of the MFD, in the sense that quite different values of f are obtained for MFD's characterized by the same $\{D_q\}$ set. Table I shows examples of some random-walk exponents. Note that for fractal media N is strictly proportional to time t, while for MFD's one can assume that the proportionality is valid on the average.[15,16]

The rate equation for the recombination of A particles, i.e.,

$$A_s + A_s \to p_g^* , \qquad (6)$$

where p^* represents products and the subscripts s and g denote surface and gas phase, respectively, can be written as

$$-\frac{d\Theta}{dt} = K\Theta^q , \qquad (7)$$

where Θ is the surface coverage of A particles, K the rate constant, and q the reaction order ($q = 2$ in the present example).

The rate constant is related to S_N through the site visitation efficiency (ϵ), that is,

TABLE I. Random-walk exponents and reaction orders for recombination reactions on different substrata. IPC and SG, 1D and 2D refer to incipient percolation cluster and Sierpinski gaskets in two dimensions, one- and two-dimensional homogeneous surfaces, respectively.

Substratum	f	x
Homogeneous		
1D	$\frac{1}{2}$	3[a,b]
2D	1	2
Fractals		
IPC	$\frac{2}{3}$[c]	2.5[a,d]
SG	0.683[c]	2.45[a]
Multifractals		
Type I		
$Q=\frac{1}{4}$	0.796[e]	2.22[f]
$Q=\frac{1}{8}$	0.693[e]	2.35[f]
$Q=\frac{1}{16}$	0.587[e]	2.56[f]
Type II		
$Q=\frac{3}{4}$	0.885[e]	2.04[d]
$Q=\frac{1}{2}$	0.769[e]	2.27[d]
$Q=\frac{1}{4}$	0.541[e]	2.79[d]
IPC plus MFD		
Type II		
$Q=\frac{3}{4}$	0.61[f]	2.64[f]
$Q=\frac{1}{2}$	0.52[f]	2.92[f]
$Q=\frac{1}{4}$	0.28[f]	4.57[f]

[a]Reference 13.
[b]Reference 17.
[c]Reference 41.
[d]Reference 16.
[e]Reference 33.
[f]Reference 45.

$$K \propto \epsilon = \frac{dS_N}{dt} \ . \tag{8}$$

Performing the derivative of Eq. (5) according to Eq. (8) and replacing in Eq. (7), one obtains[12,17]

$$-\frac{d\Theta}{dt} \propto \Theta^q t^{f-1}, \quad \Theta \to 0, \quad t \to \infty \tag{9}$$

where the proportionality between N and t has been used. Note that $\Theta \to 0$ in Eq. (9) corresponds to $t \to \infty$ [$N \to \infty$, Eq. (5)]. Integration of Eq. (9) for a recombination reaction ($q = 2$) and $\Theta \ll \Theta_0$ (Θ_0 is the initial coverage), gives

$$-\frac{d\Theta}{dt} \propto \Theta^x, \quad \Theta \to 0, \quad \Theta \ll \Theta_0 \tag{10a}$$

where now

$$x = 1 + 1/f \tag{10b}$$

is the reaction order. For a homogeneous medium in two dimensions one has $f = 1$, so that $x = q = 2$. Integration

of Eq. (10a) gives

$$\frac{1}{\Theta^{x-1}} - \frac{1}{\Theta_0^{x-1}} \propto t \ . \tag{11}$$

Equation (11) holds for $\Theta \ll \Theta_0 \ll 1$ ($f < 1$) and $\Theta \leq \Theta_0 \leq 1$ ($f = 1$). The last follows integrating Eq. (7) with $q = 2$, i.e., $f = 1$ in Eq. (10b). So, Eq. (11) is useful to observe crossover effects from homogeneous to fractal regimes (see Fig. 1, Sec. V). Also, note that for $\Theta \ll \Theta_0$ Eq. (11) becomes

$$\ln\Theta \sim -f \ln(t) \ . \tag{12}$$

Equations (11) and (12) are useful to check the validity of the theory avoiding the numerical evaluation of the reaction rate (see Sec. V).

B. Desorption of single particles

Let us now assume that the A particles can diffuse on the surface, depending on the activation energy of diffusion, and that only particles arriving at certain active sites (AS) on the surface are desorbed, that is,

$$A_s + (AS)_s \to A_g \ . \tag{13}$$

Let Θ_s be the concentration of active sites, which are assumed to be randomly distributed on the surface (Θ_s remains constant through all the procedure). Then the desorption rate can be written as

$$-\frac{d\Theta}{dt} = C\Theta_s\Theta \ , \tag{14}$$

where C is the rate constant. So one has a typical first-order reaction rate equation. Nevertheless, if the reaction takes place on a MFD one can use the definition of the site-visitation efficiency [Eq. (8)], and Eq. (14) becomes

$$-\frac{d\Theta}{dt} \propto \Theta_s t^{f-1}\Theta \ . \tag{15}$$

Integrating Eq. (15) one has

$$-\ln(\Theta) \propto t^f \ . \tag{16}$$

Replacing Eq. (16) in Eq. (15) one obtains

$$-\frac{d\Theta}{dt} \propto \Theta_s[-\ln(\Theta)]^{1-1/f}\Theta \ . \tag{17}$$

Note that for homogeneous media ($f = 1$) the usual first-order rate equation is recovered, but for $f < 1$ one expects deviations from the classical behavior.

Let us point out that for homogeneous substrata, if Θ_s is very small, one should expect that the decay of A particles would depend on the dimension of the Euclidean space in which the reaction takes place.[42] The study of this effect on MFD's lies beyond the aim of the present work.

IV. MONTE CARLO PROCEDURE

Simulations are performed on IPC's in two dimensions using square lattices of size $L \times L$ ($L = 201$). Only per-

colating clusters in both directions of the lattice are employed. Two types of MFD's generated by $P_1 = P_2 = \frac{1}{2}(1+Q)$ and $P_3 = P_4 = Q/2(1+Q)$ (type-I MFD), and $P_i = Q^{i-1}(1+Q+Q^2+Q^3)^{-1}$, $i = 1,2,\ldots,4$ (type-II MFD), respectively, are studied on square lattices of size $L \times L$ ($L = 256$, so $n = 8$), where Q is a free parameter. The studied IPC plus MFD substrata, are obtained by intersecting IPC's, which percolate in both directions of the lattice, with type-II MFD's in square lattices of size $L \times L$ ($L = 256$).

In order to study the diffusion-reaction process the substratum sites are covered at random with A particles. Interaction among adsorbed particles is neglected in all cases. For RR's, particle diffusion is simulated as follows: (i) A particle in the substratum site C is randomly chosen. (ii) One of the four nearest-neighbor (NN) sites is selected at random. (iii) If the selected NN has null measure [for example, it does not belong to the IPC; see also Eq. (4)], the trial ends and does not account for computing the Monte Carlo time. (iv) If the measure of the selected NN is different from zero one has the following possibilities: (a) for IPC's the jumping probability P_{CB} from C to the NN B is assumed to be $P_{CB} = \exp(-E/kT)$ [see Eq. (1)].[16,17] (b) For MFD's and ICP's plus MFD's one assumes[33,16]

$$P_{CB} = \begin{cases} \mu_B/\mu_C & \text{if } \mu_B < \mu_C \\ 1 & \text{otherwise.} \end{cases} \quad (18)$$

Note that, as pointed out by Meakin,[33] P_{CB} [Rq. (18)] in connection with Eq. (2) is equivalent to the method of Metropolis et al.[43] and standard Monte Carlo techniques,[44] in the sense that jumps into sites of lower (higher) energy are allowed with probability 1 (decided by comparing P_{CB} with a random number). Nevertheless, during the simulation of the present kinetic process the system can never reach any equilibrium state. (v) Finally, when two A particles are at the same site as a consequence of the movement, both particles are removed from the substratum, i.e., this is considered as a successful recombination event followed by desorption.

The desorption of single A particles is studied on MFD's. Active sites are randomly distributed on the substratum with a preset concentration. Then, the remaining sites are covered at random with A particles. After that the diffusion is simulated according to the above-discussed rules, and particles arriving at active (fixed) sites are removed from the substratum (i.e., successful desorption event).

In all cases, the Monte Carlo time is defined as proportional to the number of jumping attempts per particle, i.e., the number of successful jumping events plus the failed ones. The proportionality constant usually employed is 0.05.

V. RESULTS

A. Associative desorption

In the present work we have checked the validity of Eq. (10) on MFD's within the whole coverage regime.
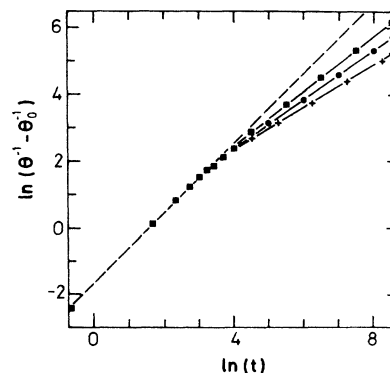

FIG. 1. Plot of $\ln(\Theta^{-1} - \Theta_0^{-1})$ vs $\ln(t)$ for recombination reactions on different MFD's of type I. ■, $Q = \frac{1}{4}$, $f = 0.82$; ●, $Q = \frac{1}{8}$, $f = 0.74$; +, $Q = \frac{1}{16}$, $f = 0.64$; $\Theta_0 = 1$ in all cases. The slopes are obtained by least-squares fits of the respectively low-coverage regime. The dashed line, with $f = 1.05$, is common for all the substrata within the high-coverage regime. Results obtained by averaging 80 different reactions in each case.

Figure 1 shows plots of $\ln(\Theta^{-1} - \Theta_0^{-1})$ versus $\ln(t)$ for MFD's of type I, with $\Theta_0 = 1$. At high coverages (short time) particles are not influenced by the heterogeneity of the substratum and the reaction becomes independent of the nature of the surface. So from the initial slope of the plot one always obtains $f \cong 1$, either for homogeneous or heterogeneous substrata, which corresponds to the classical second-order reaction. Nevertheless, at low coverages (long times), particles have traveled a long-enough distance on the substratum, before each successful recombination event, to be actually influenced by the heterogeneity of the surface. Consequently, we observe a crossover effect between the classical and the fractal behavior of the reaction. In fact, roughly at $\Theta \cong 0.15$ the plots corresponding to the different surfaces separate from the common straight line exhibiting fractal slopes, as expected, from Eq. (12). For recombination reactions on IPC's we have observed a similar crossover effect at $\Theta \cong 0.40$.[16]

It should be mentioned that in previous studies of the low coverage regime of the reaction, it has been found that Eq. (10) holds for isothermal and temperature programmed reactions on linear chains;[13,17] SG,[13] IPC,[13,16] type-II MFD's,[15,16] and type-II ICP's plus MFD's.[15] The corresponding reaction orders are also listed in Table I.

B. Desorption of single particles

In order to study the modification of the reaction rate equation for a classical first-order reaction that takes place on a MFD, we have simulated the desorption of particles from active sites randomly distributed on the surface. Figure 2 shows plots of $\ln(\Theta)$ versus t^f [see Eq. (16)] obtained through Monte Carlo simulations. Figure 2(a) corresponds to a homogeneous substratum (i.e., a trivial MFD with $Q = 1$) and the straight line is obtained using $f = 1$, as expected. For MFD's of type II, Figs. 2(b) ($Q = 0.5$) and 2(c) ($Q = 0.25$), the straight lines are obtained assuming $f = 0.80$ and $f = 0.57$, respectively.
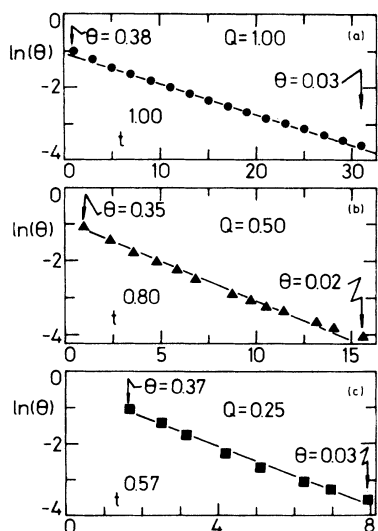
FIG. 2. Plots of $\ln(\Theta)$ vs t^f for desorption reactions of single particles from different MFD's of type II. (a) $Q = 1$ (i.e., homogeneous substratum with $f = 1.0$); (b) $Q = 0.50$, $f = 0.8$; and (c) $Q = 0.25$, $f = 0.57$. $\Theta_s = 0.15$ and $\Theta_0 = 0.50$ in all cases. The arrows at the left and right hands of each figure indicate the coverage intervals within which the straight lines are obtained. Results averaged over 80 different reactions in each case.

These random-walk exponents are in good agreement with both the results of Meakin[33] for single random walkers and with values obtained by simulating recombination reactions of adsorbed particles on the same type of substrata (see also Table I). Let us note that according to Fig. 2 the validity of the anomalous reaction rate equation covers at least the range $0.4 > \Theta > 0.03$, and theoretical arguments suggest that it may also hold for $\Theta \to 0$.

One also should mention that plots, such as those shown in Fig. 2, do not allow as precise a determination of f as for recombination reactions. Nevertheless, we have achieved enough resolution to state that on MFD substrata (with $Q < 1$) the reaction order for the desorption of single particles is different than 1, at least for $\Theta_s \leq 0.15$ and $\Theta < 0.4$. So Eq. (17) should be considered as appropriate for the description of particle desorption from energetically heterogeneous substrata with randomly distributed active sites.

VI. ADSORPTION ISOTHERMS

A. Dissociative adsorption and associative desorption

Let us consider the dissociative adsorption and recombinative desorption process of diatomic molecules on a fractal surface within the low-coverage regime. At constant temperature, when the stationary state has been reached and the surface coverage at equilibrium is Θ, one can follow the early arguments of Langmuir:[21] for a diatomic molecule approaching the surface, the rate of dis-

sociative adsorption (R_{ad}) should be proportional to the probability of finding two adjacent sites bare $[(1-\Theta)^2]$, that is,

$$R_{ad} = \alpha_0 \nu (1-\Theta)^2 , \qquad (19)$$

where ν is the number of incident molecules sticking at the unit area per second and α_0 (with $\alpha_0 \leq 1$) is the fraction of those molecules which, after finding two adjacent sites free, becomes readily adsorbed. In Eq. (19) eventual corrections to the exponent of the term $(1-\Theta)$, due to the presence of geometric or energetic heterogeneities, are neglected. Note that since α_0 [α_0' in Eq. (24)] is assumed to be constant at a given temperature, the dependence of the sticking coefficient on the energetic (adsorption) heterogeneity is neglected. This heterogeneity depends on the particular structure of the substratum itself and could eventually be induced by the adsorbate. Therefore, Eqs. (19) and (24) hold for energetically homogeneous adsorption processes but, on the other hand, with MFD's, the diffusion-limited reaction processes depend on the energetic (diffusion) heterogeneity. Adsorption on energetically homogeneous surfaces is a random process, i.e., all empty adsorption sites have the same adsorption probability, but on heterogeneous surfaces adsorption occurs at energetically favorable sites. Equations (19) and (24) would also hold for the last case when the distribution of particles on the substratum becomes independent of the initial adsorption process after a relatively short time compared with the diffusion-limited reaction.

According to the kinetic theory of gases, ν can be written as[21,24]

$$\nu = p / (2\pi m kT)^{1/2} = \eta p \qquad (20)$$

where p is the pressure and m is the mass of the incident particles. Also $\eta = (2\pi m kT)^{-1/2}$ is a constant for a fixed temperature.

Under equilibrium conditions the rate of adsorption should be equal to the rate of desorption, so using Eqs. (19) and (10), respectively, one obtains

$$\alpha_0 \nu (1-\Theta)^2 = C_0 \Theta^x , \qquad (21)$$

where C_0 is a constant. Equation (21) can be rewritten using Eq. (20), then

$$\frac{\Theta^{x/2}}{(1-\Theta)} = \left[\frac{\alpha_0 \nu}{C_0} \right]^{1/2} = ap^{1/2} , \qquad (22)$$

with $a = (\alpha_0 \eta / C_0)^{1/2}$. Therefore, the isotherm of Eq. (22) defines the relationship between the external pressure and the surface coverage in a fractal medium. It should be remembered that one expects Eq. (22) to be valid within the low-coverage regime and when the interaction between the adparticles is negligible. The fractal nature of the sample appears through the exponent x, which depends on the random-walk exponent f according to Eq. (10b). For $f = 1$ the classical result with $x = 2$ is recovered.

Since, in principle, Eq. (22) holds at low coverage, one can further approximate $(1-\Theta)^{-1} \simeq 1$, obtaining

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$$\Theta \simeq a^{2/x} p^{1/x} = b p^{1/x} , \qquad (23)$$

with $b = a^{2/x}$, which takes the form of the well-known Freundlich adsorption isotherm,[21-24] proposed in 1907, as quoted in Ref. 21, where "the constants b and x (empiric) depend on the nature of both the adsorbent-adsorbate system and temperature."[21]

Figure 3 shows plots of Θ versus $p^{1/2}$ obtained with the aid of Eq. (22), assuming $a = 1$. The nearly straight line is obtained using $x = 2$, but increasing x, marked deviations from the classical behavior are observed. The inset in Fig. 3 shows plots of Θ versus p on a logarithmic scale, for $x = 2$ and 4, obtained with both Eqs. (22) and (23). Note that the approximation $1 \simeq (1-\Theta)^{-1}$ introduced in Eq. (23) does not cause appreciable deviations from the exact behavior [Eq. (22)] for $\Theta \lesssim 0.10$. Also, the onset of adsorption becomes shifted to lower pressures for the anomalous isotherm as compared with the classical one. The employed values of x are within the typical ones for fractals and MFD's (see Table I).

B. Nondissociative adsorption and desorption processes

Using arguments similar to those employed in Sec. VI A, one has that the rate of adsorption of single particles can be written as

$$R_{ad} = \alpha_0' v (1-\theta) , \qquad (24)$$

where α_0' ($\alpha_0' \leq 1$) is the sticking coefficient and v is given by Eq. (20). Under equilibrium conditions, using Eqs. (17) and (24), one obtains

$$\alpha_0' v (1-\Theta) = C' \Theta (-\ln\Theta)^{1-1/f} , \qquad (25)$$

where C' is a constant at a fixed temperature. Regrouping Eq. (25), it follows that

$$\frac{\Theta(-\ln\Theta)^{1-1/f}}{1-\Theta} = \frac{\alpha_0' v}{C'} = b' p , \qquad (26)$$

with $b' = (\alpha_0' \eta / C')$. Note that the fractal nature of the substratum appears through the exponent f. Also, for $f = 1$ and for $f = 1$, $\Theta \to 0$ one recovers, respectively, the well-known Langmuir and Henry isotherms,[21,24] which hold for homogeneous substrata.

VII. DISCUSSION AND CONCLUSIONS

Two types of isotherms, Eqs. (22) and (26), valid in the low-coverage regime, for dissociative processes and single-particle adsorption and desorption processes, respectively, have been proposed in order to take the fractal nature of the adsorbent into account. Classical isotherms are recovered from the proposed ones for homogeneous substrata.

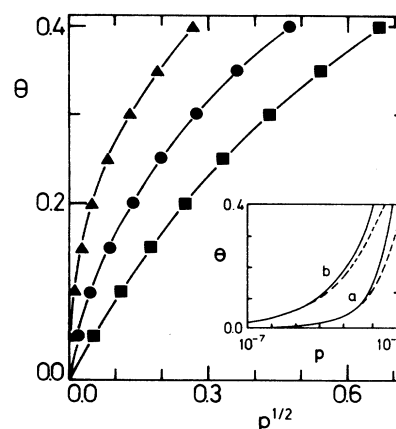For geometrically heterogeneous fractal substrata, the

FIG. 3. Plots of Θ vs $p^{1/2}$, for the adsorption isotherms defined by Eq. (22) (assuming $a = 1$) for dissociative-adsorption− associative-desorption processes on different substrata. ■, $x = 2$ (homogeneous surface with $f = 1$); ●, $x = 2.75$ ($f = \frac{4}{7}$); and ▲, $x = 4$ ($f = \frac{1}{3}$). The inset shows plots of Θ vs p on a logarithmic scale corresponding to (a) $x = 2$, Eq. (22), solid line, and Eq. (23), dashed line. The last is obtained assuming $(1-\Theta)^{-1} \approx 1$ in Eq. (22). (b) Same as (a) but for $x = 4$.

fractal behavior appears due to the dependence of the isotherms on the random-walk exponent f [note that x depends on f, Eq. (10b)], while C_0 and C' depend on E/kT through a Boltzmann term [Eq. (1)].

For MFD's and ICP's plus MFD's the isotherms also depend on f. Increasing the heterogeneity by decreasing Q, higher coverages are obtained at the same pressure, as is shown in Fig. 3, due to the diminution of the reaction rate.

We have shown that Eq. (22) takes the form of the well-known Freundlich isotherm equation (23) for $\Theta \to 0$. It has been found that this isotherm satisfactorily fits experimental data of a great variety of adsorbent-adsorbate systems, including the adsorption of atoms and complex molecules.[21] Nevertheless, it should be kept in mind that the adsorption isotherm proposed in this work [Eq. (22) or Eq. (23)] is only valid for the dissociative adsorption of diatomic species, which desorb upon recombination. The above condition could eventually be satisfied, among others, by the adsorption and desorption of H_2 and N_2 on ammonia synthesis catalysts and other microporous (fractal[1,2,4-7]) substrata.

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