

Adsorption on model fractal surfaces

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Abstract. A simple model for the adsorption of gas molecules on fractal surfaces is formulated. For surface reactions where adsorption is the rate determining step, considerations based on the probability of adsorption are sufficient to describe the kinetics. Different values of fractal dimension correspond to different values of rate constant for adsorption. A linear relationship between the dynamics and the geometric properties of a solid surface as well as a statistical mechanical relationship between internal partition functions of the gas molecule and the adsorption complex are obtained.

Keywords. Adsorption; fractal surfaces; dynamics; geometric properties; statistical mechanical relationship; internal partition functions.

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The role of fractals and fractal dimensions in heterogeneous reaction kinetics, namely surface catalysis and diffusion-limited aggregation, has been explored over the last decade [1–5]. It is now understood that rough surfaces and adsorption processes occurring on them can be categorized and analyzed using fractal behaviour. We report here a simple model regarding adsorption on a surface on which the distribution of active sites is a two-dimensional extension of a cantor set lattice [6]. We calculate rate constants for such adsorption and show that they depend on the fractal dimensions (d_f) of the corresponding lattices. A linear relationship is obtained between the logarithm of the rate constant and the fractal dimension. Finally, we show an interesting relationship involving d_f and the statistical mechanical partition functions of the reactants in the adsorption process.

The usual cantor set is constructed as follows. Take any two points (with distance between them normalized to unity) and divide the distance between them into three parts. Ignore the middle section and repeat the procedure with the other two parts. Repeated iterations generate an infinite sequence of self similar boundary points called the cantor set. The fractal dimension of this set is

$$d_f = \frac{\log(1/N)}{\log l} = \frac{\log 2}{\log 3} \quad (1)$$

where N is the number ($= 2$) and l is the length of the subintervals ($= 1/3$) chosen [6].

The distribution of active sites in our model is generated by replacing each point in the 1 D horizontal cantor lattice by a vertical cantor lattice. The fractal dimension

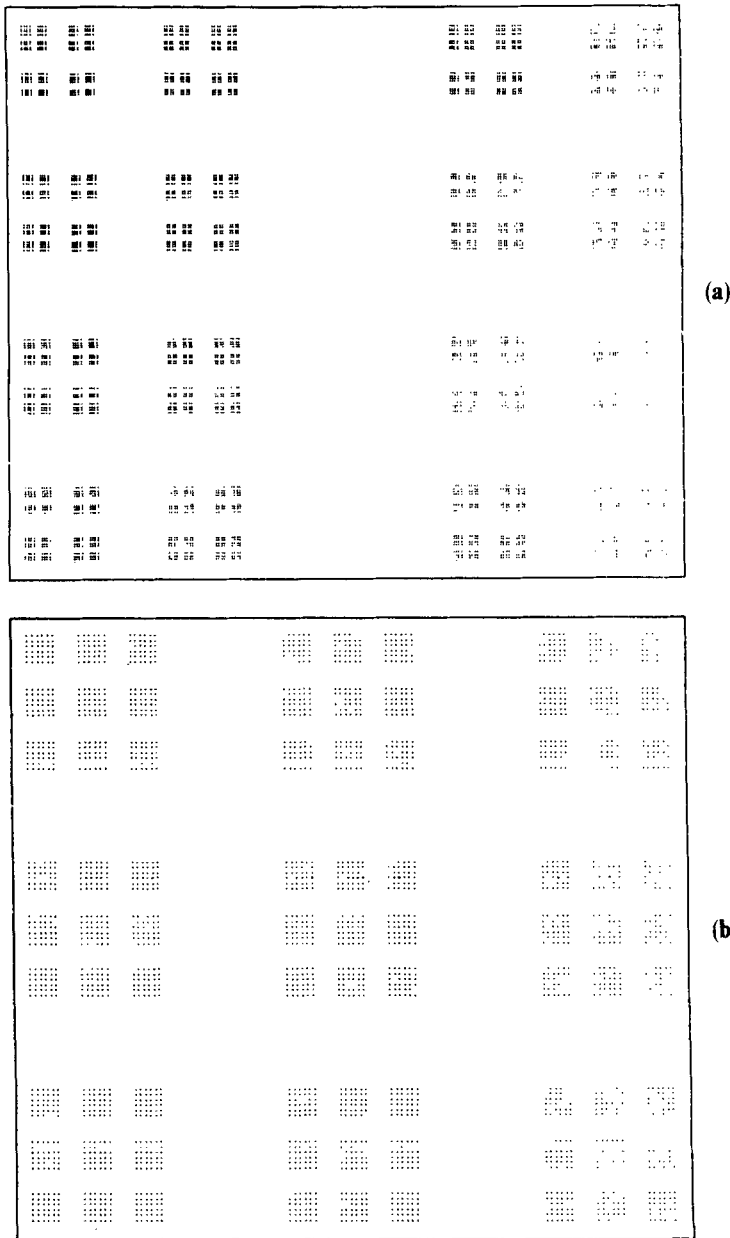


Figure 1. Fractal models of a solid surface (a) $d_f = 2 \log 2 / \log 3$, 6. iterations; (b) $d_f = 2 \log 3 / \log 5$, 4 iterations.

of the surface is

$$d_f = \frac{\log(1/2^2)}{\log(1/3)} = 2 \frac{\log 2}{\log 3}. \quad (2)$$

This construction can be generalized to sets of $d_f = 2 \log(N_1) / \log(N_2)$ with $N_2 > N_1$. Figures 1(a) and (b) show two such surfaces with $d_f = 1.26$ (6 iterations) and 1.36 (4 iterations) respectively.

Adsorption on model fractal surfaces

We consider a simple problem of heterogeneous kinetics, involving fractality. Consider molecules of a gas A landing on a surface such as the ones shown in figure 1 with a uniform density. The density is assumed to be small enough so that the amount of A adsorbed remains small. The molecules landing on the sites, where no point of the fractal lattice exists, get evaporated or desorbed instantly. Each point of the lattice is an active surface site. In other words, we have a situation such as



Once the molecule A is bound to the surface S , it can either desorb back to its gaseous state or transform to a new species B , i.e.



For simplification, we consider the case when the probabilities for desorption and reaction steps are negligible. In other words, we examine only the problem of sticking instead of a complete surface reaction.

Consider a finite number of points on the lattice (generated by a finite number of iterations of the procedure described above). In general, the fraction of the total number of active sites on the surface is

$$x = \frac{[A - S]}{[A]} = \frac{4N_1^{2(n-1)}}{(N_2^{n-1} + 1)^2} \quad (6)$$

for a surface modelled after n iterations to construct a 2D lattice of fractal dimension $2 \log(N_1)/\log(N_2)$. As long as the density of A molecules remains small, the above fraction, which can be thought of as an adsorption probability, will remain constant. Consider, for example a 2D extension of the usual cantor set, i.e., when $N_1 = 2$ and $N_2 = 3$. After 8 iterations, the value of x will be 0.014, i.e., only about .1% of the landing molecules are adsorbed on the active sites. Thus, unless the A molecules arrive in large numbers, very few sites are occupied which means that the probability and hence the rate of adsorption remains nearly constant. As long as one is dealing with a distribution of active sites with d_f reasonably less than 2 (keeping in mind that the euclidean dimension of the surface is 2) after a sufficiently large number of iterations, the set of active sites is essentially a very small fraction of the total surface. Incidentally, assuming that each site is occupied by incoming molecules of A , it can be easily shown that the area of cross-section of the base of each molecule of A is

$$\sigma \leq \frac{\mathcal{S}}{(N_2^{n-1} + 1)^2} \quad \text{where } \mathcal{S} \text{ is the surface area.}$$

The rate will also depend on the flux of A molecules, i.e., the number of molecules of A arriving on the surface per unit time. For a given concentration of the gas molecules, $[A]$, the classical dynamical rate constant k , is given by $z \exp[-E/RT]$; where z is the collision frequency, E the activation energy, T the absolute temperature and R the gas constant [7]. The collision frequency z is proportional to x in (6).

As a further simplification, we take the rate constant k to be ($E = 0$ limit)

$$k = x = \frac{4}{\{(N_2/N_1)^{n-1} + (1/N_1^{n-1})\}^2}. \quad (7)$$

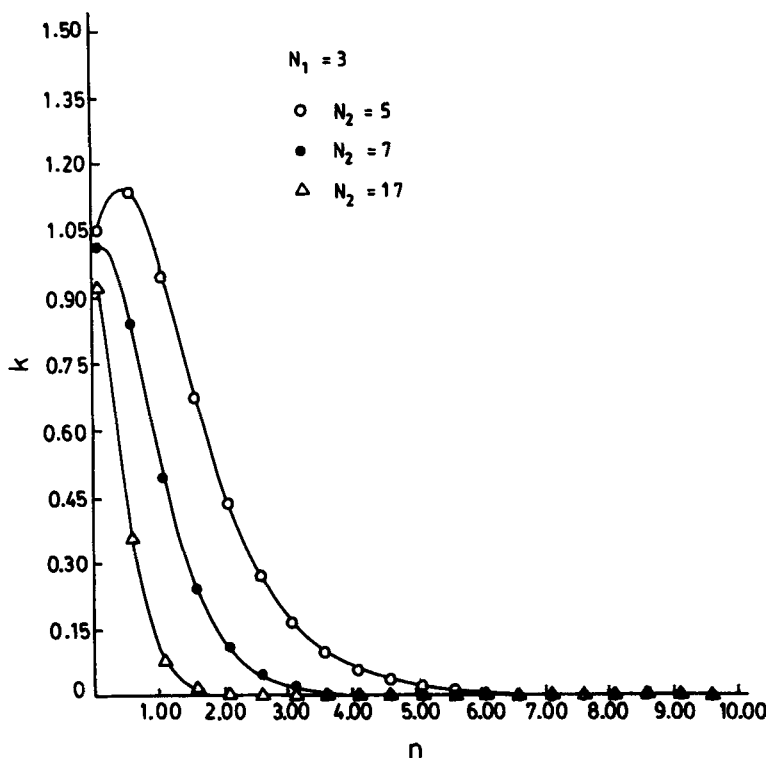


Figure 2. Variation of rate constant in eq. (5) as a function of the iterations. Only non-zero integral values of n correspond to the particular iterations.

It is easily seen that as $n \rightarrow \infty$, i.e., after a large number of iterations, k becomes negligible. This amounts to saying that we are dealing with a set of measure zero, which is a subset of all the lattice points lying in a finite interval in \mathbb{R}^2 . In figure 2, we have plotted the function on RHS of (7). It is seen that different values of d_f give rise to distinct curves. Notice that only integral values correspond to the particular iterations. The plot has been made continuous in order to point out the maximum in the curve below $n = 1$. Taking the large n limit, we have

$$k = \frac{4}{(N_2/N_1)^{2(n-1)}} \tag{8}$$

This gives

$$\frac{\log k}{\log N_2} = \frac{\log 4}{\log N_2} - 2(n-1) + (n-1)d_f. \tag{9}$$

Thus, for a given N_2 , $\log(k)$ will be linear with respect to d_f and the rate constant k will be negligibly small as $d_f \rightarrow 0$ and relatively large for $d_f \rightarrow 2$. Figure 3 shows this result for a total of 10^{20} (active and inactive) sites on a surface for two different cases of construction corresponding to $N_2 = 7$ and $N_2 = 17$ respectively. This interesting result implies that we have a dynamical quantity varying linearly with a feature which is dependent only on the geometry of the system.

Finally, a simplistic statistical mechanical analysis of the adsorption problem gives an interesting relationship between the fractal dimension and some of the relevant statistical mechanical quantities. One can write the equilibrium constant for the

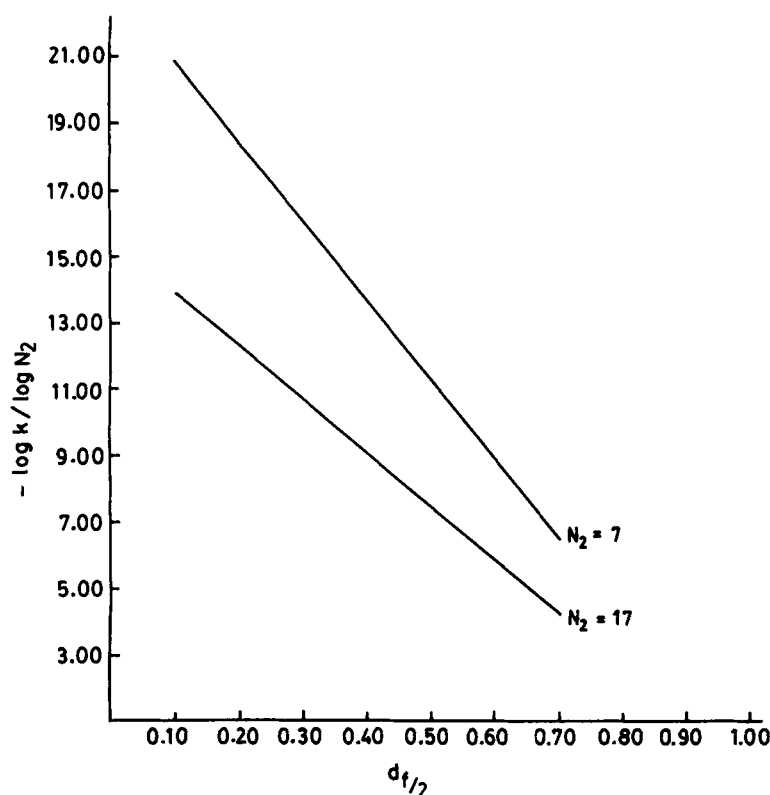


Figure 3. Logarithm of rate constant k plotted against the fractal dimension d_f for surfaces with a total of $10^{10} \times 10^{10}$ sites, corresponding to $N_2 = 7$ and 17. The quantity k has dynamical information about the adsorption process, while d_f describes only the geometric properties of the distribution of active sites on the surface.

adsorption process as

$$K = \frac{[A - S]}{[A](N/\mathcal{S} - [A - S])} \quad (10)$$

where $N = (N_2^{n-1} + 1)^2$ is the number of sites and \mathcal{S} is the surface area. Thus N/\mathcal{S} is the concentration of sites on the surface and its reciprocal gives an upper bound to the cross-sectional area of the base of the adsorbed molecule. Equating this to the statistical mechanical expression for the equilibrium constant, we have,

$$\frac{q \cdot \exp(-E/RT)}{q_g \cdot q_s} = \frac{4 \left[\frac{N_1^{n-1}}{N_2^{n-1} + 1} \right]^2 [A] c}{[A](N/\mathcal{S} - [A - S])}, \quad (11)$$

here q_g , the partition function for the gas molecule, is to be calculated for unit volume and q_s , the partition function for the unoccupied active sites on the surface, is to be calculated for unit surface area. The factor q in the numerator is the partition function for the adsorbate-adsorbent complex. The constant C is a proportionality constant

and is taken as unity in all later treatments. Also, as explained earlier, only a small fraction of the total number of sites is occupied, so that $N/\mathcal{S} - [A - S] \sim N/\mathcal{S}$. Equation (11) can then be written for a surface area normalized to unity, as ($q_s \approx 1$; [7])

$$\frac{h^3}{(2\pi m k_B T)^{3/2}} \cdot \frac{q_{\text{int}}}{q_{g(\text{int})}} \cdot \exp\left(-\frac{E}{RT}\right) = \frac{4 N_1^{2(n-1)}}{(N_2^{n-1} + 1)^4} \quad (12)$$

where m is the mass of the A molecule, $q_{g(\text{int})}$ and q_{int} are the internal partition functions of the A molecule and $A - S$ complex, and h is the Planck's constant. The factor $q_{g(\text{int})}$ at a particular temperature, is relatively easy to evaluate, by taking the relevant rotational and vibrational temperatures for the molecule from literature. On the other hand, q_{int} requires detailed understanding of the binding between the adsorbate molecule and the surface. For a given value of d_f , N_1 and N_2 can be found and given the total number of sites on the surface (active and inactive) n can be determined. Then the RHS of (12) is known. Thus the quantity $q_{\text{int}}/q_{g(\text{int})} \exp(-E/RT)$ at a given temperature can then be found out.

The above relationships further emphasize the significance of the fractal dimension in surface chemistry. Equation (12) implies that a statistical thermodynamic apparatus can be designed involving the internal dynamics of the chemisorbed complex to obtain a relationship with the fractal geometry of the adsorbent. This is not really surprising because the interaction potential for the collision of the gas molecules with the surface depends on all the active sites on the surface, whose location has a fractal geometry. These results may be modified by including a random-walk diffusion of the gas molecules to active sites as well as a definite contribution of the desorption and reaction terms.

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