

Adsorption kinetics on geometrically irregular structures studied using the Statistical Rate Theory approach

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In this work some preliminary results are reported on the adsorption kinetics in the systems with geometrically irregular surfaces. It is assumed that the adsorption kinetics is governed by the molecular transport to the interior of the fractal structure and the rate of adsorption on the surface. It appears that both these processes are strongly affected by the fractal dimension of the surface. Some model calculations are presented which show how the fractal dimension influences the adsorption kinetics, i.e., the uptake curves and the sticking probability curves. It is concluded that increasing value of the fractal dimension makes the sticking probability functions coverage independent with the initial sticking equal to unity (when the adsorption is not activated). That means all the molecules entering the interior of the fractal structure are adsorbed and the probability of escape to the bulk is almost zero. Generally, the increasing value of the fractal dimension makes to adsorption slower and entirely controlled by the rate of transport to the interior of the fractal structure.

1. INTRODUCTION

Geometrically irregular structures often reveal anomalous features due to their complex geometry. In addition to inducing energetic surface heterogeneity that geometry is also responsible for anomalous behavior of either adsorption or transport processes in such systems. To make this problem tractable the fractal geometry concepts were applied in the theoretical analysis of the interfacial phenomena on/in such structures [1-4].

The aim of this work is developing the theoretical model of adsorption kinetics on/in such media which would account for some of the most important stages of the adsorption process and next to analyze its features as a function of the fractal dimension.

2. THE MODEL

First, we have to account for diffusional transport from the bulk into the closest neighborhood of the surface of the fractal structure. The transport into the fractal media has been extensively studied in literature. Following Seri-Levi and Avnir, [5] the number of molecules $N(t)$ approaching the fractal surface is related to the diffusivity and to the fractal dimension of the structure,

$$N(t) \sim (4D_f t / \pi)^{(3-D)/2} \quad (1)$$

where D_f is the diffusivity, t is time, whereas D is the fractal dimension.

So, let us note that the diffusional transport to the surface of the fractal structure reveals anomalous behavior that is the number of molecules approaching the surface is not proportional to the square root of time.

Eq. (1) is valid when the reactant molecules change the direction of motion a number of times during their walk to the adsorbing surface. Moreover it assumes that the diffusivity is constant throughout the bulk phase. All that means that the eq. (1) is not applicable for description of transport of gas molecules when the gas phase concentration is not sufficiently high.

When the fractal adsorbing surface is in contact with a gas phase then at some distance from the surface one can distinguish some subvolume in which the concentration of molecules is lower than in the bulk (far from the surface). This is because the surface removes the adsorbate molecules from this region of the gas phase. The volume of this region can be calculated using the basic scaling laws found for fractal surfaces. Thus, when the fractal features of the surface are observed up to some distance h from the surface, then the volume of the hull of the width h scales with the fractal dimension of the surface, i.e.,

$$V = N_m a^3 \left(\frac{h}{a} \right)^{(3-D)} \quad (2)$$

where a is the diameter of the adsorbing molecules and N_m is the number of the molecules necessary to cover the adsorbing surface with monolayer blanket.

The free molecular flux to the surface is related to the pressure which is established in the subvolume adjacent to the surface. In the case of a flat surface such a flux is described by the Langmuir-Hertz equation, i.e.

$$f = \phi p = \frac{P}{\sqrt{2\pi mkT}} \quad (3)$$

where p is the pressure, m – the mass of a molecule and T – the absolute temperature.

However, the Langmuir-Hertz equation is valid only for ideally smooth surfaces. Therefore, recently Panczyk [6] has performed the molecular dynamics simulations of the collision frequency with microscopically rough/fractal surfaces. Figures 1 and 2 show how the frequency factor changes with the fractal dimension of the surface obtained using the random deposition process. These results prove that the frequency parameter is a still linear function of pressure even for highly irregular surfaces. However, as one should expect there is also some departure from the prediction given by the Langmuir-Hertz equation. Nevertheless, this departure is surprisingly small when the frequency is calculated in accordance to the actual value of the surface area. It means that, to a good approximation, the Langmuir-Hertz equation can be used provided that the correct value of the surface area is used, i.e. the fractal scaling laws are applied for the calculation/determination of the surface area.

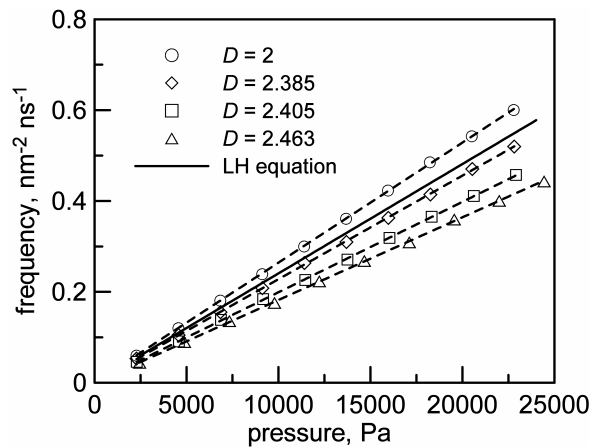


Fig. 1. The dependence of the frequency of collisions with a fractal surface as a function of pressure for various fractal dimensions of surface created by using the random deposition process

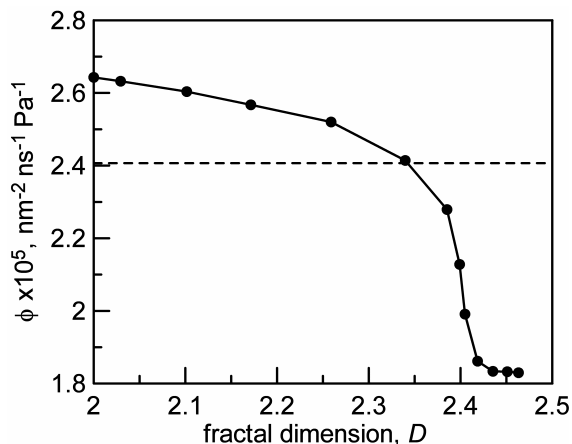


Fig. 2. The relation between the frequency factor and the fractal dimension of the surface (symbols) and the prediction given by the Langmuir-Hertz equation (dashed line).

When a molecule collides with the surface site it can be adsorbed or not. Although this process is probably very fast in many circumstances, we accounted for its potentially limited rate in the model. Thus, to describe the rate of adsorption we applied the Statistical Rate Theory (SRT) approach. [7-9] The explicit form of the SRT equation will be shaped by the energetic heterogeneity of the surface, i.e. by the adsorption energy distribution function. In 2001 Rudzinski et. al. [10] published the article where they proposed some relation between the distribution of adsorption energy and the fractal pore size distribution function. Additionally it was shown that the general adsorption energy distribution function $\chi(\epsilon)$ revealing all the most important features of the experimentally observed systems can be obtained by assuming that the fractal surfaces are partially correlated. It was postulated that the fractal pore size distribution function $\rho(r)$ takes the following form when the surface is partially correlated,

$$\rho(r) \sim \frac{(3-D)r^{2-D}}{(1+r^{3-D})^2} \quad (4)$$

where r is the pore diameter.

While applying the above relation the general form of the adsorption energy distribution has been developed,

$$\chi(\varepsilon) = (3-D)[\alpha + \beta(\varepsilon - \varepsilon_0) + \dots] \frac{\exp\left((3-D)\alpha(\varepsilon - \varepsilon_0) + \frac{3-D}{2}\beta(\varepsilon - \varepsilon_0)^2 + \dots\right)}{\left[1 + \exp\left((3-D)\alpha(\varepsilon - \varepsilon_0) + \frac{3-D}{2}\beta(\varepsilon - \varepsilon_0)^2 + \dots\right)\right]^2} \quad (5)$$

where α and β are some parameters in the Taylor expansion of the unknown relation between the pore diameter and the associated adsorption energy in this pore. The most important feature of the distribution (5) is that it predicts the existence of all the model adsorption energy distributions often used, so far in adsorption science. Particularly, it explains the existence of the Langmuir-Freundlich adsorption isotherm with the associated quasi-gaussian adsorption energy distribution. Namely, when one takes only linear terms in that Taylor expansion one arrives at the fractal version of quasi-gaussian adsorption energy distribution, i.e.

$$\chi(\varepsilon) = (3-D)\alpha \frac{\exp((3-D)\alpha(\varepsilon - \varepsilon_0))}{\left[1 + \exp((3-D)\alpha(\varepsilon - \varepsilon_0))\right]^2} \quad (6)$$

Then, by applying the Condensation Approximation one can determine the chemical potential of the adsorbed molecules on the fractal/energetically heterogeneous surface. That chemical potential calculated for the function (6) is then the following expression,

$$\mu_s(\theta) = \frac{1}{(3-D)\alpha} \ln \frac{\theta}{1-\theta} - \varepsilon_0 \quad (7)$$

To build up the model of adsorption kinetics on a fractal surface let us assume that the fractal object is in contact with the bulk gas phase at a constant and time independent pressure p_0 . The molecules from the bulk enter the subvolume, were the fractal scaling laws are obeyed, with the intensity proportional to the pressure p_0 and the area of the hull surrounding the interior of the fractal object, S_G . This area can be calculated by counting the number of artificial molecules of diameter h necessary to cover the fractal object by the monolayer blanket. While considering eq. (2) one can write,

$$S_G = \frac{V}{h^3} h^2 = N_m a^2 \left(\frac{h}{a}\right)^{2-D} \quad (8)$$

The number of the molecules in that subvolume is the result of a balance between the intensity of the transport from the bulk, escape to the bulk and the removal by the surface due to adsorption. Therefore, the pressure evolution is described by the following equation,

$$\frac{dp}{dt} = \frac{p_0 - p}{\sqrt{2\pi mkT}} \frac{kT}{h} - \frac{d\theta}{dt} \frac{kT}{a^3 (h/a)^{3-D}} \quad (9)$$

The rate of adsorption on the surface characterized by the distribution (6) can be easily developed from the SRT kinetic equation and its particular form reads,

$$\frac{d\theta}{dt} = \frac{S_A p}{N_m \sqrt{2\pi mkT}} \frac{1}{1 + (Kp)^{(3-D)akT}} \left[Kp \left(\frac{1-\theta}{\theta} \right)^{\frac{1}{(3-D)akT}} - \frac{1}{Kp} \left(\frac{\theta}{1-\theta} \right)^{\frac{1}{(3-D)akT}} \right] \quad (10)$$

In eq. (10) S_A is the area of the fractal surface, which is related to N_m , i.e. $S_A = N_m a^2$. The parameter K is only temperature dependent factor collecting the parts of the chemical potentials of both the gas and the adsorbed phases which are independent of concentration. Equations (9) and (10) form a set of differential equations describing the time evolution of the coverage of the fractal surface. While studying the behavior of this set it will be convenient to transform those equations into dimensionless forms. Thus, let us introduce the following set of substitutions:

$$\tau = \frac{a^2 t}{K \sqrt{2\pi mkT}}; \quad \eta = \frac{KkT}{a^3}; \quad \kappa = Kp; \quad \kappa_0 = Kp_0; \quad n = \frac{h}{a} \quad (11)$$

Then, we obtain the following set of differential equations;

$$\begin{cases} \frac{d\theta}{d\tau} = \frac{\kappa}{1 + \kappa^{(3-D)akT}} \left[\kappa \left(\frac{1-\theta}{\theta} \right)^{\frac{1}{(3-D)akT}} - \frac{1}{\kappa} \left(\frac{\theta}{1-\theta} \right)^{\frac{1}{(3-D)akT}} \right] \\ \frac{d\kappa}{d\tau} = (\kappa_0 - \kappa) \frac{\eta}{n} - \frac{d\theta}{d\tau} \frac{\eta}{n^{3-D}} \end{cases} \quad (12)$$

The sticking probability is thus the following function of the adsorption rate

$$S(\theta) = \frac{1}{\kappa_0 n^{2-D}} \frac{d\theta}{d\tau} \quad (13)$$

It means that the sticking probability is also function of the assumed width of the hull where the fractal scaling laws are obeyed.

3. RESULTS AND DISCUSSION

Figure 3 shows some model investigations based on eqs. (12). While performing these model investigations the following value of the parameter η has been assumed $\eta=10^6$. This value corresponds to K being of the order 1 Pa^{-1} and a of the order 10^{-9} m . The parameter αkT has been assumed to be 0.5, what implies that the condensation approximation is applicable for calculation of the chemical potential corresponding to the function (6) for $D=2$.

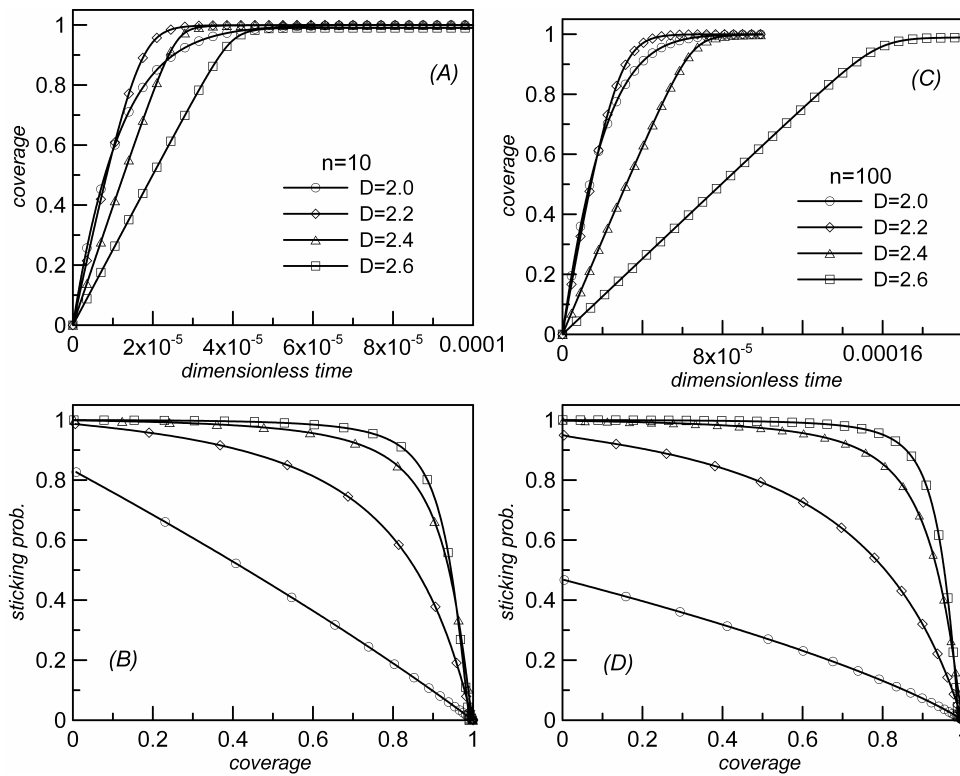


Fig. 3. Results of the model investigations based on eqs. (12) for various values of fractal dimension D and width of the hull n .

As can be seen from Figure 3 the fractal dimension of the surface has a crucial influence on the behavior of the uptake curve as well as on the sticking probability profile. Increasing the value of the fractal dimension makes the uptake curves more and more linear whereas the sticking probability becomes almost independent of the coverage. It means that all the molecules impinging the fractal surface are adsorbed even for quite high surface coverages (close to saturation).

Very important is also the width of the hull where the fractal properties of the object are revealed, i.e. n . It is expected that the higher value of the fractal dimension the wider should be that hull. However, in both cases i.e. $n = 10$ and $n = 100$, the profiles of the sticking probability are very similar for high fractal dimensions. Simultaneously, one can observe that the adsorption becomes slower when the fractal dimension takes high values. In particular when the width of the hull is long and the fractal dimension is high, the adsorption is very slow compared to the case of lower fractal dimensions.

4. SUMMARY

The general conclusions following from the presented analysis can be summarized as follows:

- In fractal structures the adsorption kinetics is slower than in non-fractal quasi-planar surfaces
- In fractal structures all the molecules entering the interior of this structure are adsorbed with the probability equal to unity, provided that the activation energy for adsorption is not very high. This probability rapidly drops at coverages close to saturation.
- Therefore, the adsorption kinetics is almost exclusively governed by the rate of the transport of the molecules to the interior of the fractal structure.

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CURRICULA VITAE



Tomasz Pańczyk was born in Zamość, Poland in 1972. Studies of chemistry in the Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin in 1992–1997. Individual course of studies supervised by professor Władysław Rudziński. Received Ph. D. degree in physical and theoretical chemistry from the Maria Curie-Skłodowska University in Lublin in 2001. At present he is employed as an assistant professor in the Institute of Catalysis and Surface Chemistry, Polish Academy of Science in Kraków. The main field of interest is the theoretical study of various dynamic processes related to the gas adsorption on solids. The investigations resulted in over 30 original papers.



Władysław Rudziński graduated from the Faculty of Chemistry of the Maria Curie Skłodowska University in Lublin. In 1979 received his Ph.D. degree in the Department of Theoretical Chemistry at Jagiellonian University in Cracow. Since 1970 he has been back at UMCS University in Lublin, where he organised his research group working on theoretical problems of adsorption. In 1979 his research group received the status of the Department of Theoretical Chemistry. He has been the Head of that Department until now. Since 1999 he has also been the Head of the Laboratory for the Theoretical Problems of Adsorption of the Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences in Cracow. He was also the Chairman of the Committee for Interface Chemistry of the Polish Chemical Society, and served also one year as the President of the Society. Professor Rudziński was a member of the Board of Directors of the International Adsorption Society, and served as a member of the Scientific Committees of such international conferences as the largest world conference on adsorption FOA (Fundamentals of Adsorption), or the Pacific Adsorption Conference. He is also a corresponding member of the European Academy of Arts Sciences and Humanities. He published over 250 papers, and the monograph co-authored by Professor D.H. Everett “Adsorption of Gases on Heterogeneous Surfaces” (Academic Press, 1992). Together with Professors W. A. Steele and G. Zgrablich, he edited the monograph “Equilibria and Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces” (Elsevier, 1997). He was the Member of Editorial Boards of “Langmuir” journal, and is now member of the Editorial Boards of “Adsorption” journal, and of the journal “Adsorption Science & Technology”.

He organised the four international symposia: "Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids"-ISSHAC (Poland, 1992, 1995, 1998, 2001, 2004), and the Polish-Israeli Symposium "Current Trends in Interface Chemistry", in 2000.

For his outstanding scientific achievements, he was awarded five times by the Polish Ministry of Education and once by the Rector of Maria Curie-Skłodowska University. He was also awarded by the Polish Chemical Society.

Besides many short visits to many Universities of the world, he also paid long-term visits to Queens University (Canada), University of Vienna (Austria), University of Leipzig (Germany), Tohoku University (Japan), CNRS Laboratory at the University of Montpellier (France), Ruhr University in Bochum (Germany), Seoul National University (Korea), Chonnam National University (Korea), CNRS Laboratory in Nancy (France), University of San Luis (Argentina), and National Chung Cheng University (Taiwan).

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