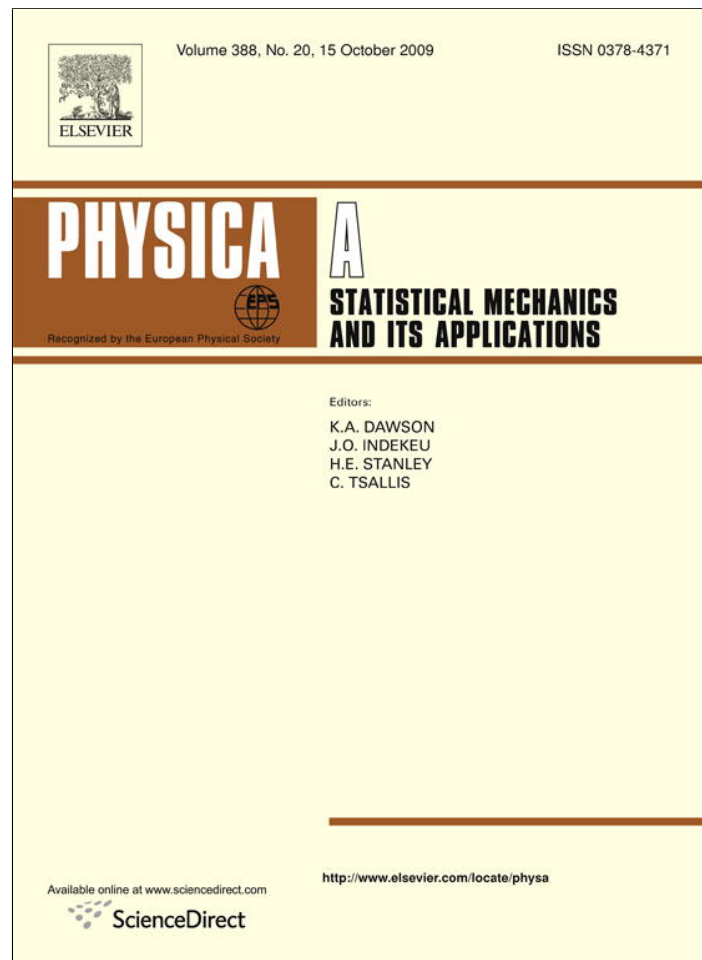


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Adsorption of interacting monomers on spanning clusters of polyatomic species

V. Cornette, A.J. Ramirez-Pastor, F. Nieto*

Departamento de Física, Instituto de Física Aplicada (INFAP), Universidad Nacional de San Luis, CONICET, Chacabuco 917, D5700BWS, San Luis, Argentina

ARTICLE INFO

Article history:

Received 21 November 2008
Received in revised form 9 June 2009
Available online 2 July 2009

Keywords:

Adsorption
Heterogeneous surfaces
Fractals
Monte Carlo simulation
Lattice-gas models

ABSTRACT

The adsorption–desorption process occurring on heterogeneous surfaces is studied by considering a special case where a fractal is used as adsorbent. The fractal surface is the spanning cluster corresponding to the random deposition of objects that occupy more than one site (k -mers) on a square lattice. Such a surface is characterized according to the deposited k -mer. Then, the adsorption of repulsively interacting particles adsorbed on the fractal surface is studied by using Monte Carlo simulations. Different thermodynamic quantities (adsorption isotherms, coverage susceptibility, etc.) are calculated and explained in terms of the characteristics of the substrate. A scheme to characterize the structure of the substrate by just considering the adsorption isotherm is presented and discussed.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Adsorption of particles on heterogeneous surfaces is one of the most important surface phenomena and plays a decisive role as a controlling mechanism in many other physical and chemical processes taking place on two-dimensional systems [1]. In addition, the study of the main features of adsorption isotherms emerges as an important tool in order to characterize solid surfaces [2].

Real surfaces are heterogeneous because of a large number of contributing factors that can be sorted into two different classes: geometrical heterogeneity (cracks, pits, vacancies, etc.) and chemical heterogeneity (impurities, substitutional atoms, etc.). The description of thermodynamic phenomena taking place on such a heterogeneous substrate is a challenging topic in surface science. Moreover, it is still an open problem to characterize the surface structure by means of the study of the surface process taking place on it. The present paper follows this line of thinking with particular attention given to geometrical heterogeneities.

On the other hand, the random sequential adsorption (RSA) of particles of different sizes on solid surfaces is a subject of considerable practical importance [3,4]. In Refs. [5,6] and Ref. [7] the percolation behavior of an RSA of linear segments with different size and the percolation of dissociative dimers have been studied, respectively. More recently, the percolation of k -mers with different structures and shapes deposited on a square lattice have been studied [8–11]. In the cases above, the dependency of the percolation threshold with the parameters of the problem and the universality of the phase transition present in the system have been discussed. In particular, it is interesting to note that for different k -mers, the spanning cluster has the same fractal dimension, d_f . However, the percolation clusters present morphological differences according to the percolating species from which they were originated.

In the present paper we study the adsorption of repulsively interacting particles (monomers) on spanning clusters of percolating species of different sizes. Adsorption phenomenon on heterogeneous surfaces has been widely treated in the literature and it is recognized as an open challenge in modern surface science. One of the most important problems is how

* Corresponding author. Tel.: +54-2652-423789-120; fax: +54-2652-431080.

E-mail addresses: cornette@unsl.edu.ar (V. Cornette), antorami@unsl.edu.ar (A.J. Ramirez-Pastor), fnieto@unsl.edu.ar (F. Nieto).

to represent a heterogeneous surface to be theoretically and/or experimentally treated and several simple approximations have been used in the past few decades. In many contributions the authors recognize the importance of determining the main parameters which influence the behavior of physical phenomena occurring in such a surface due to their practical importance. For example, the analysis of data for adsorption and chemisorption on the surfaces of heterogeneous microporous materials has been a key problem in surface science and catalysis. In this context, we mimic the heterogeneity as generated by a topological disorder in the substrate. In this context, a particular fractal is proposed as the adsorbate: the spanning cluster. However, the obtained results are expected to be useful beyond a particular choice of the fractal adsorbate. It is important to emphasize that we do not consider the adsorption on a surface formed by particles dropped on a surface at the critical threshold; we use a particular fractal as a model of heterogeneous surface. Thus, the main aims of the work are to: (a) evaluate the adsorption isotherms of repulsively interacting particles on such fractal structure; (b) collect the main features of the isotherms; (c) determine a correlation between those findings and the characteristics of the substrate; and (d) draw general conclusions for using adsorption isotherms in order to characterize surfaces which present non-controlled heterogeneities. Adsorption on fractal surfaces has been discussed in the literature by using Monte Carlo simulations [12,13] as well as experimental studies [14,15].

The outline of this paper is as follows: the substrate on which the repulsively interacting particles are deposited is described in Section 2.1. Details of the simulation technique used for mimicking the adsorption process are presented in Section 2.2. Results are discussed in Section 3 and, finally, we give our conclusions in Section 4.

2. Basic definitions and simulation details

2.1. The substrate

In this subsection we shall describe how the fractal used as substrate is built. In addition, its main properties will be analyzed, which will justify the particular choice of spanning clusters of different k -mers as a substrate where repulsive interacting monomers are adsorbed.

Let us consider a periodic square lattice of linear size L on which k -mers are deposited at random. For k -mers deposition, the following scheme is considered. A k -uple of nearest-neighbor sites is randomly selected; if it is vacant, the k -mer is then deposited on those sites (we call this polyatomics the tortuous k -mer). Otherwise, the attempt is rejected. In any case, the procedure is iterated until $N'k$ -mers are deposited and the desired concentration [given by $p = (kN')/L^2$] is reached. In addition, the particular case when linear k -uples of sites (aligned along one of the lattice axes) are dropped onto the lattice has received special attention.

The central idea of the percolation theory is based on finding the minimum concentration p for which a cluster [a group of occupied sites in such a way that each site has at least one occupied nearest-neighbor site] extends from one side to the opposite one of the system. This particular value of the concentration rate is named the *critical concentration* or *percolation threshold* and determines a phase transition in the system. In the random percolation model, a single site is occupied with probability p . For the precise value of p_c , the percolation threshold of sites, at least one spanning cluster connects the borders of the system [indeed, there exist a finite probability of finding $n (> 1)$ spanning clusters [16–19]]. In that case, a second order phase transition appears at p_c which is characterized by well defined critical exponents. This mapping to critical phenomena made percolation a full part of the theoretical framework of collective phenomena and statistical physics [20–23].

Here, the spanning cluster calculated by using the standard Hoshen and Kopelman algorithm [24] is considered while in Refs. [8,9] details of the evolution of the percolation threshold with k are presented. It is our first interest to measure the characteristic dynamic exponents for the different spanning clusters as a function of the k -mer size.

Let us suppose the motion of a particle (“an ant”) which performs a Pólya random walk (unbiased, nearest-neighbor random walk) on the sites belonging to a spanning cluster (“the labyrinth”). The root-mean-square displacement R of the random walk is related to time t through the relation [25]:

$$R \sim t^\nu, \tag{1}$$

where ν is a constant that depends only on the dimensionality d of the system. A fractal dimension d_w is defined for the random walk by $d_w = 1/\nu$. Whether this process is performed on a two dimensional regular lattice $d_w = 2$. However, on fractal structures R grows slower with time, and d_w is usually larger than 2. According to Eq. (1) the root-mean-square displacement of a random walker on a spanning cluster, as a function of the reduced lattice size L/k in a log–log scale, is a linear function whose slope allows one to determine d_w . This analysis has been done for the complete range of the studied parameters (i.e. $1 \leq k \leq 16$) and the reported exponent is $\nu = 1/d_w = 0.370 \pm 0.004$.

Another intrinsic property of a fractal structure is the well-known spectral dimension d_s , which can be calculated from [26,27]:

$$S_0(t) \sim t^{d_s/2}, \tag{2}$$

where $S_0(t)$ is the mean number of distinct sites visited by the random walker. Thus, from the slope of S_0 plotted as a function of time by using a log–log scale, the exponent d_s can be obtained for different k -mer sizes. In the studied range, $1 \leq k \leq 16$, the reported exponent is $d_s = 1.333 \pm 0.002$. Typically 10^5 different random walkers have been used for averaging the above mentioned quantities.

Finally, it is well known that the mass of the spanning cluster (number of elements belonging to such island, s_{perc}), which is also the largest cluster, increases with the lattice size L as a power law:

$$\langle s_{perc} \rangle \sim L^{d_f}, \quad (3)$$

where the angular brackets denote an average over the ensemble of different spanning clusters and d_f is the fractal dimension of the system. According to Eq. (3), d_f is determined from the slope of the “mass” of the fractal spanning cluster as a function of L (in a log–log scale). Here, the reported value for the fractal dimension of the cluster is $d_f = 1.896 \pm 0.002$.

In all considered cases the numerical results are very well correlated with the relationships Eqs. (1)–(3). The values obtained for the exponents d_w , d_s and d_f coincide with the reported ones for the case $k = 1$ [25].

In summary, the findings presented in the section lead to the conclusion that the dynamic exponents (d_w and d_s) and the fractal dimension (d_f) are not sufficiently useful for distinguishing differences between the spanning clusters of polyatomic species with different k -mer sizes. In order to characterize them, it is our purpose to use the reversible adsorption of repulsively interacting monomers on such substrates.

2.2. Monte Carlo simulations in grand canonical ensemble

One can define a set of occupation numbers $\{n_i\}$ for each site corresponding to the spanning cluster according to

$$n_i = \begin{cases} 1, & \text{if site } i \text{ is occupied} \\ 0, & \text{if site } i \text{ is empty.} \end{cases} \quad (4)$$

A given set of numbers specifies a configuration of the whole system of adparticles. In thermodynamic equilibrium, the system is described by the statistical operator ρ ,

$$\rho = Q^{-1} \exp \beta(\mu N - H), \quad (5)$$

where μ , $N = \sum_i n_i$, Q and H denote the chemical potential, the number of adparticles, the partition function and the Hamiltonian of the system, respectively. The latter is given by

$$H = -\varepsilon N + w_{nn} \sum_{nn} n_i n_j. \quad (6)$$

Here w_{nn} is the pair interaction energy of adparticles in the nearest-neighbor (nn) sites and $\beta \equiv 1/k_B T$. In this case, the adsorption energy of the site, ε , can be chosen equal zero without losing generality.

Adsorption–desorption processes on the spanning clusters described above are simulated by putting such a substrate in contact with an ideal gas phase of monomers at temperature T . Particles are characterized by their chemical potential μ . It is assumed that the surface as well as the adsorbate are inert upon adsorption. The grand partition function \mathcal{E} of interacting particles within M (being M the number of sites of the considered spanning cluster) is [28]:

$$\mathcal{E}(\mu, T, M) = \sum_{N=1}^{\infty} \frac{\exp(\beta N \mu)}{N! \Lambda^{3N}} \int_{\Omega} \exp[-\beta U(\mathbf{x}_N)] d\mathbf{x}_N, \quad (7)$$

where U is the total interaction energy of N particles with coordinates specified by $\mathbf{x}_N = \{\mathbf{x}_1, \dots, \mathbf{x}_N\}$, Ω the phase space of the system, and Λ the thermal wave-length of the particle.

The probability of finding the system in a state specified by \mathbf{x}_N is given by:

$$P(\mathbf{x}_N) = \frac{\exp(\beta N \mu) \exp[-\beta U(\mathbf{x}_N)]}{N! \Lambda^{3N} \mathcal{E}}. \quad (8)$$

Following the Metropolis scheme [29], the transition probability from a state \mathbf{x}_N to a new state $\mathbf{x}_{N'}$, $W(\mathbf{x}_N \rightarrow \mathbf{x}_{N'})$, is defined by

$$W(\mathbf{x}_N \rightarrow \mathbf{x}_{N'}) = \min \left\{ 1, \frac{P(\mathbf{x}_{N'})}{P(\mathbf{x}_N)} \right\} \quad (9)$$

in order to satisfy the Principle of Microscopic Reversibility.

In adsorption–desorption equilibrium, there are two elementary ways to perform a change of the system state: either adsorbing one particle onto the surface or desorbing one particle. The corresponding transition probabilities are, respectively,

$$\begin{aligned} W_a(\mathbf{x}_N \rightarrow \mathbf{x}_{N+1}) &= \min \{1, \exp[-\beta \Delta H + \beta \mu]\} \\ &= \min \{1, \exp[-\beta(H(\mathbf{x}_{N+1}) - H(\mathbf{x}_N)) + \beta \mu]\}; \end{aligned} \quad (10)$$

and

$$\begin{aligned} W_d(\mathbf{x}_N \rightarrow \mathbf{x}_{N-1}) &= \min \{1, \exp[-\beta \Delta H - \beta \mu]\} \\ &= \min \{1, \exp[-\beta(H(\mathbf{x}_{N-1}) - H(\mathbf{x}_N)) - \beta \mu]\}. \end{aligned} \quad (11)$$

Given a spanning cluster of M sites, the algorithm to carry out an elementary Monte Carlo (1 MCS), is the following:

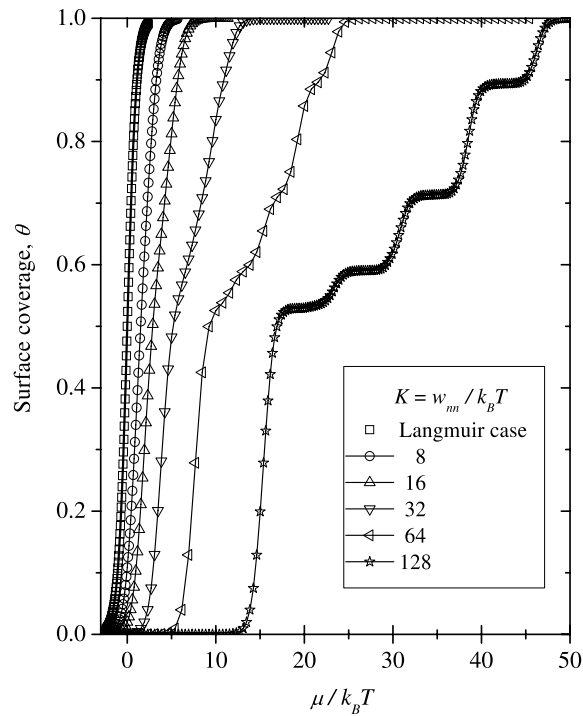


Fig. 1. Adsorption isotherms (surface coverage as a function of the reduced chemical potential $\beta\mu$) for repulsively interacting monomers on a spanning cluster built by dropping monomers ($k = 1$) and for several representative values of K as indicated.

- (1) Set the value of p^* ($p^* \equiv \exp[\beta\mu]$, proportional to the gas phase pressure) and temperature β .
- (2) Set an initial state \mathbf{x}_N by adsorbing N particles onto the lattice defined by the spanning cluster.
- (3) Choose randomly one of the M sites, and generate a random number $\xi \in [0, 1]$
 - (i) if the site is empty then adsorb a particle if $\xi \leq W_a(\mathbf{x}_N \rightarrow \mathbf{x}_{N+1})$.
 - (ii) if the site is occupied then desorb the particle if $\xi \leq W_d(\mathbf{x}_N \rightarrow \mathbf{x}_{N-1})$.
- (4) Repeat from step (3) M times.

The first m' Monte Carlo steps (MCS) of each run were discarded to allow the reaching of the equilibrium state and the next m MCS were used to compute averages.

Thermodynamic quantities, such as mean coverage, θ , and mean adsorption energy per site, u , are obtained by simple averaging:

$$\theta = \frac{1}{M} \sum_i^M \langle n_i \rangle; \quad u = \frac{1}{M} \langle H \rangle. \quad (12)$$

The equilibrium state was reached after discarding 10^5 MCS, and averages were taken over the next 10^5 MCS. At low temperatures, and in case of ordering, up to 10^6 MCS had to be used in order to let the system relax from metastable states. In addition, to obtain accurate values of the desired quantities averaging up to 10^3 different clusters generated in the same conditions has been considered.

3. Results and discussions

In this section, we shall present the adsorption isotherms of repulsively interacting particles on spanning clusters obtained with the procedure described in Section 2.1. The only interaction between the adparticles (monomers) is a pairwise repulsive energy, w_{nn} .

We shall analyze first the different thermodynamical quantities for particles adsorbed on a spanning cluster of monomers ($k = 1$) and for several representative values of $K \equiv \beta w_{nn}$. In Fig. 1, the adsorption isotherms (surface coverage, θ as a function of the reduced chemical potential $\beta\mu$) are presented. For high temperatures, the isotherms are close to the Langmuir case (homogeneous lattice gas without lateral interactions), i.e.

$$\theta(\mu) = \frac{\exp(\beta\mu)}{1 + \exp(\beta\mu)}. \quad (13)$$

Upon decreasing the temperature, the adsorption isotherms present five plateaus at characteristic coverage. This situation can be explained as follows. For low values of $\beta\mu$ (clean adsorptive surface) each incoming particle is adsorbed in such a way

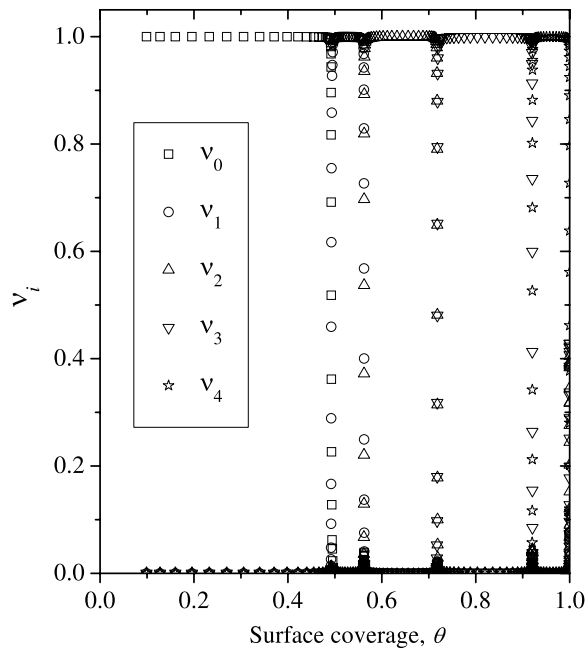


Fig. 2. v_i (the ratio of adsorbed particles on sites with i nearest-neighbor occupied sites) versus surface coverage for the lowest temperature considered in Fig. 1, $K = 128$.

that it does not have any nearest-neighbor occupied site. This occurs until all possible sites with this characteristic are filled. Then, the first plateau is formed. Due to the substrate being a fractal, the remaining empty sites can be divided into four groups according to the number of occupied nn sites that they have. Thus, upon increasing the reduced chemical potential each one of those groups will be sequentially filled. After the saturation of all sites of each group a plateau is formed. This conclusion is clearly supported by Fig. 2, where v_i (the ratio of adsorbed particles on sites with $i - nn$ occupied sites) is plotted as a function of the surface coverage for the lowest temperature considered in Fig. 1, $K = 128$. In the figure, it is clearly seen that in each range of coverage only a definite type of process is taking place. In fact, for each range of coverage just one $v_i = 1$ and the others are equal to zero, reinforcing the idea of a sequential filling of the lattice.

Another interesting quantity is the isothermal susceptibility, χ_T . This quantity is equal to the mean square density fluctuations of adparticles (or in magnetic language, to the mean square fluctuations of the magnetization of the corresponding spin system)

$$\chi_T = \frac{1}{\beta} \left(\frac{\partial^2 \tilde{f}}{\partial \mu^2} \right)_T = \langle (n_i - \theta)(n_j - \theta) \rangle, \tag{14}$$

where \tilde{f} is the “free” energy per particle of the system introduced by:

$$\tilde{f} = \frac{\ln Q}{\beta N}. \tag{15}$$

The coverage dependence of the isothermal susceptibility is shown in Fig. 3 for several characteristic temperatures. At high temperatures (Langmuir case) the mean square density fluctuations are equal to $\theta(1 - \theta)$. At low temperatures the density fluctuations are strongly suppressed at half coverage due to repulsion between the adparticles. Any density disturbance (i.e., the displacement of an adparticle from its stable position in the filled sublattice to any site of the empty sublattice) substantially increases the free energy of the system and is thermodynamically unfavorable. As the coverage is not equal to half coverage, there are fluctuations of non-stoichiometric nature that do not require additional energy for their existence and cannot be removed from the system due to the jumps of adparticles. Therefore χ_T increases when θ deviates from the half coverage. The same situation can be observed for the corresponding coverage where the isotherms exhibits a plateau. As Eq. (14) shows χ_T is the second derivative of the free energy over the chemical potential. It is a very sensitive magnitude to determine the presence of critical phases present in the problem. A detailed analysis of criticality is out of the scope of the paper.

The thermodynamic factor can be obtained by MC simulations in one of its two equivalent forms:

$$\left(\frac{\partial \beta \mu}{\partial \ln \theta} \right) = \left[\frac{\langle (\delta N)^2 \rangle}{\langle N \rangle} \right]^{-1} = \beta \theta \left(\frac{\partial^2 \tilde{f}}{\partial \mu^2} \right)^{-1} = \theta / \chi_T \tag{16}$$

either via the differentiation of adsorption isotherms obtained in the grand canonical ensemble [30] or via the normalized mean square fluctuation $\langle (\delta N)^2 \rangle / \langle N \rangle$ obtained in the canonical ensemble. Here, we have used both methodologies with

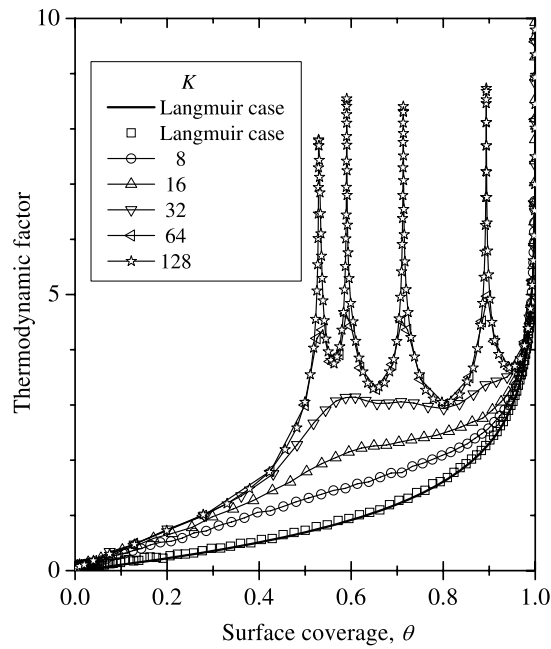


Fig. 3. Thermodynamic factor vs θ for different temperatures expressed in units of K as indicated.

the same accuracy. The thermodynamic factor entering the expression for the chemical diffusion coefficient [31–34] can be directly obtained from Fig. 3. This quantity exhibits five peaks which are consequence of the plateaus shown by the adsorption isotherms. Upon decreasing the temperature, these peaks, which correspond to the minima of χ_T become more pronounced.

The behavior of the above discussed quantities for adsorption of repulsively interacting monomers adsorbed in percolating clusters of k -mers (with $k > 1$) is quite similar to the description of those for $k = 1$. Figs. 4 and 5 show the adsorption isotherms and the thermodynamic factors for several values of k and a fixed low value of temperature ($K = 128$). In Fig. 4 (Fig. 5) five different plateaus (maxima) can be distinguished, as they are indicated, which can be explained in the same terms as that above. After the first plateau is formed (as a consequence of each incoming particle being adsorbed in such a way it does not interact with any previously adparticle) the remaining plateaus are formed after each group of empty sites (each group characterized by the number of occupied nn sites that they have) is filled. The insets in the figure magnify and illustrate the dependence of such thermodynamic quantities on k at critical coverage [values of surface coverage where a plateau in the isotherm (or a maximum in the thermodynamic factor) is present]. As is evident from the insets, those critical coverages depend on k . In other words, the critical coverage depends on the relative abundance of each group of empty sites (after the first plateaus is formed), which in turn depends on the topology of the cluster. In fact, in Fig. 6 the critical densities are shown as a function of k . Full symbols denote the critical densities of adsorption isotherms of repulsively interacting particles adsorbed on spanning clusters of tortuous k -mers. The same, for the case of adsorption on spanning clusters of linear k -mers, is presented by using empty symbols. It is important to base the understanding of the observed behavior (the difference between adsorption on a cluster formed by deposition of linear or tortuous k -mers) on an appropriate physical interpretation.

In order to give answer to this requirement, we start from basic thermodynamic relationship [28]:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,M}, \quad (17)$$

where F is the free energy. Introducing the free energy per site, $f = F/M$, the last equation can be written in terms of intensive variables in the form: $\mu = \left(\frac{\partial f}{\partial \theta} \right)_T$. Accordingly, the area to the left of each adsorption isotherm corresponding to a topography characterized by k up to a determined coverage θ is given by:

$$A(\theta, k, K) = \int_0^\theta \mu(\theta) d\theta = f(\theta, k, K) - f(0, k, K). \quad (18)$$

Therefore, this area represents the variation in the free energy per site in filling a surface, with topography characterized by size and shape (tortuous or linear) of the k -mer. If the upper limit in the integral of Eq. (18) is $\theta = 1$, the area A will represent the free energy per site at full coverage [$f(0, k)$ will be considered zero without losing generality] in such a way that:

$$A(\theta = 1, k) = f(\theta = 1, k) = 2 w_{nn} z_{eff}(k), \quad (19)$$

where $z_{eff}(k)$ is the effective coordination number for each percolating cluster, which is supposed to be function of k . Note that at this limit $\theta = 1$, the integral, Eq. (18), does not depend on K because the free energy is not affected by temperature due

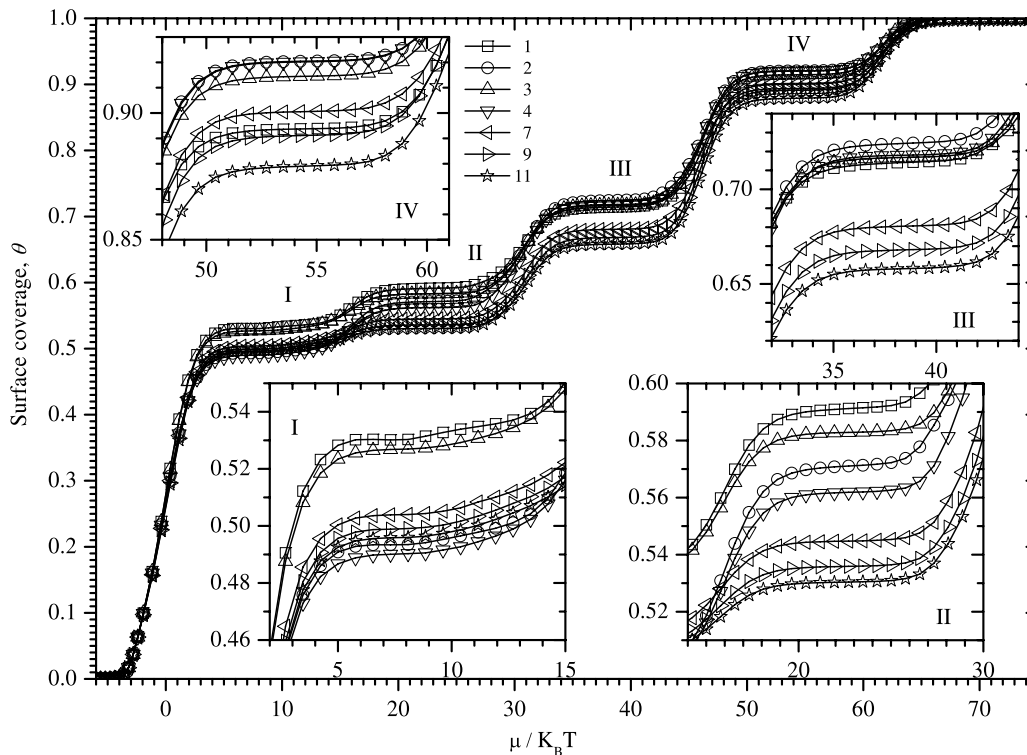


Fig. 4. Adsorption isotherms for several values of k as indicated. The temperature is fixed to $K = 128$ in all the cases considered. Insets in the figure are a zoom of the isotherms which illustrate the dependence of such a thermodynamic quantity on k . Each inset corresponds to one of the plateaus in the isotherm, as labeled.

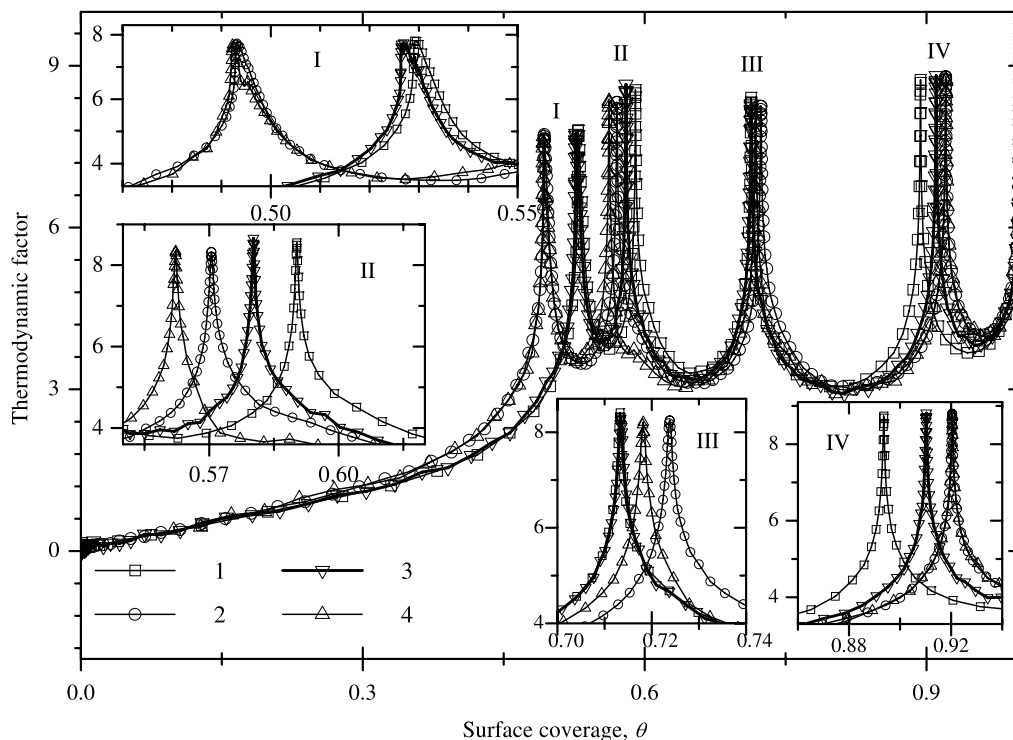


Fig. 5. Thermodynamic factors for several values of k as indicated. The temperature is fixed to $K = 128$ in all the cases considered. Insets in the figure are a zoom of the thermodynamic factors which illustrate the dependence of such a thermodynamic quantity on k . Each inset corresponds to one of the maxima, as labeled.

to the null entropic contribution of adsorption of monomers. In fact, $z_{eff}(k)$ is determined via two different measurements. In a direct way, $z_{eff}(k)$ is calculated simply by averaging the number of nearest-neighbor sites of 10^4 different realizations of percolating clusters corresponding to the deposition of k -mers, see the full symbols in Fig. 7. Alternatively, $z_{eff}(k)$ can be obtained from Eq. (19), which is shown by open symbols in Fig. 7. Both strategies to evaluate $z_{eff}(k)$ are nicely consistent. This

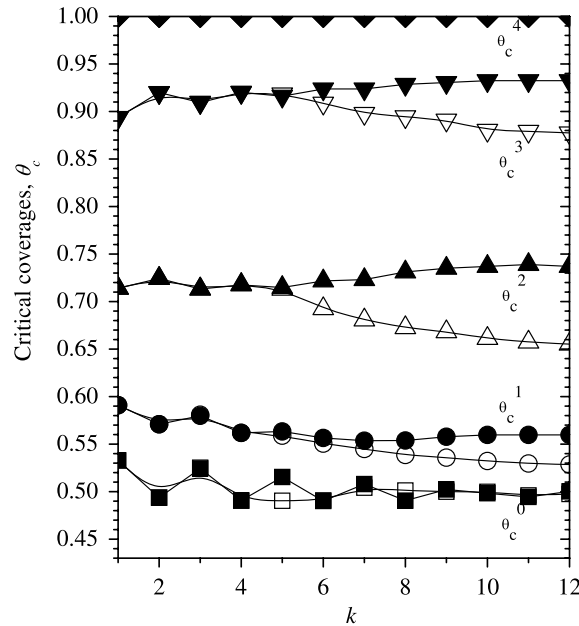


Fig. 6. Critical densities as a function of k for $K = 128$. Full (empty) symbols denote the critical densities for tortuous (linear) k -mers.

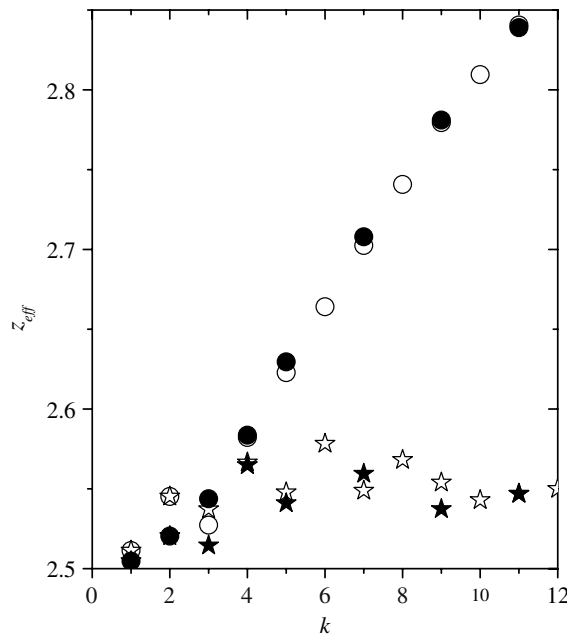


Fig. 7. z_{eff} (effective coordination number for each percolating cluster) as a function of k . Open symbols denote data from Eq. (19) while full symbols represents a direct measurement via MC simulations. Circles (stars) represent data from a surface formed by linear (tortuous) k -mers.

finding allows one to determine $z_{eff}(k)$ from a direct integration of the adsorption isotherms. This result suggests a method to calculate the effective coordination number of geometric heterogeneous substrates through adsorption measurements.

An interesting point is the different behavior of $z_{eff}(k)$ according to whether the substrate was formed by linear or tortuous k -mers. The reason of this striking result is as follows. The adsorption of linear segments shows a tendency to deposit k -mers in clusters with the same orientation along one of the principal axis. These needles tend to form compact clusters. Upon increasing k , this tendency is enhanced. This behavior produces a linear increment of $z_{eff}(k)$ in the range of k considered here. This result has already been observed and discussed in Ref.[35] and it is illustrated in Fig. 8a, where clusters formed by linear k -mers with $k = 5$ and $k = 9$ are shown. In contrast, when tortuous k -mers are deposited, this tendency is not observed and, as a consequence, $z_{eff}(k)$ remains almost constant in the range of k considered here. This is shown in Fig. 8b, where clusters formed by tortuous k -mers with $k = 5$ and $k = 9$ are shown.

4. Conclusions

In the paper we have consider the spanning clusters obtained from the deposition of k -mers on a homogeneous surface as the substrate where repulsively interacting monomers are adsorbed. The substrate is built in two alternative ways, i.e. either

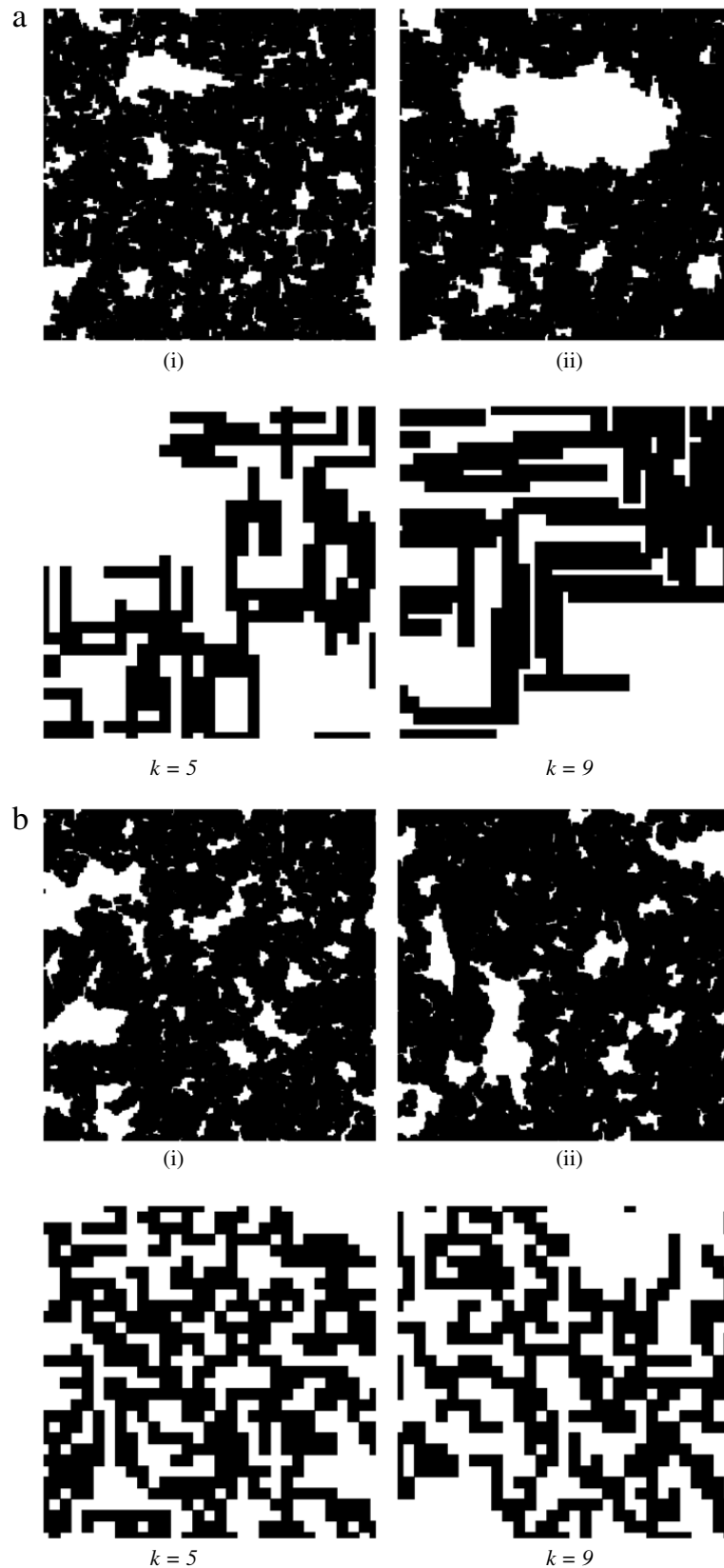


Fig. 8. Clusters formed by (a) linear and (b) tortuous k -mers with (i) $k = 5$ and (ii) $k = 9$ are shown. For each figure a small region is shown as a zoom in order to appreciate the details of the cluster.

via the deposition of linear k -mers (“needles” which are deposited along one of the two principal axis of the lattice) or by depositing k atoms in a k -uple of nearest-neighbor empty sites which are randomly selected (tortuous k -mers). The results of adsorption isotherms, coverage susceptibility, energy, etc. are obtained by means of Monte Carlo simulations. The substrate

contains a particular heterogeneity which is reflected in the study of the parameters needed to characterize it. In all the cases considered, the fractal dimension, the spectral dimension and the fractal dimension, d_w , do not change with k . However, the morphology of the clusters are quite different and such a difference is better characterized by the mean number of nearest-neighbor sites, which is clearly a function of k . In addition, this quantity allows one to distinguish between linear and tortuous k -mers and it governs the behavior of the physical process which occurs on such a surface.

The general behavior at low temperature of the adsorption isotherms of repulsively interacting particles on a fractal can be described as follows. For low values of $\beta\mu$ each incoming particle is adsorbed in such a way that it does not have any nearest-neighbor site occupied. Once all the possible sites with this characteristic are filled the first plateau is formed. Due to the substrate being a fractal, the remaining empty sites can be divided in four groups according to the number of occupied nn sites that they have. Thus, upon increasing the reduced chemical potential each one of those groups will be sequentially filled. After the saturation of all sites of each group a plateau is formed and a maximum in the thermodynamic factor is reached. Due to the relative abundance of elements of each of the mentioned groups with k , the critical coverage depends on k , as well.

It is important to emphasize that this contribution allows one to establish a criterion to determine the characteristic of the substrate from a simple analysis of the adsorption isotherms. The idea is as follows. After integrating the adsorption isotherm according to Eq. (18) one can determine the size of the object used to form the substrate and whether the surface was created by linear or tortuous k -mers by using the “calibration” curves shown in Fig. 7. It is quite obvious that the model considered here is highly idealized and is not meant to reproduce a particular experimentally studied system. However, the intention of this work is: (1) to identify and characterize the most prominent features of the adsorption process on no deterministic fractal surface; (2) to draw general conclusions on the effects of the mean coordination number on the problem, and (3) to provide a basis for the evaluation of experimental adsorption studies on fractal surfaces which are built with “massive” objects.

Acknowledgements

This work was supported in part by CONICET (Argentina) under project PIP 6294; Universidad Nacional de San Luis (Argentina) under project 322000; and the National Agency of Scientific and Technological Promotion (Argentina) under project 33328 PICT 2005. The numerical work was done using the BACO parallel cluster (composed of 60 PCs each with a 3.0 GHz Pentium-4 processor) located at Instituto de Física Aplicada, Universidad Nacional de San Luis - CONICET, San Luis, Argentina.

References

- [1] W.A. Steele, *The Interaction of Gases with Solid Surfaces*, Pergamon, Oxford, 1974.
- [2] V.P. Zhdanov, *Elementary Physicochemical Processes on Solid Surfaces*, Plenum, New York, 1991.
- [3] J.W. Evans, *Rev. Modern Phys.* 65 (1993) 1281.
- [4] V. Privman, J.-S. Wang, P. Nielaba, *Phys. Rev. B* 43 (1991) 3366.
- [5] Y. Leroyer, E. Pommiers, *Phys. Rev. B* 50 (1994) 2795.
- [6] B. Bonnier, M. Honterbeyrie, Y. Leroyer, C. Meyers, E. Pommiers, *Phys. Rev. B* 49 (1994) 305.
- [7] Z. Gao, Z.R. Yang, *Physica A* 255 (1998) 242.
- [8] V. Cornette, A.J. Ramirez-Pastor, F. Nieto, *Physica A* 327 (2003) 71.
- [9] V. Cornette, A.J. Ramirez-Pastor, F. Nieto, *Eur. Phys. J. B* 36 (2003) 391.
- [10] M. Dolz, A.J. Ramirez-Pastor, F. Nieto, *Phys. Rev. E* 72 (2005) 066129-1/5.
- [11] V. Cornette, A.J. Ramirez-Pastor, F. Nieto, *J. Chem. Phys.* 125 (2006) 204702-1/7.
- [12] H.O. Martin, E.V. Albano, *Surf. Sci.* 211 (1989) 1025.
- [13] E.V. Albano, H.O. Martin, *Phys. Rev. A* 39 (1989) 6003.
- [14] M.J. Watt-Smith, K.J. Edler, S.P. Rigby, *Langmuir* 21 (2005) 2281.
- [15] Ma Jian, Qi Hao, Wong Po-Zen, *Phys. Rev. E* 59 (1999) 2049.
- [16] M. Aizenman, *Nuclear Phys. B* 485 (1997) 551.
- [17] J. Cardy, *J. Phys. A* 31 (1998) L105–L110.
- [18] L.N. Shchur, S.S. Kosyakov, *Internat. J. Modern Phys. C* 8 (1997) 473.
- [19] L.N. Shchur, in: D.P. Landau, S.P. Lewis, H.B. Schuettler (Eds.), *Incipient Spanning Clusters in Square and Cubic Percolation*, in: Springer Proceedings in Physics, vol. 85, Springer Verlag, Heidelberg, Berlin, 2000.
- [20] A. Coniglio, *Nuclear Phys. A* 681 (2001) 451.
- [21] C.M. Fortuin, P.W. Kasteleyn, *Physica* 57 (1972) 536.
- [22] P.W. Kasteleyn, C.M. Fortuin, *J. Phys. Soc. Japan Suppl.* 16 (11) (1969).
- [23] S. Fortunato, *Phys. Rev. B* 66 (2002) 054107; *Phys. Rev. B* 67 (2003) 014102.
- [24] J. Hoshen, R. Kopelman, *Phys. Rev. B* 14 (1976) 3428.
- [25] M. Sahimi, M. McKarnin, T. Nordahl, M. Tirrel, *Phys. Rev. A* 32 (1985) 590.
- [26] R. Rammal, G. Toulouse, *J. Phys. Lett.* 44 (1983) 13.
- [27] R.B. Pandey, D. Stauffer, *J. Phys. B* 16 (1983) L511.
- [28] T.L. Hill, *J. Chem. Phys.* 17 (1949) 520.
- [29] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, E. Teller, *J. Chem. Phys.* 21 (1953) 1087.
- [30] A.J. Ramirez-Pastor, M. Nazzarro, J.R. Riccardo, V. Pereyra, *Surf. Sci.* 341 (1995) 249.
- [31] R. Gomer, *Rep. Prog. Phys.* 53 (1990) 917.
- [32] F. Nieto, A.A. Tarasenko, C. Uebing, *Phys. Chem. Chem. Phys. (PCCP)* 2 (2000) 3453.
- [33] F. Nieto, C. Uebing, *Ber. Bunsenges. Phys. Chem.* 102 (1998) 156.
- [34] F. Nieto, C. Uebing, V.D. Pereyra, R. Faccio, *Surf. Sci.* 423 (1999) 256.
- [35] G. Kondrat, A. Pekalski, *Phys. Rev. E* 63 (2001) 051108.