



Random sequential adsorption of polyatomic species with the presence of impurities

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ABSTRACT

Random sequential adsorption of k -mers (particles occupying k adsorption sites on the substrate) of different sizes and shapes deposited on square lattices is studied. Heterogeneous surfaces caused by impurities previously and randomly deposited are considered. Thus, an adsorption site occupied by an impurity is considered as forbidden for the deposition of adsorbent. As a consequence, the average coordination number for each available element depends on the concentration of impurities. For discrete models, at the late stage the surface coverage evolves according to $\theta(t) = \theta(\infty) - A \exp\left[-\frac{t}{\sigma}\right]$, where $\theta(\infty)$ is the jamming coverage while A and σ are fitting parameters. The dependence of the terminal relaxation time σ (which determines how fast the lattice is filled up to the jamming coverage) on the parameters of the problem is established.

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1. Introduction

Random sequential adsorption (RSA) is a irreversible process by which particles of different shapes and sizes are deposited on a discrete or continuous surface. The assumptions of the RSA models are easily stated: objects are placed randomly one after another in a d -dimensional volume [1]. In case that the last placed object overlaps with any of those already present, it is immediately removed; otherwise its position is permanently fixed. This model has been applied to a significant number of systems where the deposition of objects is irreversible over time scales of physical interest. Among others, a variety of physical [2], chemical [3], biological [4–6] and ecological [7] processes have been modeled by using the RSA scheme. Thus, although the problem of RSA is an old one [8–13] it has recently been attracting renewed interest [14–23].

The kinetic of the process is characterized by the time evolution of coverage (or the density of the system), $\theta(t)$, i.e. the fraction of the substrate covered by the deposited objects. For discrete models, one writes for long times

$$\theta(t) = \theta(\infty) - A \exp\left[-\frac{t}{\sigma}\right], \quad (1)$$

where $\theta(\infty)$ is the jamming coverage while A and σ are fitting parameters. Several papers have discussed the dependence of the parameter σ (which determines how fast the lattice is filled up to jamming coverage) on the main features of the system under consideration: shape and size of the adsorbing object; symmetry of the substrate; etc. In a previous paper, Ref. [24], the dependence of the rate σ on the parameters of the problem has been established. By using Eq. (1) it is straightforward to determine σ from the slope of the curve $\ln[\theta_\infty - \theta(t)]$ as a function of t . In Ref. [24], it was possible to develop a new numerical strategy to calculate σ from Monte Carlo simulations which allowed to establish its dependence on the parameters of the problem.

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In most of the cases treated in the literature, the surface where the particles are deposited has been considered to be chemically homogeneous and smooth. However, (i) for many real systems, the most important physical properties depend on the detailed geometry of the substrate; and (ii) in contrast to the statistics for simple particles, the degeneracy of arrangements of polyatomic species is strongly influenced by the structure of the lattice space. Then, it is of interest and of value to inquire how a specific lattice structure influences the properties of the kinetic deposition of k -mers [25]. Thus, the presence of impurities must be considered in many systems when the RSA process is studied. The present paper goes through this line of thinking.

The paper is organized as follows: in Section 2 the model is described in detail and the Monte Carlo simulation technique used for obtaining the desired quantities is briefly discussed. In Section 3 results for σ as a function of the concentration of impurities are presented. The paper is closed in Section 4 where concluding remarks are given.

2. The model

Periodic square lattices of linear size L which contains $N = L \times L$ sites are considered. The adsorbed molecules are assumed to be composed by k identical units arranged in two types of configurations: (i) as a linear array of monomers, which is called “linear k -mers”; and (ii) as a chain of adjacent monomers with the following sequence: once the first monomer is in place (the site in the lattice being selected at random), the second monomer occupies one of the z nearest-neighbors of the first monomer. This site is randomly selected between the z possibilities. If the chosen site is occupied, the attempt is aborted and the previous monomer is also eliminated from the lattice. The third and successive monomers occupy one of the $(z - 1)$ nearest-neighbors of the preceding monomer by using the same scheme. In other words, whether there is any overlap (or self overlap), the whole attempt will be rejected. Thus, all configurations are equally likely and this procedure constitutes a self-avoiding walk (SAW) of exactly k steps. This feature is called “SAW k -mer”. This scheme possesses a common feature property with a large number of models studied in the literature: no overlapping with previously adsorbed objects is allowed.

In the present scheme the lattice is considered as “contaminated” with impurities in a fraction c ($0 \leq c < 1$) of such N elements and those elements are considered forbidden for deposition. As the cN elements are randomly selected, the average coordination number for each available element depends on c . On such a lattice, characterized by L and c , linear (SAW) k -mers are deposited at random following the next scheme: a linear (SAW) k -uple of nearest neighbor available elements is randomly selected; if it is vacant, the linear (SAW) k -mer is then adsorbed on those elements. Otherwise, the attempt is rejected. In any case, the procedure is iterated until M k -mers are deposited and the desired concentration [given by $p = (kM)/((1 - c)N)$] is reached.

It is important to emphasize that in the experiments the ratio k/L is kept constant for avoiding spurious effects due to the k -mer size in comparison with the lattice size [26,27]. Thus, the time, t , in the experiments is related with the number of trials for deposition. However, in order to normalize the results the unit of time considered is t/N .

3. Results and discussions

3.1. Jamming coverage

The irreversible deposition described in Section 2 without detachment or diffusion is considered. Deposition of k -mer particles on one dimensional systems has been solved exactly for all times [10]. In two dimension, $d = 2$, extensive numerical studies have reported [28–33] the time dependence of the surface coverage and predicted its large-time asymptotic behavior.

In the surface coverage dependence on time, $\theta(t)$, different regimes can be distinguished. At short times, the deposited particles are, on the average far enough from each other. Then, each attempt to deposit a new particle is successful. Thus, the deposition events are largely uncorrelated and $\theta(t) \propto t$. In this regime, mean fields like low density approximation schemes are useful [5,10,28]. At very long times, the surface coverage reaches its saturation value (the jamming coverage) and it remains constant. Fig. 1 shows the time evolution of the deposition of dimers on heterogeneous surfaces with different concentrations of impurities determined by the parameter c as it is indicated. A similar behavior is reported for different k -mers. This allows us to conclude that Eq. (1) is valid for representing the time evolution of RSA of k -mers on heterogeneous surfaces.

Thus, at large coverage, only gaps smaller than the particle size are left in the monolayer. The resulting jammed-state is less dense than the fully ordered close-packed coverage. This is a characteristic feature of the RSA process when k -mers are used. In the analysis of the RSA-type models the quantity of interest is the fraction of total site lattice, $\theta(t)$, covered at time t by the deposited objects. Due to the blocking of the lattice by the already randomly adsorbed elements, the limiting or “jamming coverage”, $\theta_j = \theta(t = \infty)$, is less than that corresponding to the close packing ($\theta_j < 1$). Consequently, θ ranges from 0 to θ_j for objects occupying more than one site.

From Fig. 1 and similar data for different k -mers, which are not shown here for clarity, it can be concluded that: (a) the jamming coverage, θ_j decreases as the concentration of impurities increases for a fixed value of k , which reflects the influence of the effective coordination number of the lattice (which diminishes) as the concentration of impurities increases, and (b) θ_j is a monotonic decreasing function of k for a fixed value of c .

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