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Kinetics of random sequential adsorption on disordered substrates

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Abstract. The kinetics of the random sequential adsorption of line segments has been studied on a disordered substrate occupied with point impurities. The coverage of the surface and the jamming limits are calculated by a Monte Carlo method. The coverage $\theta(t)$ has an asymptotically exponential behaviour at low concentration of the impurities. The jamming limits depend on the concentration of the impurities p. At $p < p^*$ the jamming limits decrease as p increases. At $p > p^*$ the jamming limits increase as p increases. The one-dimensional results are in good agreement with Ben-Naim and Krapivsky's analytic results. The coverage and the jamming limits on a two-dimensional disordered lattice are similar to the one-dimensional cases. The jamming limits decrease monotonically as the length of line segments increases. The minimum locations of the jamming limits for both one and two dimensions are on the same values for a given length of the k-mer.

1. Introduction

Random sequential adsorption (RSA) of line segments without overlapping on the lattice is a famous model of non-equilibrium deposition process [1–3]. An object of a given shape is deposited randomly, sequentially and irreversibly on a substrate without diffusion and detachment. The incoming objects do not overlap previously deposited objects. The kinetics of the coverage of the surface and its infinite time limit, the so-called jamming limit, are the interesting physical quantities. The adhesion of proteins and colloidal particles on a uniform surface [4, 5], are examples of the experimental realization of RSA. RSA of the linear k-mers on a one-dimensional lattice was exactly solved by various methods [6–8]. However, the analytic solution is not known in higher dimensions. RSA on disordered substrates was studied numerically by Milošević and Švratić [9]. The jamming limits depend on the length of the segment and on the previous occupation of the substrate by the impurities. Recently, Ben-Naim and Krapivsky [10] solved the kinetics of RSA of the k-mers exactly on the one-dimensional lattice occupied initially by the point impurities with a random distribution.

In this work I have studied the kinetics of RSA on the disordered substrate on the one- and two-dimensional lattice using a Monte Carlo method.

2. Kinetics of RSA

In RSA on a lattice the kinetics of the coverage behave exponentially [1–3]

$$\theta(t) = \theta(\infty) - A\exp(-t/\sigma) \tag{1}$$

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where A and σ are parameters which may depend on the shape and size of the absording objects. In the long-time limit the coverage converges to the jamming limit $\theta(\infty)$. In one-dimensional RSA, the analytic solution of the kinetics is simply obtained by rate equations. The k-mers deposit randomly on the lattice with a constant rate. An adsorption event is successful if all k-sites are empty. Let $P_m(t)$ denote the probability that m consecutive sites are empty. The rate equations for these probabilities are [11]

$$\frac{\mathrm{d}P_m(t)}{\mathrm{d}t} = -(k-m+1)P_k - 2\sum_{j=1}^{m-1} P_{k+j} \qquad m \leqslant k \tag{2}$$

$$= -(m-k+1)P_m - 2\sum_{j=1}^{k-1} P_{m+j} \qquad m \geqslant k\,. \tag{3}$$

The first term on the right-hand side in equations (2) and (3) corresponds to the k-mer fully covering the m-site sequence ($m \leqslant k$) or filling with it ($m \geqslant k$). The second term describes the probabilities of deposition events in which the m-site sequence is occupied by a particle overlap by the incoming k-mer. The coverage is given by

$$\theta(t) = 1 - P_1(t)\,. \tag{4}$$

In the random initial distribution of the point impurities with the initial concentrations p, the initial probability is given by $P_m(t=0) = (1-p)^m$ [10]. Using these initial conditions, Ben-Naim and Krapivsky obtained the coverage as [10]

$$\theta_p(t,k) = p + k(1-p)^k \int_0^t \mathrm{d}u \exp\left[-u - 2\sum_{j=1}^{k-1} \frac{1-\mathrm{e}^{-ju}}{j}(1-p)^j\right]. \tag{5}$$

For $p = 0$, the coverage is equal to the result for the clean surface. The jamming limit for dimer deposition ($k = 2$) is

$$\theta_p(\infty, k=2) = \lim_{t\to\infty} \theta(t) = 1 - (1-p)\exp[-2(1-p)]\,. \tag{6}$$

The jamming limit has a minimum $\theta_{min}(\infty) = 1 - \mathrm{e}^{-1}/2 = 0.8160\ldots$ at $p = \frac{1}{2}$.

3. Numerical method and results

I generate a one-dimensional lattice of size $L = 10^5$ and a two-dimensional lattice of size 256×256, and randomly occupy the point impurities with concentrations p. Select randomly one of the lattice points. If the chosen site is occupied, the attempt is abandoned and a new site is selected. If the site is empty, check $(k-1)$ neighbour sites in a randomly chosen direction. If all successive k-sites are unoccupied, deposit the k-mer. The coverage $\theta(t)$ is defined as the number of points covered both by the k-mers and by the point impurities. The time is counted for the number of attempts to select the lattice sites and scaled by the total number of lattice sites. I use the periodic boundary conditions and average for 1000 configurations.

Figure 1 shows the coverage $\theta(t)$ against time on the one-dimensional lattice for the deposition of dimers. The Monte Carlo results (symbols) are in good agreement with the analytic results (curves) of (5). The coverages increase rapidly at short times and converge to the jamming limits at long times. The coverages $\theta(t)$ increase exponentially regardless of the point impurities. The jamming limits decrease as the concentrations of the point impurities increase.

In figure 2(a) I calculate the jamming limits $\theta_p(\infty)$ about the point impurities for $k = 2$ (●), 3 (□) and 4 (×). The full curves are the analytic results of (5) which are

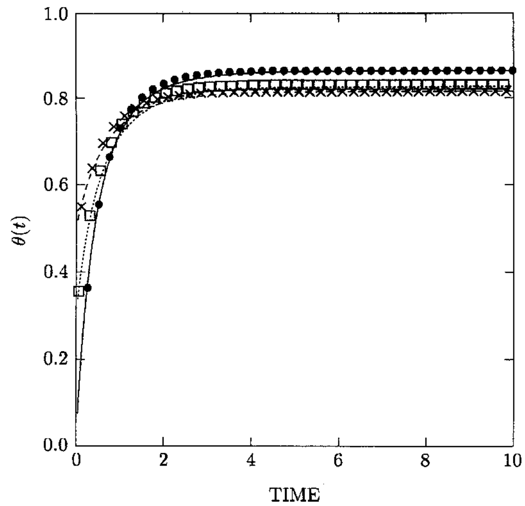

Figure 1. The coverage $\theta(t)$ versus time on a one-dimensional $L = 10^5$ lattice for the deposition of dimers. The concentrations of the point impurities are $p = 0$ (full curve, ●), 0.3 (dotted curve, □), 0.5 (short-broken curve, ×). The symbols are Monte Carlo results and the curves are analytic results.

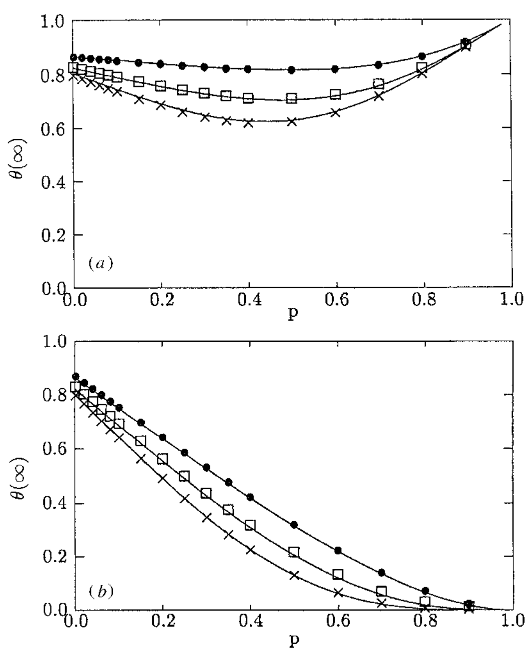

Figure 2. (*a*) The jamming limits $\theta_p(\infty)$ and (*b*) the pure k-mer jamming limits $\theta_p(\infty, k) - p$ about the point impurities for $k = 2$ (●), 3 (□), and 4 (×) on a one-dimensional lattice. The full curves are the analytic results and the symbols are Monte Carlo results.

calculated numerically using a Bode integration method. The Monte Carlo results are also in agreement with the analytic results. At low concentrations of the point impurities the jamming limits decrease with increasing p. In this regime the blocking effects by the point

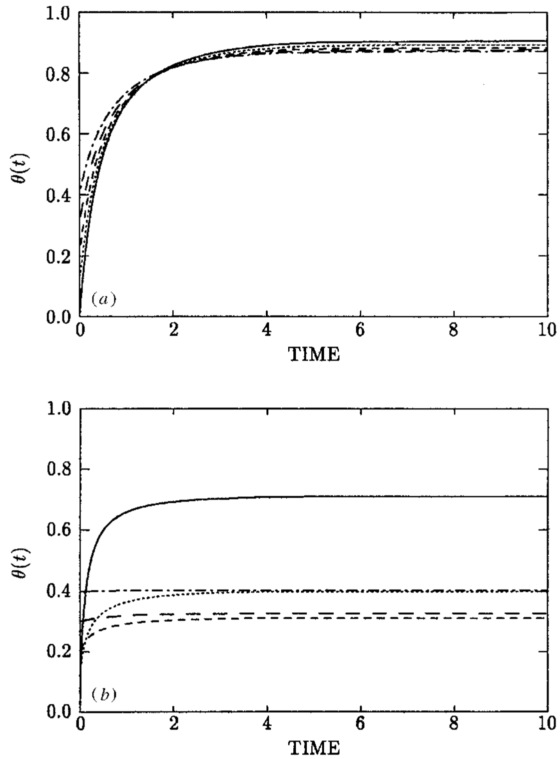

Figure 3. The coverage $\theta(t)$ versus time on a two-dimensional 256×256 square lattice for deposition of (a) dimers and (b) 16-mers for the various concentrations of the point impurities. The concentrations of the point impurities are $p = 0$ (full), 0.1 (dotted), 0.2 (short-broken), 0.3 (long-broken), and 0.4 (chain).

impurities are weak. At high concentrations of the point impurities the jamming limits increase when p increases. The blocking effects are strong at high p. The quenched impurities are already close to the jammed states. Thus, only small fractions of the k-mers are adsorbed on the surface. The minimum point of the jamming limits decreases with increasing length of the k-mers. I observed the minimum point at $p^* = 0.5$ and the jamming limit as $\theta_{min}(\infty) = 0.815(3)$ for the deposition of dimers. The previous simulation results of Milošević and Švrakić exhibit a minimum point at $p^* = 0.13$ and $\theta_{min}(\infty) = 0.8564$ [9]. Both values differ from the results of this work and the exact results of (5).

Figure 2(b) shows that the jamming limits of the pure k-mers subtracting the concentration of the point impurities from the coverages $\theta_p(\infty, k)$ plotted against the point impurities p on the one-dimensional lattice. The pure k-mer jamming limits $\theta_p(\infty, k) - p$ decrease monotonically as the point impurities increase. The analytic results (curves) and Monte Carlo results (symbols) are in good agreement with each other. The initial occupations of the impurities decrease the empty point of the substrate. Thus, the pure k-mer jamming limits decrease when the point impurities increase. At $p > p^*$, the contributions of the point impurities on the coverages are dominant and the jamming limits increase.

Figure 3 shows the coverage $\theta(t)$ versus time on the two-dimensional 256×256 lattice for deposition of (a) dimers and (b) 16-mers for various concentrations of the point impurities. For deposition of dimers ($k = 2$) the jamming limits decrease when

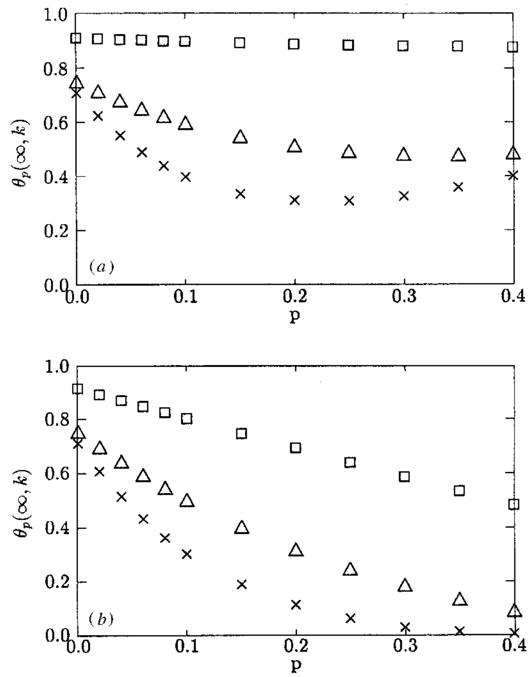

Figure 4. (a) The jamming limits $\theta_p(\infty, k)$ and (b) the pure k-mer jamming limits $\theta_p(\infty, k) - p$ versus the concentrations of the point impurities for $k = 2$ (□), 8 (△), and 16 (×) on a 256×256 square lattice.

the concentration of the point impurities increases. For deposition of 16-mers the jamming limits decrease at $p < 0.2$, but increase at $p > 0.2$. The blocking by the impurities is dominant in the deposition of the long linear k-mers.

Figure 4(a) shows the jamming limits $\theta_p(\infty)$ versus the concentration of the point impurities. At $p = 0$ the jamming limits are $\theta(\infty) = 0.904(9)$ ($k = 2$), 0.745(3) ($k = 8$), and 0.709(3) ($k = 16$) which are in good agreement with previous results [1, 2]. For deposition of dimers the jamming limits decrease up to $p = 0.4$. At $k = 8$ and 16 the jamming limits have a minimum point. The minimum points of the jamming limit are $p^* = 0.35$ at $k = 8$ and $p^* = 0.25$ at $k = 16$, respectively. The minimum points shift to smaller values of p as the length of the k-mers increases. The effects of impurities are very dominant for long k-mers.

Figure 4(b) shows the pure k-mer jamming limits $\theta_p(\infty, k) - p$ against the point impurities p for the various lengths of k-mer on a two-dimensional square lattice. The behaviour of the pure k-mer jamming limits are similar to the one-dimensional case. When the length of the k-mer increases the pure k-mer jamming limits decrease rapidly. As the point impurity p is larger than the minimum value p^*, the small fractions of the k-mer adsorb on the substrate.

Figure 5 shows the coverage $\theta_p(\infty, k)$ as a function of the length of the k-mers for various point impurities. The large k-limits of $\theta_p(\infty, k)$ have been studied previously in one [12] and two dimensions [1, 13]. The large k-limit corresponds to the continuum limit and has a $1/k$ corrective term. At $p = 0$ the jamming limits converge as $\theta_{p=0}(\infty, k) = \theta(\infty, \infty) + C_1(1/k) + C_2(1/k^2)$. Bonnier *et al* [14] obtained the coefficients as $\theta(\infty, \infty) = 0.660(2), C_1 = 1.071$, and $C_2 = 0.827$ by a Monte Carlo method and $\theta(\infty, \infty) = 0.664, C_1 = 0.827$, and $C_2 = -0.699$ by Padé analysis on the two-dimensional square lattice. In the present work I calculated the jamming limits of adsorption of infinitely long segments as $\theta(\infty, \infty) = 0.667(4)$ and the fitting coefficient as $C_1 = 0.652$ and $C_2 = -0.357$

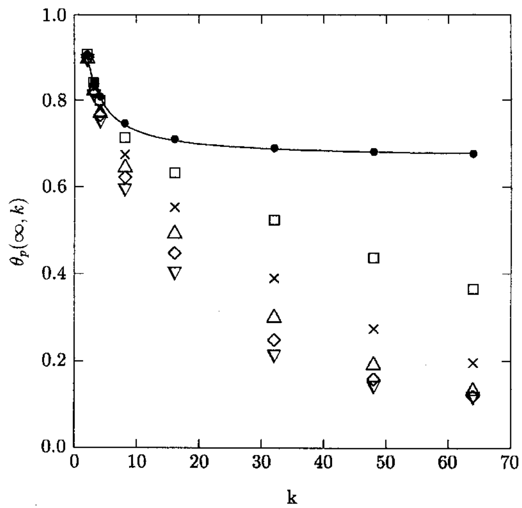

Figure 5. The coverage $\theta_p(\infty, k)$ versus the length of the k-mers for $p = 0$ (●), 0.02 (□), 0.06 (△), 0.08 (◇), and 0.1 (▽) on a 256×256 square lattice.

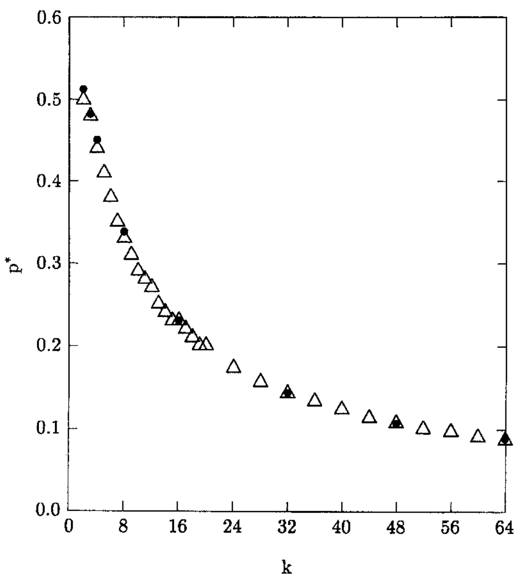

Figure 6. Plot of the minimum locations of the jamming limits as a function of k on a one-dimensional lattice (△) and a two-dimensional square lattice (●).

for the $p = 0$ case (full curve in figure 5). This result is in good agreement with the previous ones [14]. At fixed k the jamming limit $\theta_p(\infty, k)$ decreases with increasing concentration of the point impurities p. At fixed p $\theta_p(\infty, k)$ decreases as the length of the k-mers increases. The jamming limits are nearly equal values at the long length of k-mers ($k \geqslant 48$) in $p > 0.06$. When the length of the k-mer is longer, the blocking effects on the deposition of a k-mer by the point impurities are stronger. The probability of depositing the k-mers decreases abruptly at the long length of k-mers at high concentrations of the impurities. At $p > 0$ one observes that the jamming limits cannot interpolate as for the $p = 0$ case.

Figure 6 shows a plot of the minimum location of the jamming limits as a function of the k-mers. The minimum values decrease monotonically as the length of the k-mers increases in both one and two dimensions. The minimum locations of the jamming limits for a given k are at the same values for both one and two dimensions. At small k the minimum locations in both one and two dimensions are slightly different from each other. At large k the results of one and two dimensions collapse to a line. I propose that the collapse of the minimum point is because the point impurities lead to one-dimensional-like kinetics in two-dimensional adsorption at long lengths of the k-mer. I would expect that these numerical results should encourage someone else to theoretical work in these fields.

4. Conclusion

The kinetics and the jamming limit of the deposition of k-mers on a disordered substrate are studied by a Monte Carlo method. The one-dimensional results are in good agreement with the analytic predictions. At two dimensions the jamming limits have a minimum point at a particular concentration of the impurities. The minimum value decreases as the length of the k-mer increases. The jamming limits depend strongly on the blocking effects of the impurities. I observed that the jamming limits decrease monotonically with increasing length of the k-mers at $p > 0$. The pure k-mer jamming limits decrease monotonically about the point impurities. The minimum values of the jamming limits for a given k have the same values in both one and two dimensions.

Acknowledgments

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