

## Effects of impurities in random sequential adsorption on a one-dimensional substrate

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We have solved the kinetics of random sequential adsorption of linear  $k$ -mers on a one-dimensional disordered substrate for the random sequential adsorption initial condition and for the random initial condition. The jamming limits  $\theta(\infty, k', k)$  at a fixed length of linear  $k$ -mers have a minimum point at a particular density of the linear  $k'$ -mer impurity for both cases. The coverage of the surface and the jamming limits are compared to the results for Monte Carlo simulation. The Monte Carlo results for the jamming limits are in good agreement with the analytical results. The continuum limits are derived from the analytical results on lattice substrates. [S1063-651X(97)09603-7]

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Random sequential adsorption (RSA) of linear  $k$ -mers on a lattice is a model of nonequilibrium deposition process [1–3]. The linear  $k$ -mers are deposited at random, sequentially and irreversibly on a substrate without diffusion and detachment. The incoming particles do not overlap previously deposited particles. The adhesion of colloidal particles to the solid substrate serves as an experimental realization of RSA [4,5]. The surface coverages converge to the jamming limits at long times. The RSA of linear  $k$ -mers on a one-dimensional lattice has been exactly solved by various methods [6,7]. The kinetics of RSA on a one-dimensional disordered substrate occupied with point impurities has been studied numerically by Milošević and Švrtić [8], and solved analytically by Ben-Naim and Krapivsky [9]. Re-

cently, the kinetics of RSA on a two-dimensional disordered substrate with point impurities has been studied by Lee [10] using a Monte Carlo method. In the present work we studied the RSA of linear  $k$ -mers on a one-dimensional disordered substrate for the random sequential adsorption initial condition and for the random initial condition.

Let the initial density of  $k'$ -mer impurities be  $\rho_0$ . Initially,  $k'$ -mer impurities of density  $\rho_0$  are adsorbed randomly and sequentially on an empty one-dimensional substrate. Consider the elapsed time  $t_0$  at which the density of  $k'$ -mer impurities is  $\rho_0$ . Let  $P_m(t; k')$  denote the probability that  $m$  consecutive sites are empty. The  $k'$ -mers are adsorbed on a clean surface. The rate equations for these probabilities are [1,2,9]

$$\frac{dP_m(t; k')}{dt} = \begin{cases} -(k' - m + 1)P_{k'}(t; k') - 2 \sum_{j=1}^{m-1} P_{k'+j}(t; k'), & m \leq k' \\ -(m - k' + 1)P_m(t; k') - 2 \sum_{j=1}^{k'-1} P_{m+j}(t; k'), & m \geq k' \end{cases} \quad (1)$$

The first term on the right-hand side corresponds to the  $k'$ -mer fully covering the  $m$ -site sequence ( $m \leq k'$ ) or filling it ( $m \geq k'$ ). The second term describes the probabilities of deposition events in which the  $m$ -site sequence is made non-empty by a partial overlap by the incoming  $k'$ -mer. Set the trial solution  $P_m(t; k')$  as

$$P_m(t; k' \leq m) = a(t; k') e^{-mt}, \quad (3)$$

where

$$a(t; k') = \exp \left[ (k' - 1)t - 2 \sum_{j=1}^{k'-1} \frac{1 - e^{-jt}}{j} \right]. \quad (4)$$

The coverage by  $k'$ -mers is given by

$$\theta(t; k') = 1 - P_1(t; k') \quad (5)$$

$$= k' \int_0^t du \exp \left[ -u - 2 \sum_{j=1}^{k'-1} \frac{1 - e^{-ju}}{j} \right]. \quad (6)$$

The elapsed time  $t_0$  is defined as the time that the coverages of the surface reaches the initial density of the impurities,  $\rho_0$ :

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$$\rho_0 = k' \int_0^{t_0} du \exp \left[ -u - 2 \sum_{j=1}^{k'-1} \frac{1 - e^{-ju}}{j} \right]. \quad (7)$$

If  $k'=1$ , then  $t_0 = -\ln(1-\rho_0)$ . Therefore, the probability  $P_m(t_0, k'=1)$  is given by

$$P_m(t_0, k'=1) = (1-\rho_0)^m. \quad (8)$$

This result is consistent with the previous result of Ben-Naim and Krapivsky [9]. When  $k'=2$ ,  $t_0 = -\ln[1 + \frac{1}{2}\ln(1-\rho_0)]$ , and

$$P_m(t_0, k'=2) = e^{-mt_0} a(t_0; t'=2). \quad (9)$$

The probability  $P_m(t; k', k)$  for adsorption of a  $k$ -mer on a substrate occupied initially with  $k'$ -mer impurities of density  $\rho_0$ , follows the same rate equations of Eqs. (1) and (2) with  $k'$  replaced by  $k$ . Let us the initial density of impurities is  $\rho_0$ , and consider the trial solution for  $P_m(t; k', k)$  for  $m \geq k$ ,

$$P_m(t; k', k) = P_m(0) f_m(t) e^{-mt}, \quad (10)$$

where  $f_m(0)=1$  and  $P_m(0) = P_m(t_0; k')$ . Next we substitute Eq. (10) into Eq. (2), and solve for  $f_m(t)$ . We obtain

$$f_m(t) = \exp \left[ (k-1)t - 2 \sum_{j=1}^{k-1} \frac{(1-e^{jt})}{j} \frac{P_{m+j}(0)}{P_m(0)} \right]. \quad (11)$$

Therefore, the probability  $P_m(t; k', k)$  is given by

$$P_m(t; k', k) = a(t_0; k') e^{-mt_0} \exp \left[ -(m-k+1)t - 2 \sum_{j=1}^{k-1} \frac{(1-e^{-jt})}{j} \frac{P_{m+j}(0)}{P_m(0)} \right]. \quad (12)$$

If  $k \geq k'$ , then  $P_{m+j}(0)/P_m(0) = e^{-jt_0}$ . From Eq. (2) the rate equation for  $P_1(t; k', k)$  is given by

$$\frac{dP_1(t; k', k)}{dt} = -kP_k(t; k', k). \quad (13)$$

Solution of  $P_1(t; k', k)$  for  $k \geq k'$  is obtained as

$$P_1(t; k', k) = P_1(0) - ka(t_0; k') e^{-kt_0} \int_0^t du \times \exp \left[ -u - 2 \sum_{j=1}^{k-1} \frac{(1-e^{-ju})}{j} e^{-jt_0} \right], \quad (14)$$

where

$$P_1(0) = 1 - k' \int_0^{t_0} du \exp \left[ -u - 2 \sum_{j=1}^{k'-1} \frac{1 - e^{-ju}}{j} \right] \quad (15)$$

and

$$a(t_0; k') = \exp \left[ (k'-1)t_0 - 2 \sum_{j=1}^{k'-1} \frac{1 - e^{-jt_0}}{j} \right]. \quad (16)$$

The coverage for  $k \geq k'$  is obtained as

$$\theta(t; k', k) = 1 - P_1(t; k', k) \quad (17)$$

$$= \rho_0 + ka(t_0; k') e^{-kt_0} \int_0^t du \times \exp \left[ -u - 2 \sum_{j=1}^{k-1} \frac{(1 - e^{-ju})}{j} e^{-jt_0} \right]. \quad (18)$$

For  $k < k'$ , the initial probability  $P_m(0)$  is obtained from Eq. (1) as

$$P_m(0) = 1 - \int_{e^{-t_0}}^1 dv \left\{ (k' - m + 1) + 2 \sum_{j=1}^{m-1} v^j \right\} \times \exp \left[ -2 \sum_{j=1}^{k'-1} \frac{(1-v^j)}{j} \right], \quad (19)$$

where  $v = \exp(-t)$ . Substituting  $P_m(0)$  in Eq. (12), we obtain  $P_m(t; k', k)$ . Integrating Eq. (13), we calculate the coverage  $\theta(t; k', k)$  for  $k < k'$ . When  $k'=1$ ,  $t_0 = -\ln(1-\rho_0)$ , and  $a(t_0, k'=1) = 1$ . We substitute these values into Eq. (18). The coverage of surface occupied initially with point impurities then follows as

$$\theta(t; k'=1, k) = \rho_0 + k(1-\rho_0)^k \int_0^t du \times \exp \left[ -u - 2 \sum_{j=1}^{k-1} \frac{1 - e^{-ju}}{j} (1-\rho_0)^j \right]. \quad (20)$$

These results are consistent with results of Ben-Naim and Krapivsky [9]. The jamming limit for the dimer deposition ( $k=2$ ) is  $\theta(\infty, k'=1, k=2) = 1 - (1-\rho_0) \exp[-2(1-\rho_0)]$ . The jamming limits have a minimum value  $\theta_{\min}(\infty, k'=1, k=2) = 1 - e^{-1}/2 = 0.8160\dots$  at  $\rho_0 = \frac{1}{2}$ . When  $k'=2$ ,  $t_0 = -\ln[1 + \frac{1}{2}\ln(1-\rho_0)]$ , and  $a(t_0, k'=2) = (1-\rho_0)/[1 + \frac{1}{2}\ln(1-\rho_0)]$ . Substituting these values into Eq. (18), we obtain coverages for  $k'=2$  as

$$\theta(t; k'=2, k) = \rho_0 + k(1-\rho_0) e^{-(k-1)t_0} \int_0^t \exp \left[ -u - 2 \sum_{j=1}^{k-1} \frac{(1 - e^{-ju})}{j} e^{-jt_0} \right] du. \quad (21)$$

For ( $k'=2, k=1$ ) the jamming limit is trivially obtained as  $\theta(\infty; k'=2, k=1) = 1$ . For the deposition of dimer only ( $k'=2, k=2$ ), the jamming limit is consistent with the previous results as  $\theta(\infty; k'=2, k=2) = 1 - e^{-2} = 0.8646\dots$  [6,7]. For ( $k'=2, k \geq 3$ ), we obtain the jamming limits by integrating Eq. (21). The initial elapsed time  $t_0$  is numerically calculated by using Eq. (7) when  $k' > 2$ . Using the time  $t_0$ , we calculate the coverage from Eq. (18). The jamming limits  $\theta(t=\infty; k'=2, k)$  are plotted in Fig. 1. The solid lines in Fig. 1 represent results obtained by numerical integration of Eq. (18). The symbols in Fig. 1 represent the Monte Carlo results for a

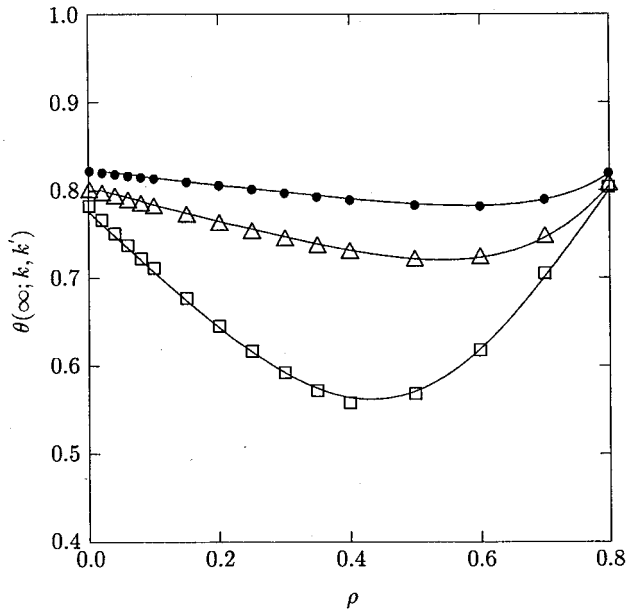


FIG. 1. The jamming limits  $\theta(\infty; k, k')$  vs the concentration of  $k'=2$  impurities  $\rho$  for  $k=3$  ( $\bullet$ ),  $4$  ( $\circ$ ), and  $8$  ( $\square$ ). The symbols are Monte Carlo results, and the lines are analytical results.

one-dimensional lattice of size  $L=10^5$  using periodic boundary conditions and  $10^3$  configurational averages. The Monte Carlo results are in good agreement with the results of numerical calculations. The appearance of the minimum point of the jamming limits is consistent with the previous exact results [9] and Monte Carlo results [8,10] on the adsorption of  $k$ -mers on a substrate occupied initially with point impurities. At low densities of  $k'$ -mer impurities, the jamming limits decrease with increasing  $\rho_0$ . In this regime effects of impurities are to reduce the available space for  $k$ -mers as compared to the empty substrate. However, at high densities of  $k'$ -mer these quenched impurities are already close to the jamming state, so that only a small fraction of  $k$ -mers is adsorbed on the substrate. The minimum point of the jamming limits decreases with increasing length of the  $k$ -mers.

Another simple solvable case is when the impurities are distributed randomly, i.e.,  $P_m(0)=\lambda^m$ , with  $\lambda=[1+k'^{-1}\rho_0(1-\rho_0)^{-1}]^{-1}$ . In this case, we obtain  $t_0=0$ ,  $P_m(0)=\lambda^m$ , and  $P_{m+j}(0)/P_m(0)=\lambda^j$ . The coverage is obtained as

$$\theta(t; k', k) = 1 - \lambda + k\lambda^k \int_0^t du \exp\left[-u - 2 \sum_{j=1}^{k-1} \frac{1 - e^{-ju}}{j} \lambda^j\right]. \quad (22)$$

When  $k=2$ , the jamming limit is given as  $\theta(\infty, k', k=2) = 1 - \lambda \exp(-2\lambda)$ . This result is the same as for the point impurity case. At  $k=2$ , the minimum value of the jamming limit is  $\theta_{\min}(\infty, k', k=2) = 1 - e^{-1}/2$  at  $\rho_0 = k'/(1+k')$ . The minimum value does not change for the length of the impurity.

Using these analytical results for lattice substrates we can obtain the coverage for the continuum case. In the continuum limit objects of unit length are deposited on a lattice initially occupied by impurities. Let the initial density of the impuri-

ties be  $\mu$  in the continuum limit. Rescale the density according to  $k\rho_0=\mu$  and the time as  $kt=\tau$  [9]. With the rescaled density and time remaining finite, we take the limit  $k\rightarrow\infty$  of Eqs. (18) and (22). When we take the continuum limit, the  $k\rightarrow\infty$  limit is primary. When the impurities are distributed randomly and sequentially, we use Eq. (18). For the case of point impurities the continuum coverage was already discussed by Ben-Naim and Krapivsky [9]. When  $k'=2$ ,  $t_0 = -\ln[1 + \frac{1}{2} \ln(1-\rho_0)]$ . The continuum coverage is obtained as

$$\theta(\tau) = \exp(-\mu/2) \int_0^\tau dv \exp\left[-2 \int_{\mu/2}^{v+\mu/2} dw \frac{1-e^{-w}}{w}\right]. \quad (23)$$

In the limit  $\mu\rightarrow 0$ , the coverage converges to the Rényi number  $\theta(\infty)=R=0.7475\dots$  [9,11]. In the limit  $\mu\rightarrow\infty$ , the coverage approaches zero exponentially according to  $\theta(\infty) = (\mu/2)\exp(-\mu/2)$ . When  $k'>2$ , it is difficult to obtain the explicit dependence of the initial time  $t_0$  on  $\rho_0$ . Thus, for  $k'\rightarrow\infty$  and  $k\rightarrow\infty$ , with  $k'/k$  finite, we cannot derive the general expression for the continuum limit when  $k'>2$ .

When the impurities are randomly distributed, we use Eq. (22). At  $k'=2$ , the continuum coverage is the same as Eq. (23). The general form of the continuum limit in the case of random initial conditions is derived by the methods of continuous RSA (not included the detailed calculations). When  $k'\rightarrow\infty$  and  $k\rightarrow\infty$ , with  $k'/k=l$  finite, we can obtain the continuum limit coverage as

$$\theta(\infty) = \rho_0 + (1-\rho_0)\exp(-\alpha) \times \int_0^\infty dt \exp\left[-2 \int_\alpha^{\alpha+t} du \frac{1-e^{-u}}{u}\right], \quad (24)$$

where  $\alpha = \rho_0/[(1-\rho_0)l]$ . When  $\rho_0=0$ , continuous RSA is recovered. When  $l\rightarrow 0$  and  $\rho_0\rightarrow 0$  such that  $\rho_0/l = \mu = \text{const}$ , then Eq. (23) is recovered. When  $\rho_0\rightarrow 1$  the coverage is only slightly higher than the initial coverage,  $\theta(\infty) = \rho_0 + (\rho_0/l)\exp(-\alpha)$ . In the continuum limit the coverage follows the algebraic decay  $\theta(\infty) - \theta(t) \sim t^{-1}$ .

In summary, we calculated the jamming limits for  $k$ -mers on one-dimensional substrates for the random sequential adsorption initial condition and for the random initial condition, by solving the appropriate rate equations. The jamming limits  $\theta(\infty; k', k)$  show a minimum value at a particular density of impurities. The Monte Carlo data are in good agreement with the analytical results. The coverage in the continuum limit was discussed using the analytical results for the lattice models.

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