Inhomogeneous random sequential adsorption on bipartite lattices

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We consider the inhomogeneous random sequential adsorption of particles on bipartite lattices. The jamming coverages of each sublattice and the total jamming coverage are calculated for a linear chain and for a square lattice as a function of the probability p of adsorbing a particle in a given sublattice. For the linear chain, we obtain an exact closed expression for the coverages as functions of time. For the square lattice, we present results coming from numerical simulations.

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I. INTRODUCTION

We consider here the problem of random sequential adsorption (RSA) of particles on a regular lattice [1–13] in which the flux of particles is not homogeneous in space. In the homogeneous RSA problem particles are irreversibly and sequentially deposited on a substrate, each one in a site of the lattice. The occupation of a certain site excludes the occupation of sites belonging to a certain neighborhood. Usually this neighborhood is chosen to be the nearest neighbor sites of a given site. One quantity of interest is the jamming coverage θ_J, that is, the density of occupied sites in the long time limit. In one dimension the exact result for the case of nearest neighbor exclusion is $\theta_J = (1-e^{-2})/2 = 0.432\,332...$ [2]. In a square lattice, numerical calculations coming from series expansions [10] give $\theta_J = 0.364\,133(3)$.

In this paper we study the problem of the inhomogeneous RSA of particles on a lattice [1,14,15]. We consider bipartite lattices and suppose that sites belonging to one of the sublattices have a higher probability to adsorb a particle than the other. Or, in other words, the flux of particles into sites of one sublattice is larger than that of the other. We treat only the case of nearest neighbor exclusion where an occupied site excludes the occupation of the nearest neighbor sites which, for bipartite lattices, belong to the other sublattice. In a square lattice, this model has been considered previously [14] for its jamming coverage behavior and percolation properties.

Let us denote by A and B the two sublattices and let p be a parameter defined in the interval $0 \leq p \leq 1$. When $p > 1/2$ the adsorption of particles in sublattice A is favored whereas when $p < 1/2$ the adsorption of particles in sublattice B is favored. At each time step of the adsorption process one site of the lattice is chosen at random. If the chosen site is empty and its nearest neighbor sites are also empty then the selected site is occupied by a particle with probability p if it belongs to sublattice A and with probability $q = 1-p$ if it belongs to sublattice B.

For the case of a linear chain, we were able to solve the problem exactly by two methods. One of them, shown in the next section, is a generalization of the original technique of Flory [1,2] and is based on the property that in a finite open chain the adsorption of one particle breaks the chain in smaller pieces. It is possible then to set up recursion relations in which the average number of adsorbed particles on a chain with a certain number of sites is written in terms of the average number of adsorbed particles on a chain with a lesser number of sites. These recursion relations are then solved by repeated iterations.

The other method, presented in Sec. III, relies on the general empty site Markov property [1] of one dimensional RSA models. One solves exactly the hierarchic set of equations for the correlations corresponding to a string of empty sites, coming from the master equation that governs the process. In this method one obtains analytical closed expressions for the coverage as functions of time. The total coverage behaves asymptotically as $\theta(t) - \theta_J \sim e^{-ct}$ where $c = \min\{a, b\}$ and a and b are the particle fluxes into sites of sublattice A and B and proportional to p and q, respectively.

In Sec. IV, we present numerical simulation for the square lattice.

II. JAMMING COVERAGE FOR A CHAIN

Let $P_A(n,\ell)$ and $P_B(n,\ell)$ be the probability of having n particles adsorbed on sites of sublattice A in a linear and open chain of ℓ sites in which the first site of the chain belongs to sublattice A and B, respectively. These probabilities refer to the final state. To set up recursive equations for these probabilities we proceed as follows.

Consider first a chain of ℓ sites beginning with a site of sublattice A, initially unoccupied. Suppose that the first particle has been adsorbed on the ℓ_1th site and let us ask for the probability of having n_1 particles adsorbed on sublattice A at left and n_2 particles adsorbed on sublattice A at right. Since the sites on the left are not adjacent to any one of the sites on the right the probability will be $P_A(n_1,\ell_1-2)P_A(n_2,\ell-\ell_1-1)$ if ℓ_1 is odd and $P_A(n_1,\ell_1-2)P_B(n_2,\ell-\ell_1-1)$ if ℓ_1 is even. To obtain, for instance, $P_A(n,\ell)$ we should consider all the possibilities of placing the first particle and all possible values of n_1 and n_2. Therefore

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$$P_A(n,\ell) = \frac{p}{D_\ell^A} \sum_{\ell' \, odd} \sum_{n'} P_A(n', \ell'-2) \times P_A(n-n'-1, \ell-\ell'-1) + \frac{q}{D_\ell^A} \sum_{\ell' \, even} \sum_{n'} P_A(n', \ell'-2) \times P_B(n-n', \ell-\ell'-1) \;, \quad (1)$$

where $q = 1-p$, and $D_\ell^A = \ell/2$ if ℓ is even and $D_\ell^A = p + (\ell-1)/2$ if ℓ is odd. The prefactor p/D_ℓ^A of the first summation stands for the probability of placing the first particle in one of the D_ℓ^A sites of sublattice A whereas the factor q/D_ℓ^A is the corresponding probability for the sites of sublattice B. We also set $P_A(0,-1) = P_B(0,-1) = P_A(0,0) = P_B(0,0) = 1$. A similar equation can be set up for $P_B(n,\ell)$, namely,

$$P_B(n,\ell) = \frac{q}{D_\ell^B} \sum_{\ell' \, odd} \sum_{n'} \times P_B(n', \ell'-2) P_B(n-n', \ell-\ell'-1) + \frac{p}{D_\ell^B} \sum_{\ell' \, even} \sum_{n'} P_B(n', \ell'-2) \times P_A(n-n'-1, \ell-\ell'-1), \quad (2)$$

where $D_\ell^B = \ell/2$ if ℓ is even and $D_\ell^B = q + (\ell-1)/2$ if ℓ is odd.

Next we set up a recursion relation for N_ℓ^A and N_ℓ^B, the average number of particles adsorbed on sites of sublattice A in chains beginning with a site of sublattice A and B, respectively, and defined by

$$N_\ell^A = \sum_n n P_A(n,\ell) \;, \quad (3)$$

$$N_\ell^B = \sum_n n P_B(n,\ell) \;. \quad (4)$$

Using Eq. (1) we get

$$N_\ell^A = \frac{p}{D_\ell^A} \sum_{\ell' \, odd} (N_{\ell'-2}^A + N_{\ell-\ell'-1}^A + 1) + \frac{q}{D_\ell^A} \sum_{\ell' \, even} (N_{\ell'-2}^A + N_{\ell-\ell'-1}^B) \;. \quad (5)$$

Similarly, we get from Eq. (2) the following equation for N_ℓ^B:

$$N_\ell^B = \frac{q}{D_\ell^B} \sum_{\ell' \, odd} (N_{\ell'-2}^B + N_{\ell-\ell'-1}^B) + \frac{p}{D_\ell^B} \sum_{\ell' \, even} (N_{\ell'-2}^B + N_{\ell-\ell'-1}^A + 1) \;. \quad (6)$$

Equations (5) and (6) can be written in the equivalent form

$$\left(\frac{\ell}{2} + p\right) N_{\ell+1}^A = \left(\frac{\ell}{2} - 1 + 3p\right) N_{\ell-1}^A + 2q N_{\ell-2}^A + p \;, \quad (7)$$

$$\left(\frac{\ell}{2} + q\right) N_{\ell+1}^B = \left(\frac{\ell}{2} - 1 + 3q\right) N_{\ell-1}^B + 2p N_{\ell-2}^A + p \;, \quad (8)$$

$$\ell N_\ell^A = \left(\frac{\ell}{2} - q\right) N_{\ell-1}^A + \left(\frac{\ell}{2} - p\right) N_{\ell-1}^B + 2N_{\ell-2}^A + p \;, \quad (9)$$

valid for $\ell = 2, 4, 6, \ldots$. We have used the property $N_\ell^B = N_\ell^A$ valid for ℓ even. Equations (7), (8), and (9) are solved numerically by repeated iterations beginning with the initial conditions $N_0^A = N_0^B = 0$, $N_1^A = 1$, $N_1^B = 0$. The jamming coverage of sublattice A can be obtained by the ratio N_ℓ^A/ℓ or N_ℓ^B/ℓ. To increase the convergence we consider, instead, a periodic chain with an even number ℓ of sites. From the average number of particles N_ℓ adsorbed on sites of sublattice A of the periodic chain, given by

$$N_\ell = p(N_{\ell-3}^A + 1) + q N_{\ell-3}^B \;, \quad (10)$$

we calculate the jamming coverage θ_J^A by

$$\theta_J^A = \lim_{\ell \to \infty} \frac{N_\ell}{\ell} \;. \quad (11)$$

The jamming coverage θ_J^B is obtained by using the property $\theta_J^B(p) = \theta_J^A(1-p)$.

Table I shows the coverages θ_J^A, θ_J^B, and the total coverage $\theta_J = \theta_J^A + \theta_J^B$ for some values of p obtained by this procedure. For $p = 1/2$ we obtain the result $\theta_J = 0.432\,332\ldots$ which should be compared with the exact result $(1-e^{-2})/2 = 0.432\,332\ldots$.

TABLE I. Jamming coverages θ_J^A of sublattice A and θ_J^B of sublattice B and total coverage $\theta_J = \theta_J^A + \theta_J^B$ as a function of p for the linear chain.

p	0	0.1	0.2	0.3	0.4	0.5
θ_J^A	0	0.029144	0.066303	0.110695	0.161142	0.216166
θ_J^B	0.5	0.447683	0.391576	0.333155	0.274095	0.216166
θ_J	0.5	0.476827	0.457879	0.443850	0.435236	0.432332

III. EXACT CLOSED SOLUTION FOR A CHAIN

Let us denote by $\xi = (\xi_1, \xi_2, \ldots, \xi_N)$ the configuration of a linear chain with N sites where the variable $\xi_i = 1$ or 0 according to whether site i is vacant or occupied by a particle. Notice that we are using a representation in which the variable ξ_i takes the value 0 when the site is occupied and the value 1 when it is empty. The flux of particle into site i is denoted by φ_i and the sticking probability by $w_i(\xi)$ which is given by

$$w_i(\xi) = \xi_{i-1}\xi_i\xi_{i+1} \;. \quad (12)$$

The time evolution of the probability $P(\xi, t)$ that the system is in configuration ξ at time t is governed by the master equation

$$\frac{d}{dt}P(\xi,t) = \sum_i \varphi_i\{w_i(\xi^i)P(\xi^i,t) - w_i(\xi)P(\xi,t)\} , \quad (13)$$

where the configuration ξ^i is obtained from ξ by the transformation $\xi_i \to 1 - \xi_i$. In the inhomogeneous model studied here we consider that particle flux into odd sites is distinct from particle flux into even sites, that is, $\varphi_i = a$ if i is even and $\varphi_i = b$ if i is odd.

Let us define now the following correlations:

$$X_n(t) = \sum_\xi \xi_0\xi_1 \cdots \xi_{n-1}P(\xi,t) \quad (14)$$

and

$$Y_n(t) = \sum_\xi \xi_1\xi_2 \cdots \xi_n P(\xi,t). \quad (15)$$

These n point correlations are, in general, distinct due to the inhomogeneity of the system. They are interpreted as the probability of finding a string of n empty sites in which the first site is even and odd, respectively. The coverages $\theta^A(t)$ and $\theta^B(t)$ of the sublattice A (even sites) and sublattice B (odd sites) are given by $\theta^A = (1-X_1)/2$ and $\theta^B = (1-Y_1)/2$, respectively, and the total coverage θ by $\theta = \theta^A + \theta^B = 1 - (X_1 + Y_1)/2$.

From the master equation one obtains the following hierarchic set of equations for the correlations:

$$\frac{d}{dt}X_1 = -aY_3 \quad (16)$$

and

$$\frac{d}{dt}Y_1 = -bX_3 \quad (17)$$

and, for $n = 2, 4, 6, \ldots$,

$$\frac{d}{dt}X_n = -bX_{n+1} - aY_{n+1} - \frac{n-2}{2}(a+b)X_n \quad (18)$$

and

$$\frac{d}{dt}Y_n = -bX_{n+1} - aY_{n+1} - \frac{n-2}{2}(a+b)Y_n \quad (19)$$

and, for $n = 3, 5, 7, \ldots$,

$$\frac{d}{dt}X_n = -aX_{n+1} - aY_{n+1} - \left(\frac{n-3}{2}a + \frac{n-1}{2}b\right) X_n \quad (20)$$

and

$$\frac{d}{dt}Y_n = -bX_{n+1} - bY_{n+1} - \left(\frac{n-3}{2}b + \frac{n-1}{2}a\right) Y_n . \quad (21)$$

These sets of equations should be solved with the initial condition that at time $t = 0$ the lattice is empty, which implies that $X_n(0) = 1$ and $Y_n(0) = 1$ for $n = 1, 2, 3, \ldots$. For n even the following property holds: $X_n(t) = Y_n(t)$. To solve this coupled set of equations one makes the following ansatz:

$$X_n(t) = A(t) \exp\left\{-\left(\frac{n-3}{2}a + \frac{n-1}{2}b\right) t\right\} \quad (22)$$

and

$$Y_n(t) = B(t) \exp\left\{-\left(\frac{n-3}{2}b + \frac{n-1}{2}a\right) t\right\} \quad (23)$$

for $n = 3, 5, \ldots$ (odd), and

$$X_n(t) = Y_n(t) = C(t) \exp\left\{-\left(\frac{n-2}{2}\right)(a+b)t\right\} \quad (24)$$

for $n = 2, 4, \ldots$ (even). Inserting these expressions into Eqs. (18), (19), (20), and (21), we obtain the following equations for the quantities $A(t)$, $B(t)$, and $C(t)$:

$$\frac{dA}{dt} = -2ae^{-at}C , \quad (25)$$

$$\frac{dB}{dt} = -2be^{-bt}C , \quad (26)$$

and

$$\frac{dC}{dt} = -ae^{-at}B - be^{-bt}A , \quad (27)$$

which should be solved with the initial condition $A(0) = 1$, $B(0) = 1$, and $C(0) = 1$. It is straightforward to show, from these equations, that $C^2(t) = A(t)B(t)$. Now, if one defines the quantities $Q(t) = \sqrt{A(t)}$ and $R(t) = \sqrt{B(t)}$ and uses the property $C^2(t) = A(t)B(t)$ one gets the equations

$$\frac{dQ}{dt} = -ae^{-at}R \quad (28)$$

and

$$\frac{dR}{dt} = -be^{-bt}Q , \quad (29)$$

which should be solved with the initial conditions $Q(0) = 1$ and $R(0) = 1$. If the solutions of these equations are obtained, then $A(t)$, $B(t)$, and $C(t)$ are determined by $A(t) = Q^2(t)$, $B(t) = R^2(t)$, and $C(t) = Q(t)R(t)$.

Let us define a new variable x by

$$x = e^{-(a+b)t} \quad (30)$$

and perform the following transformations:

$$z = 2\sqrt{pqx} \quad (31)$$

and

$$W = x^{-p/2}Q , \quad (32)$$

where $p = a/(a+b)$ and $q = b/(a+b) = 1 - p$. One concludes from Eqs. (28) and (29) that $W(z)$ obeys the modified Bessel equation

$$z^2\frac{d^2W}{dz^2}+z\frac{dW}{dz}-(p^2+z^2)W=0\ . \tag{33}$$

This equation has to be solved with the conditions

$$W(2\sqrt{pq})=1 \tag{34}$$

and

$$W'(2\sqrt{pq})=\frac{1}{2}\sqrt{\frac{p}{q}}\ . \tag{35}$$

A solution of the modified Bessel equation is $I_p(z)$, the modified Bessel function of order p [16]. For the case in which p is not an integer, another independent solution is $I_{-p}(z)$ [16]. If one denotes by $W_p(z)$ the solution of Eq. (33) with the conditions given by (34) and (35) then

$$W_p(z)=c_pI_p(z)+d_pI_{-p}(z)\ , \tag{36}$$

where c_p and d_p are constants such that conditions (34) and (35) are fulfilled. Using the usual recurrence relations [16] for Bessel functions one gets

$$c_p=\frac{\pi\sqrt{pq}}{\sin p\pi}I_{1+p}(2\sqrt{pq}) \tag{37}$$

and

$$d_p=\frac{p\pi}{\sin p\pi}I_{1+q}(2\sqrt{pq})\ . \tag{38}$$

To obtain the coverage of sublattice A we integrate Eq. (16) remembering that $\theta^A=(1-X_1)/2$. We obtain the result

$$\theta^A=\frac{1}{2}p\int_x^1 W_p^2(2\sqrt{pqy})dy\ . \tag{39}$$

A similar expression can be written for the coverage of sublattice B. Summing up the results for two sublattice coverages it is possible to write the total coverage $\theta=\theta^A+\theta^B$ in the form

$$\theta=\frac{1}{2}\left[1-\sqrt{x}W_p(2\sqrt{pqx})W_q(2\sqrt{pqx})\right]\ . \tag{40}$$

These expressions are the desired closed forms for the coverages as functions of time since $x=\exp\{-(a+b)t\}$.

Taking the limit $t\to\infty$, that is, $x\to 0$, we obtain the following closed expression for the total jamming coverage:

$$\theta_J=\frac{1}{2}\left(1-\frac{\pi\sqrt{pq}}{\sin p\pi}I_{1+p}(2\sqrt{pq})I_{1+q}(2\sqrt{pq})\right)\ . \tag{41}$$

Of course this expression gives, for the case $p=1/2$, the well known result for the coverage of the homogeneous RSA on a chain, $\theta_J=(1-e^{-2})/2$.

The asymptotic behavior of θ^A can be obtained from Eq. (39), which gives

$$\theta^A(t)-\theta_J^A\sim e^{-at}\ . \tag{42}$$

Similarly one gets

$$\theta^B(t)-\theta_J^B\sim e^{-bt}\ . \tag{43}$$

Since $\theta(t)=\theta^A(t)+\theta^B(t)$, the asymptotic behavior of the total coverage will be $\theta(t)-\theta_J\sim e^{-ct}$ where $c=\min\{a,b\}$.

TABLE II. Jamming coverages θ_J^A of sublattice A and θ_J^B of sublattice B and total coverage $\theta_J=\theta_J^A+\theta_J^B$ as a function of p for a square lattice.

p	0	0.1	0.2	0.3	0.4	0.5
θ_J^A	0	0.0157(1)	0.0399(2)	0.0756(7)	0.1234(8)	0.1820(5)
θ_J^B	0.5	0.4459(4)	0.3845(6)	0.3175(9)	0.2482(9)	0.1821(6)
θ_J	0.5	0.4616(3)	0.4244(3)	0.3931(4)	0.3716(2)	0.3641(1)

IV. NUMERICAL SIMULATIONS

According to the definition of the RSA process, a site of the lattice should be chosen at random at each time step of the process. If the chosen site is blocked no particle is adsorbed. The numerical simulation of the model becomes, therefore, inefficient for later times when the number of blocked sites is large. To avoid this problem one uses a procedure in which one particle is added at each time step so that the process terminates in a number of time steps smaller then $N/2$. At each time step, we first select which sublattice to place a particle. Sublattice A is chosen with probability $p'=pR_A/(pR_A+qR_B)$ and sublattice B with probability $1-p'$ where R_A and R_B are the number of available adsorption sites of sublattice A and B, respectively. After that, we choose at random one of the available adsorption sites of the selected sublattice to place a particle.

We have performed numerical simulation on a square lattice for several values of p. We used periodic lattices with $L\times L$ sites with sizes sufficiently large so that the finite size deviations were always smaller than the statistical errors. Table II shows results obtained for $L=100$ for some values of p. For $p=1/2$ the value 0.364 1(1) should be compared with the value $\theta_J=0.364\,133(3)$ obtained from series expansion [10].

V. CONCLUSION

We have studied the inhomogeneous random sequential adsorption of particles on a bipartite lattice in which the fluxes of particles in each one of the sublattices are distinct. The coverage of each sublattice and the total coverage were calculated as a function of the fluxes for a linear chain and for a square lattice. For the linear chain, we have have solved the problem by two methods: one which generalizes a technique due to Flory and the other which relies on the general empty site Markov property. For the square lattice we have presented numerical results coming from simulations.

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