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Random Sequential Adsorption on a Ladder

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We study the asymptotic coverage of a lattice to which particles are randomly and irreversibly attached, under the constraint of nearest neighbor exclusion. After reviewing the case of a one-dimensional lattice, we extend the treatment first to a triangular ladder and then to a square ladder. The former maps onto a previously solved one-dimensional case, the latter does not. We also determine the time-dependent coverage of the square ladder. Implications as to the process on a full 2-dimensional square lattice are discussed.

1. INTRODUCTION

Random sequential adsorption (RSA) has been studied extensively because of its wide applicability to diverse aspects of physics, chemistry, biology, etc.(1) It is defined by a sequence of random placements of particles on a surface, a move being accepted if the particle does not fall into the geometric exclusion region of another particle (or with appropriate probability distribution for probabilistic acceptance(2)), else rejected. On the time scale considered, the process is irreversible—an accepted particle stays where it has fallen; various obvious reversible generalizations are of potential importance,(3) but will not be considered here. The process is normally imagined as starting with an empty surface. Since the placement is random, there will be a distribution of configurations at each time and a distribution of time-asymptotic final states. The question that one focuses on is the time dependence of the coverage—the mean particle density on the surface—and in particular the asymptotic coverage. The asymptotic state is not an eqilibrium state in the usual sense of the term, since one cannot test against

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removal of particles—indeed, standard equilibrium would result in asymptotic close packing—and so the problem of finding it without the necessity of carrying out stochastic dynamics has received considerable attention.

Various analytic solutions for both continuum and lattice versions of RSA have been found, starting with the elegant work of Flory,[4] but these have all been in one-dimensional space. They proceed by decomposing the system into unit configurations, whose statistics is assessed. For higher dimension, the class of unit configurations becomes enormous, and only numerical or approximate results are available.[5] In this note, we use similar techniques to extend the analytic results for RSA on a lattice space to the class of two-row ladders, a very modest entree into two-dimensional space, but with suggestive implications. The paper is organized as follows. In Section 2, we briefly recall Flory's approach, and then solve the asymptotic model for a finite triangular ladder. By mapping this onto a one-dimensional chain with next nearest neighbor exclusion, in the thermodynamic limit, we reproduce an earlier result given by Gonzalez *et al.*[6] In Section 3, we do similar calculations for a square ladder, and then in Section 4 carry out the full time dependence with suitable rate equations. We conclude with a brief extension to a multirow ladder and a discussion of the implications of our results.

2. THE TRIANGULAR LADDER

Flory's technique[4] for the direct evaluation of the asymptotic state, originally applied to the closely related problem of irreversible dimer packings, focuses on the iterative filling up of initially empty lattice regions. In particular, consider, for a nearest neighbor exclusion one-dimensional lattice, a segment of $k > 2$ unoccupied sites, say $1,..., k$, with sites 0 and $k+1$ occupied, which on being filled to a "jammed" configuration (one to which no particle can be added) has on the average A_k vacant sites remaining. Clearly $A_1 = 1$, $A_2 = 2$. A particle dropped randomly will adhere with probability $1/(k-2)$ to one of the sites $2,..., k-1$. If this occurs at site j, there results an empty sublattice of $j-1$ sites and one of $k-j$ sites. It follows that $A_k = [1/k-2)] \sum_{j=2}^{k-1} (A_{j-1} + A_{k-j})$, or

$$A_k = \frac{2}{k-2} \sum_{j=1}^{k-2} A_j \qquad \text{for} \quad k > 2 \tag{2.1}$$

By mimicking Flory's analysis, or by generating function techniques (see later), it can be shown that

$$\Delta_k = A_{k+1} - A_k = 1 + \frac{1}{2} \sum_{j=1}^{k-1} \frac{(-2)^j}{j!} \tag{2.2}$$

and the thermodynamic limit of mean occupation density is given by

$$\rho_\infty = 1 - \lim_{k \to \infty} \Delta_k = \tfrac{1}{2}(1 - e^{-2}) \tag{2.3}$$

We proceed next to the triangular ladder with nearest neighbor exclusion. A vacant strip of the ladder with k empty sites, terminated by occupied sites on both sides, is characterized by mean asymptotic vacancy number A_k, as illustrated in Fig. 1. For $k > 4$, an incoming particle can adhere with equal probability to any of $k - 4$ sites, in each case decomposing the region into two smaller vacant regions. Thus,

$$A_k = [1/(k-4)][(A_2 + A_{k-3}) + (A_3 + A_{k-4}) + \cdots + (A_{k-3} + A_2)]$$

or

$$(k-4)A_k = 2 \sum_{j=2}^{k-3} A_j \qquad \text{for} \quad k > 0 \tag{2.4}$$

with $A_2 = 2$, $A_3 = 3$, $A_4 = 4$.

To solve (2.4), let us use the generating function approach. We define

$$A(x) = \sum_{k=4}^{\infty} A_k x^{k-4} \tag{2.5}$$

multiply (2.4) by x^{k-5}, and sum over k, obtaining

$$\begin{aligned} A'(x) &= \frac{2x^2}{1-x} A(x) + \frac{2}{1-x}(2+3x) \\ A(0) &= 4 \end{aligned} \tag{2.6}$$

The solution of (2.6) is readily found,

$$A(x) = e^{-(2x + x^2)}(1-x)^{-2} \left[4 + 2 \int_0^x (1-y)(2+3y) e^{2y + y^2} \, dy \right] \tag{2.7}$$

But $\lim_{k \to \infty} A_k/k = \lim_{x-1}(1-x)^2 A(x)$, and so we have

$$\begin{aligned} \rho_\infty &= 1 - 4e^{-3} - 2 \int_0^1 (1-y)(2+3y) e^{y^2 + 2y - 3} \, dy \\ &= \int_0^1 e^{y^2 + 2y - 3} \, dy \end{aligned} \tag{2.8}$$

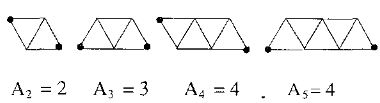

Fig. 1. Low-order vacancy regions on the triangular ladder.

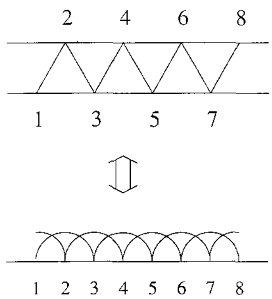

Fig. 2. Mapping of the triangular ladder onto one dimension.

It is to be noted that (see Fig. 2) the nearest neighbor exclusion triangular ladder maps onto the nearest plus next nearest neighbor exclusion one-dimensional lattice, showing that our solution is directly related to the elegant work of Gonzalez *et al.*,[6] who also used a modified Flory technique to solve for the full stochastic dynamics.

3. THE SQUARE LADDER

The mapping just mentioned is not suitable for the square ladder, which must therefore be handled *ab initio*. Now again there are two types of termination of k-column empty strips: on the same row or on opposite rows, but here they can be associated with the same vacancy number (see Fig. 3). Since the asymptotic mean vacancy numbers A_k and B_k are not the same, the two types of configuration must be distinguished. However, the procedure is precisely as with the triangular ladder. Adding the separate contributions from occupying the lower jth and upper jth sites, the opposite site always remaining empty, we clearly have

$$A_k = [1/(2k-2)][(B_{k-1}+1)+(B_1+A_{k-2}+1)+(A_1+B_{k-2}+1)+\cdots + (A_{k-2}-B_1+1)+(B_{k-1}+1)]$$

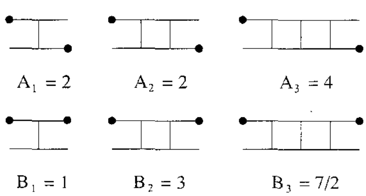

Fig. 3. Low-order vacant configuration for the square ladder.

or

$$(k-1)A_k=\sum_{j=1}^{k-2} A_j+\sum_{j=1}^{k-1} B_j+k-1, \qquad k\geqslant 2 \tag{3.1}$$

Similarly,

$$B_k=[1/(2k-2)][(A_{k-1}+1)+(B_1+B_{k-2}+1)+(A_1+A_{k-2}+1)+\cdots$$
$$+(B_{k-2}+B_1+1)+(A_{k-1}+1)]$$

or

$$(k-1)B_k=\sum_{j=1}^{k-1} A_j+\sum_{j=1}^{k-2} B_j+k-1, \qquad k\geqslant 2 \tag{3.2}$$

Equations (3.1) and (3.2) can of course be solved by generating functions, but since it is not hard to do so directly, let us choose the latter route. To start with, set $C_k=\frac{1}{2}(A_k+B_k)$, so that (3.1) and (3.2) combine to

$$\begin{aligned}(k-1)C_k&=2\sum_{j=1}^{k-2} C_j+C_{k-1}+k-1, \qquad k\geqslant 2\\ C_1&=3/2\end{aligned} \tag{3.3}$$

The thermodynamic limits of A_k, B_k, and C_k are of course identical. Now subtract (3.3) at k from (3.3) at $k+1$, giving

$$\begin{gathered}kC_{k+1}-kC_k-C_{k-1}=1, \qquad k\geqslant 2\\ C_1=\tfrac{3}{2}, \qquad C_2=\tfrac{5}{2}\end{gathered} \tag{3.4}$$

which can be extended to $k\geqslant 0$ by setting $C_{-1}=-1$. $C_0=0$. Then introduce

$$\Delta_k=C_k-C_{k-1} \tag{3.5}$$

converting (3.4) to

$$\begin{gathered}k\Delta_{k+1}-(k-1)\,\Delta_k-\Delta_{k-1}=0\\ \Delta_0=1, \qquad \Delta_1=3/2\end{gathered} \tag{3.6}$$

In the form

$$\Delta_{k+1}-\Delta_k=-\frac{1}{k}(\Delta_k-\Delta_{k-1}) \tag{3.7}$$

the solution is immediate:

$$\Delta_{k+1} - \Delta_k = \frac{1}{2} \frac{(-1)^k}{k!} \tag{3.8}$$

so that

$$\Delta_{k+1} = 1 + \frac{1}{2} \sum_0^k \frac{(-1)^j}{j!} \tag{3.9}$$

Since

$$\lim_{k \to \infty} \frac{A_k}{2k} = \lim_{k \to \infty} \frac{C_k}{2k} = \frac{1}{2} \lim_{k \to \infty} \Delta_k = \frac{1}{2}\left(1 + \frac{1}{2e}\right)$$

we conclude that

$$\rho_\infty = 1 - \lim_{k - \infty} \frac{A_k}{2k} = \frac{1}{2}\left(1 - \frac{1}{2e}\right) \tag{3.10}$$

4. TIME EVOLUTION ON SQUARE LADDER

Now let us consider the RSA kinetics on an (infinite) square ladder. The corresponding calculation for triangular ladders can be found in ref. 6 because of the mapping mentioned above. We will use a procedure analogous to that employed above for the asymptotic state, now defining $u_k(t)$ as the mean number of k-column gaps of type A per site at time t, and $v_k(t)$ for the B type. Clearly, u_k decays by particle accretion to any of its $2k-2$ available sites, and similarly for v_k, except that v_1 has only one site available. Furthermore, u_k is produced as a left or right fragment of any u_j with $j \geqslant k+2$ or any v_j with $j \geqslant k+1$. Similarly, v_k is produced from v_j with $j \geqslant k+2$ or u_j with $j \geqslant k+1$. We then have at once, under suitable scaling of time,

$$\begin{aligned}
\frac{du_k}{dt} &= 2 \sum_{j=k+1}^{\infty} v_j + 2 \sum_{j=k+2}^{\infty} u_j - (2k-2) u_k, \qquad k \geqslant 1 \\
\frac{dv_k}{dt} &= 2 \sum_{j=k+1}^{\infty} u_j + 2 \sum_{j=k+2}^{\infty} v_j - (2k-2) v_k, \qquad k \geqslant 2 \\
\frac{dv_1}{dt} &= 2 \sum_{j=2}^{\infty} u_j + 2 \sum_{j=3}^{\infty} v_j - v_1
\end{aligned} \tag{4.1}$$

As initial conditions, we may choose

$$\begin{aligned} &u_k(0)=0 \\ &\qquad \text{but} \quad \lim_{t\to 0} \sum_{k=K}^{\infty} [u_k(t)+v_k(t)]\,2k=1 \\ &v_k(0)=0 \end{aligned} \tag{4.2}$$

for any finite lower bond K.

The solution of (4.1), (4.2) is accomplished by extending the ansatz of Gonzalez *et al.*[6]:

$$\begin{aligned} u_k(t)&=u(t)e^{-(2k-2)t}, \qquad k\geqslant 1 \\ v_k(t)&=v(t)e^{-(2k-2)t}, \qquad k\geqslant 2 \end{aligned} \tag{4.3}$$

Equations (4.1) thereby reduce to

$$\begin{aligned} u'(t)&=2u(t)/(e^{2t}-1)+2v(t)e^{-2t}/(e^{2t}-1) \\ v'(t)&=2v(t)/(e^{2t}-1)+2u(t)e^{-2t}/(e^{2t}-1) \end{aligned} \tag{4.4}$$

It suffices to solve for $w=u+v$, which thereby satisfies

$$w'(t)=2w(t)(e^{-2t}+1)/(e^{2t}-1) \tag{4.5}$$

having the solution

$$w(t)=C(1-e^{-2t})^2\exp(e^{-2t}) \tag{4.6}$$

To satisfy (4.2), we need

$$\begin{aligned} &\lim_{t\to 0}\sum_{k=K}^{\infty} 2ke^{-(2k-2)t}C(1-e^{-2t})^2\exp(e^{-2t}) \\ &\qquad =\lim_{t\to 0} C(1-e^{-2t})^2\,2(1-e^{-2t})^{-2}e=1 \end{aligned}$$

or

$$C=1/2e \tag{4.7}$$

completing our solution.

The mean coverage is of course given by

$$\rho(t)=\frac{1}{2}\left\{1-2\sum_{k=1}^{\infty}[u_k(t)+v_k(t)]\right\} \tag{4.8}$$

which is readily evaluated. In particular, if $t \to \infty$,

$$\rho(\infty) = \frac{1}{2}[1 - 2u_1(\infty)] = \frac{1}{2}\left(1 - \frac{1}{2e}\right) \tag{4.9}$$

coinciding with our previous result.

5. DISCUSSION

The first observation we have from the present work is the reduction of the boundary effect when row number increases. It was noticed that the boundary effect of the 1D chain RSA model is very small and ten sites are enough to give very accurate results.[4,7] Now, comparing (2.2) with (3.9), one can see that a two-row ladder converges even more rapidly. If we consider the ladder as a lattice with two columns and infinite rows, we can reasonably expect the boundary effect to be even smaller and very few "columns," certainly less than ten, are required in order to mimic a full 2D square lattice. Notice that it is Δ_k rather than A_k in (2.2) and (3.9) that leads to very rapid convergence: we correspondingly consider

$$\begin{aligned} \Delta_1 &= 2\rho(\text{two row}) - \rho(\text{one row}) \\ &= \tfrac{1}{2}(1 - e^{-1} + e^{-2}) = 0.384 \end{aligned} \tag{5.1}$$

tolerably close to the simulation result 0.364.[8]

For lattices with more than two rows, a single particle deposition may or may not break the strip, which is the key to ref. 4 and this work. Therefore, the present technique seems not easily extendable. However, there is one simple case, and it even has the required four neighbors—namely that of three rows with periodic boundary condition in the vertical direction. It is easy to see that all "jammed" configurations have precisely one occupied site per column, so that $\rho = 1/3$. But this is not yet close to the numerical result. It seems evident that techniques which can deal with the full lattice are required, and we will report one such possibility in a separate publication.

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