Asymptotic coverage in random sequential adsorption on a lattice

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Series expansions for the time-dependent coverage in random sequential adsorption on a lattice are reviewed. A transformation is carried out, resulting in combinatorial expressions in which only nonrepeating lattice walks are required. Convergence is greatly accelerated, and application is made to the asymptotic coverage of previously solved lattices as well as Bethe lattices and cactuses, or Bethe lattices with the bonds replaced by triangles. The method is extended to multisite correlations as well.

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I. INTRODUCTION

The process of random sequential adsorption (RSA) appears in many guises in the physical sciences [1]. Most important are rather literal manifestations in which molecules randomly arriving at a surface are irreversibly adsorbed on the time scale of interest, unless previously adsorbed molecules keep them from reaching the surface, in which case they leave and try again. But local-bond formation on a polymer chain can be cast in the same form [2], as can other analogous processes. Theoretical analysis of this irreversible phenomenon has remained an active, if surprisingly refractory, area. The point of course is that local-equilibrium approximations, which can be so effective in reversible dynamics, are not suitable. Even if one only desires the true asymptotic adsorbed-particle distribution, and this is what we will focus upon, dynamical memory, or its equivalent, is a crucial component and cannot be neglected—true equilibrium for this effectively zero-temperature phenomenon would always result in close packing.

Exact theoretical results have been largely confined to one-dimensional systems [3–5], making use of Flory's original idea [2], in which one followed the attrition of unoccupied intervals. Recently, extension was made to two-row lattices, or ladders [6], but it seems very difficult to exactly solve anything more complex. What one would like is some sort of systematic expansion method, perhaps along the lines of classical [7], and quantum [8] statistical mechanics. Indeed, such expansions have been obtained [9,10], but only at short times in the dynamical process, requiring poorly controlled extrapolation techniques for the more interesting long-time regime.

In this article, we indicate how a certain amount of progress can be made in direct evaluation of asymptotic coverage (mean occupation per site) when the adsorbing sites form a translation-invariant lattice. We first review the short time series that are available, and then show how to transform them into convergent expansions for the asymptotics. We apply this, analytically and numerically, to two previously solved cases as a check, and then to Bethe lattices and a cactus, in which the enormous surface provides a very severe test of convergence properties. We conclude with a brief extension to multisite correlations.

II. TIME-SERIES EXPANSION

Let us consider a regular lattice, initially unoccupied, to which particles are being randomly adsorbed under the restriction of nearest-neighbor exclusion. The condition that site y is a nearest neighbor of x will be denoted by $\langle y,x\rangle$. If, in the usual notation, $\nu_x=1$ or 0 as a particle is present or absent at site x, a configuration of the lattice can be given the occupation-number representation

$$|\Psi\rangle=|\{\nu_x\}\rangle\ , \tag{2.1}$$

which is a unit vector in the space of weighted configurations. Explicitly, each $|\{\nu_x\}\rangle$ is the direct product over all sites of two-component unit vectors $|0\rangle=\binom{1}{0}$ or $|1\rangle=\binom{0}{1}$. Suppose that $\{a_x,a_x^\dagger\}$ are the standard boson annihilation and creation operators, but that matters are arranged so that no state with $\nu_x>1$ ever occurs. Then

$$a=\begin{bmatrix}0&1\\0&0\end{bmatrix},\quad a^\dagger=\begin{bmatrix}0&0\\1&0\end{bmatrix}$$

per site on our restricted state space, and the particle number and vacancy number operators are

$$n_x=a_x^\dagger a_x,\quad \bar{n}_x=a_x a_x^\dagger\ , \tag{2.2}$$

satisfying

$$n_y|\{\nu_x\}\rangle=\nu_y|\{\nu_x\}\rangle,\bar{n}_y|\{\nu_x\}\rangle=(1-\nu_y)|\{\nu_x\}\rangle\ .$$

We follow quite directly the derivation of Dickman, Wang, and Jensen [10]. The initial state is

$$|\Psi_0\rangle=|\{0\}\rangle\ ; \tag{2.3}$$

a transition adds a particle at x at unit rate if x and its nearest neighbors are vacant, corresponding to the transition operator

$$T^+=\sum_x a_x^\dagger\left[\prod_{\langle y,x\rangle}\bar{n}_y\right]\ . \tag{2.4}$$

On the other hand, a configuration is removed by accretion at any site x which, with its nearest neighbors, is vacant:

$$T^- = \sum_x \bar{n}_x \left[\prod_{\langle y,x \rangle} \bar{n}_y \right] . \tag{2.5}$$

It follows that if the ensemble of system states is given by the weighted average

$$|\Psi(t)\rangle = \sum_{\{\nu_x\}} P(\{\nu_x\},t)|\{\nu_x\}\rangle \tag{2.6}$$

with normalized probability

$$\sum_{\{\nu_x\}} P(\{\nu_x\},t)=1 , \tag{2.7}$$

then

$$\frac{\partial}{\partial t}|\Psi(t)\rangle = \sum_x (a_x^\dagger - \bar{n}_x) \left[\prod_{\langle y,x \rangle} \bar{n}_y \right] |\Psi(t)\rangle \tag{2.8}$$

with $\Psi(0)=|\{0\}\rangle$.

We will first be interested in the time dependence of the coverage of the lattice, the mean occupation per site, which for a translation-invariant system is the mean occupation at any site, say at the origin $x=0$:

$$\rho(t) = \sum_{\{\nu_x\}} \nu_0 P(\{\nu_x\},t) . \tag{2.9}$$

In terms of the unnormalized universal state defined by

$$|\Psi_u\rangle = |\{u_x\}\rangle \tag{2.10}$$

where

$$u = \begin{bmatrix}1\\0\end{bmatrix} + \begin{bmatrix}0\\1\end{bmatrix} = \begin{bmatrix}1\\1\end{bmatrix} ,$$

this is simply

$$\rho(t) = \langle \Psi_u | n_0 | \Psi(t) \rangle . \tag{2.11}$$

Now (2.8), with time-independent transition operator, can be solved at once in exponential form, so that on expanding out the exponential,

$$\begin{aligned}\rho(t) &= \langle \{u\}| n_0 \exp\left[t \sum_x (a_x^\dagger - \bar{n}_x) \left[\prod_{\langle y,x \rangle} \bar{n}_y \right] \right] |\{0\}\rangle \\ &= \sum \frac{t^k}{k!} \langle \{u\}| n_0 \left[\sum_x (a_x^\dagger - \bar{n}_x) \left[\prod_{\langle y,x \rangle} \bar{n}_y \right] \right]^k |\{0\}\rangle \\ &= \sum \frac{t^k}{k!} \langle \{u\}| n_0 \sum_{\{x_j\}} \prod_{j=1}^{k} \left[(a_{x_j}^\dagger - \bar{n}_{x_j}) \left[\prod_{\langle y,x_j \rangle} \bar{n}_y \right] \right] |\{0\}\rangle .\end{aligned} \tag{2.12}$$

This is evaluated [10] by commuting successive factors $a_{x_j}^\dagger - \bar{n}_{x_j}$ through to the left. Since

$$\langle u | a^\dagger - \bar{n} | 0 \rangle = 0 , \tag{2.13}$$

but $\langle u|\bar{n}(a^\dagger - \bar{n})|0\rangle = -1$, a contribution of -1 results whenever x_j is identical to a previous x_i or one of its next neighbors; otherwise 0 results. The case $x=0$ is special, but here

$$\langle u | n_0 (a_x^\dagger - \bar{n}_x) = \langle u | \bar{n}_0 \delta_{x,0} , \tag{2.14}$$

so that necessarily $x_1 = 0$, with an associated + sign.

We conclude with Evans [9] and Dickman, Wang, and Jensen [10] that

$$\rho(t) = \sum_{k=1}^{\infty} \frac{(-1)^{k-1}}{k!} S(k-1) t^k , \tag{2.15}$$

where $S(k-1)$ is the number of paths, starting at 0, with $k-1$ further sites, each a repeat or a nearest neighbor of a previous site.

III. ASYMPTOTIC COVERAGE

The combinatorial quantity $S(k)$ grows very rapidly with k. Computer evaluations [10] have thus focused on various building blocks to reduce the work involved; such reductions are also useful for analytic purposes, and then serve as well to organize computations more effectively. In the above formulation, the fact that $S(k)$ allows repeats of a given site is obviously inefficient. To eliminate this redundancy, it is useful to first take the Laplace transform of (2.15), term by term, assuming convergence:

$$\begin{aligned}\tilde{\rho}(s) &= \int_0^\infty \rho(t) e^{-st} dt \\ &= -\frac{1}{s} \sum_{n=0}^{\infty} S(n)/(-s)^{n+1}\end{aligned} \tag{3.1}$$

for sufficiently large s. Now suppose N_k represents the number of length $k+1$ nonrepeated paths starting at the origin, where each site visited must be a strict neighbor of a previous site, and associate with it the weight $N_k/(-s)^{k+1}$. The $S(n)/(-s)^{n+1}$ are then produced from the $N_k/(-s)^{k+1}$ by choosing to repeat none, one, two, or more of the $l+1$ distinct sites available after the lth step of the N_k walk, and giving each choice a weight of $(-1/s)$. Hence

$$\sum_{n=0}^{\infty} S(n)/(-s)^{n+1} = \sum_{k=0}^{\infty} N_k \Big/ (-s)^{k+1} \prod_{l=0}^{k} \left[1 + \frac{l+1}{-s} + \left[\frac{l+1}{-s} \right]^2 + \cdots \right]$$
$$= \sum_{k=0}^{\infty} N_k \Big/ (-s)^{k+1} \prod_{l=0}^{k} \frac{s}{s+l+1}$$
$$= \sum_{k=0}^{\infty} (-1)^{k+1} N_k \Big/ \prod_{l=0}^{k} (s+l+1) , \tag{3.2}$$

yielding the transformed expression

$$\tilde{\rho}(s) = \frac{1}{s} \sum_{k=0}^{\infty} (-1)^k N_k \Big/ \prod_{l=0}^{k} (s+l+1) . \tag{3.3}$$

A quick estimate of N_k can be made. Each member path has a "volume" of $k+1$ sites, and hence a "surface" of next neighbors which would go as $A(k+1)^{\alpha} N_k$, where $\alpha = (d-1)/d$ for a compact d-dimensional cluster, may be closer to 1 for a fractal diffusion-limited-aggregation-type accumulation (but in N_k, filling can also occur at internal sites), and $\alpha = 1$ for a Bethe lattice. In other words, one anticipates $n_k \propto A^k (k!)^{\alpha}$, where $\alpha \leq 1$. If $\alpha < 1$, $s\tilde{\rho}(s)$ of (3.3) will converge, even as $s \to 0$, but when $\alpha = 1$, the situation is more delicate.

The expansion (3.3) can be revealingly simplified. We note that

$$1/\textstyle\prod_{l=0}^{k}(s+l+1) = \Gamma(s+1)/\Gamma(s+k+2)$$
$$= (1/k!)\Gamma(s+1)\Gamma(k+1)/\Gamma(s+k+2)$$
$$= (1/k!)B(s+1,k+1)$$
$$= (1/k!)\textstyle\int_0^1 (1-x)^s x^k dx ,$$

so that

$$\tilde{\rho}(s) = \frac{1}{s} \int_0^1 (1-x)^s \left[\sum_{k=0}^{\infty} \frac{(-1)^k x^k}{k!} N_k \right] dx . \tag{3.4}$$

Hence, taking the inverse Laplace transform,

$$\rho(t) = \int_0^1 \epsilon \left[t - \ln \frac{1}{1-x} \right] \sum_{k=0}^{\infty} \frac{(-1)^k x^k}{k!} N_k dx , \tag{3.5}$$

telling us that if we define

$$N(x) = \sum_{k=0}^{\infty} \frac{(-1)^k x^{k+1}}{(k+1)!} N_k , \tag{3.6}$$

then we have simply

$$\rho(t) = N(1-e^{-t}) . \tag{3.7}$$

It is clear from (3.7) that the appropriate expansion variable is not t, but rather $1-e^{-t}$, a remark that has been made before [11], and further that the asymptotic density, assuming convergence of the series for $N(x)$, is just

$$\rho_{\infty} = \lim_{x \to 1} N(x) . \tag{3.8}$$

The expression (3.6) was used in a special case by Dickman, Wang, and Jensen [10] for organizing computations. It has also been obtained [11] in a rather different fashion and some of its properties assessed, the definition of N_k being, however, somewhat obscure. From our derivation, it is clear that the validity of (3.6) is not restricted to nearest-neighbor exclusion or to single-particle deposition.

IV. EXAMPLES

Consider a one-dimensional lattice. An N_k configuration must consist of a string of $k+1$ occupied sites. Each such configuration gives rise to two of N_{k+1} by placing a particle either on the left edge or the right. Hence $N_k = 2^k$, so that

$$N'(x) = \sum_{k=0}^{\infty} \frac{(-1)^k x^k}{k!} N_k$$
$$= e^{-2x} \tag{4.1}$$

and

$$\rho_{\infty} = \int_0^1 N'(x) dx$$
$$= \tfrac{1}{2}(1-e^{-1}) , \tag{4.2}$$

a familiar result [2].

Let us proceed to a square ladder, for which RSA has recently been solved [6]. Here one can have holes inside a connected N_k configuration, so that N_k grows more rapidly. However, computer counting of configurations is readily organized, and N_k has been determined for $k \leq 30$. By this stage, the convergence of $N(x)$, or of ρ_{∞} directly from (3.8), has become evident (see Table I), yielding a value within 10^{-9} of the exactly known

$$\rho_{\infty} = \tfrac{1}{2} \left[1 - \frac{1}{2e} \right] . \tag{4.3}$$

The case of a Bethe lattice (infinite regular Cayley tree) has interest of its own, for now the surface is enormous, leading to rapid growth of the N_k. This problem was previously solved by Evans [12], in a somewhat different version. Suppose we have a q-neighbor Bethe lattice. Then it is readily shown by induction that a connected fragment of size n has precisely $n(q-2)+2$ sites available at its outer surface (adding a site destroys the availability of one site, but produces $q-1$ new ones). Hence

TABLE I. Terms and partial sums in series expansion of ρ_∞. Here $\rho(k)\equiv\sum_{l=0}^{k}(-1)^l N_l/(l+1)!$, and the numbers in square brackets denote power-of-10 factors.

k	$\rho(k)$	$N_k/(k+1)!$
0	1	1
1	−0.5	1.5
2	1.5	2
3	−0.6667	2.1667
4	1.3333	2
5	−0.3	1.6333
6	0.9016	1.2016
7	0.0915	8.1012[−1]
8	0.5972	5.0569[−1]
9	0.3021	2.9508[−1]
10	0.4641	1.6203[−1]
11	0.3799	8.4234[−2]
12	0.4215	4.1649[−2]
13	0.4018	1.9669[−2]
14	0.4108	8.9016[−3]
15	0.4069	3.8726[−3]
16	0.4085	1.6236[−3]
30	0.4080	1.5225[−9]
∞	$\frac{1}{2}(1-\frac{1}{2e})$	0

$$N_k/N_{k-1}=k(q-2)+2 \quad \text{for } k>1\ ,\quad N_0=1,\ N_1=q \tag{4.4}$$

so that

$$N_k=\prod_{j=1}^{k}[j(q-2)+2] =(q-2)^k(-1)^k\Gamma\left[-\frac{2}{q-2}\right]\Big/\Gamma\left[-\frac{2}{q-2}-k\right] . \tag{4.5}$$

It follows that

$$N'(x)=[1+(q-2)x]^{-q/(q-2)} \quad \text{for } |x|<1/(q-2)\ . \tag{4.6}$$

Now the singularity that produces the divergence of the MacLaurin series for $x>1/(q-2)$ is at $x=-1/(q-2)$, out of the range of relevance. If $q=3$, this is no problem at all: $N'(x)$ converges for $|x|<1$, and we have at once from (4.6)

$$\rho_\infty=\int_0^1 N'(x)dx =\tfrac{1}{2}(1-\tfrac{1}{4})\ . \tag{4.7}$$

If $q>3$, the analytic continuation of $N'(x)$ must be used instead, and we find

$$\rho_{\infty,q}=\tfrac{1}{2}[1-(q-1)^{-2/(q-2)}]\ . \tag{4.8}$$

A major reason for interest in the Bethe lattice, as Evans [9] has observed, is of course for the light it may shed on regular lattices with the same local structure. For example, a square lattice with local $q=4$ would have a Bethe lattice image, according to (4.6), with

$$N_4(x)=\tfrac{1}{2}\left[1-\frac{1}{1+2x}\right] =x/1+2x\ , \tag{4.9}$$

suggesting that a Padé expansion in x for a true square lattice would be a reasonable strategy. It would also give an estimated asymptotic coverage of 0.33, tolerably close to the simulation value of 0.36.

Pursuing the same line of argument, a triangular lattice, with $q=6$ and a corresponding Bethe lattice generating function

$$N_6(x)=\tfrac{1}{2}\left[1-\frac{1}{\sqrt{1+4x}}\right] \tag{4.10}$$

(and $\rho_\infty=0.28$ compared with a simulation value of 0.23) would raise questions as to the legitimacy of a Padé expansion. These would not, however, be compelling. Suppose we go to the next level of approximation for a regular triangular lattice, a cactus, or Bethe lattice with bonds replaced by triangles, in which three triangles meet at each vertex. This, by happenstance, can be analyzed in very similar fashion to (4.4)–(4.8). It is readily seen that occupation of a lattice site always increases the number of available surface sites by 3. It easily follows that $N_k/N_{k-1}=3(k+1)$, so that $n_k=3^k(k+1)!$ and

$$N_{6,\text{cactus}}(x)=\frac{x}{1+3x}\ . \tag{4.11}$$

Thus Padé expansion might again be appropriate, and incidentally an improved value of $\rho_\infty=0.25$ results.

V. DISCUSSION

The mean coverage in RSA, even in its time-dependent version, is rather sparse information as to the structure of the process. An extension that is relatively direct is to the multisite mean coverage correlations. See also Hoffman [13] and Evans, Burgess, and Hoffman [14]. For instance, suppose we ask for the pair coverage density at sites 0 and p,

$$\rho_{0p}(t)=\langle\Psi_u|n_0n_p|\Psi(t)\rangle \tag{5.1}$$

in our previous notation. Following the path (2.11)–(2.15), this becomes

$$\rho_{0p}(t)=\sum_{k=2}^{\infty}\frac{(-1)^k}{k!}S_{0p}(k-2)t^k\ , \tag{5.2}$$

where $S_{0p}(k-2)$ is the number of paths of length k starting with sites 0 and p occupied, for which each entry is identical with or a next neighbor of a previous site. Proceeding in the same fashion as (3.1)–(3.7), Eq. (5.2) translates to

$$\rho_{0p}(t)=N_{0p}(1-e^{-t})$$

where

$$N_{0p}(x)=\sum_{0}^{\infty}\frac{(-1)^k}{k+2!}N_{0p,k}x^{k+2}\ , \tag{5.3}$$

$N_{0p,k}$ denoting the number of nonrepeating length $k+2$ walks starting with sites 0, p occupied, and requiring each entry to be a next neighbor of a previous entry. The density-density correlation $\rho_{0p}-\rho_0\rho_p$ has even a simpler structure, since disconnected configurations do not appear. This opens the door to a much more detailed analysis of structure, which is now being developed.

Finally, it should be noted that the reduction from $S(n)$ to N_k greatly improves the convergence properties of the series encountered, but that, consistent with the high-density expansion that is required, many terms are needed in practice. This means that further transformations, numerically or preferably physically motivated, are mandatory if any qualitative understanding is to accompany the numerical values. One such approach, based upon the Bethe-lattice results quoted in Sec. IV is quite effective and is planned to be reported in a subsequent publication.

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