Random Sequential Adsorption,  
Series Expansion and Monte Carlo Simulation  

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Abstract  
Random sequential adsorption is an irreversible surface deposition of extended objects. In systems with continuous degrees of freedom coverage follows a power law, \( \theta(t) \approx \theta_J - c t^{-\alpha} \), where the exponent \( \alpha \) depends on the geometric shape (symmetry) of the objects. Lattice models give typically exponential saturation to jamming coverage. We discuss how such function \( \theta(t) \) can be computed by series expansions and analyzed with Padé approximations. We consider the applications of efficient Monte Carlo computer simulation method (event-driven method) to random sequential adsorptions with high precision and at very long-time scale.  

Keywords: random sequential adsorption, surface irreversible deposition, series expansion, event-driven algorithm.  
PACS numbers: 05.70.Ln, 82.20.Mj.  

1. Introduction  
Random sequential adsorption\(^1,2\) (RSA) refers to a type of irreversible adsorptions of spatially extended objects. Two features characterize RSA: (1) the objects, once on the surface, are permanently stick to the surface without further thermal relaxation; (2) only a single layer is deposited, and the objects have hardcore volume exclusion.  

A standard example\(^3\) of RSA is the adsorption of spherical macromolecular particles in solution on a glass surface. Some surface reaction dynamics may be described by RSA on lattices. In comparison with a corresponding equilibrium system of particles, RSA shows unusual properties, most notably the existence of a jamming coverage and a super-exponential correlation of particle density.  

One of the central theoretical problems in RSA is the computation of the coverage \( \theta(t) \). Such problems are intractable for exact solutions except perhaps some one-dimensional systems.\(^4,5\) Series expansion and Monte Carlo simulation offer semi-numerical or numerical results which can be improved systematically. They are perhaps
the best methods available. In this article, we describe some of the advanced techniques of attaining that goal.

2. Series Expansions

Earlier calculations\(^2,6\) in RSA were based on truncation of an infinite hierarchy of rate equations together with mean-field type approximations (and shielding property) to close the equations. It is only recently that these equations are systematically used, resulting very long series.\(^7\)\(^\text{-}\)\(^10\)

To illustrate the series expansion method,\(^9\) let us consider the deposition of dimer on square lattice. The basic quantity of interest in computing a series is the probability \(P(A)\) that the given set \(A\) of sites are empty; we do not care other sites being occupied or empty. It is a marginal probability of the full probability distribution. Such probability can only decrease. The rate of decrease is proportional to the probability that the current configuration \(A\) can be destroyed by depositing a dimer with at least one site in \(A\). Thus we have

\[
- \frac{dP(A)}{dt} \propto \sum \text{ways of destroying } A P(A').
\]

where the summation is over all possible ways of depositing a dimer at a pair of empty sites such that at least one site is in \(A\); \(A' = A\) if two of the dimer sites of a deposition attempt are within \(A\), or \(A'\) is one site more than \(A\) so that the deposition with one site in \(A\) and one site outside \(A\) can be carried out. The proportionality constant sets the time scale. Without loss of generality, we can take it to be unity. The first two equations look like these:

\[
- \frac{dP(o)}{dt} = 4 P(oo),
\]

\[
- \frac{dP(oo)}{dt} = P(oo) + 2 P(ooo) + 4 P(0o).
\]

There are four ways to destroy a single empty site, provided that the nearest neighbor site is also empty. Using the assumption that initial conditions are lattice symmetry invariant, we can write them simply as \(4P(oo)\). The second equation is derived similarly.

For a general discussion, we write the rate equations symbolically as

\[
\frac{dP(A)}{dt} = \mathcal{L} P(A),
\]

where \(\mathcal{L}\) is a linear operator defined by

\[
\mathcal{L} P(A) = \sum_{A'} c_{A'} P(A').
\]

The \(n\)-th derivative is then

\[
\frac{d^n P(A)}{dt^n} = \mathcal{L}^n P(A), \quad \text{with} \quad P(A')\big|_{t=0} = 1 \quad \text{for all } A'.
\]
The initial conditions are such that all sites are empty at $t = 0$.

The above scheme can be implemented on computer as follows: starting from some initial pattern (or called configuration) $A^{0}$, we apply $\mathcal{L}$ to get $A^{1}$, from which we obtain the first derivative at $t = 0$, as $dP(A^{0})/dt|_{t=0} = \sum_{j} c_{j}P(A_{j}^{1})|_{t=0} = \sum_{j} c_{j}^{1}$. The second derivative is obtained recursively by applying $\mathcal{L}$ again to the new patterns as

$$
\frac{d^{2}P(A^{0})}{dt^{2}} = \sum_{j} c_{j}^{1}\frac{dP(A_{j}^{1})}{dt},
$$

(6a)

$$
\frac{dP(A_{j}^{1})}{dt} = \mathcal{L}P(A_{j}^{1}) = \sum_{k} c_{k}^{2}P(A_{k}^{2}).
$$

(6b)

The superscript 2 in $c_{k}^{2}$ refers to the second generation of patterns. The relationship of the patterns and the rate equations can be represented as a tree with arbitrary number of branches. Each node of a tree contains a pattern $A$, and its associated derivatives $d^{i}P(A)/dt^{i}$ for $i = 0, 1, 2, \ldots, n$. Each node, if its derivative has been computed, has a list of pointers to the children nodes and associated coefficients $c_{j}$. Thus a node together with its children symbolically represents one rate equation.

If the tree nodes are traversed in a depth-first manner, then we need not store all the nodes at the same time. The memory requirement is proportional to the number of levels of the tree. Simple counting method usually uses this strategy. The same node may have to be expanded many times, and repeated work has to be done. However, minimum book-keeping is needed.

Computation can be performed faster if we do not repeat the same expansion and calculation. However, it is necessary then that all nodes are kept; the tree can be generated in a breadth-first fashion one level at a time. Equivalent nodes due to lattice symmetry are treated as the same node. If a particular node is already generated before, a pointer reference is made to the existing node. Such strategy is known as dynamic programming in computer science.

The most practical and efficient algorithm is a combination of several methods. To conserve memory, depth-first expansion after every $D$ levels is made; while the highest levels use a simple counting algorithm which uses a negligible amount of memory.

The above method is applicable to a wide range of problems, such as diffusion-reaction models, Ising relaxation dynamics, and other dynamic processes described by a hierarchy of rate equations.

Summary of Results

Series$^{10}$ for the dimer on square lattice (17 orders), monomer with nearest neighbor exclusion on square lattice (20 orders), dimer on honeycomb lattice (20 orders), and monomer with nearest neighbor exclusion on honeycomb lattice (23 orders) are obtained. To our knowledge, there series are the longest known.

The discrete counting problem for RSA on lattice can be generalized to RSA on continuum, where summations are replaced by integrals. We note that these integrals
can be related to the cluster integrals with a diagrammatic rule similar to the Mayer theory for fluid. A five-order series for disks and a seven-order series for aligned squares or cubes are available.\textsuperscript{7,11}

Padé Analysis of Series

Given a finite number of terms in a series, how can we say anything about the whole time domain \( t \) from 0 to \( \infty \)? Clearly it is not possible in general. Our experience with RSA series suggests that we can give reliable estimates from the series for all times.\textsuperscript{7}

The method of Padé approximants\textsuperscript{12,13} is very useful in this respect. Given a series \( f(x) \) to order \( L \), we determine two polynomials \( P_N(x) \) and \( Q_D(x) \) of degree \( N \) and \( D \) respectively, such that

\[
f(x) - \frac{P_N(x)}{Q_D(x)} = O(x^{L+1}), \quad N + D \leq L.
\]

It is a powerful way of extending the domain of convergence of the original series. To accelerate the convergence further, new variables are introduced,\textsuperscript{7} e.g.,

\[
s = 1 - \exp(-b(1 - e^{-t})).
\]

The functional form is chosen in such a way so that the series in the new variable \( s \) is most closely resemble the asymptotic behavior of the coverage \( \theta(t) \) at large \( t \). The above specific form is encouraged by the exact solution of the one-dimensional dimer problem. In fact we have \( \theta = s \) with \( b = 2 \) in such case. The convergence among various Padé approximants is improved greatly by the transformation.

Here is an example of Padé approximant for the dimer on square lattice

\[
\left( 2.962963 \ s + 0.03206897 \ s^2 - 2.195246 \ s^3 - 1.073721 \ s^4 + 0.9207869 \ s^5 + 0.5556586 \ s^6 \\
- 0.043856743 \ s^7 - 0.05303456 \ s^8 \right) / \left( 1 + 1.733045 \ s - 0.2568919 \ s^2 - 1.942572 \ s^3 \\
- 0.5852424 \ s^4 + 0.7908992 \ s^5 + 0.4421557 \ s^6 - 0.0493306 \ s^7 - 0.0513337 \ s^8 \right),
\]

where \( s \) is given by Eq. (8) with \( b = 1.35 \). The result is stable against variation in \( b \). Error can be estimated from the convergence of various Padé approximants and Monte Carlo simulation results. The above Padé approximant is accurate to \( 10^{-5} \) for all \( t \geq 0 \). Such a high degree of accuracy embedded in a simple formula is remarkable.

3. Monte Carlo Simulation

Monte Carlo simulation\textsuperscript{14–16} is a simple and useful method to get a quick result on an otherwise difficult problem by analytical means. RSA model can be simulated rather easily with a simple program. Our emphasis here is how to make Monte Carlo simulation more efficient. During late stage of simulation, most of the sites are already
occupied or blocked and few adsorption attempts may succeed. The dynamics thus becomes very slow, especially for deposition on continuum.

To overcome such slow dynamics, event-driven algorithms\textsuperscript{16–19,22} are devised where the deposition attempts can be chosen in such a way so that it is accepted with a high probability.

To illustrate the method, let us look at the dimer RSA on square lattice again. At late stage, the number of places where a dimer can be placed is small. We can afford to enumerate them and store them in a list. In the next stage of simulation, we pick a possible dimer position from the list randomly, and make the deposition attempt. The difference between the new method and the original is that time step has to be different. In particular, each deposition attempt taken from the list should advance the time step stochastically by

\[ \delta t = \frac{1}{N_{\text{tot}}} \left( \left\lfloor \frac{\ln \xi}{\ln(1 - r)} \right\rfloor + 1 \right), \]

where \( N_{\text{tot}} \) is total number of lattice sites, and \( r \) is the ratio of the number of ways of possible depositions on the list to the total number of ways of depositions. \( \xi \) is a uniformly distributed random number between 0 and 1. The original method has a constant time step \( 1/N_{\text{tot}} \).

Similar idea is used for RSA of disks on continuum,\textsuperscript{18} where the area is divided into small squares. Each square is classified as available or unavailable for further deposition. The classification is nontrivial, but can be done efficiently in two dimensions. The new algorithm enable us to simulate the system until jamming state in finite computer time. We confirmed the Feder’s law\textsuperscript{14}

\[ \theta(t) - \theta_J \propto t^{-1/2}, \]

and also obtained a very precise value for the jamming coverage \( \theta_J \approx 0.547069 \).

An important application of the event-driven algorithms in RSA is the deposition of more complex objects\textsuperscript{19} like polymers and macromolecules represented as random walks. A lattice RSA model that we have proposed describes an irreversible adsorption of polymer chains in good solvent (self-avoiding random walks). The coverage is a very slow function of time. Thus a straightforward simple algorithm can only probe the short-time behavior. The event-driven algorithm requires to list all the available ways of deposit polymers on the lattice. Clearly such enumeration is not possible for long chains due to the huge number of possible configurations a polymer can take. Thus we only enumerate the first few steps of the chain, and sample remaining sites stochastically. The length of the stored segments of the chains is dictated by the computer memory available. The event-driven method substantially extends the time scale, and is able to simulate the process over 12 decades in time. Our numerical results suggest that the coverage as a function of time obeys

\[ \theta - \theta_J \propto t^{-2/N}, \]
in a broad time domain for long chains, where $N$ is the length of the self-avoiding walks. The jamming coverage is consistent with $\theta_J \propto N^{-0.1}$.

When the objects in RSA deposition are allowed to relax, specifically, a random diffusion on the surface, the picture changes a lot. In particular, a full coverage can be reached (depends on the geometry of the objects). RSA with diffusional relaxation is studied by Monte Carlo simulations\textsuperscript{20,21} as well as series expansions.\textsuperscript{22} Unlike simple RSA, the late stage dynamics typically obeys a power law even on discrete lattices. Some of the peculiar behavior\textsuperscript{21} have not been understood very well. Other research direction is the adsorption involving multi-layers.\textsuperscript{23,24} It is interesting to investigate new phenomena and to develop efficient methods for such more complex problems.

Acknowledgements

The author would like to thank R. Dickman, C.-K. Gan, P. Nielaba, and V. Privman for many of the collaborative work. This work is supported in part by an Academic Research Grant, No. PR950601, of National University of Singapore.

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