Exact bounds from a new series-expansion method for random sequential adsorption

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Abstract. We present a new series-expansion method for the analysis of the covering fraction Θ in a random sequential adsorption process with nearest-neighbour exclusion on a lattice. It is the first method to yield sequences of increasing lower bounds and decreasing upper bounds on Θ. It is illustrated by numerical calculations for the hexagonal lattice.

1. Introduction

Random sequential adsorption (RSA) in its simplest form is the process in which a surface, represented by a two-dimensional lattice, is successively filled with particles. The particles are deposited irreversibly onto randomly picked lattice sites, with the condition that an occupied site makes the subsequent occupation of a neighbouring site impossible. Hence the process comes to a natural standstill when a final state is reached in which no particles can be deposited any more. The theoretical interest in this process focuses first of all on the average fraction $\Theta(t)$ of lattice sites occupied after a time t, and in particular on its value $\Theta(\infty)$ in the final state. In the absence of exact solutions in two dimensions Monte Carlo simulations, approximate closed-form solutions, and series expansions have been used. An excellent overview of all this and other RSA work has been given recently by Evans [1]. New experimental techniques in RSA have recently been reviewed by Ramsden [2].

This work deals with an expansion method for the covering fraction. Series expansions for lattice RSA have been considered previously by Widom [3], by Evans [4], by Hoffman [5], by Baram and Kutasov [6], and by Dickman, Wang and Jensen [7]. All these authors write the deposition rate $d\Theta(t)/dt$ in the form of an initial time expansion

$$\frac{d\Theta(t)}{dt} = 1 + c_1 t + c_2 t^2 + \dots \tag{1.1}$$

and construct algorithms for the calculation of the coefficients c_i. When the first few coefficients are known, $\Theta(\infty)$ can be estimated by an extrapolation method.

Here we present a new expansion method which focuses directly on the covering fraction $\Theta(\infty)$ of the final state. The method leads to exact upper and lower bounds on $\Theta(\infty)$ and is, to our knowledge, the first one that does so. The bounds presented in this paper still leave a rather wide interval for $\Theta(\infty)$ and cannot, at lowest orders, compete with other estimates. However, they can be successively improved, even though the diagrams to be considered

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become rapidly more complicated. The method starts from the observation, explained in section 2, that the final states on a lattice of N sites may be viewed as resulting from the permutations of N objects. The method's general principles are explained in sections 3 and 4, and it is applied to the hexagonal lattice in sections 5 and 6. In section 7 we present various comments and a conclusion.

2. Basis of expansion method

2.1. How a final state is determined by a permutation

We consider a random sequential adsorption (RSA) process with nearest-neighbour exclusion on a lattice of N sites, numbered from 1 to N. Let the lattice be regular and with periodic boundary conditions in such a way that all sites are equivalent. Let the adsorption process take place in continuous time, so that each site i, in each time interval dt, is occupied with a probability γdt. Upon rendering the time t dimensionless we may choose $\gamma = 1$. Let the process start at $t = 0$. We associate with each site i the instant of time τ_i at which the *first attempt* was made to occupy it. The τ_i are independent random variables distributed according to the probability law

$$p(\tau_i)d\tau_i = e^{-\tau_i}d\tau_i. \tag{2.1}$$

We now note that, whereas the *first* attempt to adsorb a particle on site i may be successful or not, any subsequent attempt to adsorb a particle on that site has no effect on the configuration. Therefore the full adsorption process, from the initially empty lattice until the final or 'jammed' state, is uniquely determined by the N-component vector

$$\tau \equiv (\tau_1, \tau_2, \cdots, \tau_N). \tag{2.2}$$

Hence averages on all realizations of the process can be calculated as averages on all τ. If one is not interested in the full time evolution of the adsorption process but only in the final state, then it suffices to know the ordering relation between the τ_i, that is, the permutation $\mathcal{P}$ of N elements for which

$$\tau_{\mathcal{P}_1} < \tau_{\mathcal{P}_2} < \cdots < \tau_{\mathcal{P}_N}. \tag{2.3}$$

Hence there is a mapping from the set of permutations to the set of final states. All $N!$ permutations will occur with the same probability $1/N!$. Since the total number of final states grows only exponentially with N, the permutations determine the final states via a many-to-one relation.

Finally, it is clear that instead of obtaining all permutations from τ, one may just as well obtain them from the N-component vector

$$x = (x_1, x_2, \cdots, x_N) \tag{2.4}$$

whose components are identically distributed independent random variables with an arbitrary distribution $\tilde{p}(x_i)$. Later on we shall take for $\tilde{p}(x_i)$ the uniform distribution on the interval $[0, 1]$.

2.2. Implementation: the 'sweep' algorithm

We now describe an algorithm for generating RSA final states that is useful both for implementation in computer simulations and for the theoretical analysis of this work. Let an integer $\mathcal{P}_i$ be assigned to each site i of a lattice of N sites, where $\mathcal{P}$ is a permutation of N elements. We now ask how, for this $\mathcal{P}$, one can obtain the final state. From the construction of the permutations it is clear that this can be done by an iterative procedure consisting of performing alternately two types of sweeps through the lattice, numbered $1, 2, 3, \ldots$. In an odd sweep, only the number of occupied sites is allowed to increase; in an even sweep, only the number of blocked sites. The sweeps are defined as follows.

Sweep 1. Occupy each site i whose $\mathcal{P}_i$ is less than the $\mathcal{P}_j$ of all its neighbours j.

Sweep 2. Block the neighbours of all sites that have been occupied in sweep 1.

For $k = 2, 3, 4, \ldots$:

Sweep $2k - 1$. Go through all sites i that are not yet occupied or blocked; occupy site i if $\mathcal{P}_i$ is less than the $\mathcal{P}_j$ of all its neighbours j that are neither occupied nor blocked.

Sweep $2k$. Block the neighbours of all sites that have been occupied in sweep $2k - 1$.

We have observed in practice, for a hexagonal lattice of 480 sites, that after the first two sweeps the sites that are neither blocked nor occupied form small disjoint clusters. Typically about five occupying sweeps alternating with blocking sweeps suffice to reach the final state.

3. Arrow configurations

For one to be able to construct the final state according to the above algorithm, it suffices to know, for each pair of neighbouring sites i and j, the value ($+1$ or -1) of

$$a_{ij}(\mathcal{P}) = \text{sign}(\mathcal{P}_i - \mathcal{P}_j). \tag{3.1}$$

We can represent this sign by an arrow on the bond (i, j), pointing from the site with the lower one of $\mathcal{P}_i$ and $\mathcal{P}_j$ to the site with the higher one. The set $\mathcal{A}$ of arrow configurations $a \equiv \{a_{ij}\}$ is intermediate between the set of permutations and the set of final states. Each permutation $\mathcal{P}$ leads to a unique $a(\mathcal{P})$ and from there to a unique final state. The relation between the $\mathcal{P}$'s and the a's is many-to-one and the relation between the a's and the final states is also many-to-one. Whereas all permutations have the same weight, the weight $P(\alpha)$ of an arrow configuration $\alpha \equiv \{\alpha_{ij}\}$ is

$$P(\alpha) = \frac{1}{N!} \sum_{\mathcal{P}} \prod_{\langle i,j \rangle} \delta(\alpha_{ij}, a_{ij}(\mathcal{P})). \tag{3.2}$$

Here $\delta(.\,,.)$ is the Kronecker delta and $\langle i, j \rangle$ denotes a pair of neighbouring lattice sites. Returning to the continuous formulation of the sum on permutations (see the final paragraph of section 1) we can write equation (3.2) alternatively as

$$P(\alpha) = \int_0^1 dx_1 \cdots \int_0^1 dx_N \prod_{\langle i,j \rangle} \vartheta(\alpha_{ij}(x_i - x_j)) \tag{3.3}$$

where ϑ is the unit step function. The weight of a subset $\mathcal{A}' \subset \mathcal{A}$ of arrow configurations is obtained by summing $P(a)$ on all $a \in \mathcal{A}'$. Obviously we have the normalization

$$\sum_{a \in \mathcal{A}} P(a) = 1. \tag{3.4}$$

The final state average of any observable $X(a)$ is

$$\langle X \rangle \equiv \frac{1}{N!} \sum_{\mathcal{P}} X(a(\mathcal{P})) = \sum_{a \in \mathcal{A}} X(a) P(a). \tag{3.5}$$

The arrow configurations a and their weights (3.3) will be at the basis of our explicit calculations.

4. The covering fraction

Consider the final state determined by an arrow configuration a. Let $n(a)$ be equal to 1 if in this state the origin is occupied (and equal to 0 otherwise), and let $\bar{n}(a)$ be equal to 1 if the origin is blocked (and equal to zero otherwise). Obviously, $n(a) + \bar{n}(a) = 1$. Since all sites are equivalent, the covering fraction $\Theta(\infty)$ is equal to

$$\Theta(\infty) = \sum_{a \in \mathcal{A}} n(a) P(a) \tag{4.1a}$$

$$= 1 - \sum_{a \in \mathcal{A}} \bar{n}(a) P(a). \tag{4.1b}$$

Let $n_k(a)$ and $\bar{n}_k(a)$ be defined in the same way as $n(a)$ and $\bar{n}(a)$, but with respect to the state that prevails after sweep $2k$ of the sweep algorithm. Obviously, $n_k(a) + \bar{n}_k(a) \leqslant 1$. Let

$$\Theta_k \equiv \langle n_k \rangle$$
$$\bar{\Theta}_k \equiv 1 - \langle \bar{n}_k \rangle. \tag{4.2}$$

Then, for $k = 1, 2, 3, \ldots$, the Θ_k form an increasing sequence and the $\bar{\Theta}_k$ a decreasing sequence such that

$$\lim_{k \to \infty} \Theta_k = \lim_{k \to \infty} \bar{\Theta}_k = \Theta(\infty). \tag{4.3}$$

There now remains to be found a way to determine the Θ_k and $\bar{\Theta}_k$. It is here that the arrow configurations play an important rôle.

We first make the following general remark. If the summation on a in (4.1) is restricted to some subset of $\mathcal{A}$, then (4.1a) obviously gives a lower bound and (4.1b) an upper bound on the coverage $\Theta(\infty)$. Hence from a nested sequence of subsets that tends to $\mathcal{A}$ one can deduce, in principle, an increasing sequence of lower bounds and a decreasing sequence of upper bounds on $\Theta(\infty)$. We shall now explicitly identify the subsets which will enable us to numerically calculate the bounds Θ_k and $\bar{\Theta}_k$. It will appear that these subsets are determined by imposing the arrow directions in certain finite neighbourhoods of the origin. Our discussion will be for the example of the hexagonal lattice, but can easily be adapted to other lattices.

5. Lower bounds

5.1. Diagrams representing subsets of arrow configurations

We introduce the following notation. A diagram consisting of a finite number of lattice sites joined by nearest-neighbour bonds, some or all of which carry arrows, will represent the set of all arrow configurations that coincide with the diagram on the arrow-carrying bonds (and are arbitrary otherwise). We shall denote such subsets of $\mathcal{A}$ by script letters.

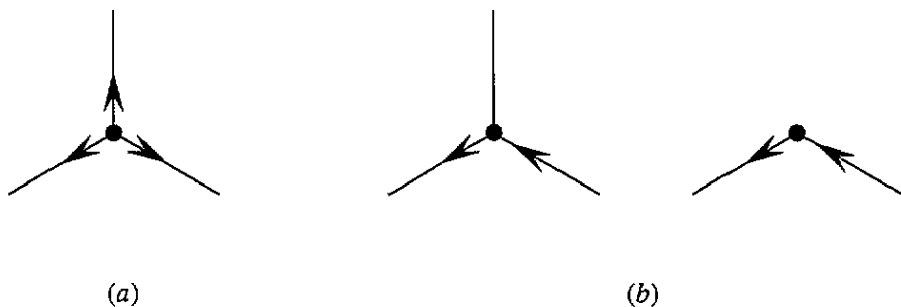(a)   (b)

Figure 1. Examples of sets of arrow configurations. (a) Diagram representing the set of arrow configurations with the origin surrounded by three outgoing arrows. (b) Two equivalent diagrams representing the set of arrow configurations having the origin surrounded by two arrow-carrying bonds oriented as indicated, the orientation of the vertical bond remaining arbitrary.

For example, the diagram of figure 1(a) represents the set of all arrow configurations where the origin (indicated here and henceforth by a heavy dot) is surrounded by three outgoing arrows; the diagrams of figure 1(b) both represent the set of all arrow configurations where the origin has one arrow incoming from the right and one outgoing to the left, the orientation of the third one remaining arbitrary.

5.2. The lower bound Θ_1

In the algorithm of section 2, the origin is occupied in the first sweep if and only if the arrow configuration is in the subset of $\mathcal{A}$ shown in figure 1(a). We call this subset $\mathcal{A}_1$. One can immediately see that the probability for this to happen is $\frac{1}{4}$, and hence we have the lower bound

$$\Theta_1 = \frac{1}{4}. \tag{5.1}$$

For the formal derivation of this result, we associate with the origin and with the three surrounding sites the variables x_0 and x_1, x_2, x_3, respectively. Θ_1 is equal to the total weight of the set $\mathcal{A}_1$, for which we get, from equation (3.3) and the remark following it,

$$\Theta_1 = \int_0^1 dx_0 \int_0^1 dx_1 \int_0^1 dx_2 \int_0^1 dx_3\, \vartheta(x_1 - x_0)\vartheta(x_2 - x_0)\vartheta(x_3 - x_0)$$

$$= \frac{1}{4}. \tag{5.2}$$

5.3. Simplified notation

In order to calculate increasingly better lower bounds $\Theta_2, \Theta_3, \ldots$, it is useful to introduce the following simplified notation.

(1) A star of three bonds joining at a central lattice site will be replaced by a triangle. The arrows on the bonds will be represented on the triangle in the following way.

(1a) A vertex connected to the central site by an ingoing arrow will be decorated by an arc.

(1b) A vertex connected to the central site by an outgoing arrow will not be decorated.

(1c) A vertex connected to the central site by an unoriented bond will be circled. A vertex common to two or more triangles will never be of this type, so that no confusion can arise.

These rules are illustrated by figure 2.

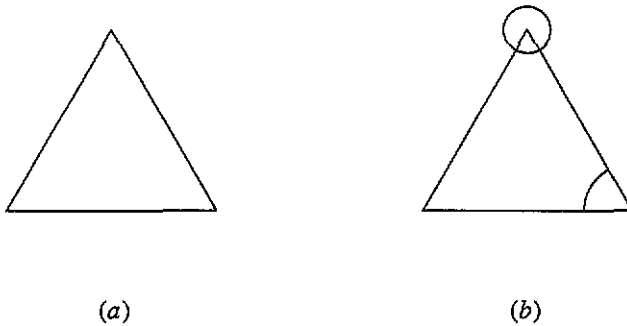(a)   (b)

Figure 2. Examples of the alternative notation introduced in subsection 5.3. The diagrams (a) and (b) represent the same sets of arrow configurations as figures 1(a) and (b), respectively.

(2) A set symbol $\mathcal{B}$, or the diagram representing it, when occurring in an arithmetic expression or equation, will henceforth stand not for the set $\mathcal{B}$ itself, but for its contribution $\Theta_{\mathcal{B}}$ to $\Theta(\infty)$. That is, we shall write

$$\mathcal{B} \equiv \sum_{a \in \mathcal{B}} n(a) P(a). \tag{5.3}$$

By contrast, the usual identity between sets, when it occurs, will be written with the aid of the symbol $\overset{s}{=}$. Obviously, to the set identity $\mathcal{B} \overset{s}{=} \mathcal{C} \cup \mathcal{D}$ corresponds the arithmetic identity

$$\mathcal{B} = \mathcal{C} \cup \mathcal{D}$$

$$= \sum_{a \in \mathcal{C} \cup \mathcal{D}} n(a) P(a)$$

$$= \mathcal{C} + \mathcal{D} - \mathcal{C} \cap \mathcal{D}. \tag{5.4}$$

In the particular case where

$$\mathcal{D} = \sum_{a \in \mathcal{D}} n(a) P(a) = 0 \tag{5.5}$$

equation (5.4) reduces to

$$\mathcal{B} = \mathcal{C} \tag{5.6}$$

which holds even if the *sets* $\mathcal{B}$ and $\mathcal{C}$ are distinct.

5.4. General method and lower bound Θ_2

We now present an expansion method that leads to increasingly better upper bounds. Its principle is to decompose the full set $\mathcal{A}$ of all arrow configurations into disjoint subsets, some of the subsets into smaller subsets, etc. The purpose is to identify progressively subsets of which all arrow configurations have the origin occupied, and other subsets of which all arrow configurations have the origin blocked. Subsets of the first type contribute to $\Theta(\infty)$ an amount equal to their weight, and subsets of the second type contribute zero.

We begin by expressing $\Theta(\infty)$ as the sum of the contributions from the eight disjoint subsets having specified arrows on the three bonds around the origin. This gives, with the notation convention of the preceding subsection,

$$\Theta(\infty) = \triangle \cup 3 \triangle \cup 3 \triangle \cup \triangle \tag{5.7}$$

where the coefficients 3 indicate that three copies of the same set, related by lattice symmetry operations, have to be considered. We shall denote the sets represented by the diagrams of equation (5.7) by $\mathcal{A}_1$, $\mathcal{R}_1$, $\mathcal{R}_2$, and $\mathcal{R}_3$, respectively. All arrow configurations of $\mathcal{A}_1$, because of the three arrows coming out of the origin, have the origin occupied in the first sweep. The contribution of $\mathcal{A}_1$ to $\Theta(\infty)$ was easily found to be equal to $\Theta_1 = \frac{1}{4}$ in subsection 5.2. In the three remaining sets in equation (5.7) the origin is not occupied in the first sweep, and it may or may not be in a later sweep. Therefore, in order to find the contributions of $\mathcal{R}_1$, $\mathcal{R}_2$, and $\mathcal{R}_3$ to $\Theta(\infty)$, a further expansion is required. We first look at $\mathcal{R}_1$. In this set the origin will be occupied if and only if the upper vertex is blocked in a later sweep, which in turn can happen only if at least one of the two bonds that join the upper vertex from the upper right and left carries an arrow pointing towards that vertex. This condition defines the subset

$$\triangle \quad \cup \quad \triangle$$

of $\mathcal{R}_1$, whose contribution to $\Theta(\infty)$ is equal to that of $\mathcal{R}_1$ itself. Therefore we have, with the notation convention of subsection 5.3,

$$\mathcal{R}_1 \stackrel{s}{=} \triangle \quad \cup \quad \triangle \tag{5.8}$$

We note now the set identity

$$\triangle \stackrel{s}{=} \triangle \cup \triangle \cup \triangle \cup \triangle \tag{5.9}$$

and its counterparts obtained by rotations over multiples of $2\pi/3$. By substituting this identity into equation (5.8) we can further expand the set $\mathcal{R}_1$. We shall not pursue here the analysis of the full expansion, but only extract directly the contribution of $\mathcal{R}_1$ to Θ_2, which we shall call $\Theta_2^{(1)}$. This contribution is characterized by the fact that the origin is occupied in the third sweep, which happens if and only if at least one of the two upper triangles has its centre occupied in the first sweep. (We recall that the second sweep blocks the neighbours of the sites occupied in the first sweep.) This defines a subset in the above expansion, and we find

$$\Theta_2^{(1)} = \quad \triangle \quad \cup \quad \triangle \tag{5.10a}$$

$$= 2 \quad \triangle \quad - \quad \triangle \triangle \tag{5.10b}$$

where the second equality is obtained by using the general identity (5.4) as well as lattice symmetry. The numerical values of the diagrams are equal to the weights of the corresponding sets. These are easily calculated according to equation (3.3) and we find

$$\Theta_2^{(1)} = \frac{3}{140}. \tag{5.11}$$

The remaining diagrams in $\mathcal{R}_1$ will contribute only to $\Theta_3, \Theta_4, \ldots$.

We turn now to $\mathcal{R}_2$ in equation (5.7), and shall directly extract from it its contribution $\Theta_2^{(2)}$ to $\Theta(\infty)$. The origin will be occupied in the third sweep if and only if each of the two bottom vertices has at least one neighbouring site that is occupied in the first sweep. Therefore $\Theta_2^{(2)}$ comes from the union of $2^2 = 4$ subsets and is given by

$$\Theta_2^{(2)} = \quad \triangle\triangle\triangle \quad \cup \quad \triangle\triangle\triangle \quad \cup \quad \triangle\triangle \quad \cup \quad \triangle\triangle \tag{5.12a}$$

$$= 3 \quad \triangle\triangle\triangle \quad + \quad \triangle\triangle \quad - 2 \quad \triangle\triangle$$

$$- 2 \quad \triangle\triangle\triangle \quad + \quad \triangle\triangle\triangle \tag{5.12b}$$

where the expansion of the second equality comes from a repeated application of equation (5.4) and use of lattice symmetry. The numerical values are again easily calculated and we find

$$\Theta_2^{(2)} = 0.009\,963. \tag{5.13}$$

By extending these considerations one can also determine successively the contributions of $\mathcal{R}_2$ to $\Theta_3, \Theta_4, \ldots$.

We finally consider $\mathcal{R}_3$ in equation (5.7) and we shall extract from it its contribution $\Theta_2^{(3)}$ to Θ_2. The origin will be occupied in the third sweep if and only if each of the three vertices has at least one neighbouring site occupied in the first sweep. Therefore $\Theta_2^{(3)}$ comes from the union of $2^3 = 8$ subsets whose expression is readily written down analogously to (5.10a) and (5.12a). Upon expanding as in (5.10b) and (5.12b) one finds

$$\Theta_2^{(3)} = 2 \quad [\text{diagram}] \quad + 6 \quad [\text{diagram}] \quad - 6 \quad [\text{diagram}] \tag{5.14}$$

$$- 3 \quad [\text{diagram}] \quad - 3 \quad [\text{diagram}]$$

$$+ 6 \quad [\text{diagram}] \quad - \quad [\text{diagram}]$$

Upon putting in the numerical values one finds

$$\Theta_2^{(3)} = 0.015\,439. \tag{5.15}$$

By extending these considerations one can also determine successively the contributions of $\mathcal{R}_3$ to $\Theta_3, \Theta_4, \dots$.

By combining equations (5.1), (5.11), (5.13), and (5.15) we find for the lower bound Θ_2 the value

$$\Theta_2 = \Theta_1 + 3\Theta_2^{(1)} + 3\Theta_2^{(2)} + \Theta_2^{(3)}$$
$$= 0.359\,613 \tag{5.16}$$

which is a considerable improvement over $\Theta_1 = 0.25$ (equation (5.1)).

6. Upper bounds

The method used to calculate successively better lower bounds can also be applied, with some obvious modifications, to calculate the upper bounds $\bar{\Theta}_1, \bar{\Theta}_2, \dots$. The upper bound $\bar{\Theta}_1$ is equal to one minus the probability that the origin gets blocked in the second sweep. This happens if and only if at least one of the sites neighbouring the origin gets occupied in the first sweep. Therefore, with the same notation convention as before and indicating the location of the origin again by a heavy dot, we have

$$\bar{\Theta}_1 = 1 \quad - \quad [\text{diagram}] \quad \cup \quad [\text{diagram}] \quad \cup \quad [\text{diagram}]$$

$$= 1 - \quad 3 \quad [\text{diagram}] \quad + \quad 3 \quad [\text{diagram}] \quad - \quad [\text{diagram}] \tag{6.1}$$

The first diagram on the RHS is equal to $\frac{1}{4}$. The two remaining ones are new. They can be calculated, as in equation (3.3), by associating a variable x_i with each centre and each vertex, and integrating on a product of ϑ functions that impose the arrow directions. The

result is that the two diagrams are equal to $\frac{1}{14}$ and $\frac{3}{140}$, respectively, which gives the final result

$$\bar{\Theta}_1 = \frac{31}{70} = 0.442\,857 . \tag{6.2}$$

7. Comments and conclusion

The equations (5.2), (5.16), and (6.2) represent the numerical values of exact bounds on the final state covering fraction of an RSA process with nearest-neighbour exclusion on a hexagonal lattice. The two lower bounds $\Theta_1 = 0.25$ and $\Theta_2 = 0.3596$, and the upper bound $\bar{\Theta}_1 = 0.4429$ should be compared with the estimates $\Theta(\infty) = 0.379$ and $\Theta(\infty) = 0.3759$ [4].

The low order bounds presented here are not yet competitive with the precision of a Monte Carlo simulation. However, our main purpose has been to show that exact bounds *can* be calculated. Higher-order bounds on $\Theta(\infty)$ can be found in a systematic way. For the one-dimensional RSA process of particles with nearest-neighbour exclusion, we have calculated all the lower bounds Θ_k and found that they converge exponentially with k to the exactly known value [3] of $\Theta(\infty)$. We strongly expect that the convergence is also exponential in two dimensions. We have not considered here the related question of how best to extrapolate towards $\Theta(\infty)$ on the basis of a finite number of Θ_k and $\bar{\Theta}_k$.

We briefly address the question of how to use the method of this work to find bounds on the time-dependent covering fraction $\Theta(t)$. At time t, the RSA process will have attempted to fill a fraction $1 - e^{-t}$ of all sites. A site i belongs to this fraction iff $0 \leqslant x_i \leqslant 1 - e^{-t}$ (we again take all x_j's uniformly distributed between 0 and 1). Finding the bounds on $\Theta(t)$ then amounts to calculating the same diagrams as for $\Theta(\infty)$, but the integrations on the x_j are carried out subject to the condition that sites i with $x_i > 1 - e^{-t}$, as well as the bonds joining them, be deleted from the diagrams. In this way it is easy to generalize the most elementary of our bounds (equation (5.2)), to

$$\Theta(t) \geqslant \Theta_1(t) = \tfrac{1}{4}(1 - e^{-4t}). \tag{7.1}$$

We do not pursue these questions here, nor shall we attempt to discuss applications of this method to RSA in continuous space.

A final comment concerns the relation between our expansion and existing ones (see Evans [1] for an overview). As far as we know, the existing expansions are all, implicitly or explicitly, in powers of the time t, and therefore different from ours. The question of how it is possible, if at all, to establish a correspondence between them is therefore left open.

Acknowledgments

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