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Random sequential adsorption of k-mers on a square lattice: The large k regime

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The random sequential adsorption of k-mers on a two-dimensional lattice is studied in the regime of large k, up to infinity where the coverage has a finite limit. A simple and accurate representation of the coverage as a function of the time is given for any value of k. Its parametrization is a consequence, through the master equations, of the particular behavior that we find for the deposited clusters in Monte Carlo simulations of the process. The parameters are fixed by matching a seventh-order time series expansion. [S1063-651X(96)11507-5]

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Random sequential adsorption (RSA) is a model in which objects are deposited on a given substrate one at a time, with random positions, such that new objects cannot overlap previously adsorbed ones [1]. A variety of large molecules adsorbs in an essentially irreversible manner, and the RSA model may be appropriate [2] to describe this process. When the substrate is one-dimensional, the model is generally solvable, as the well known deposition of k-mers (line segments of k sites) or its continuous version (the car parking problem) [3]. In higher dimensions, no model has been solved, but a great amount of information has been collected, especially for the coverage $\Theta(T)$: at low coverage, exact but finite perturbative series can be derived (time or virial-like expansions) [4], and at large time the asymptotic approach to the jamming limit can be guessed from heuristic arguments [5]. In many cases, it then appears feasible to invent an interpolating function for the coverage in agreement with the Monte Carlo (MC) data at any time [6].

There is a noticeable exception to this scheme, when the deposition involves very anisotropic objects, such as for example, rectangles with a large aspect ratio α, where $\alpha=$(length)/(width). In the RSA of such unoriented rectangles on the plane, when $\alpha\geqslant 4$, no satisfactory interpolation has been found [7] between the low coverage regime, known from a third-order virial-like expansion, and the asymptotic regime where saturation occurs as $T^{-1/3}$. This failure is attributed to the very different nature of the two regimes. In fact, intuitive arguments and MC simulations [8] indicate that at low coverage the orientations of the adsorbed rectangles are weakly correlated but that at long time an ordering effect occurs: the adsorbed rectangles have orientations similar to those of their preadsorbed neighbors. This regime becomes more pronounced as the aspect ratio increases, and some shrinkage of the low coverage regime weakens the ability of the low time expansion at moderate order to fix the scale of the coverage at large time.

The model we consider in this work suffers *a priori* this kind of problem: it is the RSA of k-mers on a two-dimensional lattice for large values of k, i.e., the RSA of oriented rectangles of length k and width 1, when the aspect ratio goes to infinity. Indeed, a standard Padé summation of the seventh-order expansion of $\Theta_k(T)$ in powers of the time T cannot be trusted at any time when k is large: it appears that T has to be smaller than 1 when k is greater than 10. It is however possible to derive the jamming limit Θ_k from this expansion, as we have shown in our previous work [9], where we performed MC simulations of this model in the range $2\leqslant k\leqslant 512$. In agreement with the MC simulations, we have shown that

$$\Theta_k=0.664+0.83/k-0.7/k^2, \tag{1}$$

which implies a finite coverage for infinite k-mers, that we interpret as a consequence of the alignment constraint. In order to complete our previous analysis, we want to report here the very simple behavior that we find for the coverage in the large k regime, $k>10$:

$$\Theta_k(T)=T\Theta_k/(T+\chi_k), \quad T\geqslant 2/\ln(k), \tag{2}$$

where the constant χ_k, which can be estimated from the series expansion, is given by

$$\chi_k=1.22-11.07/k+63.7/k^2. \tag{3}$$

The representation (2) is an approximation whose accuracy increases with k, according to our MC simulations, and which appears as an approximate solution of the master equations that we derive below.

The k-mer deposition is done along two orthogonal lattice orientations (i,j) and let E_n^i be a cluster of n consecutive empty sites aligned with the direction i. On an initially empty lattice, the averaged probabilities of such sets are position and orientation free, and they can be denoted by $P_n(T)$, with $P_n(T=0)=1$. We use a dimensionless time variable $T=Rkt$, where R is the rate of random deposition attempts of k-mers per site and per unit time t, such that $-k(d/dT)P_n(T)$ counts all the possible ways of filling at least one of the n sites of E_n^i through a k-mer deposition. Then $-k(d/dT)P_1(T)=2kP_k(T)$, which gives for the coverage

$$\Theta_k(T)=2\int_0^T P_k(T')dT'=\Theta_k-2\int_T^\infty P_k(T')dT'. \tag{4}$$

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When $n \geqslant k$, two kinds of events have to be considered: the deposition occurs with orientation i and the k-mer is inside or overlapping E_n^i, or it occurs with another orientation j and it intersects E_n^i at some site s. This last contribution can be written as $\Sigma_s P(E_n^i E_k^j)$, where the s summation is performed on the nk possible intersections of a pair of orthogonal clusters E_n^i and E_k^j. In order to truncate the hierarchy at the $P_n(T)$ level, we put $\Sigma_s P(E_n^i E_k^j) = nkP_n(T)\varphi(T)$, where the k-dependent conditional probability $\varphi(T)$ is left unspecified. This approximation will be justified later on, and we end up with

$$-k\frac{d}{dT}P_n(T) = (n-k+1)P_n(T) + 2\sum_{l=1}^{k-1} P_{n+l}(T) + nkP_n(T)\varphi(T), \tag{5}$$

which is solved as its one-dimensional analog. Inserting in the system (5) the ansatz $P_n(T) = z^{n-k}(T)P_k(T)$ for $n \geqslant k$, one obtains

$$-k\frac{d}{dT}\ln z(T) = 1 + k\varphi(T), \tag{6}$$

$$-k\frac{d}{dT}\ln P_k(T) = 1 + 2\sum_{l=1}^{k-1} z^l(T) + k^2\varphi(T). \tag{7}$$

Defining the function $\chi(T)$ as $\chi(T) = k\int_0^T \varphi(T')dT'$ and taking into account the initial conditions, one arrives at

$$z(T) = \exp\{-[T+\chi(T)]/k\} \tag{8}$$

and finally

$$P_k(T) = \exp\left(-\frac{T}{k} - \chi(T) - S(\chi;T)\right), \tag{9}$$

where we have defined $S(\chi;T)$ as

$$S(\chi;T) = \frac{2}{k}\int_0^T \sum_{l=1}^{k-1} z^l(T')dT' = \frac{2}{k}\int_0^T \frac{z(T') - z^k(T')}{1 - z(T')} dT'. \tag{10}$$

At this point we can mention the experimental tests of the truncation hypothesis that we have made. In the course of MC simulations of the model, for various choices of k and T, we have measured some ratios $z_n = P_{n+1}(T)/P_n(T)$ for $n \geqslant k$. As a consequence of this hypothesis, they must be independent of n, since they are all equal to $z(T)$ given by Eq. (8). The simulations indicate a small discrepancy between z_k and z_{k+1}, increasing with T, but always less than 5%, the remaining measured ratios z_{k+1} to z_{k+5} being practically equal. They also show that $\chi(T)$ increases with T, in agreement with its definition, and quickly saturates some finite limit χ_k. This behavior, which implies the rapid decrease of $\varphi(T)$, indicates the tendancy to align for the deposited k-mers.

In the large k regime, where from (8) $z(T) \simeq 1 - [T+\chi(T)]/k$, $S(\chi;T)$ becomes

$$S(\chi;T) = 2\int_0^T \frac{1 - e^{-[x+\chi(x)]}}{x+\chi(x)} dx + 0\left(\frac{1}{k}\right), \tag{11}$$

which can be written $S(\chi;T) = S_k + 2\ln(T+\chi_k)$ for T sufficiently large and greater than T_k, under the assumption that for $T \geqslant T_k$, $\chi(T)$ saturates its limit χ_k, and where S_k is a time-independent constant. Thus from Eq. (9), $P_k(T) \simeq A_k/(T+\chi_k)^2$, which inserted in Eq. (4) gives for the coverage

$$\Theta_k(T) = \Theta_k - 2A_k/(T+\chi_k), \quad T \geqslant T_k. \tag{12}$$

One can eliminate the constant A_k in favor of $\Theta_k(T_k)$ in the previous expression to obtain

$$\Theta_k(T) = \frac{T\Theta_k}{T+\chi_k} + \frac{T_k+\chi_k}{T+\chi_k}\left(\Theta_k(T_k) - \frac{T_k\theta_k}{T_k+\chi_k}\right), \quad T \geqslant T_k. \tag{13}$$

Thus, if one can find T_k such that $\Theta_k(T_k) = T_k\Theta_k/(T_k+\chi_k)$, then

$$\Theta_k(T) = T\Theta_k/(T+\chi_k) \ \text{ for } \ T \geqslant T_k. \tag{14}$$

In order to test this assumption we have performed MC simulations, within the method already explained in our previous work [9], for k running from 12 to 128. In all cases, taking for Θ_k the values given in (1), one can find a constant χ_k such that the expression Eq. (14) fits perfectly with the data for $T \geqslant 1$. It is an interpolation of these values which is given in expression Eq. (3). It also appears that T_k, defined as the smallest value of T where the data and the fit Eq. (14) coincide, shrinks to 0 approximatively as $T_k \simeq 2/\ln(k)$, suggesting a very simple form for the asymptotic coverage $\Theta_\infty(T) \simeq 0.664T/(T+1.22)$. A sample of these results is displayed in Table I, where T is restricted to $T \leqslant 1$, as the data and the fit coincide at higher values.

It remains to show that the values of χ_k can be obtained from the expansion of $\Theta_k(T)$ in powers of T. In the large k regime, the Padé resummation of this series is not reliable at large T, but it works in the region $T \simeq T_k$ in such a way that a comparison of these approximants and the form Eq. (14) fixes Θ_k and χ_k. A direct evaluation of χ_k is also possible, and we give here as an example its determination in the most difficult case $k = \infty$. In this case, up to $O(1/k)$ terms, the series of $\chi(T)$, obtained by matching the expansion of $P_k(T)$ [known from the series of $\Theta_k(T)$] with the parametrization (9), reads in the variable $u = kT$

$$\chi(T) = u - \frac{1}{2}u^2 + \frac{5}{27}u^3 - \frac{23}{432}u^4 + \frac{481}{36000}u^5 - \frac{24097}{5832000}u^6 + O(u^7). \tag{15}$$

As χ_∞ is the limit of Eq. (15) at $u = \infty$, we use the mapping $v = y(1 - e^{-u/y})$, which transforms the series (15) into a v series $\chi(v)$. Then χ_∞ is the value of $\chi(v)$ at $v = y$. As this

TABLE I. For the values of k given on top of each double column, the MC values of the coverage (first column) are compared with the expression Eq. (2) (second column). The sign = indicates that the data and the fit are equal within one unit on the last digit, which is the maximum uncertainty on the MC results, which are obtained as in our Ref. [9] where details can be found. For any choice of k, the values for Θ_k and χ_k used to compute expression Eq. (2) are given by the interpolations Eq. (1) and Eq. (3), respectively.

T	$k=12$		$k=48$		$k=80$		$k=128$		$k=\infty$
0.1	0.124	0.087	0.082	0.061	0.072	0.057	0.065	0.054	0.050
0.2	0.190	0.155	0.129	0.112	0.116	0.104	0.107	0.100	0.093
0.3	0.237	0.210	0.168	0.155	0.153	0.145	0.143	0.140	0.131
0.4	0.275	0.255	0.201	0.192	0.186	0.181	0.176	0.174	0.164
0.5	0.307	0.294	0.230	0.225	0.215	0.212	0.205	=	0.193
0.6	0.335	0.326	0.256	0.253	0.241	0.239	0.231	=	0.219
0.7	0.358	0.354	0.280	0.278	0.264	=	0.255	=	0.242
0.8	0.380	0.378	0.300	=	0.285	=	0.276	=	0.263
0.9	0.399	=	0.320	=	0.305	=	0.295	=	0.282
1.0	0.418	=	0.338	=	0.322	=	0.313	=	0.299

value must be independent of the mapping parameter y, y is fixed at finite order by a stationarity condition. One obtains

$$\chi(v=y)=\frac{49}{20}y-\frac{203}{90}y^2+\frac{245}{216}y^3-\frac{805}{2592}y^4+\frac{3367}{72000}y^5-\frac{24097}{5832000}y^6 \tag{16}$$

and one can check that this polynom has only one extremum for positive y at $y=2.13$. It is a maximum with the value 1.218 and the Padé table gives $\chi_\infty=1.22\pm0.01$, in agreement with the interpolation given in Eq. (3).

More generally, for any value of k, $\chi_k(T)$ can be recovered from its time series expansion, assuming that it has a finite limit. This has to be contrasted with its usual self-consistent determinations which, even if they work for small k-mers, fail in the large k regime since χ_k becomes unbounded and the coverage vanishes. For example in the ''shielding'' approximation [10], where $\varphi=z^{k-1}$, one finds $\Theta_2=\frac{8}{9}\simeq0.8889$ (MC value [9] =0.9068) but as k increases $\chi_k\simeq\ln(k)$ and $\Theta_k\simeq1/k$. This is also the case for the mean-field approximation $\varphi=P_k$, which gives P_k throughout the nonlinear equation (5), and it can be proven that the coverage is bounded by $4\ln(k)/k$. These approximations fail because the probabilities of the empty clusters are independent of their shape, which eliminates any ordering effect, but a realistic self-consistent determination of $\chi(T)$ at large k is still an open problem.

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