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LETTER TO THE EDITOR

On the dynamics of random sequential absorption

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Abstract. The dynamics of random sequential absorption on d-dimensional lattices is represented by a simple graphical expansion. Results for the entire filling process, and in particular its saturation limit are easily obtained. It is shown that the large-d limit of the saturation density is $\ln 2d/2d$. The expression gives an accurate approximation for $d \geqslant 3$.

Random sequential absorption (RSA) of particles on d-dimensional lattices occurs in many chemical, physical and biological processes. In many systems the binding of the particles to the lattice sites is very strong, and as a result desorption and intersite diffusion effects are negligible, resulting in an essentially irreversible process. Usually, the particles extend over several lattice sites, so the occupancy of a site affects the binding probability of its neighbours for the entire process. One-dimensional (1D) RSA models describe irreversible reactions between segments of polymers and binding ligands [1, 2]. Chemisorption of molecules on surfaces [3, 4] and adsorption of particles on natural membranes [5] are examples of 2D RSA processes. In 3D the model describes photochemical reactions in crystals [6].

The dynamics of the RSA models has been studied by several authors. For 1D systems of this kind exact solutions have been obtained [1, 7]. These analytical solutions are based on simple recursion relations among chains of different lengths. Evans *et al* [8] extended this approach to 2D lattices to obtain a hierarchy of recursive relations. Truncation of the hierarchy results in an approximate solution. Meakin *et al* [9] performed numerical simulations to estimate the density of maximal coverage of RSA models with nearest-neighbour exclusion for $1 \leqslant d \leqslant 4$.

The aim of this letter is to present a formalism for the dynamics of the RSA process. We apply Glauber dynamics [10] to this problem and construct a simple graphical expansion for the density of occupied ('reacted') sites in terms of the elementary excitations of the model. The expansion is valid for all dimensions d.

The basic point is that Glauber dynamics simplifies considerably when applied to a system with local interactions, with two states at each site (like the Ising model), which can only pass irreversibly from one state to the other (unlike the Ising model). We use this simplification to calculate quantities of interest, in particular the density of maximal coverage. This is done by calculating a few coefficients of the formal expansion and then summing the series using convergence acceleration methods. In addition we calculate the leading term in a $1/d$ expansion for the maximal coverage density. Both methods give excellent agreement with Monte Carlo results. Finally we discuss the RSA model at finite temperature within a Hamiltonian approach.

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The dynamics is formulated in terms of a time-dependent distribution function $P(\{s_i\}, t)$. s_i are occupation variables which are defined as 1 for *empty* sites and 0 for full ones. We will explicitly discuss the case when the index i runs over the sites of a d-dimensional hypercubic lattice; the generalisation to other cases is straightforward.

P satisfies a master equation [10]

$$\frac{\mathrm{d}}{\mathrm{d}t} P(\boldsymbol{s}, t) = \sum_{i=1}^{N} [W(1-s_i)P(s_1, \ldots, 1-s_i, \ldots, s_N, t) - W(s_i)P(\boldsymbol{s}, t)]. \tag{1}$$

The transition rates W are given by

$$W(s_i) = s_i \prod_{\delta} s_{i+\delta} \equiv B_i \tag{2}$$

where δ runs over the $2d$ nearest neighbours of s_i. Correlation functions are defined by $\langle F(\boldsymbol{s})\rangle = \mathrm{Tr}_s F(\boldsymbol{s})P(\boldsymbol{s}, t)$. The density $\rho(t)$ is given by

$$\rho(t) = 1 - M(t) \tag{3}$$

where $M(t) = \langle s_i \rangle$. We will next derive a hierarchical set of equations for $M(t)$. To do this consider a general connected correlator $M(C, t) = \langle s_1, \ldots, s_n \rangle$, where C is an 'animal' on the lattice consisting of the points $1, \ldots, n$. Using (1) and (2) it is easy to see that

$$\frac{\mathrm{d}M(C, t)}{\mathrm{d}t} = -\sum_{i=1}^{n} M(C_i, t) \tag{4}$$

where $M(C_i, t) = \langle s_1, \ldots, s_i B_i, \ldots, s_n \rangle$. Equation (4) means that $\mathrm{d}M(C, t)/\mathrm{d}t$ is given by a sum of correlators of larger animals C_i, which are obtained by adding a d-dimensional cross at each site i of C. Obviously, if C is connected, so are the C_i. Equation (4) can be further simplified. Define $N_I(C)$ the number of inner points of C, i.e. those points with $2d$ neighbours. Since $s^2 = s$, for i which is one of the N_I inner points, $C_i = C$. Using this fact and redefining $F(C, t) = \exp[N_I(C)t]M(C, t)$ and $u = \exp(-t)$, (4) turns into

$$\frac{\mathrm{d}F(C, u)}{\mathrm{d}u} = \sum_{i=1}^{N_B} u^{N_I(C_i) - N_I(C) - 1} F(C_i, u) \tag{5}$$

where $N_B(C)$ is the number of boundary points of C, i.e. the number of points with less than $2d$ neighbours. Thus the time dependence of $F(C, u)$ is related to the bigger animals which can be generated from the boundaries of C. Equation (5) is almost what we need; using it we can compute the coefficients in the expansion of M (3):

$$M(u) = \sum_{n=0}^{\infty} \frac{a_n}{n!} (u-1)^n \tag{6}$$

where $a_n = \mathrm{d}^n M/\mathrm{d}u^n|_{u=1}$. By sequential application of (5), we can reduce the calculation of a_n to that of counting animals on the lattice, because $F(C_i, 1) = 1$ for all C_i which are generated from $M(t)$ (this is just the statement that the initial conditions are compatible with the dynamics).

The last simplification we need is expressing the C in terms of correlators of B. It is easy to see that for all descendants of $M(t)$, $M(C, t) = \langle \Pi_{i=1}^{N_I} B_i \rangle$. In this form, the animal is characterised by its inner points only. Each of the C_i is generated from C by adding one point to it in all possible directions (configurations with $C_i = C$ are not counted). After adding the point, one has to check whether some other points (in addition to the one added explicitly) become inner points of C_i in the process. The

power of u in (5) is determined by the difference in the number of inner points between C_i and C (minus 1). Non-vanishing values of this power affect the calculation of a_n.

To clarify the procedure, we illustrate it in several special cases. First, we calculate the first few coefficients for generic d. $a_0 = 1$ for all d since $M(1) = 1$. $dM/du = F_1(u)$, where $F_1 = \langle B \rangle$ (the animal is one point). Therefore $a_1 = 1$ too. To calculate a_2 we use $d^2M/du^2 = dF_1/du$. F_1 is one point and there are $2d$ possible directions to add a point to it. Thus $a_2 = 2d$. The third cofficient follows from $d^3M/du^3 = 2d\, dF_2/du$. There are two different animals consisting of three points which can be obtained from the one with two points. At this order only their total number which is $2(2d-1)$ is important, therefore $a_3 = 2 \times 2d \times (2d-1)$. From these coefficients we can deduce the short-t behaviour of the filling process: $\rho(t) = t - (d+\frac{1}{2})t^2 + O(t^3)$ (in terms of single flip (computer) time we have to replace $t \to t/N$). For higher n, a_n can be counted by a computer.

In $d = 1$ the a_n can be computed exactly. The power of u in (5) is then (and only then) zero identically. The animals are labelled by the number of points n and (5) takes the form $dF_n/du = 2F_{n+1}$. The solution to (6) is $a_n = 2^{n-1}$ $(n \geq 1)$ and $M(u) = \frac{1}{2}(1 + e^{2(u-1)})$. At $t \to \infty$ $(u \to 0)$ we find $\rho(\infty) = \frac{1}{2}(1 - e^{-2})$.

For $d = 2$ we computed the first 10 coefficients and summed the resulting series (6) using the Levin convergence acceleration method [11]. The table below presents the a_n and the corresponding Levin approximants for $\rho(\infty)$. The approximants form a fast converging monotonically increasing series, whose limit is estimated to be $\rho(\infty) = 0.3641(1)$. The uncertainty in the last digit is enclosed in parentheses.

n	3	4	5	6	7	8	9	10
a_n	24	176	1504	14 560	156 768	1852 512	23 783 264	329 070 176
$\rho_n(\infty)$	0.3443	0.3545	0.3602	0.3630	0.3637	0.3639	0.36400	0.36405

Another regime in which our expansion can be summed is that of large d. To leading order in $1/d$ the $a_n(d)$ can be obtained by the following argument. For large d, the effect of curling up of the animals that generate the a_n is negligible. The different animals can be labelled solely by the number of points in them, N_I. In addition, because of the large number of independent directions in which one can add points to the animals, we can (with the above accuracy) make the following two simplifying assumptions. (i) Neglect the directions in which the animals cannot grow since they are already occupied; thus the number of new animals obtained from a single point in C is $2d$. (ii) Assume that $N_I(C_i) - N_I(C) = 1$ for most C. This is the assumption that curled animals are rare at large d. Both assumptions can be quantified. Applying these assumptions to (5), we get the asymptotic relation $dF_n/du = n \times 2dF_{n+1}$. This gives in (6) $a_n = (n-1)!(2d)^{n-1}$ $(n \geq 1)$. Summing (6) we get $M(u) = 1 - (1/2d)\ln[1 - 2d(u-1)]$, and from (3), $\rho(\infty) = \ln(1+2d)/2d$. Strictly speaking we should drop the 1 in comparison with $2d$, so that the final result is $\rho(\infty) \simeq \ln 2d/2d$. We found however that for all values of $1 \leq d \leq 6$ for which we checked, the correct $\rho(\infty)$ was bounded by $\ln 2d/2d \leq \rho(\infty) \leq \ln(2d+1)/2d$ as in the table below.

We see that for $d \geq 3$ the approximation is very good and the error in the approximate values is less than 1.5%. The relationship between $\rho(\infty)$ and the density of the glass transition will be discussed elsewhere [12].

d	1	2	3	4	5	6
$\ln 2d/2d$	0.3466	0.3466	0.2986	0.2599	0.230	0.207
$\rho(\infty)$	0.4323	0.3641(1)	0.304(1)	0.264(1)	0.233(1)	0.209(1)
$\ln(2d+1)/2d$	0.549	0.40235	0.3243	0.275	0.240	0.2137

Finally, we would like to discuss a different aspect of our problem, by comparing it with a similar equilibrium model. Consider the Hamiltonian

$$H = \beta \left[\sum_i B_i + \sum_{(i,j)} (1-s_i)(1-s_j) \right] \tag{7}$$

in the large-β limit ($\beta = 1/T$ is a coupling constant). The first term in (7) suppresses configurations in which a site and all its nearest neighbours are empty. The second reflects a repulsion which tends to forbid configurations with occupation of nearest neighbours. In the limit of infinite β, the configurations which contribute to correlation functions of the Hamiltonian H are precisely the allowed final states of the dynamics (1) and (2). One can now define Glauber dynamics for this Hamiltonian (e.g. by $W(s) = e^{-1/2\beta\Delta H(s)}$). It is easy to see that this dynamics coincides for infinite β (after an irrelevant rescaling of time) with (2). For finite β it incorporates the effect of diffusion and desorption of particles in a way consistent with detailed balance. For $d = 1$ one can easily calculate (using the transfer matrix) the one-point function $\langle s \rangle$ exactly. One obtains for the density $\rho_H(\infty) = 0.4115\ldots$ which is smaller than the saturation density of the corresponding RSA model $\rho(\infty) = 0.43233\ldots$. The discrepancy results from the fact that although the allowed configurations are identical in both models their relative weights are different. This is a typical zero-temperature phenomenon. For any finite T, the W matrix is not reducible and thus from any initial configuration (in particular $\{s_i\} = 1$), P evolves to the unique stationary distribution $P(s) \propto \exp(-\beta H)$. The corresponding $\rho(\infty)$ is (for large β), $\rho_H(\infty) + O(T)$. For $T = 0$, W is highly reducible and $\rho(\infty)$ does depend on the initial conditions. Thus, for the above initial conditions, $\rho(\infty, T)$ has a jump as $T \to 0$ from $\rho_H(\infty)$ to $\rho(\infty)$. The relationship between the two processes in higher dimensions as well as the properties at finite T are under investigation [12].

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