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LETTER TO THE EDITOR

An algorithm for series expansions based on hierarchical rate equations

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Abstract. We propose a computational method to obtain series expansions in powers of time for general dynamical systems described by a set of hierarchical rate equations. The method is generally applicable to problems in both equilibrium and non-equilibrium statistical mechanics such as random sequential adsorption, diffusion-reaction dynamics, and Ising dynamics. A new result for random sequential adsorption of dimers on a square lattice is presented.

Most dynamical models in equilibrium and non-equilibrium statistical mechanics can be described by a set of hierarchical rate equations: random sequential adsorptions (RSA) and their variants [1], diffusion–reaction models [2], and kinetic Ising models [3]. The specifications of interactions between the components of the system or interactions between the environment and the system give a deterministic time evolution for the distribution functions once the initial condition of the system is given. Exact solutions are often restricted to simple models, while one has to use approximate methods for those that resist exact analyses.

Power series expansion is one of the methods of controlled approximations. There are a number of systematic methods to obtain time power series [4–7]. Long series were usually obtained by reducing a problem to an enumeration problem similar to the series expansions in equilibrium statistical mechanics [8].

Lattice enumeration problems are typically limited by CPU time due to their exponential growth. In this letter, we discuss a general method to obtain series expansions based on rate equations for lattice models. Our method differs from previous approaches in that the limiting factor is memory space, but it is faster in time. The method is applicable to many different problems, in particular RSA, RSA with diffusional relaxation, reaction–diffusion problems, and general Ising dynamics.

To illustrate the method, we take the RSA of random dimer filling on a square lattice as an example [9]. Dimers of random orientations are dropped randomly and sequentially, at a rate of k per lattice site per unit time, onto an initially empty, infinite square lattice. Hereafter we set k equal to unity without loss of generality. If the chosen two nearest neighbour sites are unoccupied, the dimer is adsorbed on the lattice. If one of the chosen sites is occupied by a previously adsorbed dimer, the adsorption attempt is rejected. The first few of an infinite number of rate equations for this process are given as follows:

$$\frac{\mathrm{d}P(\circ)}{\mathrm{d}t} = -4P(\circ\circ) \tag{1}$$

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$$\frac{\mathrm{d}P(\circ\circ)}{\mathrm{d}t} = -P(\circ\circ) - 2P(\circ\circ\circ) - 4P(\overset{\circ}{\circ\circ}) \tag{2}$$

$$\frac{\mathrm{d}P(\circ\circ\circ)}{\mathrm{d}t} = -2P(\circ\circ\circ) - 2P(\circ\circ\circ\circ) - 4P(\overset{\circ}{\circ\circ\circ}) - 2P(\underset{\circ}{\circ\circ\circ}) \tag{3}$$

$$\frac{\mathrm{d}P(\overset{\circ}{\circ\circ})}{\mathrm{d}t} = -2P(\overset{\circ}{\circ\circ}) - 2P(\overset{\circ\circ}{\circ\circ}) - 2P(\underset{\circ}{\circ\circ\circ}) - 2P(\overset{\circ}{\circ\circ\circ}) - 2P(\underset{\circ}{\circ}\overset{\circ}{\circ}) \tag{4}$$

...

where $P(C)$ stands for the probability of finding a configuration C of sites specified empty or filled. An '$\circ$' denotes an empty site. We have taken into account the symmetries of the problem, i.e. the invariance of $P(C)$ under all lattice group operations (e.g. rotation and reflection). For notational convenience we will use $P_C \equiv P(C)$.

Let C_0 denote a particular configuration of interest, then P_{C_0} is the configuration probability associated with C_0. On physical grounds, we expect P_{C_0} to be a well behaved function of time t, and one would expect to obtain the Taylor expansion $P_{C_0}(t) = \sum_{n=0}^{\infty} {P_{C_0}}^{(n)} t^n/n!$, with the nth *derivative* of P_{C_0} given by

$${P_{C_0}}^{(n)} = \left.\frac{\mathrm{d}^n P_{C_0}(t)}{\mathrm{d}t^n}\right|_{t=0}. \tag{5}$$

The zeroth derivative of P_{C_0} is determined by the initial condition. The first derivative of P_{C_0} is obtained by the rate equation associated with C_0. For the random dimer deposition problem, we choose the configuration of an empty site to be C_0. We have, from equations (1)–(4), $P(\circ)^{(0)} = 1$ and $P(\circ)^{(1)} = -4$, $P(\circ\circ)^{(1)} = -7$, $P(\circ\circ\circ)^{(1)} = -10$, and $P(\overset{\circ}{\circ\circ})^{(1)} = -10$. To compute the second derivative of $P(\circ)$, we take the first derivative of equation (1) and use the result of $P(\circ\circ)^{(1)}$ to obtain $P(\circ)^{(2)} = (-4)(-7) = 28$. For the third derivative $P(\circ)^{(3)}$, we take the second derivative of equation (1), which in turn needs the first derivative of equation (2). Using equations (2)–(4) for the first derivatives, we get $P(\circ)^{(3)} = -268$.

To computerize the calculations with high efficiency, we make the following important observations. For any configuration C, the rate equation is always of the form

$$\frac{\mathrm{d}P_C}{\mathrm{d}t} = \sum_{C'} \lambda_{C'} P_{C'}. \tag{6}$$

This immediately gives us the first derivative of P_C; in particular the first derivative of P_{C_0} of interest. Since the derivative operator is linear, the second derivative of P_C is a linear combination of the first derivatives of $P_{C'}$ on the right-hand side of the rate equation (6). For each higher derivative, new rate equations and new configurations are involved. Let G_i denote the set of new configurations generated in the calculation of the ith derivative of P_{C_0}, and G_i^j the corresponding jth derivatives of the set of configurations. We observe that $G_0^{n-1}, G_1^{n-2}, \ldots, G_{n-1}^0$ (determined at the $(n-1)$th derivative), $G_0^{n-2}, G_1^{n-3}, \ldots, G_{n-2}^0$ (determined at the $(n-2)$th derivative), $\ldots, G_0^0$ are known before calculating the nth derivative. In other words, G_i^j are predetermined where $0 \leqslant i + j \leqslant n-1$ at this stage. The derivatives $G_0^n, G_1^{n-1}, \ldots, G_{n-1}^1, G_n^0$, would then be determined in a *bottom-up* fashion by recursive use of the rate equations. The method is efficient in the sense that each value in G_i^{n-i}, $0 \leqslant i \leqslant n$, is calculated exactly once and the rate equation for a configuration C is also generated exactly once. By repeated use of this procedure, we can in principle calculate G_0^n for any $n \geqslant 1$.

In most cases, knowledge of the initial condition of the system (usually one starts with an initially empty lattice) can further improve the efficiency of the method. For example,

let h be the highest order of derivative of P_{C_0} for which we wish to compute. Then only a subset $G_i{}'$, $i \leqslant h$, of G_i needs to be considered, once it is known that an element in $G_i - G_i{}'$ gives a zero contribution in the subsequent calculations. This observation is particularly useful for models which *introduce* particles in the rate equations; this is typical in models involving desorption or diffusion.

To implement the above scheme, we store symbolically the rate equations and the intermediate derivatives G_i^j. For each configuration C, we store the configuration and its first j derivatives known so far. The rate equation for C is generated when the first derivative of P_C is needed, and the equation is represented as an array of pointers to other configurations corresponding to the right-hand side of equation (6), and the corresponding array of coefficients $\lambda_{C'}$.

The structural part implementing the recursive use of rate equations is independent of the details of a model. The function calls for a core routine to generate a rate equation if it is not available. Symmetries of the problem are treated here. This routine is called only once for each configuration C. To facilitate this, only a pointer of reference is used for each unique configuration. Configurations are searched with the help of a hash table or a tree data structure.

Table 1. Taylor expansion coefficients for the probability of finding an empty site of random dimer filling on a square lattice.

n	$P(\circ)^{(n)}$
0	1
1	−4
2	28
3	−268
4	3 212
5	−45 868
6	756 364
7	−14 094 572
8	292 140 492
9	−6 653 993 260
10	164 952 149 516
11	−4 416 119 044 972
12	126 863 203 272 268
13	−3 889 473 277 203 116
14	126 677 386 324 657 804

Table 2. CPU time and memory usage on a DEC3000/900 for the dimer problem.

Order	Memory (Mbytes)	Time (s)
9	1	1.0
10	3	4.4
11	12	22.0
12	47	114.7
13	182	612.8
14	706	3131.3

The merit of the approach allows us to obtain a series up to t^{14} for the RSA of dimers on a square lattice (table 1). Results for other models will be published elsewhere. The

computational costs are presented in table 2. Poland obtained the same series up to t^7 [10]. For the RSA of monomer filling with nearest-neighbour exclusion on a square lattice, the efficiency of our algorithm is comparable to the algorithm based on the operator formalism [7], but it is not as good as the method used by Baram and Fixman [11]. However, the power of our method is its generality.

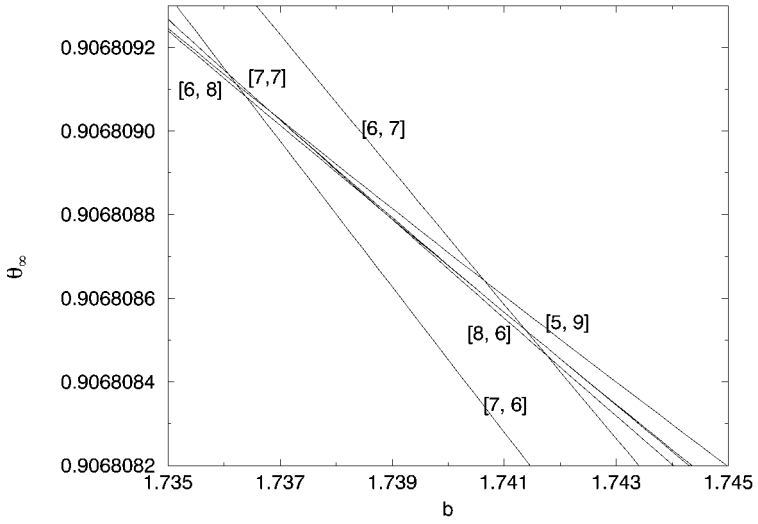

Figure 1. Padé approximant estimates for the jamming coverage θ_∞ as a function of the transformation parameter b, in the crossing region.

The approach to the jamming state for lattice RSA is often exponential. We follow the analysis of series by Dickman *et al* [7]. First we transform the coverage $\theta(t) = 1 - P(\circ, t)$ into a function of $y = 1 - \mathrm{e}^{-t}$. Another transformation, via $z = (1 - \mathrm{e}^{-by})/b$, is performed for the second time, and we examine various Padé approximants to the z series. As we see from figure 1, the resulting estimates for θ_∞ are excellent for $1.736 < b < 1.742$. The intersections of $[6, 8]$, $[7, 7]$, $[7, 6]$, $[8, 6]$, $[6, 7]$, and $[5, 9]$ approximants around this range of b yield an estimate of $\theta_\infty = 0.906\,8088(4)$, where the last digit denotes the uncertainty. This result is in good agreement with the simulation result of $0.906\,873 \pm 0.000\,138$ [12] or the result of 0.9068 obtained via approximate truncation procedures [9].

In summary, we introduced a new approach to deriving power series expansions in time, and we have applied the method to a RSA problem. For the RSA of dimers on a square lattice, we are able to generate a 15-term series, thence to derive the most precise estimate for the jamming coverage yet presented. Our computational method is general and it can be used to handle a variety of problems based on rate equations, especially those that deal with the kinetics of the lattice models.

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