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Asymptotic behaviour of $A + B \rightarrow O$ type reaction-diffusion systems from time-power series

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Abstract. Lattice models for reaction-diffusion systems of the type $A + B \rightarrow O$ are studied using power series in time and techniques developed for determining critical exponents from series. By inverting the series to give time as a function of the appropriate density variable, the terms in the new series yield successive estimates of the exponents that characterize the asymptotic (long-time) behaviour of these systems. The estimates converge rapidly to the expected limiting values.

1. Introduction

The analysis of lattice models in which species hop (diffuse) from site to site and then react irreversibly (either coalescing or annihilating one another) when they are on nearest-neighbour sites has shown that the long-time behaviour of such systems is very different from that predicted by the use of a mean-field or rapid-mixing approximation. These reaction-diffusion models thus illuminate an interesting chemistry to be found in such systems. For the $A + B \rightarrow O$ model, where two different species A and B diffuse on a lattice and annihilate one another on closest approach, it is well established (Ovchinnikov and Zeldovich 1978, Toussaint and Wilczek 1983, Kang and Redner 1984, 1985, Zumofen *et al* 1985, Branson and Lebowitz 1988, Clement *et al* 1989, Lindenberg *et al* 1990) that the asymptotic behaviour for the case where the initial concentrations are equal ($A_0 = B_0$) is given by

$$\rho_A \sim t^{-d/4} \quad (d \leq 4) \quad (1.1)$$

where ρ_A is the number density of A particles and d is the dimension of space. For rapid, random mixing (see the appendix) one expects $\rho_A \sim t^{-1}$ independent of dimension. Thus for $d \geq 4$ one has the mean-field result, but in dimensions one, two, and three one obtains a very much slower decay to the final state.

Variants on the $A + B \rightarrow O$ model are $A + A \rightarrow O$ (annihilation) and $A + A \rightarrow A$ (coagulation). These models both have the following asymptotic behaviour (Rasaiah *et al* 1990, Lin 1991, Ohtsuki 1991, Zhou 1991)

$$\rho_A \sim t^{-d/2} \quad (d < 2). \quad (1.2)$$

In two dimensions the asymptotic behaviour is $t^{-1} \ln t$ while for $d > 2$ one has the mean-field behaviour, i.e. t^{-1} .

Thus a number of reaction-diffusion lattice models have the asymptotic form

$$\rho_A \sim t^{-\nu}. \quad (1.3)$$

The values of the exponent ν quoted above have been deduced mainly from scaling arguments. The validity of these results are supported by exact solutions for special cases (reactions of the A + A type: Spouge 1988, Balding and Green 1989, ben-Avraham *et al* 1990) and computer simulations (Argyrakis and Kopelman 1990, Jiang and Ebner 1990, Becker *et al* 1991).

In the appendix we review, for purposes of comparison, the kinetics of the A + B \rightarrow O reaction when one can assume that the distribution of A and B is random at all stages of the reaction (well-stirred limit). Models of the mixing process (Argyrakis and Kopelman 1989, Sokolov and Blumen 1991) indicate that the approach to the t^{-1} limit is a complex process.

In the present work we explore the utility of using time-power series for reaction-diffusion lattice models to determine the exponent ν in (1.3). If $c(t)$ is the concentration of the species of interest, we construct the time-power series

$$c(t) = \sum_{n=0}^{\infty} c^{(n)} t^n / n! \quad (1.4)$$

where

$$c^{(n)} = \left(\frac{d^n c}{dt^n} \right)_{t=0}. \quad (1.5)$$

We have recently treated the construction of time-power series for lattice models of co-operative sequential adsorption (Poland 1989, 1990a, b, 1991a, b, c, d). In that case one starts with the empty lattice and adds particles in stepwise fashion, as illustrated in figure 1(a). The first derivative in (1.4) is associated with the first step, the second derivative with the second step, and so on (the details are given in Poland 1990b). In fact the $c^{(n)}$ are similar to virial coefficients in the density expansion of equilibrium thermodynamic functions (e.g. the second virial coefficient involves the interaction of two particles, while $c^{(2)}$ involves the addition of two particles). For the models under consideration here, we start out with a full or partially full, infinitely long lattice; sample initial configurations are illustrated in figure 1(b). For this case, $c^{(1)}$ involves a single change in the system averaged over all possible initial conditions (rather than the addition of a single particle to the empty lattice as is the case with sequential adsorption). It might seem that in this case $c^{(1)}$ would be a very complicated quantity (because of the requirement to average over all initial conditions). In fact this turns out not to be the case and one can obtain a finite number of the $c^{(n)}$ for the models of interest here with only a little more effort than that required to treat sequential adsorption. We illustrate the construction of the series for the A + B \rightarrow O reaction in one dimension in the following section.

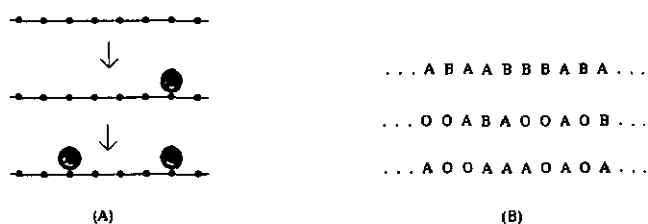


Figure 1. (a) Illustration of sequential addition of particles to an empty lattice; (b) Illustration of sample initial conditions for the A + B \rightarrow O reaction.

2. Time-power series

In this section we construct a hierarchy of differential equations for the $A + B \rightarrow O$ model in one dimension that enable us to evaluate exactly a finite number of the coefficients $c^{(n)}$ in (1.4). We begin by constructing an equation for the rate of change of the density of A-particles. We denote this density as ρ_A ; this is a normalized density (or probability) that can vary from zero (no A's on the lattice) to one (all lattice sites occupied by A). In figure 2 we show all the reactions that change the occupation of a given site (shown underlined in figure 2) by species A. As indicated in the introduction, there are two types of reaction possible, annihilation which can occur when A and B are nearest neighbours and diffusion which can occur when A or B have a least one unoccupied nearest neighbour. We assume homogeneous initial conditions which means that the density of the various lattice configurations shown in figure 2 are independent of position and orientation on the lattice, i.e.

$$\rho_{AB} = \rho_{BA} \quad \rho_{AO} = \rho_{OA} \tag{2.1}$$

Using (2.1), the sum of the reactions shown in figure 2 reduces simply to the following differential equation (note that the reactions involving ρ_{AO} and ρ_{OA} cancel because of (2.1))

$$\frac{d\rho_A}{dt} = -4\rho_{AB} \tag{2.2}$$

Taking the generic $c(t)$ in (1.4) as ρ_A we thus have immediately

$$c^{(1)} = \left(\frac{d\rho_A}{dt} \right)_{t=0} = -4(\rho_{AB})_{t=0} \tag{2.3}$$

We can use any model we wish to describe the initial density. For example, we could use a Markov chain with nearest-neighbour conditional probabilities that reflect a tendency for the A's and B's to cluster (or to repel one another) on the lattice. We

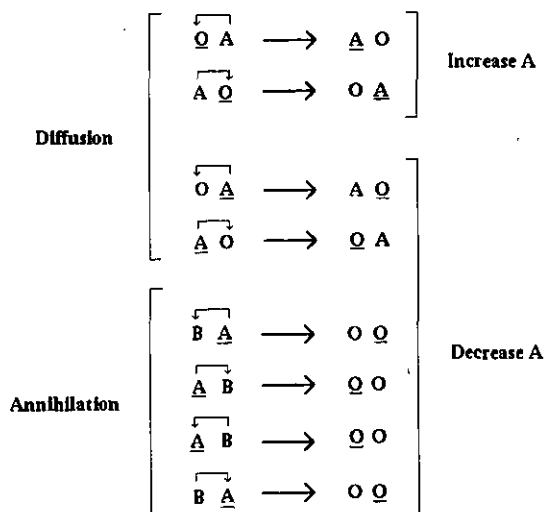


Figure 2. The various types of reaction that can occur in the $A + B \rightarrow O$ system. The reference site is underlined.

stress that one does not need to assume a random initial condition. However for simplicity, that is what we will do. We let the *a priori* probabilities that a given lattice site is occupied by A, B, or is empty (O) at zero time be given by

$$(\rho_A)_{t=0} = \alpha \quad (\rho_B)_{t=0} = \beta \quad (\rho_o)_{t=0} = \gamma \quad (2.4)$$

with the conservation relation

$$\alpha + \beta + \gamma = 1. \quad (2.5)$$

Because of the relation (2.5) we can eliminate γ and describe the initial probabilities solely in terms of α and β . Assuming a random initial distribution one has then

$$(\rho_{AB})_{t=0} = \alpha\beta \quad (2.6)$$

giving

$$c^{(1)} = -4\alpha\beta. \quad (2.7)$$

This gives the first derivative averaged over all initial configurations.

To proceed we take the derivative of (2.2) giving

$$c^{(2)} = \left(\frac{d^2 \rho_A}{dt^2} \right)_{t=0} = -4 \left(\frac{d \rho_{AB}}{dt} \right)_{t=0}. \quad (2.8)$$

Thus we need a differential equation for ρ_{AB} . Proceeding as before, we obtain

$$\left(\frac{d \rho_{AB}}{dt} \right)_{t=0} = 2(\rho_{AOB})_o - [2(\rho_{AB})_o + (\rho_{OAB})_o + (\rho_{ABO})_o + 2(\rho_{BAB})_o + 2(\rho_{ABA})_o]. \quad (2.9)$$

Again assuming a random initial configuration we have

$$\begin{aligned} (\rho_{AB})_o &= \alpha\beta \\ (\rho_{AOB})_o &= (\rho_{OAB})_o = (\rho_{ABO})_o = \alpha\beta\gamma \\ (\rho_{ABA})_o &= \alpha^2\beta \quad (\rho_{BAB})_o = \alpha\beta^2 \end{aligned} \quad (2.10)$$

which when used in (2.9) and (2.8) gives the second derivative

$$c^{(2)} = 8\alpha\beta + 8\alpha^2\beta + 8\alpha\beta^2. \quad (2.11)$$

To go on we need differential equations for ever larger chunks of lattice. The final results for the next three terms are

$$\begin{aligned} c^{(3)} &= -32\alpha\beta - 24\alpha\beta^2 - 8\alpha\beta^3 - 24\alpha^2\beta - 48\alpha^2\beta^2 - 8\alpha^3\beta \\ c^{(4)} &= 144\alpha\beta + 168\alpha\beta^2 - 64\alpha\beta^3 + 8\alpha\beta^4 + 168\alpha^2\beta + 136\alpha^2\beta^2 \\ &\quad + 80\alpha^2\beta^3 - 88\alpha^3\beta + 104\alpha^3\beta^2 + 32\alpha^4\beta \\ c^{(5)} &= -784\alpha\beta - 840\alpha\beta^2 + 632\alpha\beta^3 - 24\alpha\beta^4 - 8\alpha\beta^5 - 848\alpha^2\beta - 560\alpha^2\beta^2 - 160\alpha^2\beta^3 \\ &\quad - 224\alpha^2\beta^4 + 824\alpha^3\beta - 312\alpha^3\beta^2 - 464\alpha^3\beta^3 - 208\alpha^4\beta - 256\alpha^4\beta^2 - 8\alpha^5\beta. \end{aligned} \quad (2.12)$$

For the special case of $\alpha = \beta$ the above expressions become

$$\begin{aligned} c^{(1)} &= -4\alpha^2 & c^{(2)} &= 8\alpha^2 + 16\alpha^3 & c^{(3)} &= -32\alpha^2 - 48\alpha^3 - 64\alpha^4 \\ c^{(4)} &= 144\alpha^2 + 336\alpha^3 - 16\alpha^4 + 224\alpha^5 \\ c^{(5)} &= -784\alpha^2 - 1688\alpha^3 + 896\alpha^4 - 704\alpha^5 - 960\alpha^6. \end{aligned} \quad (2.13)$$

We see that these quantities are polynomials in α .

At the special value $\alpha = \beta = 1/2$ (lattice filled at $t=0$, half A, half B) the coefficients in (2.13), when used in the general series (1.4), give (where we also give the sixth term for this special case)

$$\text{(Diffusion)} \quad c(t) = 1/2 - t + 2t^2 - 3t^3 + (7/2)t^4 - (97/30)t^5 + (837/360)t^6 + \dots \quad (2.14)$$

For comparison we give the corresponding results for the well-stirred limit (see the appendix):

$$\text{(Well stirred)} \quad c(t) = 1/2 - t + 2t^2 - 4t^3 + 8t^4 - 16t^5 + 32t^6 + \dots \quad (2.15)$$

One sees that for this special case the first difference between the two forms is in the t^3 term.

3. Matrix formulation

One can also write the required hierarchy of different equations in terms of the appropriate vectors and matrices. We consider the example of the previous section ($A + B \rightarrow O$ in one dimension). The main difference here from the approach of the previous section is that instead of considering an infinite lattice we treat finite chunks of lattice wrapped in a circle (periodic boundary conditions). This will allow us to calculate a finite number of derivatives (powers of time in the time series); specifically, if we treat a ring of n sites, we obtain $(n-1)$ exact derivatives for the infinite system (Poland 1989, 1990a).

First one must list the rings required to treat a given number of sites. These are illustrated for $n=2$ and $n=3$ in figure 3. One sees that not all possible rings are required. For example, rings that contain only A's or only B's are deleted since these do not contribute to a change in the number of A or B particles (since one must have

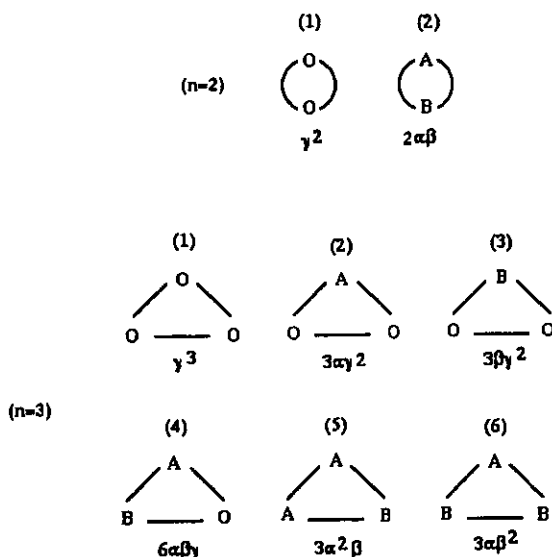


Figure 3. Configurations of finite rings for $n=2$ and $n=3$ sites required to construct the appropriate matrices for the $A + B \rightarrow O$ system. The initial probabilities the various rings are indicated.

a mixture of A and B to get the annihilation reaction). Also, we require only one orientation of each ring; the combinatorics of different rotational orientations and reflections will be introduced in the initial conditions.

We define a row vector, p , whose elements are the probabilities of the appropriate rings. The initial probabilities of the rings are given in terms of the parameters α and β (see (2.4)) for random initial configurations; also included in the initial probabilities are the number of rotations and reflections of a given ring. The appropriate initial values are indicated in figure 3; note that the sum of the probabilities does not add up to one since we are not required to include all of the possible rings (as just explained). We then introduce the matrix of transition probabilities

$$W = (w_{ij}) \tag{3.1}$$

where

$$\begin{aligned} w_{ij} &= \text{rate constant for reaction ring } i \rightarrow \text{ring } j \\ w_{ii} &= -\sum w_{ij} \text{ (sum over } j \text{ with } j \neq i). \end{aligned} \tag{3.2}$$

The differential equation for the time evolution of the rings is then given by

$$dp/dt = pW \tag{3.3}$$

In terms of the vector p , the net density of A sites is then

$$\rho_A = (1/N)p v \tag{3.4}$$

where v is a column vector whose i th element is the number of A's in the i th ring. The derivatives of ρ_A (hence the coefficients in the time-power series) are then

$$\rho_A^{(n)} = \left(\frac{d^n \rho_A}{dt^n} \right)_{t=0} = \frac{1}{N} p(0) W^n v \tag{3.5}$$

where $p(0)$ is the vector of initial ring probabilities.

As an example, from figures 3 for $n = 2$ one has

$$p(0) = ([1 - \alpha - \beta] \ 2\alpha\beta) \quad W = \begin{pmatrix} 0 & 0 \\ 4 & -4 \end{pmatrix} \quad v = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{3.6}$$

Using (3.6) in (3.5) gives

$$\rho_A^{(1)} = -4\alpha\beta \tag{3.7}$$

which is the result of (2.7). A two-site ring gives us only the correct first derivative. To obtain through $\rho_A^{(2)}$ we require rings with three sites. From figure 3 we have

$$\begin{aligned} p(0) &= (\gamma^3 \quad 3\alpha\gamma^2 \quad 3\beta\gamma^2 \quad 6\alpha\beta\gamma \quad 3\alpha^2\beta \quad 3\alpha\beta^2) \\ W &= \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & -2 & 0 & 0 \\ 0 & 4 & 0 & 0 & -4 & 0 \\ 0 & 0 & 4 & 0 & 0 & -4 \end{pmatrix} \quad v = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \\ 2 \\ 1 \end{pmatrix}. \end{aligned} \tag{3.8}$$

From these equations we obtain the following derivatives for the infinite system

$$\rho_A^{(0)} = \alpha \quad \rho_A^{(1)} = -4\alpha\beta \quad \rho_A^{(2)} = 8\alpha\beta(1 + \alpha + \beta) \tag{3.9}$$

which reproduce the results of (2.7) and (2.11) obtained in a different manner. Note that while all of the initial probabilities are cubic in the initial densities, the lower order derivatives contain terms that are not cubic (reflecting the use of (2.5)).

In summary, the matrix method gives a systematic alternative means of deriving the coefficients in the time-power series. The fact that one has two independent ways of deriving the $c^{(n)}$ serves as a useful check on the accuracy of the results. We turn now to the question of how to determine the exponent ν from the time-power series.

4. Asymptotic form

We continue to use the reaction $A+B \rightarrow O$ in one dimension as an example. We take the case $\alpha = \beta$ (equal initial concentrations of A and B). From the discussion in the introduction we expect the long-time asymptotic behaviour

$$\rho_A(t) \sim t^{-\nu} \quad (4.1)$$

with $\nu = 1/4$ for the one-dimensional case. Our goal is to determine ν from the power series (1.4). To this end we introduce the variable

$$y = 1 - \rho_A/\alpha \quad (4.2)$$

which varies from zero at $t=0$ to one at $t=\infty$. Writing the time series for ρ_A as

$$\rho_A = \sum_{n=0}^{\infty} a_n t^n \quad (4.3)$$

where $a_0 = \rho_A(0) = \alpha$, we then invert this relation using (4.2) to give

$$t = \sum_{n=1}^{\infty} b_n y^n. \quad (4.4)$$

From (4.1) we have

$$t \sim \left(\frac{1}{1-y} \right)^{1/\nu} \quad (4.5)$$

For a singularity of the form of (4.5) the ratios of successive terms

$$r_n = b_n/b_{n-1} \quad (4.6)$$

are given by (Stanley 1971, Gaunt and Guttmann 1974)

$$r_n = y_\sigma^{-1} \left[1 + \frac{1}{n} \left(\frac{1}{\nu} - 1 \right) \right] \quad (4.7)$$

where y_σ is the radius of convergence. From (4.5) we have $t_\sigma = 1$ and hence

$$1/\nu = 1 - n(1 - r_n). \quad (4.8)$$

Thus the various r_n give a series of estimates of ν which one hopes will converge rapidly to the true value.

For example, for the case $\alpha = \beta = 1/2$ we use $c(t)$ given in (2.14) with the variable $y = 1 - 2c$ to give a time-power series for y

$$y = 2t - 4t^2 + 6t^3 + \dots \quad (4.9)$$

Introducing a scaled time $t' = 2t$, but then dropping the prime for simplicity, gives

$$y = t - t^2 + (3/4)t^3 + \dots \quad (4.10)$$

which can be inverted to give t as a function of y

$$\begin{aligned} t &= y + y^2 + (5/4)y^3 + (27/16)y^4 + (1133/480)y^5 + (38\,721/11\,520)y^6 + \dots \\ &= y + y^2 + (1.25)y^3 + (1.688)y^4 + (2.360)y^5 + (3.361)y^6 + \dots \end{aligned} \quad (4.11)$$

The series is seen to be very well-behaved with the coefficients all positive and monotonically increasing. Applying (4.8) we obtain the following series of estimates of ν

$$\nu = 1, 0.571, 0.417, 0.334, 0.282 \quad (4.12)$$

which indeed are rapidly converging toward the expected value of $\nu = 0.25$. The values of ν given in (4.12) are plotted as a function of n (determined by the r_n value used) in figure 4 (the curve marked 1-d).

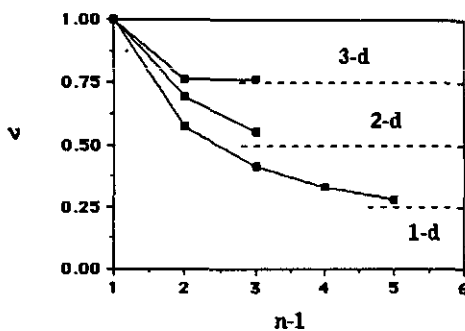


Figure 4. Estimates of the exponent ν for the $A + B \rightarrow O$ system in one, two and three dimensions using equation (4.8) and the series (4.11), (5.11), and (5.12) respectively. The limiting values shown by the dashed lines are $\nu = 1/4$, $1/2$, and $3/4$ respectively in one, two, and three dimensions.

5. $A + B \rightarrow O$ in two and three dimensions

The procedure used in section 2 to construct a time-power series from a hierarchy of coupled differential equations for the $A + B \rightarrow O$ reaction in one dimension is easily extended to two and three dimensions (using the square and cubic lattices, respectively). The basic equations are (analogues of (2.2))

$$(2D) \quad d\rho_A/dt = -6\rho_{AB} \quad (5.1)$$

$$(3D) \quad d\rho_A/dt = -8\rho_{AB} \quad (5.2)$$

where ρ_A is again the number of lattice sites occupied by A and ρ_{AB} is the density of nearest neighbour AB pairs. One then proceeds to construct differential equations for the rate of change of ρ_{AB} on the appropriate lattice.

For general α and β , assuming the same random initial conditions as we did for the one-dimensional model (see (2.4)) one obtains

$$\begin{aligned}
 (2D) \quad c^{(0)} &= \alpha & c^{(1)} &= -8\alpha\beta & c^{(2)} &= 16\alpha\beta + 48\alpha\beta^2 + 48\alpha^2\beta \\
 c^{(3)} &= -128\alpha\beta - 144\alpha\beta^2 - 240\alpha\beta^3 - 144\alpha^2\beta - 1056\alpha^2\beta^2 - 240\alpha^3\beta \\
 c^{(4)} &= 1216\alpha\beta + 1296\alpha\beta^2 + 480\alpha\beta^3 + 1104\alpha\beta^4 + 1296\alpha^2\beta \\
 &\quad + 4224\alpha^2\beta^2 + 14\,256\alpha^2\beta^3 + 480\alpha^3\beta + 14\,256\alpha^3\beta^2 + 1104\alpha^4\beta.
 \end{aligned} \tag{5.3}$$

$$\begin{aligned}
 (3D) \quad c^{(0)} &= \alpha & c^{(1)} &= -12\alpha\beta & c^{(2)} &= 24\alpha\beta + 120\alpha\beta^2 + 120\alpha^2\beta \\
 c^{(3)} &= -288\alpha\beta - 360\alpha\beta^2 - 1080\alpha\beta^3 - 360\alpha^2\beta - 4560\alpha^2\beta^2 - 1080\alpha^3\beta \\
 c^{(4)} &= 3456\alpha\beta + 3240\alpha\beta^2 + 4320\alpha\beta^3 + 9240\alpha\beta^4 + 3240\alpha^2\beta \\
 &\quad + 89\,280\alpha^2\beta^2 + 34\,920\alpha^2\beta^3 + 4320\alpha^3\beta + 34\,920\alpha^3\beta^2 + 9240\alpha^4\beta.
 \end{aligned} \tag{5.4}$$

For the special case of $\alpha = \beta$ the above results reduce to the following polynomials in α :

$$\begin{aligned}
 (2D) \quad c^{(0)} &= \alpha & c^{(1)} &= -8\alpha^2 & c^{(2)} &= 16\alpha^2 + 96\alpha^3 \\
 c^{(3)} &= -128\alpha^2 - 288\alpha^3 - 1536\alpha^4 \\
 c^{(4)} &= 1216\alpha^2 + 2592\alpha^3 + 5184\alpha^4 + 30\,720\alpha^5
 \end{aligned} \tag{5.5}$$

$$\begin{aligned}
 (3D) \quad c^{(0)} &= \alpha & c^{(1)} &= -12\alpha^2 & c^{(2)} &= 24\alpha^2 + 240\alpha^3 \\
 c^{(3)} &= -288\alpha^2 - 720\alpha^3 - 6720\alpha^4 \\
 c^{(4)} &= 3456\alpha^2 + 6480\alpha^3 + 97\,920\alpha^4 + 88\,320\alpha^5
 \end{aligned} \tag{5.6}$$

Finally, when $\alpha = \beta = 1/2$ we obtain the following numerical coefficients:

$$\begin{aligned}
 (2D) \quad c^{(0)} &= 1/2 & c^{(1)} &= -2 & c^{(2)} &= 16 \\
 c^{(3)} &= -164 & c^{(4)} &= 2080
 \end{aligned} \tag{5.7}$$

$$\begin{aligned}
 (3D) \quad c^{(0)} &= 1/2 & c^{(1)} &= -3 & c^{(2)} &= 36 \\
 c^{(3)} &= -582 & c^{(4)} &= 10\,554
 \end{aligned} \tag{5.8}$$

Using the coefficients of (5.7) and (5.8) in the general time-power series (1.4), scaling the time ($t' = 4t$ in 2D and $t' = 6t$ in 3D), and introducing the variable y of (4.2) (where $y = 1 - 2c$ in both 2D and 3D for $\alpha = \beta = 1/2$) gives (dropping the prime on t for simplicity)

$$(2D) \quad y(t) = t - t^2 + (41/48)t^3 - (239/384)t^4 + \dots \tag{5.9}$$

$$(3D) \quad y = t - t^2 + (97/108)t^3 - (1759/2592)t^4 + \dots \tag{5.10}$$

Inverting the above series gives our working equations

$$(2D) \quad t = y + y^2 + (55/48)y^3 + (529/384)y^4 + \dots \tag{5.11}$$

$$(3D) \quad t = y + y^2 + (119/108)y^3 + (3079/2592)y^4 + \dots \tag{5.12}$$

The ratios of successive coefficients in the above equations give series of estimates of the exponent ν of (4.1) using (4.7)

$$\begin{aligned}
 (2D) \quad \nu &= 1, 16/23, 110/199, \dots \\
 &= 1, 0.696, 0.553, \dots
 \end{aligned} \tag{5.13}$$

$$\begin{aligned}
 (3D) \quad \nu &= 1, 36/47, 714/937, \dots \\
 &= 1, 0.765, 0.762, \dots
 \end{aligned} \tag{5.14}$$

The numbers given above are plotted in figure 4 as a function of n , the summation index in (4.7). One sees that in one, two, and three dimensions the estimates of the exponents from the time-power series rapidly converge to the general result $d/4$, i.e. $\nu = 1/4, 1/2$ and $3/4$ respectively in one, two and three dimensions. Since the value of ν for three dimensions is close to the mean-field result, the sequence of estimates of ν converge rapidly in that case.

6. $A + A \rightarrow O$ and $A + A \rightarrow A$ in one dimension

As mentioned in the introduction, the reactions $A + A \rightarrow O$ and $A + A \rightarrow A$ in one dimension are both expected to give $\rho_A \sim t^{-1/2}$. To construct the hierarchy of differential equations for these systems we proceed exactly as we did with the $A + B \rightarrow O$ reaction in section 2. We begin with $A + A \rightarrow O$. The reactions changing the occupancy of A at a given lattice site are the same as those given in figure 2, except that for the annihilation reactions, B is replaced by A. Assuming that the lattice is homogeneous, i.e. $\rho_{AO} = \rho_{OA}$ one then has in analogy with (2.2)

$$(A + A \rightarrow O) \quad d\rho_A/dt = -4\rho_{AA}. \tag{6.1}$$

For the case of $A + A \rightarrow A$ the diffusion reactions in figure 2 apply. But in this case the annihilation reactions are (the site selected to monitor the change of occupancy by A is underlined)



One sees that only the first two reactions lead to a change in the occupancy by A at the chosen site. The basic differential equation is then

$$(A + A \rightarrow A) \quad d\rho_A/dt = -2\rho_{AA} \tag{6.3}$$

where, again, since $\rho_{OA} = \rho_{AO}$, the contribution of the diffusion terms exactly cancels.

One then proceeds to form differential equations for $d\rho_{AA}/dt$ in the two cases. We assume random initial conditions with

$$\begin{aligned} \rho_A(0) &= \alpha & \rho_O(0) &= \gamma \\ \alpha + \gamma &= 1. \end{aligned} \tag{6.4}$$

For general α we obtain

$$\begin{aligned} (A + A \rightarrow O) \quad c^{(0)} &= \alpha & c^{(1)} &= -4\alpha^2 & c^{(2)} &= 8\alpha^2 + 16\alpha^3 \\ c^{(3)} &= -32\alpha^2 - 64\alpha^3 - 64\alpha^4 \end{aligned} \tag{6.5}$$

$$\begin{aligned} (A + A \rightarrow A) \quad c^{(0)} &= \alpha & c^{(1)} &= -2\alpha^2 & c^{(2)} &= 4\alpha^2 + 4\alpha^3 \\ c^{(3)} &= -16\alpha^2 - 16\alpha^3 - 8\alpha^3 \\ c^{(4)} &= 80\alpha^2 + 80\alpha^3 + 48\alpha^4 + 16\alpha^5. \end{aligned} \tag{6.6}$$

At the special value $\alpha = 1$ we obtain a few more terms:

$$\begin{aligned} (A + A \rightarrow O) \quad c^{(0)} &= 1 & c^{(1)} &= -4 & c^{(2)} &= 24 & c^{(3)} &= -160 \\ c^{(4)} &= 1120 & c^{(5)} &= -8064 & c^{(6)} &= 60\,592 \end{aligned} \tag{6.7}$$

$$\begin{aligned} (A + A \rightarrow A) \quad c^{(0)} &= 1 & c^{(1)} &= -2 & c^{(2)} &= 8 \\ c^{(3)} &= -40 & c^{(4)} &= 224 & c^{(5)} &= -1344 \end{aligned} \tag{6.8}$$

For the case of $\alpha=1$ we take $y=1-c$ and scale time appropriately ($t'=4t$ for $A+A\rightarrow O$, and $t'=2t$ for $A+A\rightarrow A$, dropping the prime for simplicity) giving

$$(A+A\rightarrow O) \quad y = t - (3/4)t^2 + (5/12)t^3 - (35/192)t^4 - (21/320)t^5 \\ - (3787/184\,320)t^6 + \dots \quad (6.9)$$

$$(A+A\rightarrow A) \quad y = t - t^2 + (5/6)t^3 - (7/12)t^4 + (7/20)t^5 + \dots \quad (6.10)$$

which when inverted give

$$(A+A\rightarrow O) \quad t = y + (3/4)y^2 + (17/24)y^3 + (35/48)y^4 + (47/60)y^5 \\ + (158\,963/184\,320)y^6 + \dots \quad (6.11)$$

$$(A+A\rightarrow A) \quad t = y + y^2 + (7/6)y^3 + (17/12)y^4 + (26/15)y^5 + \dots \quad (6.12)$$

The ratio method then gives the following estimate of the exponent ν :

$$(A+A\rightarrow O) \quad \nu = 2, 6/5, 17/19, 35/48, 24\,064/38\,643, \dots \\ = 2, 1.2, 0.895, 0.731, 0.623, \dots \quad (6.13)$$

$$(A+A\rightarrow A) \quad \nu = 1, 2/3, 7/13, 17/36, \dots \\ = 1, 0.667, 0.538, 0.472, \dots \quad (6.14)$$

The exponents given above are plotted as a function of the summation index (n) in figure 5; the values for both models are seen to be converging toward the expected value of $1/2$ (we note in (6.14) that the estimate of ν is actually slightly below the value $1/2$). There is no guarantee that the estimates of the exponents will extrapolate monotonically to the limiting values. Sometimes nearby roots in the complex plane cause a small background oscillation in the values obtained. For the case of a random walk of a single particle on a lattice, the probability that the particle remains at the original site goes to zero asymptotically as $t^{-1/2}$. One can show exactly that Padé approximants for the exponent do not approach $1/2$ monotonically (instead the function has a single maximum before settling down to the value of $1/2$).

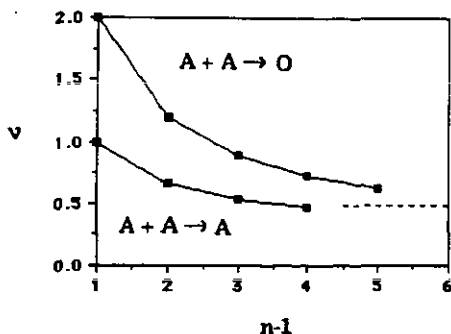


Figure 5. Estimation of the exponent ν for the systems $A+A\rightarrow O$ and $A+A\rightarrow A$ in one dimension using equation (4.8) and the series of (6.11) and (6.12) respectively. The dashed line gives the limiting value of $\nu=1/2$ for both.

7. $A + B \rightarrow B$, one species immobile

For the 1D systems

$$\text{(mobile A, immobile B)} \quad A + B \rightarrow B \quad (7.1)$$

$$\text{(immobile A, mobile B)} \quad A + B \rightarrow B \quad (7.2)$$

the expected asymptotic behaviour is (Sokolov *et al* 1991)

$$\text{(immobile B)} \quad \rho_A \sim \exp(-t^{1/3}) \quad (7.3)$$

$$\text{(immobile A)} \quad \rho_A \sim \exp(-t^{1/2}). \quad (7.4)$$

For these models the asymptotic form is thus a stretched exponential of the general form

$$\rho_A \sim \exp(-t^\nu) \quad (7.5)$$

and we enquire here if our series method can give estimates of the exponent ν for the functional form of (7.5). Taking $u = 2\rho_A$ we first form the series for $-\ln u$ which has the property

$$-\ln u \sim t^\nu \quad (7.6)$$

and then introduce the variable w with the asymptotic form of

$$w = 1/(1 - \ln u) \sim t^{-\nu}. \quad (7.7)$$

We now proceed as before forming

$$y = 1 - w \sim 1 - t^{-\nu} \quad (7.8)$$

which when inverted gives

$$t \sim \left(\frac{1}{1-y} \right)^{1/\nu} \quad (7.9)$$

as before. The net transformation is

$$y = \frac{1}{1 - \left(\frac{1}{\ln u} \right)}. \quad (7.10)$$

The series are obtained in the manner described for the previous models. The final results are

$$\text{(immobile B)} \quad t = y + (5/4)y^2 + (19/12)y^3 + (97/48)y^4 + (827/320)y^5 + \dots \quad (7.11)$$

$$\text{(immobile A)} \quad t = y + (5/4)y^2 + (37/24)y^3 + (121/64)y^4 + (895/384)y^5 + \dots \quad (7.12)$$

Again these series are seen to be very well-behaved with the coefficients increasing monotonically. Using (4.8) gives the following estimates of the exponent ν :

$$\begin{aligned} \text{(immobile B)} \quad \nu &= 2/3, 10/17, 19/40, 388/929, \dots \\ &= 0.667, 0.556, 0.475, 0.418, \dots \end{aligned} \quad (7.13)$$

$$\begin{aligned} \text{(immobile A)} \quad \nu &= 2/3, 10/17, 74/141, 726/1571, \dots \\ &= 0.667, 0.588, 0.525, 0.462, \dots \end{aligned} \quad (7.14)$$

The sequences in (7.13) and (7.14) should be asymptotic to $1/3$ and $1/2$ respectively. Clearly they are headed in the correct direction (we note that the last estimate of ν in (7.14) has dropped below the expected value). We give an alternative estimate of these exponents in the next section.

8. Summary

We have shown that power series in the time of moderate length (5 or 6 terms), when properly manipulated, can give estimates of power-law exponents and even exponents for stretched exponentials, that converge rapidly to the expected limits. We have determined the series here by hand by constructing the hierarchy of different equations to a given order. (For the case of $A+B \rightarrow O$ in one dimension we have also checked the series through the fourth order by using the independent matrix method of section 3.) In order to obtain longer series one would have to computerize the construction of the differential equations (or, in one dimension, the construction of the appropriate matrix). The method outlined here can be applied to many other reaction-diffusion models. For example, we have successfully applied the method of using time-power series to determine power law exponents to aggregation models governed by the Smoluchowski equation.

We have seen that that ratio method of (4.7) works well for the models considered here. The ratio method assumes that the singularity of interest, e.g. (4.5), is the dominant one (nearest singularity to the origin). If that is not the case, one can use Padé approximants to concentrate the influence of the desired singularity (Stanley 1971). Given the general series $t = t(y)$ one can construct the function

$$f(y) = t/y \quad (8.1)$$

and then form the series for

$$(1-y) \, d \ln f / d \ln y = g(y) \quad (8.2)$$

where

$$g(1) = 1/\nu. \quad (8.3)$$

This method in principle will work for power law singularities as in (4.1) or for the stretched exponential of (7.5), where in the latter case one uses $t(y)$ as constructed in (7.8).

The $(1/2)$ Padé approximants to $g(y)$ are shown in figure 6 for the stretched-exponential models of (7.1) and (7.2). The horizontal dashes at $y=1$ give the expected values ($1/\nu=3$ for immobile B and $1/\nu=2$ for immobile A; the Padé approximants give respectively the values 3.69 and 1.85). Clearly a longer series on which to base the Padé approximants could be expected to give a much better estimate of the exponents.

Oddly the above approach does not work well for the power-law models (the Padé approximants seem to develop obscuring roots). A practical approach that allows one to construct a good approximate form for $\rho_A(t)$ over the whole time range for these models is as follows. We define the function $h(y)$ by

$$t = y \left(\frac{1}{1-y} \right)^{h(y)}. \quad (8.4)$$

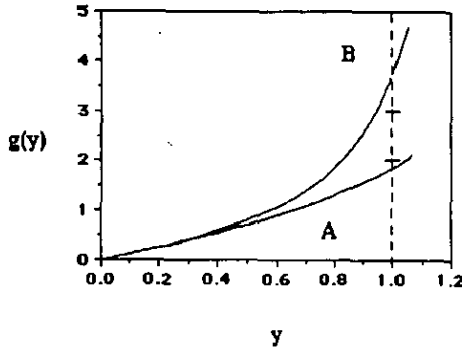


Figure 6. Padé approximants to the function $g(y)$ defined in (8.2) for the models of (7.1) and (7.2) (immobile B and immobile A respectively, labelled B and A). The value of the exponent in the stretched exponential is given by $1/\nu = g(y=1)$. The correct values are indicated by the horizontal dashes at $y=1$.

We can construct $h(y)$ so that $t(y)$ defined by (8.4) has the first N derivatives exact and the correct asymptotic behaviour. By constructing the function $h(y)$ and seeing how rapidly it approaches a limiting value we learn how rapidly the asymptotic form of (4.5) is attained. Given N exact terms for $t(y)$ one obtains $(N-2)$ terms in the series for $h(y)$. For the $A+B \rightarrow O$ reaction in one dimension, using the numbers given in (2.14), one obtains

$$h(y) = 1 + 0.25y + 0.3125y^2 + 0.40209y^3 + 0.52370y^4 + [(0.79281y)^5 / (1 - 0.79281y)]. \quad (8.5)$$

The term in square brackets is a correction term of fifth order and higher in y that forces $h(1)=4$ (without the correction the truncated series gives $h(1)=2.49$). The function $h(y)$ is shown in figure 7(a) while the function $\rho_A(s)$ is plotted in figure 7(b) (recall that $y = 1 - 2\rho_A$; $s = t/(1+t)$). The function $\rho_A(s)$ shown in figure 7(b), calculated using (8.5), has the first six derivatives with respect to s (time) exact and gives the correct asymptotic form, i.e. $t^{-1/4}$. The mean-field form (see (A-11) in the appendix) is (using the scaled time $t' = 2t$)

$$\rho_A = \frac{1}{2}(1-s) \quad (8.6)$$

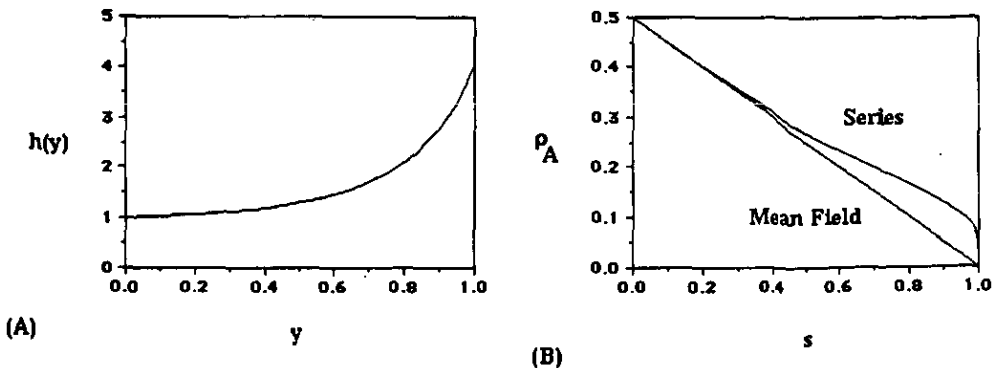


Figure 7. (a) A plot of the function $h(y)$ defined in (8.5); $h(1)=4$; (b) Plots of ρ_A for the $A+B \rightarrow O$ reaction as a function of the variable $s = t/(1+t)$ for the function of (8.4) (labelled as series) and the mean-field result of (8.6).

which is also shown in figure 7(b). From equations (2.14) and (2.15) we know that the mean-field result and the exact series agree through the second-order terms, and this is evident in figure 7(b). Since $h(y)$ is an effective exponent, one sees that this quantity only approaches the limiting value of $1/\nu = 4$ as y is almost equal to one. It is thus striking that the successive estimates of ν from the series, as shown in figure 3, approach the value $\nu = 1/4$ is rapidly.

Appendix. Well-stirred limit

As a limiting case we consider the system where the occurrences of A and B on the lattice are random for all times. This means physically that the system is continually randomized, a condition we refer to as the well-stirred limit. We treat the reaction $A + B \rightarrow O$ on the 1D lattice. We begin with the general equation

$$d\rho_A/dt = -4\rho_{AB}. \quad (\text{A1})$$

The assumption of instantaneous randomization gives (for all times)

$$\rho_{AB} = \rho_A \rho_B. \quad (\text{A2})$$

We introduce the variables

$$\begin{aligned} x &= \rho_A = x_0 - \xi \\ y &= \rho_B = y_0 - \xi \end{aligned} \quad (\text{A3})$$

where

$$x_0 = \rho_A(t=0) = \alpha \quad y_0 = \rho_B(t=0) = \beta \quad (\text{A4})$$

and ξ is the progress variable. Using (A2) and (A3) in (A1) gives

$$d\xi/dt = 4(\alpha - \xi)(\beta - \xi) \quad (\text{A5})$$

which can be integrated to give (where we assume $\alpha > \beta$)

$$\xi = \frac{\beta[1 - e^{-4(\alpha-\beta)t}]}{1 - (\beta/\alpha)e^{-4(\alpha-\beta)t}}. \quad (\text{A6})$$

For $\alpha > \beta$ gives the asymptotic behaviour

$$y \sim \exp(-t/\tau) \quad (\text{A7})$$

where one has the relaxation time

$$\tau = \frac{1}{4(\alpha - \beta)}. \quad (\text{A8})$$

As $\alpha \leftarrow \beta$ the relaxation time goes to infinity, and in that limit one obtains a power-law behaviour.

For $\alpha = \beta$, (A1) gives

$$dx/dt = -4x^2 \quad (\text{A9})$$

which can be integrated to yield

$$x = \left(\frac{\alpha}{1 + 4\alpha t} \right) \sim t^{-1}. \quad (\text{A10})$$

For the special case of $\alpha = \beta = 1/2$ one has

$$\rho_A = \frac{1}{2} \left(\frac{1}{1 + 2t} \right). \quad (\text{A11})$$

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