

# Finite-Size Scaling Studies of One-Dimensional Reaction–Diffusion Systems. Part II. Numerical Methods

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The scaling exponent and the scaling function for the 1D single-species coagulation model ( $A + A \rightarrow A$ ) are shown to be universal, i.e., they are not influenced by the value of the coagulation rate. They are independent of the initial conditions as well. Two different numerical methods are used to compute the scaling properties of the concentration: Monte Carlo simulations and extrapolations of exact finite-lattice data. These methods are tested in a case where analytical results are available. To obtain reliable results from finite-size extrapolations, numerical data for lattices up to ten sites are sufficient.

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**KEY WORDS:** Reaction–diffusion systems; finite-size scaling; Monte Carlo simulations; nonequilibrium statistical mechanics; coagulation model.

## 1. INTRODUCTION

The study of reaction–diffusion systems has become a field of intense research in recent years. Since analytical solutions are only possible in special cases, numerical methods are a useful tool in the investigation of these systems.<sup>(1–3)</sup> In continuation of our previous paper<sup>(4)</sup> (denoted by paper I in the sequel), we concentrate on the coagulation model defined on a one-dimensional lattice of length  $L$ . This model allows the description of exciton concentration decay in porous media, a phenomenon experimentally studied in refs. 5–8. In the coagulation model only the following two processes on adjacent sites take place with left–right-symmetric rates:

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- Diffusion with rate  $D$



- Coagulation with rate  $c$



One of the two reaction rates can be eliminated by choosing the time scale such that  $D = 1$ . So there remains only one parameter describing the reaction rates. A convenient choice for this parameter is the asymmetry  $\Delta'$  between the diffusion rate and the coagulation rate:

$$\Delta' = 1 - c \quad (1.3)$$

In paper I it was shown that this model is analytically solvable only for  $\Delta' = 0$ . In this case the finite-size scaling behavior was investigated. In this article these investigations are extended to the case  $\Delta' \neq 0$ , using Monte Carlo techniques. We also present a new interesting method based on extrapolation of data obtained by numerical diagonalization.

Up to now theoretical and numerical methods have concentrated on the thermodynamic and the continuum limits. Thus Monte Carlo simulations were performed on large lattices with  $L \geq 10^3$  in order to avoid finite-size effects. In this article we use the opposite approach: We are able to show that by studying the dependence of the concentration on the length  $L$  of the lattice one can get information about the behavior of the system in the thermodynamic limit. The key point here is the validity of the finite-size scaling hypothesis of the concentration for reaction-diffusion systems with critical dynamics. Following Alcaraz *et al.*,<sup>(9)</sup> the concentration behaves according to

$$c(z, L) = L^x [F_0(z) + L^{-y}F(z) + \dots] \quad (1.4)$$

in the limit  $L \rightarrow \infty$ ,  $t \rightarrow \infty$  with  $z = 4t/L^2$  fixed. In this equation  $x$  denotes the scaling exponent,  $F_0(z)$  the scaling function, and  $L^{-y}F(z)$  the leading correction term.

We point out that the finite-size scaling hypothesis is only valid for systems which do not have a finite energy gap in their spectrum. Such systems are commonly said to be massless. Therefore the spectrum allows us to decide whether the finite-size scaling hypothesis can be applied or not.

The finite-size scaling behavior can be studied in a new way which we will now briefly explain. The master equation describing a reaction-

diffusion system can be written as a Euclidean Schrödinger equation in the  $2^L$ -dimensional configuration space<sup>(9)</sup>:

$$\frac{\partial}{\partial t} |P(t)\rangle = -H |P(t)\rangle \quad (1.5)$$

where  $H$  is the Hamiltonian describing the system. For small lattices the equation can be solved by numerical diagonalization of the Hamiltonian. This gives us a way to compute expectation values of various observables for arbitrary chemical processes and lattice lengths  $L$  up to 10–20 sites. (The minimal value of the lattice length needed for this computation depends on the number of particle species, the maximal possible value is limited by the computer capacity.) The scaling exponent, the scaling function, and the correction term are obtained through extrapolation of the finite-lattice data.

In paper I we showed that the spectrum of the Hamiltonian  $H$  describing the coagulation model is given by that of the  $XXZ$  quantum chain in an external magnetic field. The first aim of the present paper is to investigate the scaling behavior (1.4) of the concentration for different choices of the coagulation rate  $c$ , i.e., different values of  $\Delta'$ . As long as no decoagulation reaction ( $A \rightarrow A + A$ ) occurs, the system is on the Pokrovsky–Talapov line<sup>(9)</sup> for any  $\Delta'$ . It can be shown<sup>(10)</sup> that in the continuum, along the Pokrovsky–Talapov line, the system is always massless with the same quadratic dispersion relation. We expect that this fact is reflected in the scaling properties. For  $\Delta' = 0$  the spectrum can be obtained in terms of free fermions. This fact allows the analytical solutions presented in paper I. For  $\Delta' \neq 0$  these calculations do not apply. Therefore we use Monte Carlo simulations to determine the scaling exponent and function as well as the corrections.

The case  $0 < \Delta' < 1$  corresponds to a coagulation reaction taking place with probability  $c < 1$  on two-particle encounters, a subject which has drawn much attention in recent years. Some of the approaches studying this situation<sup>(11,12)</sup> are based on mean-field approximations for infinite lattices and treat the crossover from the reaction-controlled to the diffusion-controlled reaction regime. An approximate equation for the particle concentration derived from empty interval probabilities is considered in ref. 13. In refs. 14–16 the self-organization of the model in the continuum limit was investigated by studying the nearest-neighbor distance distribution. Interesting conclusions were drawn from Monte Carlo simulations. The decay of the concentration at intermediate times as a  $t$ -dependent effective exponent law was proposed in ref. 17. The determination of the steady-state densities was used in ref. 18 in order to get the “effective reaction order,” i.e., the effective exponent of the density replacing the classical exponent in the rate equation.

It is a well-known fact that at large times the particle concentration in the thermodynamic limit behaves like  $(2\pi t)^{-1/2}$ . The results we obtained from finite-size scaling analysis of Monte Carlo data show that this behavior occurs independently of the value of  $\Delta'$ . Moreover, we show that the next-to-leading term is of the order  $t^{-1}$  with a coefficient dependent on  $\Delta'$  and independent of the initial conditions. Thus we are in perfect agreement with the analytical results of refs. 13 and 14.

Up to now only the case of  $\Delta' > 0$ , i.e., coagulation rate less than the diffusion rate, has been studied in the literature. We extend the investigation to the case of negative values of  $\Delta'$ , i.e., coagulation rate larger than the diffusion rate, and find a similar behavior. This is an important observation because the model can clearly be interpreted as a system with a short-range attractive force between the particles.

Our second point of interest is to figure out how the choice of initial conditions influences the scaling properties. For  $\Delta' = 0$  the case of uncorrelated initial conditions with arbitrary initial occupation probability  $p$  was treated analytically in paper I. Now we use Monte Carlo simulations and extrapolations from finite lattices to study initial configurations with small clusters. Due to lack of computer time, these studies are carried out for  $\Delta' = 0$  only.

It was pointed out in paper I that scaling relations allow us to compute estimates for critical exponents of an infinite system from the scaling behavior of a finite one. An important purpose of the present paper is therefore to figure out what lattice sizes are necessary to compute the scaling properties numerically. The case of  $\Delta' = 0$  is used to test the accuracy of finite-lattice extrapolations. It is shown that finite-size analysis allows us to determine the scaling properties already from numerical data for lattices of length smaller than ten sites.

We decided to organize the paper according to the different numerical methods we use. In Section 2 we discuss Monte Carlo simulations of reaction-diffusion systems and present the results obtained by this method. Section 3 is devoted to extrapolations from finite lattices. The accuracy of the extrapolations is studied and the investigation of different initial conditions in the case of open boundary conditions is presented. We close with the discussion of our results.

## 2. MONTE CARLO SIMULATIONS

Before we present the results of the Monte Carlo simulations, we briefly explain how the simulations are performed. The dynamics of the system is determined by the rates  $\Gamma_{\gamma,\delta}^{\alpha,\beta}$  for the nearest-neighbor interactions:

$$(\alpha, \beta) \rightarrow (\gamma, \delta) \quad (2.1)$$

Here a value of  $\alpha, \beta, \gamma, \delta = 1$  corresponds to a particle and a value of 0 to a vacancy.

We consider two types of initial conditions: in an uncorrelated initial state all sites are occupied with equal probability  $p$  at  $t=0$ ; a weakly correlated state consists of a pairwise alternating sequence of particles and vacancies ( $AA\emptyset\emptyset AA\emptyset\emptyset \dots$ ).

We only study vacuum-driven processes, i.e., no reactions occur on a pair of empty sites. Therefore we use the "direct method"<sup>(1,2)</sup> for our simulations. By  $\Delta t$  we denote a discrete time step. Each Monte Carlo step consists of the following operations:

1. A particle is chosen at random and afterward, with equal probability, one of its neighbors. The resulting pair  $(\alpha, \beta)$  cannot consist of two vacancies.

2. A new configuration  $(\gamma, \delta) \neq (\alpha, \beta)$  is chosen with the probability

$$n(\alpha, \beta) \Gamma_{\gamma, \delta}^{\alpha, \beta} \Delta t \quad (2.2)$$

or the pair remains unchanged with probability

$$1 - n(\alpha, \beta) \Delta t \sum_{(\gamma, \delta) \neq (\alpha, \beta)} \Gamma_{\gamma, \delta}^{\alpha, \beta} \quad (2.3)$$

Here  $n(\alpha, \beta)$  is defined by

$$n(\alpha, \beta) = \begin{cases} 1 & \text{if } (\alpha, \beta) = (1, 1) \\ 2 & \text{if } (\alpha, \beta) = (1, 0) \\ 2 & \text{if } (\alpha, \beta) = (0, 1) \end{cases} \quad (2.4)$$

This factor<sup>(19)</sup> simply accounts for the fact that a pair containing only a single particle is chosen with half the probability of choosing one that consists of two particles.

3. Finally the time is increased:

$$t \rightarrow t + \Delta t/N \quad (2.5)$$

where  $N$  is the total number of particles on the lattice.

If the coagulation process has been chosen in a Monte Carlo step, the average concentration decreases by an amount of

$$q_c = \frac{1}{LN_s} \quad (2.6)$$

Table I. Maximum Error of the Simulated Concentration for Periodic Boundaries and  $\Delta' = 0$

$\Delta t$	$L$	$t_{\max}$	Maximum error in %
$5 \times 10^{-3}$	6	0.9	0.36
$5 \times 10^{-2}$	200	$10^3$	0.42
$5 \times 10^{-1}$	1000	$25 \times 10^3$	0.44

where  $N_s$  denotes the number of samples (i.e., program runs) used in the simulation. Therefore the simulated time  $t$  should not reach values where the concentration  $c(t)$  becomes of the order of  $q_c$ . Because we are interested in the scaling behavior and the corrections, it is necessary to perform the simulations on small lattices ( $L < 100$ ). Therefore the number of samples  $N_s$  has to be large. A large number of samples is advantageous because the standard deviation of the mean decreases like  $(N_s)^{-0.5}$ . The limit is set by the growth of the necessary CPU time. Averaging over  $N_s = 20,000$  samples provides very accurate results, as the test described in the sequel will show.

The time discretization  $\Delta t$  clearly influences the quality of the simulations. For smaller lattices this influence grows, because the number of particles is small [cf. Eq. (2.5)]. As a test, we perform simulations for  $\Delta' = 0$  and periodic boundary conditions and compare the results with the exact expressions from paper I. The difference of the concentration averaged over 20,000 program runs and the exact value is used as a measure for the accuracy of the simulation. Table I shows the maximum value of the relative deviation which is observed during simulations up to a value of  $z_{\max} = 0.1$ . Then the maximum simulated time is  $t_{\max} = z_{\max} L^2 / 4$ . It can be seen that  $\Delta t$  has to be decreased to obtain results with equal accuracy for smaller lattices. The table shows typical values for  $\Delta t$  which are used for different lattice lengths.

However, for very small values of  $\Delta t$  the probability that "something" will happen in a Monte Carlo step becomes very small in comparison with the probability that "nothing" will happen. Therefore the fact that a random generator never provides perfectly uniformly distributed numbers limits the possibility to improve the simulations by decreasing  $\Delta t$ .

Another serious limitation is the growth of the necessary CPU time, which is proportional to  $(\Delta t)^{-1}$ . As an example, take the CPU time of 80 sec for  $L = 3$ ,  $N_s = 20,000$ ,  $\Delta t = 5 \times 10^{-3}$ , and  $z_{\max} = 0.1$ .

We are interested not only in the scaling function, but in the corrections as well. The latter can only be determined for values of the scaling variable  $z$  for which the corrections are much larger than the numerical errors. Values of  $z = 0.01, \dots, 0.1$  turn out to be suitable.

**Table II. Monte Carlo Data and Exact Results for Periodic Boundaries and  $\Delta' = 0$**

$z$	Scaling function $F_0(z)$		Corrections $F_2(z, 0)$	
	Analytical	MC	Analytical	MC
0.01	7.979	$7.839 \pm 0.005$	-99.8	$-103.2 \pm 0.3$
0.02	5.642	$5.680 \pm 0.004$	-35.3	$-45.0 \pm 0.3$
0.03	4.607	$4.635 \pm 0.004$	-19.2	$-24.3 \pm 0.3$
0.04	3.989	$4.006 \pm 0.003$	-12.5	$-15.0 \pm 0.3$
0.05	3.568	$3.577 \pm 0.003$	-8.9	$-10.1 \pm 0.3$
0.06	3.257	$3.264 \pm 0.003$	-6.8	$-7.4 \pm 0.2$
0.07	3.016	$3.022 \pm 0.003$	-5.4	$-5.8 \pm 0.2$
0.08	2.821	$2.825 \pm 0.003$	-4.4	$-4.7 \pm 0.2$
0.09	2.660	$2.661 \pm 0.003$	-3.7	$-3.7 \pm 0.2$
0.10	2.523	$2.525 \pm 0.003$	-3.2	$-3.2 \pm 0.2$

To demonstrate the accuracy, we made simulations for  $L = 9, 10, \dots, 16$  with  $\Delta t = 5 \times 10^{-3}$  and averaged over 20,000 samples. The difference between the simulated concentration and the exact expression is always less than 0.4% and less than the standard deviation of the mean. With the help of a  $\chi^2$  fit we compute approximations for the scaling function and the corrections in  $1/L^2$  for fixed values of  $z$ . The results are given in Table II along with the exact expressions from paper I. It can clearly be seen that Monte Carlo simulations provide reliable information about the scaling properties.

The programs were written in Fortran using the RAN random number generator and executed on DEC workstations.

## 2.1. The Influence of the Coagulation Rate

To solve the coagulation model exactly in paper I it was necessary to choose the coagulation rate equal to the diffusion rate, i.e.,  $\Delta' = 0$ . Now we use Monte Carlo simulations to study the way the scaling properties change for different choices of the coagulation rate, i.e.,  $\Delta' \neq 0$ .

We use a full lattice as initial configuration corresponding to an occupation probability of  $p = 1$ . Both periodic and open boundary conditions are considered. Averages are always taken over  $N_s = 20,000$  samples, except where other numbers are stated. The exponents and the scaling functions are calculated for different values of  $z$  and  $\Delta'$  by applying the  $\chi^2$  fit to the data obtained for different lattice lengths.

The first step is to determine the scaling exponent  $x$  in Eq. (1.4). For this purpose, for each value of  $\Delta'$  we perform simulations for

$L = 500, 550, \dots, 950$  taking  $\Delta t = 0.5$ . Averaging over 400 samples is sufficient in this case, whereas in all other simulations we use 20,000 samples. For each value of  $z$ ,  $x$  is determined with the help of the  $\chi^2$  fit according to

$$\log[c(z)] = \text{const} + x \log(L) \quad (2.7)$$

With an accuracy of 5% or better we obtain  $x = -1$ , for any  $\Delta'$ .

The second step is to find the leading term of the corrections. In order to do so, we need an approximation  $\tilde{F}_0$  for the scaling function  $F_0$ . For this purpose we use the value of  $Lc(z, \Delta')$  obtained from simulations on a lattice of length  $L = 1000$ . Then we perform another set of simulations on lattices of length  $L = 30, 35, \dots, 85$  with  $\Delta t = 5 \times 10^{-3}$ . Using this second set of data, we make a logarithmic fit of the type

$$\log[Lc(z) - \tilde{F}_0] = \text{const} - y \log(L) \quad (2.8)$$

In all cases the correction exponent  $y$  is found to be equal to  $+1$  with an error of 15% or less. Observe the contrast to the case of  $\Delta' = 0$ , where the leading correction exponent is  $y = 2$ . So the dominant correction for  $\Delta' \neq 0$  is of the order of  $1/L$ .

Therefore we finally approximate the second set of data by

$$Lc(z, \Delta') = F_0(z, \Delta') + \frac{F_1(z, \Delta')}{L} + \frac{F_2(z, \Delta')}{L^2} \quad (2.9)$$

The scaling function  $F_0$  is found to be independent of  $\Delta'$  and has the value given in paper I, i.e.,  $F_0(z, \Delta') = F_0(z, 0)$ . This can be seen in Tables III and IV, where the values obtained for  $F_0$  are given for periodic and for open boundary conditions, respectively.

Table III. Scaling Function  $F_0(z)$  for Periodic Boundaries

$z$	$\Delta' = 0.75$	$\Delta' = 0.5$	$\Delta' = 0$	$\Delta' = -1$	$\Delta' = -2$
0.01	$7.95 \pm 0.06$	$7.87 \pm 0.03$	7.98	$7.97 \pm 0.02$	$7.88 \pm 0.03$
0.02	$5.43 \pm 0.04$	$5.58 \pm 0.02$	5.64	$5.62 \pm 0.02$	$5.57 \pm 0.02$
0.03	$4.50 \pm 0.04$	$4.55 \pm 0.02$	4.61	$4.58 \pm 0.02$	$4.60 \pm 0.02$
0.04	$3.91 \pm 0.04$	$3.94 \pm 0.02$	3.99	$3.95 \pm 0.02$	$3.96 \pm 0.02$
0.05	$3.50 \pm 0.03$	$3.55 \pm 0.02$	3.57	$3.54 \pm 0.02$	$3.56 \pm 0.02$
0.06	$3.20 \pm 0.03$	$3.25 \pm 0.02$	3.26	$3.23 \pm 0.02$	$3.24 \pm 0.02$
0.07	$2.97 \pm 0.03$	$3.00 \pm 0.02$	3.02	$2.98 \pm 0.02$	$3.00 \pm 0.02$
0.08	$2.78 \pm 0.03$	$2.80 \pm 0.02$	2.82	$2.80 \pm 0.02$	$2.79 \pm 0.02$
0.09	$2.64 \pm 0.03$	$2.63 \pm 0.02$	2.66	$2.63 \pm 0.01$	$2.63 \pm 0.02$
0.10	$2.49 \pm 0.03$	$2.51 \pm 0.02$	2.52	$2.51 \pm 0.01$	$2.50 \pm 0.02$



Table IV. Scaling Function  $F_0(z)$  for Open Boundaries

$z$	$\Delta' = 0.5$	$\Delta' = 0$	$\Delta' = -1$
0.01	$8.33 \pm 0.04$	8.34	$8.27 \pm 0.05$
0.02	$5.98 \pm 0.03$	6.01	$6.00 \pm 0.04$
0.03	$4.92 \pm 0.03$	4.97	$4.99 \pm 0.04$
0.04	$4.28 \pm 0.02$	4.35	$4.41 \pm 0.04$
0.05	$3.89 \pm 0.02$	3.93	$3.96 \pm 0.03$
0.06	$3.60 \pm 0.02$	3.62	$3.65 \pm 0.03$
0.07	$3.36 \pm 0.02$	3.38	$3.40 \pm 0.03$
0.08	$3.15 \pm 0.02$	3.18	$3.18 \pm 0.03$
0.09	$3.01 \pm 0.02$	3.02	$3.01 \pm 0.03$
0.10	$2.88 \pm 0.02$	2.89	$2.85 \pm 0.03$

The first-order correction function  $F_1$  behaves according to the following scheme:

$$\begin{aligned}
 F_1(z, \Delta') &> 0 & \text{for } \Delta' > 0 \\
 F_1(z, \Delta') &= 0 & \text{for } \Delta' = 0 \\
 F_1(z, \Delta') &< 0 & \text{for } \Delta' < 0
 \end{aligned}
 \tag{2.10}$$

The first and second correction functions are shown in Figs. 1 and 2 for periodic boundaries and in Figs. 3 and 4 for open boundaries, together with the analytic results for  $\Delta' = 0$ . Since the second-order correction term, i.e.,  $F_2(z, \Delta')/L^2$ , becomes already of the order of the statistical errors of the simulations, the correction function  $F_2$  can only be determined with large numerical errors.

As explained in paper I, the scaling limit for small  $z$  and the long-time behavior in the thermodynamic limit ( $L \rightarrow \infty$ ) are related. For periodic boundaries and  $\Delta' = 0$  we found the following expansion for the concentration:

$$c(t) = \left(\frac{1}{2\pi t}\right)^{1/2} \left[ 1 - \frac{1}{16t} \left( \frac{(p-2)^2}{p^2} - \frac{1}{2} \right) + \dots \right]
 \tag{2.11}$$

The leading term is obtained from the scaling function and the second term from the expansion of the corrections is  $1/L^2$ . For  $\Delta' \neq 0$  the leading correction is of the order of  $1/L$ . A  $\chi^2$  analysis of the corresponding correction function  $F_1$  shows that it behaves like  $1/z$ . Therefore we obtain an expansion of the form

$$c(t) = \left(\frac{1}{2\pi t}\right)^{1/2} \left[ 1 + \frac{a(\Delta')}{\sqrt{t}} + O(t^{-1}) + \dots \right]
 \tag{2.12}$$

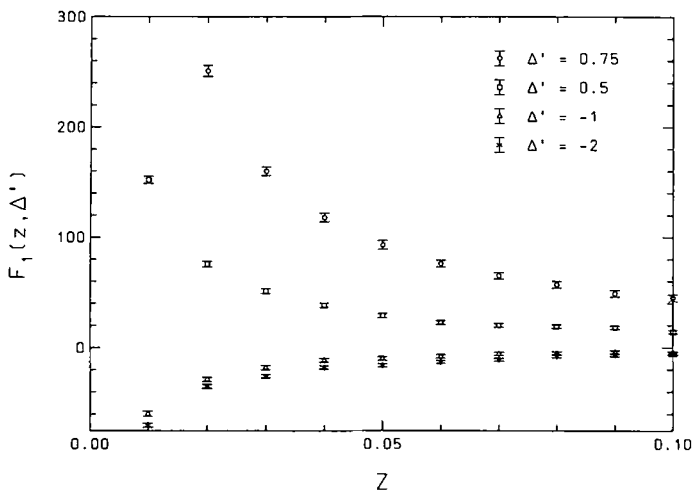


Fig. 1. First-order correction function  $F_1(z, \Delta')$  for periodic boundary conditions and different values of  $\Delta'$ .

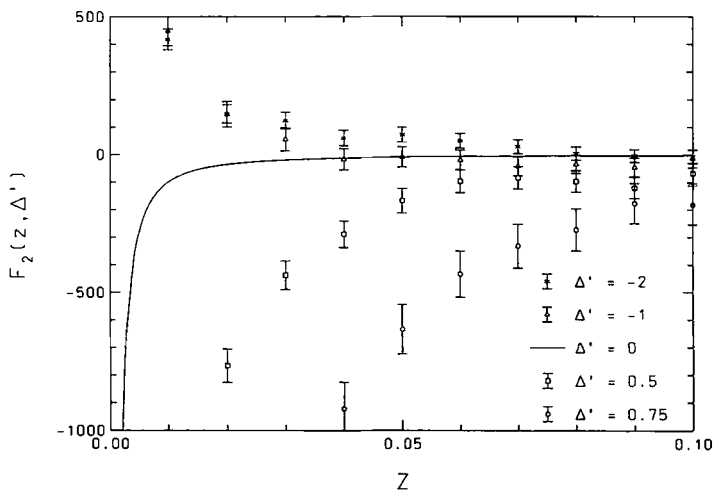


Fig. 2. Second-order correction function  $F_2(z, \Delta')$  for periodic boundary conditions and different values of  $\Delta'$ .

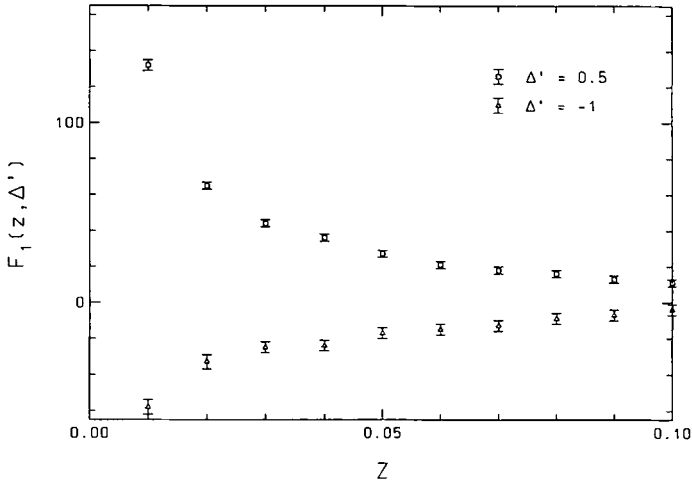


Fig. 3. First-order correction function  $F_1(z, \Delta')$  for open boundary conditions and different values of  $\Delta'$ .

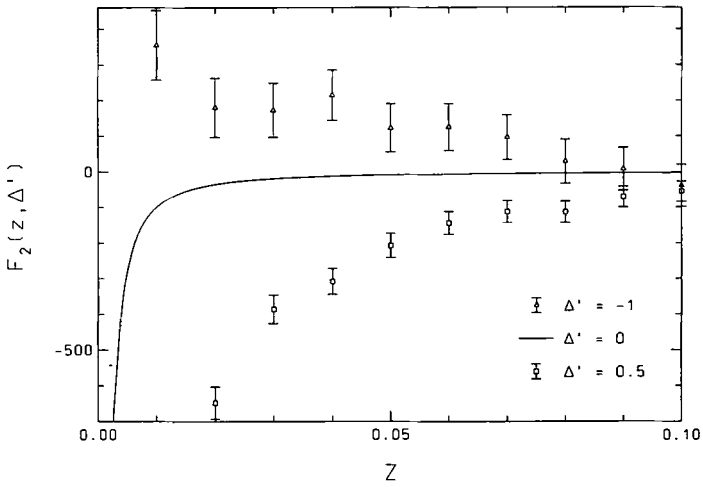


Fig. 4. Second-order correction function  $F_2(z, \Delta')$  for open boundary conditions and different values of  $\Delta'$ .

Thus the change of the coagulation rate does not affect the leading term of the large-time expansion of the concentration in the thermodynamic limit. However, the next-to-leading term is no longer of the order of  $t^{-3/2}$  as for  $\Delta' = 0$ , but of the order of  $t^{-1}$ . The coefficient  $a$  depends on the value of  $\Delta'$ , but it is found to be independent of the initial occupation probability  $p$ . Our conclusions are in perfect agreement with the large-time expansion of the analytical results obtained by Privman *et al.*<sup>(14)</sup> from a diffusion-equation-type approximation scheme (where a random distribution of particles is chosen as initial configuration). Taking the lattice spacing equal to 1, their result can be rewritten in the form:

$$a(\Delta') = \left(\frac{2}{\pi}\right)^{1/2} \frac{\Delta'}{1 - \Delta'} \quad (2.13)$$

For periodic boundary conditions we present the values of  $a$  for different  $\Delta'$  in Table V. These data have been computed using a  $\chi^2$  fit of the values for the first correction function  $F_1$  starting with an initially fully occupied lattice. They are in good agreement with Eq. (2.13). Moreover, we see that these results hold also for values of  $c$  greater than 1, i.e.,  $\Delta' < 0$ .

If one is interested in the time dependence of systems in the thermodynamic limit ( $L \rightarrow \infty$ ) only, of course there is no need to calculate the scaling expansion first. Instead one performs simulations on large lattices. We found that  $L = 2000$  is sufficient to obtain reliable results. For both periodic and open boundaries we collected data for several values of  $\Delta'$  between  $-7$  and  $0.875$  starting with initial occupation probabilities between  $0.05$  and  $1.0$ . In each case we averaged over  $20,000$  runs, each of them performed up to values of  $t \simeq 10^4$ . Using  $\chi^2$  fits, we checked again that  $a$  is independent of  $p$ . Concerning the  $\Delta'$  dependence of the coefficient  $a$  we also found that the difference from (2.13) is smaller than  $5\%$ , i.e., smaller than those of the finite-size scaling data. For times larger than  $\sim 100$  the Monte Carlo data are in very good agreement with Eq. (2.12).

**Table V. First Correction Term  $a(\Delta', 1)$  of the Large-Time Expansion for Periodic Boundaries**

$\Delta'$	$a(\Delta')$	
	MC	Analytical
$-2.00$	$-0.512 \pm 0.060$	$-0.53$
$-1.00$	$-0.414 \pm 0.083$	$-0.40$
$0.50$	$0.894 \pm 0.070$	$0.80$
$0.75$	$2.831 \pm 0.130$	$2.40$

**Table VI.** Influence of the Initial Conditions on the Scaling Properties for Periodic Boundaries and  $\Delta' = 0$

$z$	Scaling function $F_0(z)$		Corrections $F_2(z, 0)$	
	$p = 0.5$ Analytical	$AA\emptyset\emptyset\dots$ MC	$p = 0.5$ Analytical	$AA\emptyset\emptyset\dots$ MC
0.01	7.979	$7.967 \pm 0.008$	-212.5	$-836.7 \pm 12.6$
0.02	5.642	$5.623 \pm 0.007$	-106.3	$-304.8 \pm 10.7$
0.03	4.607	$4.607 \pm 0.006$	-70.8	$-164.4 \pm 9.7$
0.04	3.989	$3.988 \pm 0.006$	-53.1	$-109.8 \pm 9.0$
0.05	3.570	$3.556 \pm 0.006$	-42.4	$-77.2 \pm 8.6$
0.06	3.257	$3.245 \pm 0.005$	-35.4	$-61.7 \pm 8.2$
0.07	3.016	$3.006 \pm 0.005$	-30.4	$-48.8 \pm 7.9$
0.08	2.821	$2.808 \pm 0.005$	-26.6	$-40.6 \pm 7.6$
0.09	2.660	$2.647 \pm 0.005$	-23.6	$-27.7 \pm 7.4$
0.10	2.523	$2.517 \pm 0.005$	-21.3	$-17.6 \pm 7.2$

## 2.2. The Influence of the Initial Conditions

For periodic boundaries and  $\Delta' = 0$  we use Monte Carlo simulations to study the influence of a weakly correlated initial state. The configuration at  $t = 0$  is chosen to be a pairwise alternating sequence of particles and vacancies ( $AA\emptyset\emptyset AA\emptyset\emptyset\dots$ ).

Lattice lengths of  $L = 36, 40, \dots, 80$  ( $\Delta t = 5 \times 10^{-3}$ ) are used. We analyze the data using the procedure described in the previous section. The results, shown in Table VI, confirm that the scaling function is not influenced by an initial state with small clusters. The corrections are still of the order of  $1/L^2$ , but they are different from those given in paper I for  $p = 0.5$ , although the initial concentration is the same,  $c(0) = 0.5$ .

## 3. EXTRAPOLATION FROM FINITE LATTICES

The coagulation model, being exactly solvable, provides a good experimental field to test the accuracy of numerical extrapolation from finite lattices to determine scaling functions and exponents. Our special interest is to find out from what size of lattices it is possible to obtain reliable information about the scaling exponent and the scaling function of the particle concentration as well as about the corrections.

The extrapolations are performed using the algorithm proposed by Bulirsch and Stoer<sup>(20)</sup> (BST).

### 3.1. Test of Extrapolations for Periodic Boundary Conditions

The BST extrapolations are performed with seven input values ( $L = 2, \dots, 8$ ) and with eight input values ( $L = 2, \dots, 9$ ). For small values of  $z$  the BST algorithm is convergent only in the latter case. The input values are calculated using the exact expression for the concentration in the coagulation model with  $\Delta' = 0$  derived in paper I.

For  $z$  the values  $z = 0.1, 0.2, \dots, 1.0$  were chosen, covering a sufficiently large range in time between  $t = 0.1$  and  $t = 25$  where the behavior of the scaling function and its corrections are investigated.

Let us now describe the extrapolations in detail:

(a) *Scaling exponent.* In order to get a higher precision in our estimates, we write the scaling exponent as  $x = -1 + \tilde{x}$  and try to determine the difference  $\tilde{x}$  from the theoretical value for the scaling exponent  $x = -1$ , using the following expression to form the extrapolants:

$$\tilde{x}_0^{(L)} = \frac{\ln[(L + 1) c(L + 1, z) / Lc(L, z)]}{\ln[(L + 1) / L]} \tag{3.1}$$

The only inconvenience of this method is the fact that one obtains one input value less than for the extrapolation of the scaling function. The results are shown in Table VII for each  $z$ . We find  $\tilde{x} = 0$  with a numerical error less than  $3 \times 10^{-3}$ .

(b) *Scaling function.* The scaling function  $F_0$  is extrapolated from

$$T_0^{(L)} = Lc(z, L) \tag{3.2}$$

**Table VII. Extrapolants from Finite Lattices ( $L = 2, \dots, 9$ ) for Periodic Boundary Conditions and  $\Delta' = 0$**

$z$	$1 + x$ Extrapolated	Scaling function $F_0(z)$		$y - 2$ Extrapolated	Corrections $F_2(z)$	
		Extrapolated	Analytical		Extrapolated	Analytical
0.1	0.004547	2.5210	2.5231	-0.134	-2.776	-3.154
0.2	0.002986	1.784283	1.784286	-0.011	-1.1011	-1.1017
0.3	0.0000353	1.46043902	1.46043901	-0.005	-0.51697	-0.51697
0.4	0.0000003	1.27857491	1.27856700	0.005	-0.22442	-0.22246
0.5	0.0000477	1.169713390	1.169713392	0.026	-0.07196	-0.07196
0.6	-0.000002	1.103560880	1.103560906	0.145	-0.00291	-0.00291
0.7	0.0000304	1.0632169524	1.0632169522	-0.003	0.023694	0.023694
0.8	0.0000726	1.0385928840	1.0385928831	0.005	0.030097	0.030097
0.9	0.0000522	1.02356074810	1.02356074816	-0.002	0.0279317	0.0279317
1.0	0.0000988	1.01438377205	1.01438377206	0.006	0.0228893	0.0228893

The results are compared to the analytical values of the scaling function  $F_0(z)$  calculated from paper I in Table VII. The bigger the values of  $z$  are, the higher the precision of the extrapolants becomes: for small  $z$ , the difference from the theoretical value is of the order of  $2 \times 10^{-3}$ ; for  $z = 1.0$  we even get a precision of ten digits in comparison to the exact scaling function. This can easily be understood by looking at the definition of  $z = 4t/L^2$ . For small values of  $z$  and  $L$  the time  $t$  is small as well and the concentration of the system is close to 1. Therefore we expect large corrections to the leading term

$$c(L, z) \xrightarrow{L \rightarrow \infty} \frac{1}{L} F_0(z)$$

i.e., the convergence of the finite-size scaling expansion becomes worse if  $z$  decreases.

(c) *Correction exponent.* Similar to (a), we extrapolate the difference  $\tilde{y} = y - 2$  to the theoretical correction exponent  $y = 2$ . The input values are calculated according to

$$\tilde{y}_0^{(L)} = \frac{\ln\{(L+1)^2 [(L+1) c(L+1, z) - F_0(z)] / L^2 [Lc(L, z) - F_0(z)]\}}{\ln([L+1]/L)} \quad (3.3)$$

For the value of the scaling function  $F_0(z)$  we use the result obtained in (b). So there is already a numerical error in the input values leading to a lower precision for the correction exponent in comparison to the scaling exponent. We find  $\tilde{y} = 0$  with an error of  $10^{-3}$ . Because the correction function  $F_2(z)$  has a zero close to  $z = 0.6$ , it can be understood easily that the correction exponent can only be extrapolated with a smaller accuracy at this point.

(d) *Correction function.* We are interested in the corrections  $F_2(z)$  to the scaling function, i.e., we extrapolate

$$T_0^{(L)} = L^2 (Lc(L, z) - F_0(z)) \quad (3.4)$$

For  $F_0(z)$  we again use the result obtained in (b). Arguing similarly to the approximation of the scaling function, we can understand the high precision of the extrapolated correction function for large values of  $z$ . But even for small values of  $z$  (except for  $z = 0.1$ ) the precision is in the range of  $6 \times 10^{-4}$ . The bad value for the extrapolated corrections for  $z = 0.1$  can be understood by looking at the corresponding extrapolated scaling function, which is known only with a precision of  $2 \times 10^{-3}$ . Since this value enters the input values for the extrapolation of the corrections, the algorithm cannot lead to a reasonable result.

In conclusion, we can say that the BST algorithm provides a powerful tool for extrapolations from finite lattices. Already from ten sites, for which the Hamiltonian can easily be diagonalized explicitly in order to get a value for the concentration, we obtain extrapolations with a very high precision. This knowledge can be used especially to examine nonintegrable chemical models and to determine their critical exponents and finite-size scaling properties.

### 3.2. Influence of the Initial Conditions for Open Boundary Conditions

Once having tested the accuracy of the BST algorithm, we now use it to examine the influence of a weakly correlated initial state on the scaling and the correction function for open boundary conditions. For this purpose, we numerically calculate the concentration for finite lattices using the expressions found in paper I for the eigenfunctions of the system of differential equations describing the time evolution of the coagulation model. Analytically, these calculations become too cumbersome. Afterward, we extrapolate the finite-lattice data with BST. This time we use for the input values lattice lengths between 20 and 40 sites in order to get a higher precision for the extrapolated values.

Table VIII. Influence of the Initial Conditions on the Scaling Properties for Open Boundaries and  $\Delta' = 0$

$z$	Scaling function $F_0(z)$		Corrections $F_2(z)$	
	$p = 0.5$ Analytical	$AA\emptyset\emptyset\dots$ Extrapolated	$p = 0.5$ Analytical	$AA\emptyset\emptyset\dots$ Extrapolated
0.01	8.342226	8.344116	-1950.15	-1050.17
0.02	6.005276	6.005276	-726.78	-381.02
0.04	4.352803	4.352803	-275.60	-144.03
0.07	3.379100	3.379100	-127.93	-66.66
0.10	2.886513	2.886513	-79.08	-41.12
0.20	2.147403	2.147403	-31.71	-16.41
0.30	1.818125	1.818125	-18.94	-9.79
0.40	1.617195	1.617195	-13.21	-6.81
0.50	1.475872	1.475872	-9.83	-5.04
0.60	1.369969	1.369969	-7.50	-3.82
0.70	1.288534	1.288534	-5.77	-2.91
0.80	1.225287	1.225287	-4.45	-2.23
0.90	1.175981	1.175981	-3.44	-1.70
1.00	1.137489	1.137489	-2.66	-1.30



Using the same procedure as described in Section 3.1, we determine the scaling function and the corrections for the weakly correlated initial condition  $AA\emptyset\emptyset AA\emptyset\emptyset\dots$ . The results are shown in Table VIII in comparison to the analytical values for uncorrelated initial conditions (initial occupation probability  $p = 0.5$ ).

The scaling function is again found to be *independent of the initial conditions* with a precision of  $10^{-6}$  for values of  $z$  larger than  $z = 0.1$ .

On the other hand, the corrections are influenced by the different choice of initial conditions. They are even different for uncorrelated and weakly correlated initial conditions with the same initial concentration. The corrections are smaller for the pairwise alternating sequence of particles and holes than for the random distribution in the case of open boundary conditions.

#### 4. CONCLUSIONS

In this paper, we presented the numerical examination of the finite-size scaling behavior of the coagulation model.

We showed on the one hand the universality of the scaling function with the help of Monte Carlo simulations. On the other hand, we were able to determine critical exponents already from lattices of ten sites, using finite-lattice extrapolations. The test of these two numerical methods (Monte Carlo simulations and finite-lattice extrapolations) revealed that they can be successfully applied to characterize the finite-size scaling behavior of reaction–diffusion processes.

Let us discuss our results in detail.

- *Universality of the scaling function and the corrections.* As a first application of the Monte Carlo simulations, we examined the scaling function for periodic and open boundary conditions for different tuning of the rates in order to answer the question of whether the scaling function is universal (i.e., independent of the details of the model): we varied the parameter  $\Delta'$  that reflects the difference between the diffusion rate  $D$  and the coagulation rate  $c$ . The scaling function was found to be universal.

As far as the corrections to the scaling function are concerned, we obtained a leading correction term of the order  $1/L$  in the case of  $\Delta' \neq 0$ . The corresponding correction function (the coefficient of  $1/L$ ) depends on the values of  $\Delta'$ . However, it has always the same sign as  $\Delta'$  [cf. Eq. (2.10)]. In particular, for  $\Delta' = 0$  it is zero as well. This explains the fact that we obtained leading corrections of the order of  $1/L^2$  in the case  $\Delta' = 0$  which was treated analytically in paper I.

From the results mentioned above we conclude that in the thermodynamic limit the leading term of the large-time expansion is universal, i.e., independent of  $\Delta'$ . The next-to-leading term is of the order of  $t^{-1}$  as long as there is an asymmetry between the coagulation and the diffusion rate. Using Monte Carlo simulations on lattices of  $L=2000$ , we have checked that its coefficient is independent of the initial concentration. Comparing our values with the analytical results of ref. 14, we find a perfect agreement. Thus we can explain the apparent  $t$ -dependent exponent law of the concentration decay observed in ref. 17 through the combination of a  $t^{-1/2}$  and a  $t^{-1}$  term.

- *Influence of the initial conditions.* We examined the influence of weakly correlated initial states both for open and periodic boundary conditions. A configuration with small clusters ( $AA\emptyset\emptyset AA\dots$ ) was used as initial state. We showed that the scaling function is not influenced by the initial conditions. So we observe again the phenomenon of self-organization. The system develops according to its intrinsic dynamics and is independent of the initial conditions for large times and large lattices.

- *Test of numerical methods.* In order to test the accuracy of Monte Carlo simulations, we compared the results obtained by simulation to the data that are analytically known. This comparison revealed that the Monte Carlo method provides reliable results that approximate very well the exact expressions. So this method can successfully be used to investigate the finite-size scaling behavior of chemical models.

As far as finite-lattice extrapolations are concerned, we demonstrated that the algorithm of Bulirsch and Stoer<sup>(20)</sup> is a useful method to determine the scaling and the correction exponents and functions already from very small lattices. The only condition one has to impose is that the input values (for small lattices) have to be known with a sufficiently high precision. The accuracy of the extrapolated values depends on the number of input values. However, in our case it was sufficient to take the values from lattices of length up to nine sites as input values to determine the exponents with a precision of at least  $10^{-3}$ . So this method is very suitable for the analysis of the finite-size scaling regime for models that cannot be treated analytically. In this case a numerical diagonalization is still possible for small lattices and can be used to generate the input values for the BST extrapolation.

- *Best choice of the parameters for the numerical examination.* The analysis of the coagulation model allows us to decide which is the best choice of the parameters (tuning of the rates, initial conditions, boundary conditions, and value of the scaling variable  $z$ ) for the numerical determination of the finite-size scaling data.

1. *Tuning of the rates.* As far as this model is concerned, the scaling function can best be determined if the rates are tuned in a way that  $\Delta' = 0$ . Then the leading correction term is of the order  $L^{-2}$ , i.e., small for large  $L$ ; furthermore, the correction function (the coefficient of  $L^{-2}$ ) is smallest for  $\Delta' = 0$ .

2. *Choice of initial conditions.* As far as the choice of the initial conditions is concerned, the corrections become smallest for large values of the initial occupation probability  $p$ , as can be seen in Fig. 5. The effect of correlated initial conditions (an interpolating sequence of particles and holes) cannot be easily understood and requires a more detailed analysis: for periodic boundary conditions, the corrections become smaller for uncorrelated initial conditions (when the initial concentration is kept the same), while for open boundary conditions, the cluster configuration gives rise to smaller correction terms (cf. Tables VI and VIII). So in general the most promising choice of initial conditions for the determination of the scaling function and the scaling exponent is the full lattice.

3. *Choice of boundary conditions.* The discussion of which boundary conditions are more convenient for a numerical examination of the scaling and the correction exponent (the scaling functions are different for different boundary conditions) is very difficult and depends on the other parameters as well. If the initial occupation probability  $p$  is smaller than 1 and  $\Delta' = 0$ , the corrections are smaller for periodic boundaries. For  $\Delta' \neq 0$  and  $p = 1$ ,

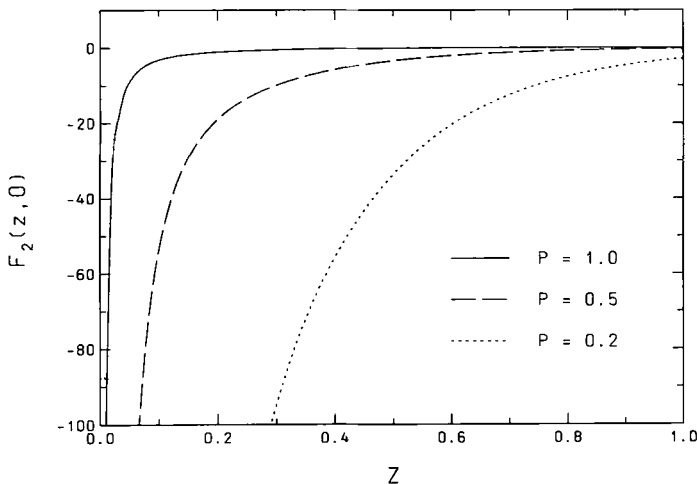


Fig. 5. Correction function  $F_2(z, \Delta')$  for periodic boundary conditions,  $\Delta' = 0$ , and different values of the initial occupation probability  $p$ .

however, the corrections are smaller for open boundary conditions (cf. Figs. 1 and 3). These cases are interesting for the determination of the correction exponent. Taking  $p = 1$  and  $\Delta' = 0$  (the best choice of  $\Delta'$  and  $p$  for the determination of the scaling exponent), we find that the corrections are almost identical for different boundary conditions. In Figs. 2 and 4 values for  $z$  between 0.01 and 0.1 are given where the corrections are exactly the same. For larger values of  $z$ , however, they become slightly different (cf. paper I). Taking into account that periodic boundaries usually allow a Fourier transformation of the equations and therefore a reduction of the number of degrees of freedom of the system, it is more convenient to work with periodic boundary conditions here.

4. *Value of the scaling variable  $z$ .* For the determination of the scaling exponent, one has to choose a value of  $z$  where the corrections are small, i.e., a value around  $z = 0.6$  should be convenient. Since the zero of the correction function occurs at a smaller value of  $z$  for periodic boundary conditions, these boundary conditions better allow a Monte Carlo simulation: the smaller the value of  $z$  is, the smaller the simulated time can be made and the more precise the results of the simulation are. For the determination of the correction exponent the situation is quite different. Here the correction function should be large in order to allow a numerical fit of the simulated data. So one has to choose small values of  $z$  for a Monte Carlo simulation ( $z \leq 0.1$ ). The BST algorithm, however, converges better for large values of  $z$  ( $z \geq 0.2$ ).

Whether these observations hold for more complicated chemical systems still has to be investigated.

Summing up, we can say that the numerical treatment presented here completes the picture of the finite-size scaling behavior of the coagulation model. Both analytical and numerical methods can be successfully applied to chemical models. The results obtained in our work now open the way toward the investigation of more complex chemical systems. The methods tested here provide a powerful tool to gain deeper insight into nonequilibrium physics.

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