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Finite-Size Scaling Studies of One-Dimensional Reaction-Diffusion Systems.

Part I. Analytical Results

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We consider two single-species reaction-diffusion models on one-dimensional lattices of length L : the coagulation-decoagulation model and the annihilation model. For the coagulation model the system of differential equations describing the time evolution of the empty interval probabilities is derived for periodic as well as for open boundary conditions. This system of differential equations grows quadratically with L in the latter case. The equations are solved analytically and exact expressions for the concentration are derived. We investigate the finite-size behavior of the concentration and calculate the corresponding scaling functions and the leading corrections for both types of boundary conditions. We show that the scaling functions are independent of the initial conditions but do depend on the boundary conditions. A similarity transformation between the two models is derived and used to connect the corresponding scaling functions.

KEY WORDS: Reaction-diffusion systems; finite-size scaling; nonequilibrium statistical mechanics; coagulation model; annihilation model.

1. INTRODUCTION

Since Smoluchowski⁽¹⁾ demonstrated that the macroscopic phenomenon of diffusion can be explained on the microscopic scale by Brownian motion of particles, reaction-diffusion systems have been a field of intense research in nonequilibrium statistical mechanics. There are numerous applications in physical chemistry and physics: in deposition-evaporation phenomena,^(2,3) diffusion-controlled chemical reactions,⁽⁴⁻⁶⁾ catalysts,⁽⁷⁾ or in the description of polymers,⁽⁸⁾ to name only a few. Recently experimental studies of

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one-dimensional systems have been reported.^(9,10) In these experiments, the particles correspond to excitons moving along "chains" inside a crystal. In this way, direct applications are found for calculations that are restricted to one dimension because of technical difficulties.

Since analytic calculations are often cumbersome, even in the simplest models exact results are very scarce. Monte Carlo simulations and mean-field calculations or truncation schemes for an infinite hierarchy of n -point functions⁽¹¹⁾ have been the most promising methods for a long time.

Reaction-diffusion systems can be described by lattice models. The dynamics is given by a master equation for the probability $P(\{\beta\}, t)$ to have the configuration $\{\beta\}$ realized at time t .^(12,13)

Concerning one-dimensional systems, the master equation can be mapped onto a Euclidean Schrödinger equation:

$$\frac{\partial}{\partial t} P(\{\beta\}, t) = -HP(\{\beta\}, t) \quad (1.1)$$

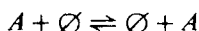
where the Hamiltonian is the one of a quantum chain.⁽¹⁴⁾ This formulation has been used already to study different models, for example, in refs. 2, 15, and 16. It has the advantage that many techniques developed for the investigation of quantum chains can be applied to study reaction-diffusion systems and vice versa.⁽¹⁷⁾

The Hamilton formalism allows us to define the equivalence of two reaction-diffusion models, namely that the corresponding Hamiltonians are related by a similarity transformation. In general the existence of such a transformation does not imply a simple rule of correspondence for observables: operators as well as initial conditions have to be transformed. As an example, we show in the present paper that the coagulation and the annihilation models are equivalent and derive the transformation law for observables explicitly.

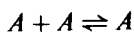
On the other hand, methods which have been restricted to equilibrium statistical mechanics can be applied to a new class of problems. In this context quantum groups and Hecke algebras, which appear quite artificially in equilibrium problems (since unusual boundary conditions or bulk interactions have to be introduced) and have mainly been of mathematical interest up to now, arise naturally in the present case.⁽¹⁸⁾ It is possible as well to use Bethe Ansatz techniques in nonequilibrium problems.^(19,20)

In this paper, we will concentrate on systems with a single type of particle (denoted by A) and the following reactions:

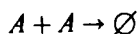
- Diffusion:



- Coagulation and decoagulation:



- Annihilation:



where \emptyset denotes a state without any particles.

We are interested in the dynamics of these systems. Therefore the most important physical quantity is the particle concentration (i.e., the mean number of particles) as a function of time. One way to compute the concentration would be to diagonalize the Hamiltonian directly. This turns out to be very complicated because one has to know all eigenvectors. Therefore we use a different approach to the coagulation model proposed by ref. 21: we investigate the probability of finding empty intervals on the lattice. The time evolution of these empty interval probabilities is given by a closed set of linear differential equations which can be decoupled into L sets of $L - 1$ equations in the case of periodic boundary conditions. For open boundary conditions, however, one obtains a set of $L(L + 1)/2$ equations. It is the first time that such a system is solved in the theory of reaction-diffusion processes.

The long-time behavior of the concentration can be studied by a finite-size scaling approach which allows us to extrapolate from finite systems to infinite ones. The concentration $c(t)$ for an infinite system with a massless spectrum is characterized by an algebraic decay

$$c(t) \simeq t^{-\alpha}$$

The exponent α can be determined with the help of a finite-size scaling expansion of the concentration. In the theory of chemical models finite-size expansions of this type have been introduced by Alcaraz *et al.*⁽¹⁴⁾

Finite-size scaling was originally proposed in equilibrium statistical mechanics. There one is interested in phase transitions, i.e., the singularities of thermodynamic quantities at the critical temperature T_c . These singularities become smooth if the system has a finite size. The idea is to extract critical exponents of an infinite system by studying how thermodynamic quantities—in particular, the ground-state energy—vary with the size of the finite system.^(22,23) The behavior of the finite system is then determined by the ratio of the system size L and the correlation length ξ , which diverges at the critical point. Therefore finite-size scaling studies in equilibrium statistical mechanics are always characterized by the presence of a large length scale, the correlation length.

The scaling limit we consider in the investigation of reaction-diffusion processes differs from the one used in equilibrium statistical mechanics: Here we relate the limits $t \rightarrow \infty$ and $L \rightarrow \infty$ by keeping the scaling variable $z = 4Dt/L^2$ constant while t and L go to infinity. D denotes the diffusion constant. This limit can be understood as comparing the dynamics of a system with a pure diffusion process described by $D\Delta c(t) = \partial_t c(t)$. The average of the square of the distance traveled by a particle in time t is then given by $\langle (x_t - x_0)^2 \rangle = 2Dt$. Thus $z = 4Dt/L^2$ appears naturally as the square of the "correlation length" divided by L^2 . It is obvious that this kind of limit is only reasonable in the case of diffusion-limited systems where the decay to the steady state is algebraic and thus involves a diverging "correlation length." In the present work we therefore have to restrict ourselves to systems with diffusion and pure coagulation or diffusion and pure annihilation, respectively. In the presence of particle-creating reactions (i.e., decoagulation, birth, or pair production) the systems are no longer diffusion limited and no large length scale appears.

Applying the scaling hypothesis to the concentration of particles gives

$$c(z, L) = L^x [F_0(z) + L^{-y}F(z) + \dots] \quad (1.2)$$

Here F_0 denotes the scaling function, x is the scaling exponent, and $L^{-y}F(z)$ is the leading correction term. F_0 and the correction function F depend only on the scaling variable z . The scaling exponent x and the "critical" exponent α , which describes the large-time behavior of an infinite system, are connected by the scaling relation

$$\alpha = \frac{x}{2} \quad (1.3)$$

Similar to equilibrium statistical mechanics, the existence of finite-size scaling relations allows the numerical determination of critical exponents (α in the present case) from finite lattices. The question of universality arises immediately. Do the exponents and scaling functions depend on the details of the model and the initial conditions?

Our results are published in two parts. The present article contains the results we have achieved by analytical calculations. In the second article we focus on those situations where only numerical methods can be applied. Monte Carlo simulations and extrapolations from finite lattices are used to investigate the dependence of the scaling function on the choice of the reaction rates (universality) as well as on the initial conditions (self-organization).

The present article is organized as follows: In Section 2, we present the general framework we use to study reaction-diffusion processes. In Section 3, we define the models, derive the corresponding Hamiltonians, and

investigate their spectra. These results are used to construct the similarity transformation between the coagulation model and the annihilation model in Section 4. Using the empty interval approach in Section 5, we solve the resulting system of differential equations for the coagulation model for both periodic and open boundary conditions. The finite-size scaling behavior of the coagulation and annihilation models is investigated in Section 6. In an appendix we present a derivation of the scaling function based on the continuous version of the coagulation model. We close with a discussion of our results, where open questions and possible directions of further research are outlined.

2. MASTER EQUATION AND ONE-DIMENSIONAL QUANTUM CHAINS

The models studied in this paper are defined on an one-dimensional lattice of length L . To each site i we attach a variable β_i taking two values: $\beta_i=0$ corresponds to a vacancy, $\beta_i=1$ to a particle of type A .

The dynamics of the system is determined by the rates for the allowed reactions: The probability that a state (α, β) on two adjacent sites will change into the state (γ, δ) after one unit of time is denoted by

$$\Gamma_{\gamma, \delta}^{\alpha, \beta}, \quad (\alpha, \beta) \neq (\gamma, \delta) \quad (2.1)$$

So we only consider nearest-neighbor interactions. All reactions changing the state (α, β) into any other state are summarized in the rate $\Gamma_{\alpha, \beta}$:

$$\Gamma_{\alpha, \beta} = \sum'_{\gamma, \delta=0} \Gamma_{\gamma, \delta}^{\alpha, \beta} \quad (2.2)$$

where the prime is always used to indicate that in the sum the case $(\alpha, \beta) = (\gamma, \delta)$ is excluded. This definition ensures the conservation of probabilities. Clearly all rates have to be nonnegative and real.

Let $P(\{\beta\}; t)$ be the probability to find the system at time t in the configuration $\{\beta\} = \{\beta_1, \beta_2, \dots, \beta_L\}$. The dynamics of the system is then determined by the following master equation⁽¹⁴⁾ describing the time evolution of the probability distribution $P(\{\beta\}; t)$:

$$\begin{aligned} \frac{\hat{c}}{\hat{c}t} P(\{\beta\}; t) = & \sum_{k=1}^L \left[-\Gamma_{\beta_k, \beta_{k+1}} P(\beta_1, \dots, \beta_L; t) \right. \\ & \left. + \sum_{\alpha_k, \alpha_{k+1}=0}^1 \Gamma_{\beta_k, \beta_{k+1}}^{\alpha_k, \alpha_{k+1}} P(\beta_1, \dots, \beta_{k-1}, \alpha_k, \alpha_{k+1}, \beta_{k+2}, \dots, \beta_L; t) \right] \end{aligned} \quad (2.3)$$

All arithmetic operations on the α_k and β_k are performed modulo 2.

In this article we deal with periodic as well as with open boundary conditions. Different choices of boundaries are reflected in the upper limit of the summation. For periodic boundary conditions, the summation has to be performed up to $k = L$. For open boundary conditions the sum only runs up to $L - 1$.

2.1. Mapping on a Schrödinger Equation

It is possible to rewrite the master equation in the form of a Euclidean Schrödinger equation with a quantum-chain Hamiltonian. The configuration space is constructed by attaching a two-dimensional vector space V_i to each site i . The vector $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ corresponds to a vacancy, $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ to a particle. The configuration space has the structure of an L -fold tensor product $V_1 \otimes \cdots \otimes V_L$. We choose an orthonormal basis, which we are going to call the spin basis⁽¹²⁾:

$$|\{\beta\}\rangle = |\beta_1, \dots, \beta_L\rangle; \quad \langle\{\beta\}|\{\beta'\}\rangle = \delta_{\{\beta\}, \{\beta'\}} \quad (2.4)$$

and define the ket state

$$|P\rangle = \sum_{\{\beta\}} P(\{\beta\}; t) |\{\beta\}\rangle \quad (2.5)$$

Using the 2×2 matrices E^{kl} with entries $(E^{kl})_{nm} = \delta_{k,n} \delta_{l,m}$, it was shown in ref. 14 that a quantum-chain Hamiltonian H can be defined as follows:

$$H = \sum_{i=1}^L H_i \quad (2.6)$$

$$H_i = \sum_{\alpha, \beta=0}^1 \left[\Gamma_{\alpha, \beta} E_i^{\alpha, \alpha} E_{i+1}^{\beta, \beta} - \sum_{\gamma, \delta=0}^1 \Gamma_{\alpha, \beta}^{\gamma, \delta} E_i^{\alpha, \gamma} E_{i+1}^{\beta, \delta} \right] \quad (2.7)$$

The operator H operates on the L -fold tensor product $V_1 \otimes \cdots \otimes V_L$. The H_i operate locally on $V_i \otimes V_{i+1}$. The master equation (2.3) can now be replaced by the Euclidean Schrödinger equation:

$$\frac{\partial}{\partial t} |P(t)\rangle = -H |P(t)\rangle \quad (2.8)$$

Thus the time evolution of the system is given by

$$|P(t)\rangle = \exp(-Ht) |P_0\rangle \quad (2.9)$$

where $|P_0\rangle$ denotes the initial state. Since $|P\rangle$ already denotes a probability distribution, whereas in quantum mechanics the wave function

represents a probability amplitude, the calculation of expectation values differs from ordinary quantum mechanics. Let X be an observable of the system. Instead of $\langle X \rangle(t) = \langle \Psi | X | \Psi \rangle$, as in quantum mechanics, the expectation value of X is now defined as

$$\langle X \rangle(t) = \sum_{\{\beta\}} X(\{\beta\}) P(\{\beta\}; t) \quad (2.10)$$

If we introduce the bra ground state

$$\langle 0 | = \sum_{\{\beta\}} \langle \{\beta\} | \quad (2.11)$$

we can write the expectation value (2.10) in the form

$$\langle X \rangle(t) = \langle 0 | X | P(t) \rangle \quad (2.12)$$

The notion of $\langle 0 |$ as a bra ground state is justified by the fact that

$$\langle 0 | H = 0 \quad (2.13)$$

which is a simple consequence of the conservation of probabilities (2.2).

The calculation of expectation values can often be simplified as follows. If X is an operator with matrix elements $\langle \{\alpha\} | X | \{\beta\} \rangle$, we define a new operator \bar{X} with matrix elements

$$\langle \{\alpha\} | \bar{X} | \{\beta\} \rangle := \delta_{\{\alpha\}, \{\beta\}} \sum_{\{\gamma\}} \langle \{\gamma\} | X | \{\beta\} \rangle \quad (2.14)$$

It is clear that \bar{X} is diagonal. Each diagonal element is obtained from the matrix representing X by summing up all entries of the corresponding column. The expectation values of both operators are equal, namely

$$\langle 0 | X | \{\beta\} \rangle = \langle 0 | \bar{X} | \{\beta\} \rangle \quad (2.15)$$

The proof is straightforward. As a consequence of this identity one has to consider only diagonal operators.

3. TWO-STATE HAMILTONIANS

We will now derive the Hamiltonians for both models considered in this article: the coagulation-decoagulation model and the annihilation model. The reaction rates are always chosen to be left-right symmetric, i.e., $\Gamma_{\alpha\beta}^{\gamma} = \Gamma_{\beta\alpha}^{\gamma}$. In both models we have the following:

- Diffusion with rate $\Gamma_{10}^{01} = D = 1$

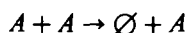


The diffusion rate can be used to fix the time scale in the models and thus is set equal to 1.

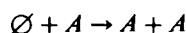
3.1. The Coagulation–Decoagulation Model

We start with the coagulation–decoagulation model, where diffusion and the following processes are possible:

- Coagulation with rate $\Gamma_{01}^{11} = c$



- Decoagulation with rate $\Gamma_{11}^{01} = d$



This model has been discussed in various contexts. In refs. 4, 24, and 25 results of Monte Carlo simulations are reported. Analytical calculations have been performed predominantly for infinite, continuous models,^(21, 26–28) where in ref. 21 the formalism of the empty interval probabilities was described for the first time. We will use this formalism in Section 5. In refs. 29 and 30, approximations for the density functions of the model are derived. Exact results for a lattice formulation of the coagulation model can be found in ref. 31 as well as in ref. 32, where the lattice model is investigated by means of probability arguments. Recently field-theoretic methods have been applied to the coagulation model.^(33, 34)

The Hamiltonian of the coagulation model can immediately be calculated from the definitions (2.6) and (2.7). It is convenient to rewrite it in terms of Pauli matrices:

$$\begin{aligned}
 H_{\text{cong}} = & -\frac{1}{2} \sum_{i=1}^L [\sigma_i^x \sigma_{i+1}^x + \sigma_i^y \sigma_{i+1}^y + (1-c+d) \sigma_i^z \sigma_{i+1}^z \\
 & + c(\sigma_i^z + \sigma_{i+1}^z) - 1 - c - d \\
 & + (c\sigma_i^+ + d\sigma_i^-)(1 - \sigma_{i+1}^z) + (1 - \sigma_i^z)(c\sigma_{i+1}^+ + d\sigma_{i+1}^-)] \quad (3.1)
 \end{aligned}$$

Notice that this operator is non-Hermitian, but it can be brought to a Hermitian form by a rescaling of the spin basis. For this purpose we use the transformation $G = g^{\otimes L}$, where g is a diagonal matrix given by

$$g = \begin{pmatrix} 1 & 0 \\ 0 & (c/d)^{1/2} \end{pmatrix} \quad (3.2)$$

such that GHG^{-1} is found to be Hermitian (a more general type of this transformation was discussed in ref. 14). In the second step we perform a rotation around the y axis in the space of σ -matrices:

$$\sigma^y = \tilde{\sigma}^y; \quad \sigma^x = \frac{\tilde{\sigma}^x + \sqrt{\delta} \tilde{\sigma}^z}{(1 + \delta)^{1/2}}; \quad \sigma^z = \frac{\tilde{\sigma}^z - \sqrt{\delta} \tilde{\sigma}^x}{(1 + \delta)^{1/2}} \quad (3.3)$$

where

$$\delta = \frac{d}{c} \quad (3.4)$$

The $\tilde{\sigma}^i$ still obey the same commutation relations as the Pauli matrices. After dropping the tildes, we can write the resulting Hamiltonian as

$$H_{\text{coag}} = -\frac{1}{2} \eta \sum_{i=1}^L \left[\eta \sigma_i^x \sigma_{i+1}^x + \frac{1}{\eta} \sigma_i^y \sigma_{i+1}^y + \frac{D'}{\eta} \sigma_i^z \sigma_{i+1}^z + \frac{[(1 - D')(\eta^2 - D')]^{1/2}}{\eta} (\sigma_i^z + \sigma_{i+1}^z) - \eta - \frac{1 - D'}{\eta} \right] \quad (3.5)$$

with

$$D' = 1 - c, \quad \eta = (1 + d)^{1/2} \quad (3.6)$$

For $D' = 0$ we find the Hamiltonian of the XY chain in an external magnetic field, which has been studied in refs. 35–37. This Hamiltonian is known to be integrable in terms of free fermions and will be the subject of Section 3.2.

The calculations above are only valid in the case of a nonvanishing decoagulation rate because the matrix G becomes singular if $d = 0$. Since the case of a vanishing decoagulation rate will be essential throughout this paper (since only in this case are the derivation of the similarity transformation and the finite-size scaling studies possible), we will give the corresponding Hamiltonian explicitly. It is obtained from Eq. (3.1) by putting $d = 0$. It can be written as $H_{\text{coag}} = H_0 + H_1$, where H_0 is the Hamiltonian of the XXZ chain in an external magnetic field in the z direction studied in ref. 38:

$$H_0 = -\frac{1}{2} \sum_{i=1}^L [\sigma_i^x \sigma_{i+1}^x + \sigma_i^y \sigma_{i+1}^y + D' \sigma_i^z \sigma_{i+1}^z + (1 - D')(\sigma_i^z + \sigma_{i+1}^z) + D' - 2] \quad (3.7)$$

$$H_1 = -\frac{1}{2} (1 - D') \sum_{i=1}^L [\sigma_i^+ (1 - \sigma_{i+1}^z) + (1 - \sigma_i^z) \sigma_{i+1}^+] \quad (3.8)$$

with

$$\Delta' = 1 - c \quad (3.9)$$

The spectrum of the total Hamiltonian is determined by H_0 alone. This fact can be understood in the following way: Since H_0 conserves the total number of particles $N = \frac{1}{2} \sum (1 - \sigma_i^z)$, it can be brought into block-diagonal form, each block corresponding to a fixed number of particles. If we arrange the blocks in an increasing order, it is clear that H_1 leads only to blocks above the diagonal because it decreases the total number of particles by one.

Of course the eigenvectors of H_0 are changed due to the presence of H_1 . For a detailed discussion see Appendix A in ref. 14.

3.2. Spectrum of the Coagulation–Decoagulation Model

The Hamiltonian of the coagulation–decoagulation model can be diagonalized in terms of free fermions if we put $\Delta' = 0$, i.e., $c = 1$. This choice of rates corresponds to a model where the coagulation–reaction takes place instantaneously when two particles meet. A continuous version of this model has been studied in refs. 39 and 40. Imposing periodic boundary conditions, we can write the Hamiltonian (3.5) as

$$H = -\frac{\eta}{2} \sum_{i=1}^L \left(\eta \sigma_i^x \sigma_{i+1}^x + \frac{1}{\eta} \sigma_i^y \sigma_{i+1}^y + \sigma_i^z + \sigma_{i+1}^z - \eta - \frac{1}{\eta} \right) \quad (3.10)$$

Using a Jordan–Wigner transformation and a Fourier transformation, we can write the Hamiltonian in the diagonal form^(35–37,41)

$$H = P^+ \sum_{q \text{ even}} A_q \chi_q^+ \chi_q P^+ + P^- \sum_{q \text{ odd}} A_q \chi_q^+ \chi_q P^- \quad (3.11)$$

where χ_q^+ and χ_q are fermionic operators obeying the anticommutation relations

$$\{\chi_q^+, \chi_k\} = \delta_{q,k}, \quad \{\chi_q^+, \chi_k^+\} = 0, \quad \{\chi_q, \chi_k\} = 0 \quad (3.12)$$

The A_q are fermionic excitation energies given by

$$A_q = \eta(\eta + \eta^{-1} - 2 \cos(q)) \quad (3.13)$$

P^\pm denote the projection operators onto the sectors with charge $Q = \pm 1$, respectively, where Q is given by

$$Q = (-1)^N \quad (3.14)$$

N counts the number of particles. By q_{even} and q_{odd} we denote the values q takes in the different Q -sectors. These values also depend on the lattice length:

$$q_{\text{even}} = \begin{cases} \pm \frac{(2k+1)\pi}{L}, & k=0, 1, 2, \dots, \frac{L-2}{2}, \quad Q=+1, \quad L \text{ even} \\ \pm \frac{(2k+1)\pi}{L}, & k=0, 1, 2, \dots, \frac{L-1}{2}, \quad Q=+1, \quad L \text{ odd} \end{cases} \quad (3.15)$$

$$q_{\text{odd}} = \begin{cases} 0, \pm \frac{2k\pi}{L}, \pi, & k=0, 1, 2, \dots, \frac{L-2}{2}, \quad Q=-1, \quad L \text{ even} \\ 0, \pm \frac{2k\pi}{L}, & k=0, 1, 2, \dots, \frac{L-1}{2}, \quad Q=-1, \quad L \text{ odd} \end{cases} \quad (3.16)$$

Due to the projection operators in Eq. (3.11), *all excitations are only combinations of an even number of fermions* in the sector $Q=+1$ as well as in the sector $Q=-1$. This can be understood taking into account that in both sectors we have a ground state with energy zero but with different charge. So the zero-energy state in the sector $Q=-1$ has already charge -1 . Consequently, all excitations in this sector are combinations of an even number of fermions. The same applies to the sector $Q=+1$.

The situation is different for open boundary conditions. Here the Hamiltonian is again given by (3.10), but the sum only runs up to $L-1$. Using standard techniques, we can write the Hamiltonian in the diagonal form⁽⁴²⁾

$$H^{XY} = \sum_{k=0}^{L-1} A_k a_k^\dagger a_k \quad (3.17)$$

where a_k^\dagger and a_k are fermionic operators:

$$\{a_k^\dagger, a_l\} = \delta_{k,l}, \quad \{a_k^\dagger, a_l^\dagger\} = 0, \quad \{a_k, a_l\} = 0 \quad (3.18)$$

Here the fermionic excitation energies A_k are given by

$$A_0 = 0 \quad (3.19)$$

$$A_k = \eta \left(\eta + \eta^{-1} - 2 \cos \frac{\pi k}{L} \right), \quad k=1, \dots, L-1 \quad (3.20)$$

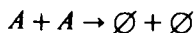
The fact that one obtains an eigenvalue zero for arbitrary η is related to a hidden quantum group symmetry⁽⁴³⁾ and implies that the levels of the spectrum are at least twofold degenerate.

Equations (3.13) and (3.20) are just the dispersion relation of the XY chain and we observe that the system is massless for $\eta=1$ ($d=0$).

3.3. The Annihilation Model

In the annihilation model the only possible reaction besides diffusion is as follows:

- Annihilation with rate $\Gamma_{00}^{11} = a$:



For an initially fully occupied lattice and the choice of the rates $a = 2D$ some exact results have been found in refs. 32, 44, and 45. The influence of the annihilation rate was investigated by Monte Carlo simulations⁽⁴⁶⁾ and for lattice models with discrete time.^(47,48) Furthermore, there are renormalization group calculations for higher dimensions.^(34,49)

From the definitions (2.6) and (2.7) we derive the Hamiltonian $H_{\text{ann}} = H_0 + H_1$ with

$$H_0 = -\frac{1}{2} \sum_{i=1}^L [\sigma_i^x \sigma_{i+1}^x + \sigma_i^y \sigma_{i+1}^y + \Delta' \sigma_i^z \sigma_{i+1}^z + (1 - \Delta')(\sigma_i^z + \sigma_{i+1}^z) + \Delta' - 2] \quad (3.21)$$

$$H_1 = -(2 - 2\Delta') \sum_{i=1}^L \sigma_i^+ \sigma_{i+1}^+ \quad (3.22)$$

where

$$\Delta' = 1 - \frac{a}{2} \quad (3.23)$$

The same arguments as in Section 3.1 show that the spectrum again is determined by H_0 only (here the operator H_1 decreases the number of particles by two). Since for

$$c = \frac{a}{2} \quad (3.24)$$

the operators H_0 of the coagulation model (3.7) and the annihilation model (3.21) are identical, H_{coag} and H_{ann} have the same spectrum in this case.

If we put additionally $\Delta' = 0$, i.e., $a = 2$ (corresponding to instantaneous annihilation when two particles meet), the Hamiltonian of the annihilation model can be written in terms of free fermions. In this case the spectrum can be obtained from Section 3.2 by putting $\eta = 1$ (vanishing decoagulation rate) there.

4. TRANSFORMATION BETWEEN TWO-STATE MODELS

As the comparison of the Hamiltonians (3.7), (3.8) and (3.21), (3.22) revealed in the previous section, the coagulation and the annihilation models have identical spectra if the annihilation rate is chosen to be twice the coagulation rate.

In this section we are going to show that both Hamiltonians are related by a similarity transformation, i.e., they are equivalent from an algebraic point of view. We will discuss the consequences this transformation implies for the relation between the expectation values of observables in the two chemical models.

Kang and Redner⁽⁴⁾ conjectured for the first time that the coagulation and the annihilation models are equivalent because they observed a $t^{-1/2}$ decay of the concentration in both models. For the special case $c=1$ and $a=2$ the transformation law for the concentration for certain initial conditions⁽³²⁾ as well as for special correlation functions averaged over translationally invariant initial conditions⁽³¹⁾ are known exactly.

We point out that we relate two complete families of models because Δ' remains as a free parameter. Furthermore, we give the transformation law for arbitrary observables and arbitrary initial conditions [cf. Eq. (4.9)].

The fact that both Hamiltonians are equivalent can be seen easily: We define the matrices

$$h = \begin{pmatrix} 1 & -1 \\ 0 & 2 \end{pmatrix}, \quad h^{-1} = \begin{pmatrix} 1 & \frac{1}{2} \\ 0 & \frac{1}{2} \end{pmatrix} \quad (4.1)$$

and their L -fold tensor product:

$$B = h^{\otimes L}, \quad B^{-1} = (h^{-1})^{\otimes L} \quad (4.2)$$

Using the relations

$$h\sigma^+ h^{-1} = \frac{1}{2}\sigma^+ \quad (4.3)$$

$$h\sigma^- h^{-1} = -\sigma^- + 2\sigma^+ - \frac{1}{2}\sigma^+ \quad (4.4)$$

$$h\sigma^z h^{-1} = \sigma^z + \sigma^+ \quad (4.5)$$

it is straightforward to prove that

$$H_{\text{coag}} = BH_{\text{ann}}B^{-1} \quad (4.6)$$

Thus both Hamiltonians are equivalent. Notice that this transformation is nonunitary but local and independent of the sites. Therefore it can be applied in the case of periodic as well as of open boundary conditions.

We now study how the expectation values transform under application of B . Let us first consider a special case of initial conditions. We introduce a state $|\mathbf{P}_0\rangle$ of the product form:

$$|\mathbf{P}_0\rangle = \begin{pmatrix} 1-p_1 \\ p_1 \end{pmatrix} \otimes \dots \otimes \begin{pmatrix} 1-p_L \\ p_L \end{pmatrix} \quad (4.7)$$

with $\mathbf{P}_0 = (p_1, \dots, p_L)$. If we take $0 \leq p_i \leq 1$, this is a state where site i is occupied with probability p_i . The generalization to an arbitrary initial state is straightforward because every state $|\{\beta\}\rangle$ of the spin basis is of the product form (4.7) if the values $p_i = \beta_i$ are used. Therefore an arbitrary initial state $|\mathbf{P}_0\rangle$ can be expressed as a linear combination of product states (4.7).

The operator B^{-1} acts on $|\mathbf{P}_0\rangle$ according to

$$B^{-1}|\mathbf{P}_0\rangle = |\frac{1}{2}\mathbf{P}_0\rangle \quad (4.8)$$

For the expectation value $\langle X \rangle(\mathbf{P}_0, t)$ of an observable X at time t and for a given initial state $|\mathbf{P}_0\rangle$ we find

$$\begin{aligned} \langle X \rangle_{\text{coag}}(\mathbf{P}_0, t) &= \langle 0 | X e^{-H_{\text{coag}} t} | \mathbf{P}_0 \rangle \\ &= \langle 0 | X B e^{-H_{\text{ann}} t} B^{-1} | \mathbf{P}_0 \rangle \\ &= \langle X B \rangle_{\text{ann}}(\frac{1}{2}\mathbf{P}_0, t) \end{aligned} \quad (4.9)$$

This relation can be applied to an arbitrary n -point function. The operator of the occupation number of the i th site is given by

$$n_i = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}_i \quad (4.10)$$

Using the relations $\langle 0 | b = \langle 0 |$ and $n_i b = 2n_i$, we find

$$\begin{aligned} \langle n_{i_1} \dots n_{i_k} \rangle_{\text{coag}}(\mathbf{P}_0, t) &= \langle (n_{i_1} \dots n_{i_k}) B \rangle_{\text{ann}}(\frac{1}{2}\mathbf{P}_0, t) \\ &= 2^k \langle n_{i_1} \dots n_{i_k} \rangle_{\text{ann}}(\frac{1}{2}\mathbf{P}_0, t) \end{aligned} \quad (4.11)$$

As a special case, we obtain for the concentration $c = (1/L) \sum_{i=1}^L n_i$

$$c_{\text{coag}}(\mathbf{P}_0, t) = 2c_{\text{ann}}(\frac{1}{2}\mathbf{P}_0, t) \quad (4.12)$$

We finally remark that if probabilities larger than 1/2 occur in the annihilation model [cf. Eq. (4.8)], the application of the transformation B leads to probabilities larger than 1 in the coagulation model. Therefore the range of the physical correspondence between both models is restricted. However,

the calculations of expectation values are valid for any state, since, according to Eq. (2.12), they do not depend on the interpretation of the state $|P\rangle$ as a probability distribution.

5. PROBABILISTIC APPROACH TO THE COAGULATION-DECOAGULATION MODEL WITH $\Delta' = 0$

The calculation of expectation values according to Eq. (2.12) requires the knowledge of the full probability distribution $P(\{\beta\}; t)$. One way to compute $P(\{\beta\}; t)$ from a given initial state $P_0(\{\beta\})$ would be to diagonalize the Hamiltonian, i.e., to find all 2^L eigenvectors. These calculations become very cumbersome even for small lattice sizes.

In the special case of the coagulation model with $\Delta' = 0$ it was shown in refs. 27, 39, 40, and 50 that a subset of observables can be found for which the time evolution is described by a closed system of differential equations. Furthermore, the so-called empty interval probabilities were introduced, the corresponding differential equations were solved, and the concentration for infinite systems was computed.

In this section we will adapt this formalism to finite systems, derive the differential equations for the time evolution of the empty interval probabilities, and present a complete set of solutions for periodic as well as for open boundary conditions. The solutions will be identified as one- or two-fermionic excitations of the corresponding quantum chain.

5.1. Empty Interval Probabilities

The empty interval probability function $\Omega(j, n, t)$ is defined as the probability to find n consecutive sites $j - n/2 + 1, \dots, j + n/2$ empty at time t . (In the case of periodic boundary conditions, the arithmetic operations on the numbering of the sites are performed modulo L .) Notice that j takes half-integer values if n is odd. For example, $\Omega(5/2, 3, t)$ is the probability to find sites 2, 3, and 4 empty at time t .

Obviously the probability to have site j occupied is just $1 - \Omega(j - \frac{1}{2}, 1, t)$. Therefore we can calculate the concentration as

$$c(t) = 1 - \frac{1}{L} \sum_{j=1}^{L-1} \Omega(j, 1, t) \quad (5.1)$$

The probability $\Omega(j, n, t)$ is the expectation value $\langle O(j, n) \rangle(t)$ of the empty interval operator

$$O(j, n) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}_{j-n/2+1} \otimes \dots \otimes \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}_{j+n/2} \quad (5.2)$$

From the Schrödinger equation (2.8) and Eq. (2.10) it follows immediately that the time evolution of $\Omega(j, n, t)$ is given by

$$\frac{\partial}{\partial t} \Omega(j, n, t) = -\langle 0 | O(j, n) H | P \rangle \quad (5.3)$$

By a series of purely algebraic manipulations we will show that the right-hand side can be expressed in terms of empty interval probabilities Ω so that we obtain a closed system of differential equations.

The Hamiltonian is rewritten as $H = \sum_i H_i$, where H_i operates locally on the sites i and $i + 1$ and has the matrix representation

$$H_i = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \eta^2 & -1 & -1 \\ 0 & -1 & \eta^2 & -1 \\ 0 & 1 - \eta^2 & 1 - \eta^2 & 2 \end{pmatrix} \quad (5.4)$$

where we used the notation $\eta^2 = 1 + d$. We can now write down the system of differential equations describing the time evolution of $\Omega(j, n, t)$. For $n = 2, \dots, L - 1$ we obtain

$$\frac{\partial}{\partial t} \Omega(j, n, t) = - \sum_{i=1}^L \langle 0 | O(j, n) H_i | P \rangle \quad (5.5)$$

$$= -\langle 0 | O(j, n) H_{j-n/2} | P \rangle - \langle 0 | O(j, n) H_{j+n/2} | P \rangle \quad (5.6)$$

$$= \eta^2 \langle 0 | O(j-1/2, n+1) | P \rangle + \eta^2 \langle 0 | O(j+1/2, n+1) | P \rangle$$

$$- 2(\eta^2 + 1) \langle 0 | O(j, n) | P \rangle$$

$$+ \langle 0 | O(j-1/2, n-1) | P \rangle + \langle 0 | O(j+1/2, n-1) | P \rangle \quad (5.7)$$

For $i = 1, \dots, j - n/2 - 1$ and $i = j + n/2 + 1, \dots, L$, H_i operates directly to the left on the bra ground state $\langle 0 |$. Because we have $\langle 0 | H_i = 0$ [cf. Eq. (2.13)] these terms vanish. For $i = j - n/2 + 1, \dots, j + n/2 - 1$ we have

$$\left[\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}_i \otimes \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}_{i+1} \right] H_i = 0 \quad (5.8)$$

Therefore there are only two terms left, and Eq. (5.6) follows. Remembering the fact that it is sufficient for the calculation of expectation values to

consider diagonal operators [cf. Eq. (2.15)], we finally arrive at Eq. (5.7). For $n = 1$ we get

$$\begin{aligned} \frac{\partial}{\partial t} \Omega(j, 1, t) = & \eta^2 \langle 0 | O(j - \frac{1}{2}, 2) | P \rangle + \eta^2 \langle 0 | O(j + \frac{1}{2}, 2) | P \rangle \\ & - 2(\eta^2 + 1) \langle 0 | O(j, 1) | P \rangle + \langle 0 | P \rangle + \langle 0 | P \rangle \end{aligned} \quad (5.9)$$

If we formally put

$$O(j, 0) = 1 \quad (5.10)$$

the case $n = 1$ is included in Eq. (5.7).

Due to the last two terms in Eq. (5.9), which contain the normalization of probability,

$$\langle 0 | P \rangle = 1 \quad (5.11)$$

the system of differential equations is inhomogeneous.

The way the equations were derived here is rather formal and differs from the derivation given in refs. 27, 39, 40, and 50. The advantage of our formalism is that the calculations are independent of the interpretation of the functions Ω as probabilities. The final equation (5.12) is valid for every state $|P\rangle$ satisfying Eq. (5.11). This is an important remark because it shows that the results for the coagulation model can be extended to the annihilation model with the help of the similarity transformation B (cf. Section 4). The transformed state $B|P\rangle$ satisfies Eq. (5.11) if the state $|P\rangle$ does.

In summary we have the following equations:

$$\begin{aligned} \frac{\partial}{\partial t} \Omega(j, n, t) = & +\eta^2 \Omega(j - \frac{1}{2}, n + 1, t) + \eta^2 \Omega(j + \frac{1}{2}, n + 1, t) \\ & - 2(\eta^2 + 1) \Omega(j, n, t) \\ & + \Omega(j - \frac{1}{2}, n - 1, t) + \Omega(j + \frac{1}{2}, n - 1, t), \\ & n = 1, \dots, L - 1 \end{aligned} \quad (5.12)$$

The range of the center coordinate j depends on the boundary conditions:

- For *periodic boundaries* we have

$$j = \begin{cases} \frac{1}{2}, \dots, L - \frac{1}{2} & \text{if } n \text{ is odd} \\ 1, \dots, L & \text{if } n \text{ is even} \end{cases} \quad (5.13)$$

• For open boundaries we have

$$j = \frac{n}{2} + 1, \dots, L - \frac{n}{2} - 1 \quad (5.14)$$

In the latter case we obtain additional equations if the interval touches the boundaries:

$$\begin{aligned} \frac{\partial}{\partial t} \Omega \left(\frac{n}{2}, n, t \right) &= \eta^2 \Omega \left(\frac{n+1}{2}, n+1, t \right) + \Omega \left(\frac{n-1}{2}, n-1, t \right) \\ &\quad - (\eta^2 + 1) \Omega \left(\frac{n}{2}, n, t \right) \end{aligned} \quad (5.15)$$

$$\begin{aligned} \frac{\partial}{\partial t} \Omega \left(L - \frac{n}{2}, n, t \right) &= \eta^2 \Omega \left(L - \frac{n+1}{2}, n+1, t \right) + \Omega \left(L - \frac{n-1}{2}, n-1, t \right) \\ &\quad - (\eta^2 + 1) \Omega \left(L - \frac{n}{2}, n, t \right) \end{aligned} \quad (5.16)$$

Neither can all particles disappear, because there is always one left in the coagulation reaction, nor can particles be created from the vacuum. Hence for $n = L$ (empty lattice) the time evolution decouples trivially:

$$\frac{\partial}{\partial t} \Omega \left(\frac{L}{2}, L, t \right) = 0 \quad (5.17)$$

The general case of chemical systems for which a system of differential equations for empty interval probabilities can be obtained is discussed in ref. 17.

5.2. Solution for Periodic Boundary Conditions

Because of translational invariance we can use a Fourier transformation with respect to the center coordinate j :

$$\hat{\Omega}(k, n, t) = \frac{1}{L} \sum_j \Omega(j, n, t) \exp \left(i \frac{2\pi k j}{L} \right); \quad k = 0, 1, \dots, L-1 \quad (5.18)$$

For $n = L$ there is only one independent empty interval probability. Therefore we put

$$\hat{\Omega}(k, L, t) = \begin{cases} \Omega(L/2, L, 0) & \text{if } k = 0 \\ 0 & \text{if } k = 1, \dots, L-1 \end{cases} \quad (5.19)$$

The fact that the system of differential equations is inhomogeneous due to Eq. (5.10) is reflected only in the sector corresponding to the momentum $k = 0$:

$$\hat{\Omega}(k, 0, t) = \begin{cases} 1 & \text{if } k = 0 \\ 0 & \text{if } k = 1, \dots, L-1 \end{cases} \quad (5.20)$$

Now the system of differential equations (5.12) splits up into L independent systems, one for each momentum k :

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\Omega}(k, n, t) &= 2\eta^2 \cos\left(\frac{\pi k}{L}\right) \hat{\Omega}(k, n+1, t) - 2(\eta^2 + 1) \hat{\Omega}(k, n, t) \\ &\quad + 2 \cos\left(\frac{\pi k}{L}\right) \hat{\Omega}(k, n-1, t) \\ n &= 1, \dots, L-1, \quad k = 0, \dots, L-1 \end{aligned} \quad (5.21)$$

From Eq. (5.17) follows in addition

$$\frac{\partial}{\partial t} \hat{\Omega}(0, L, t) = 0 \quad (5.22)$$

The first step in solving these equations is to determine a particular solution for the inhomogeneous problem in the $k = 0$ sector. It can be easily seen that the constant function

$$\Psi_{\text{part}}^0(n) = 1 \quad (5.23)$$

is a solution. From now on we have only to consider the homogeneous systems $\hat{\Omega}(k, 0, t) = 0$. The time dependence is separated by the ansatz

$$\hat{\Omega}(k, n, t) = \Psi_l^k(n) \exp(-\lambda_l^k t) \quad (5.24)$$

The homogeneous problem is now turned into a simple eigenvalue problem where the index l enumerates the different eigenvalues λ_l^k and eigenfunctions Ψ_l^k in each momentum sector:

$$\begin{aligned} -\lambda_l^k \Psi_l^k(n) &= 2\eta^2 \cos\left(\frac{\pi k}{L}\right) \Psi_l^k(n+1) - 2(\eta^2 + 1) \Psi_l^k(n) \\ &\quad + 2 \cos\left(\frac{\pi k}{L}\right) \Psi_l^k(n-1) \end{aligned} \quad (5.25)$$

From Eq. (5.22) we have $-A_l^0 \Psi_l^0(L) = 0$. Thus $\Psi_l^0(L)$ can be nonzero only if $A_l^0 = 0$, i.e., if the solution is stationary. We find

$$\Psi_{\text{stat}}^0(n) = \frac{1 - \eta^{-2n}}{1 - \eta^{-2L}} \quad (5.26)$$

For $k \neq 0$ we have from Eq. (5.19) anyway $\hat{\Omega}(k, L, t) = 0$. The solution for $A \neq 0$ therefore have to obey $\Psi_l^k(0) = \Psi_l^k(L) = 0$. These boundary conditions suggest an ansatz with plane sine waves which have to be deformed because of the factor η^2 in Eq. (5.25). We find

$$\Psi_l^k(n) = \eta^{-n} \sin\left(\frac{\pi l n}{L}\right) \quad (5.27)$$

with eigenvalues

$$A_l^k = \eta \left(2 \left(\eta + \frac{1}{\eta} \right) - 2 \cos \frac{\pi(k+l)}{L} - 2 \cos \frac{\pi(k-l)}{L} \right) \quad (5.28)$$

Here the index l enumerates the different eigenvalues for fixed k :

$$k = 0, \dots, L-1, \quad l = 1, \dots, L-1$$

The various solutions can now be compared to the fermionic excitations of the quantum chain (3.10) from Section 3.2:

- The particular solution (5.23) corresponds to a completely empty lattice and thus to the vacuum of the quantum chain.
- The stationary solution (5.26) is related to the charged ground state of the sector $Q = -1$ of the chain.
- The eigenfunctions (5.27) can be identified as representations of two-fermionic excitations, as the comparison of Eqs. (3.13) and (5.28) shows.

The stationary solution (5.26) and the $L(L-1)$ two-fermionic excitations (5.27) together with the particular solution (5.23) form a complete set of solutions of the differential equations (5.21) for the Fourier-transformed empty-interval probabilities. The general solution can always be expressed as a linear combination of these special solutions:

$$\hat{\Omega}(k, n, t) = \delta_{k,0} + \delta_{k,0} A_0^0 \Psi_{\text{stat}}^0(n) + \sum_{l=1}^{L-1} A_l^k \Psi_l^k(n) \exp(-A_l^k t) \quad (5.29)$$

The initial condition $\hat{\Omega}_0(k, n)$ at $t=0$ determines the coefficients A_j^k . The first term $\delta_{k,0}$ and the second term take into account the particular solution (5.23) and the stationary solution (5.26), which appear only in the sector with momentum $k=0$.

The coefficients A_j^k can be easily calculated if we use the scalar product

$$(f|g) := \frac{2}{L} \sum_{n=1}^{L-1} \eta^{2n} f(n) g(n) \quad (5.30)$$

in each momentum sector. The eigenfunctions (5.27) obey the orthogonality relation

$$(\Psi_l^k | \Psi_m^k) = \delta_{l,m} \quad (5.31)$$

with respect to this scalar product. Since all solutions except the stationary and the particular one vanish for $n=L$, the coefficient A_0^0 is determined only by the initial value of $\hat{\Omega}_0(0, L)$ according to

$$A_0^0 = \hat{\Omega}_0(0, L) - 1 \quad (5.32)$$

The other coefficients are computed using the relation (5.31):

$$A_j^k = (\Psi_j^k | \hat{\Omega}_0(k) - \delta_{k,0}(1 + A_0^0 \Psi_{\text{stat}}^0)) \quad (5.33)$$

Using the inverse transformation

$$\Omega(j, n, t) = \sum_k \hat{\Omega}(k, n, t) \exp\left(-i \frac{2\pi j k}{L}\right) \quad (5.34)$$

we obtain from Eq. (5.29) the empty interval probabilities $\Omega(j, n, t)$. This completes the solution of the differential equations for periodic boundary conditions.

5.3. Solution for Open Boundary Conditions

Notice that, in opposition to the case of periodic boundary conditions, where the Fourier-transformed system has only $L-1$ degrees of freedom, the system (5.12), (5.15)–(5.17) has $L(L+1)/2$ degrees of freedom. The loss of translational invariance causes the system of differential equations to grow quadratically with lattice length L . Naturally it is more difficult to solve this system than the previous one for periodic boundary conditions.

Because of Eq. (5.10) the system of equations is inhomogeneous. The particular solution is the same as in the case of periodic boundaries:

$$\phi_{\text{part}}(j, n) = 1 \quad (5.35)$$

So we only have to deal with the homogeneous system of differential equations by setting $\Omega(j, 0, t) = 0$. As one can easily check, the system of differential equations (5.12), (5.15)–(5.17) is invariant under space reflection P , which is described by the map

$$P: (j, n) \mapsto (L - j, n) \quad (5.36)$$

Therefore we can find solutions which are eigenfunctions of P as well.

It is convenient to change the variables. Instead of the center j and the length n of the interval we now use the positions of its left and right boundary,

$$x = j - \frac{n}{2}, \quad y = j + \frac{n}{2} \quad (5.37)$$

where x and y take the values $0 \leq x \leq y \leq L$. In this notation the space reflection becomes $P: (x, y) \mapsto (L - y, L - x)$. As in the case of periodic boundary conditions the ansatz

$$\Omega(x, y, t) = \phi_A(x, y) e^{-At} \quad (5.38)$$

is used to separate the time dependence and we are left with an eigenvalue problem:

- For $0 < x < y < L$

$$-A\phi_A(x, y) = \eta^2(\phi_A(x-1, y) + \phi_A(x, y+1)) + \phi_A(x+1, y) + \phi_A(x, y-1) - 2(\eta^2 + 1)\phi_A(x, y) \quad (5.39)$$

- For the boundary terms $x=0$ or $y=L$

$$-A\phi_A(0, y) = \eta^2\phi_A(0, y+1) + \phi_A(0, y-1) - (\eta^2 + 1)\phi_A(0, y) \quad (5.40)$$

$$-A\phi_A(x, L) = \eta^2\phi_A(x-1, L) + \phi_A(x+1, L) - (\eta^2 + 1)\phi_A(x, L) \quad (5.41)$$

$$-A\phi_A(0, L) = 0 \quad (5.42)$$

For easy reference we illustrate the organization of the complete system for $L=6$ sites in Fig. 1. Here the $L(L+1)/2$ boxes represent the degrees of freedom $\phi_A(x, y)$. The number in each box denotes the strength of the diagonal contribution in the differential equations, where $g = -(2+d) = -(1+\eta^2)$, while the arrows denote the flow of probability to the neighbors with respect to the couplings

$$\rightarrow, \downarrow: \quad 1 + d = \eta^2$$

$$\leftarrow, \uparrow: \quad 1$$

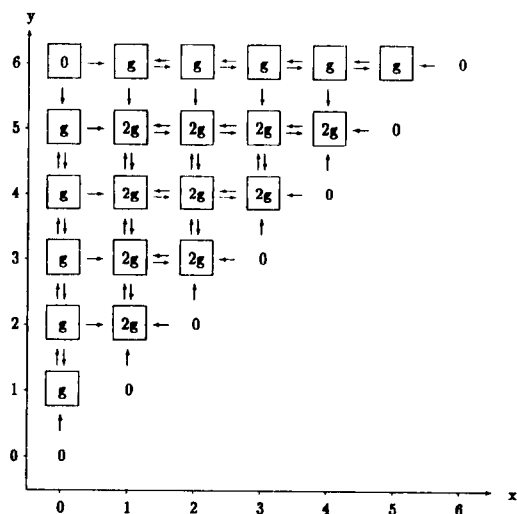


Fig. 1. Structure of the system of differential equations for $L = 6$ sites. The figure is explained in the text.

The zeros on the hypotenuse $x = y$ represent the contributions from the inhomogeneous part of the system. Since we consider only the homogeneous equation, we will drop these terms in the following.

Before calculating the solutions of Eqs. (5.39)–(5.42) we give a short description of how to proceed. Looking at Fig. 1, we find that the boxes on the short sides of the triangle form a closed $(2L - 1)$ -dimensional subsystem of differential equations. As a consequence we expect two kinds of solutions:

- The first kind is obtained by solving the subsystem separately. Since each solution imposes inhomogeneous Dirichlet boundary conditions, it can be extended uniquely to the interior of the triangle. This procedure yields a set of $2L - 1$ solutions of Eqs. (5.39)–(5.42) forming a complete set of eigenfunctions for the short sides of the triangle.
- The second kind of solution is now calculated using the completeness of the first kind of solution. They are forced to vanish on the boundary and therefore to obey homogeneous Dirichlet boundary conditions.

Let us now study the solution of Eqs. (5.39)–(5.42) in more detail. For the moment we choose $\eta = 1$ (i.e., decoagulation rate $d = 0$). Then the differential equations acting on the short sides of the triangle are

$$\begin{aligned} D_x^2 \phi_A(x, L) &= -A \phi_A(x, L) \\ D_y^2 \phi_A(0, y) &= -A \phi_A(0, y) \end{aligned} \quad (5.43)$$

where $x, y = 1, \dots, L - 1$. Here D_x and D_y are discrete derivative operators in the x and y directions, respectively. For example, D_x^2 is given by

$$D_x^2 \phi(x, y) = \phi(x + 1, y) + \phi(x - 1, y) - 2\phi(x, y)$$

The probability for an empty lattice $\phi_A(0, L)$ decouples completely and remains constant in time. Thus $\phi_A(0, L)$ takes nonzero values only if $A = 0$. In this case the second derivative of ϕ vanishes and we find the stationary solution which is a linear function of x and y with $\phi_{\text{stat}}(x, x) = 0$. Thus $\phi_{\text{stat}}(x, y) \sim y - x$. For $A \neq 0$ the condition $\phi_A(0, L) = 0$ gives an additional constraint which determines the solution of Eq. (5.43) to be simple oscillations:

$$\begin{aligned} \phi(x, L) &\sim \sin \frac{\pi k_x x}{L}, & \phi(0, y) &\sim \sin \frac{\pi k_y y}{L} \\ A_k &= 2 \left(1 - \cos \frac{\pi k}{L} \right) \end{aligned} \quad (5.44)$$

where $k = 1, \dots, L - 1$. Since the eigenfunctions are determined by two independent equations, they are twofold degenerate if $A \neq 0$. However, we can choose the solutions to be eigenfunctions of P . It will be convenient to introduce the notation $P\phi_k^\pm = \pm(-1)^k \phi_k^\pm$. So far we have determined the required $2L - 1$ solutions on the short sides of the triangle, which still have to be extended to the interior. Here the differential equations act according to $(D_x^2 + D_y^2)\phi = -A\phi$, where the operator on the left side is just the discretized Laplacian.

The remaining $(L - 1)(L - 2)/2$ solutions of the interior of the triangle are plane waves vanishing on the boundary of the triangle. Collecting all the solutions and comparing them with the excitations of the XY chain Eq. (3.13), we find the following structure:

- The particular solution

$$\phi_{\text{part}}(x, y) = 1 \quad (5.45)$$

corresponds to the vacuum of the quantum chain.

- The stationary solution

$$\phi_{\text{stat}}(x, y) = \frac{y-x}{L} \quad (5.46)$$

is related to the fermion with vanishing energy.

- The eigenfunctions

$$\phi_k^+(x, y) = \frac{1}{\sqrt{L}} \left(\sin \frac{\pi k}{L} x - \sin \frac{\pi k}{L} y \right) \quad (5.47)$$

$$\phi_k^-(x, y) = \frac{1}{\sqrt{L}} \left[\left(1 - \frac{2y}{L} \right) \sin \frac{\pi k}{L} x - \left(1 - \frac{2x}{L} \right) \sin \frac{\pi k}{L} y \right] \quad (5.48)$$

represent the one-fermion excitations ($k = 1, \dots, L-1$).

- The second kind of eigenfunctions

$$\Phi_{kl}(x, y) = \frac{2}{L} \left(\sin \frac{\pi k}{L} x \sin \frac{\pi l}{L} y - \sin \frac{\pi l}{L} x \sin \frac{\pi k}{L} y \right) \quad (5.49)$$

correspond to the two-fermion excitations ($k, l = 1, \dots, L-1$; $k < l$).

This is the complete set of $L(L+1)/2$ solutions. For $\eta \neq 1$ we obtain deformations of them. In order to avoid too much detail, we only present our results:

- The stationary solution:

$$\phi_{\text{stat}}(x, y) = \frac{1 - \eta^{2(x-y)}}{1 - \eta^{-2L}} \quad (5.50)$$

with eigenvalue $\lambda = 0$ and parity $P = +1$.

- One-fermionic excitations ($k = 1, \dots, L-1$):

$$\phi_k^\pm(x, y) = \frac{1}{\sqrt{L}} \frac{\eta^{x-y}}{1 \pm \eta^L} \left[(\eta^x \pm \eta^{L-x}) \sin \frac{\pi k}{L} x - (\eta^y \pm \eta^{L-y}) \sin \frac{\pi k}{L} y \right] \quad (5.51)$$

with eigenvalue $\lambda_k = \eta[\eta + \eta^{-1} - 2 \cos(\pi k/L)]$ and parity $P = \pm(-1)^k$.

- Two-fermionic excitations ($k, l = 1, \dots, L-1$; $k < l$):

$$\Phi_{kl}(x, y) = \frac{2}{L} \eta^{x-y} \left(\sin \frac{\pi k x}{L} \sin \frac{\pi l y}{L} - \sin \frac{\pi l x}{L} \sin \frac{\pi k y}{L} \right) \quad (5.52)$$

with eigenvalue $\lambda_{kl} = \eta[2\eta + 2\eta^{-1} - 2 \cos(\pi k/L) - 2 \cos(\pi l/L)]$ and parity $P = (-1)^{k+l+1}$.

It is easy to check that these solutions reduce to Eqs. (5.46)–(5.49) in the limit $\eta \rightarrow 1$.

Let us now study the orthogonality relations of the different types of solutions. The functions ϕ_k^\pm , $k \neq 0$, form a complete system of eigenfunctions on the short sides of the triangle except the point $(0, L)$. Therefore we define a scalar product $(\cdot | \cdot)_{\text{boundary}}$ which takes only these points into account:

$$(f | g)_{\text{boundary}} = \sum_{x=1}^{L-1} \eta^{2(L-x)} f(x, L) g(x, L) + \sum_{y=1}^{L-1} \eta^{2y} f(0, y) g(0, y) \quad (5.53)$$

The solutions (5.50)–(5.52) are normalized so that

$$(\phi_k^\alpha | \phi_l^\beta)_{\text{boundary}} = \delta_{kl} \delta_{\alpha\beta} \quad (5.54)$$

where $k, l = 1, \dots, L-1$ and $\alpha, \beta = \pm$. For the functions Φ_{kl} we define a scalar product on the interior of the triangle:

$$(f | g)_{\text{bulk}} = \sum_{x=1}^{L-1} \sum_{y=x+1}^{L-1} \eta^{-2(x+y)} f(x, y) g(x, y) \quad (5.55)$$

The functions Φ_{kl} then obey the relation

$$(\Phi_{kl} | \Phi_{k'l'})_{\text{bulk}} = \delta_{kk'} \delta_{ll'} \quad (5.56)$$

These relations are independent of the value of η .

Every solution can be expanded in terms of the eigenfunctions (5.50)–(5.52):

$$\begin{aligned} \Omega(x, y, t) = & 1 + \omega_0 \phi_{\text{stat}}(x, y) + \sum_{k=1}^{L-1} \sum_{\alpha=\pm} \omega_k^\alpha \phi_k^\alpha(x, y) e^{-A_k t} \\ & + \sum_{k=1}^{L-2} \sum_{l=k+1}^{L-1} \omega_{kl} \Phi_{kl}(x, y) e^{-(A_k + A_l)t} \end{aligned} \quad (5.57)$$

Here the constant 1-function is just the particular solution (5.35) and A_k is defined in Eq. (3.13). The scalar products (5.53) and (5.55) allow the coefficients ω_0 , ω_k^\pm , and ω_{kl} to be computed if the initial values $\Omega_0(x, y)$ are known. We obtain

$$\omega_0 = \Omega_0(0, L) - 1 \quad (5.58)$$

$$\omega_k^\pm = (\phi_k^\pm | \Omega_0 - 1 - \omega_0 \phi_{\text{stat}})_{\text{boundary}} \quad (5.59)$$

$$\omega_{kl} = (\Phi_{kl} | \Omega_0 - 1 - \omega_0 \phi_{\text{stat}})_{\text{bulk}} - \sum_{k'=1}^{L-1} \sum_{\alpha=\pm} \omega_{k'}^\alpha (\Phi_{kl} | \phi_{k'}^\alpha)_{\text{bulk}} \quad (5.60)$$

We will apply this procedure for a special choice of the initial conditions in the next section.

6. FINITE-SIZE SCALING

In this section we study the finite-size scaling behavior of the concentration for the coagulation model with periodic and open boundary conditions and for the annihilation model for periodic boundary conditions (the latter case illustrates the consequences of the similarity transformation). The finite-size scaling limit is obtained by taking the limit $L \rightarrow \infty$, $t \rightarrow \infty$ while the scaling variable $z = 4t/L^2$ is kept fixed. As explained in the introduction, the expansion of the concentration in the scaling limit, Eq. (1.2), reads

$$c(z, L) = L^x [F_0(z) + L^{-y}F(z) + \dots] \quad (6.1)$$

where F_0 is the scaling function and x the scaling exponent. The leading correction term is denoted by $L^{-y}F$, where y is the correction exponent and F the correction function.

Since the finite-size scaling hypothesis is only valid for systems corresponding to massless quantum chains, we have to restrict ourselves to the case $\eta = 1$, where the decoagulation rate d vanishes. In general, only models without backreactions correspond to massless quantum chains.

6.1. The Coagulation Model with Periodic Boundary Conditions

Before calculating the finite-size scaling expansion for the concentration, an exact expression for the particle concentration has to be found for a special choice of the initial condition. According to Eqs. (5.1) and (5.29), we have

$$\begin{aligned} c(t, L) &= \frac{1}{L} \sum_{j=1}^{L-1/2} [1 - \Omega(j, 1, t)] \\ &= 1 - \hat{\Omega}(0, 1, t) \\ &= -A_0^0 \Psi_{\text{stat}}^0(n) - \sum_{k=1}^{L-1} A_k^0 \Psi_k^0(n) \exp(-A_k^0 t) \end{aligned} \quad (6.2)$$

As initial condition we choose a state where each site is occupied with probability p :

$$\hat{\Omega}(0, n, 0) = \Omega(j, n, 0) = (1 - p)^n \quad (6.3)$$

The coefficients A_k^0 can be calculated with the help of Eqs. (5.32) and (5.33). For the concentration we find

$$\begin{aligned}
 c(t, L) = & \frac{(1 - \eta^{-2})[1 - (1 - p)^L]}{1 - \eta^{-2L}} \\
 & - \frac{1}{L} \sum_{k=1}^{L-1} \left[\frac{1 + (-1)^{k+1} \eta^L (1 - p)^L}{[1 + \eta^2(1 - p)^2]/2\eta(1 - p) - \cos(\pi k/L)} \right. \\
 & \left. - \frac{1 + (-1)^{k+1} \eta^L (1 - p)^L}{(\eta^2 + 1)/2\eta - \cos(\pi k/L)} \right] \\
 & \times \sin^2 \left(\frac{\pi k}{L} \right) \exp(-A_k^0 t) \quad (6.4)
 \end{aligned}$$

where the A_k^0 are calculated from Eq. (5.28):

$$A_k^0 = \eta \left[2(\eta + \eta^{-1}) - 4 \cos \frac{\pi k}{L} \right] \quad (6.5)$$

This expression for the concentration is exact for all lattice sizes L . In the limit $\eta \rightarrow 1$ we derive from Eq. (6.4)

$$\begin{aligned}
 c(z, L) = & \frac{1 - (1 - p)^L}{L} \\
 & - \frac{1}{L} \sum_{k=1}^{L-1} \left[\frac{1 + (-1)^{k+1} (1 - p)^L}{[1 + (1 - p)^2]/2(1 - p) - \cos(\pi k/L)} \right. \\
 & \left. - \frac{1 + (-1)^{k+1} (1 - p)^L}{1 - \cos(\pi k/L)} \right] \\
 & \times \sin^2 \left(\frac{\pi k}{L} \right) \exp \left[-zL^2 \left(1 - \cos \frac{\pi k}{L} \right) \right] \quad (6.6)
 \end{aligned}$$

We now perform the scaling limit in Eq. (6.6). For this purpose we write $Lc(z, L)$ as a power series in $1/L$ with coefficients depending only on the scaling variable z . The coefficients can be identified as Jacobi theta functions and their derivatives:

$$\begin{aligned}
 Lc(z, L) = & \theta_3 \left(0, \frac{i\pi z}{2} \right) + \frac{1}{L^2} \left[\frac{z}{6} \frac{\partial^2}{\partial z^2} \theta_3 \left(0, \frac{i\pi z}{2} \right) \right. \\
 & \left. + \frac{(p-2)^2}{2p^2} \frac{\partial}{\partial z} \theta_3 \left(0, \frac{i\pi z}{2} \right) \right] + O \left(\frac{1}{L^4} \right) \quad (6.7)
 \end{aligned}$$

where $\theta_3(u, \tau)$ is defined by the series

$$\theta_3(u, \tau) = \sum_{l=-\infty}^{\infty} e^{i\pi\tau l^2} e^{2ilu} \quad (6.8)$$

Comparing this result with Eq. (6.1), we find the scaling exponent and the correction exponent to be $x = -1$ and $y = 2$. Observe that the initial probability p (to find a particle at a site at time $t = 0$) enters only in the corrections. So the scaling function for this model is independent of the initial conditions as far as an uncorrelated initial state is concerned. It reflects the phenomenon of self-organization: with increasing time and lattice length, the influence of the initial conditions vanishes.

At this point, it is interesting to mention that it is possible as well to obtain the scaling function by using the continuum limit of the lattice model.⁽⁴⁰⁾ These calculations are presented in the appendix.

Before closing this section, we relate the concentration in the scaling limit, taking additionally small z , to the long-time behavior of the concentration in the thermodynamic limit. For this purpose, we apply the Poisson resummation formula to the scaling function $\theta_3(0, i\pi z/2)$:

$$\theta_3\left(0, \frac{i\pi z}{2}\right) = \left(\frac{2}{\pi z}\right)^{1/2} \left[1 + 2 \sum_{m=1}^{\infty} \exp\left(-\frac{2m^2}{z}\right) \right] \quad (6.9)$$

With the help of this expression, we can now take the limit for small z in Eq. (6.7):

$$c(z, L) = \frac{1}{L} \left(\frac{2}{\pi z}\right)^{1/2} \left[1 - \frac{1}{4zL^2} \left(\frac{(p-2)^2}{p^2} - \frac{1}{2}\right) + \dots \right] \quad (6.10)$$

Inserting the definition of z yields

$$c(t) = \left(\frac{1}{2\pi t}\right)^{1/2} \left[1 - \frac{1}{16t} \left(\frac{(p-2)^2}{p^2} - \frac{1}{2}\right) + \dots \right] \quad (6.11)$$

The leading term was already obtained in refs. 29 and 40.

This relationship illustrates the fact already mentioned in ref. 14: the scaling exponent $x = -1$ is twice the exponent α of t in the long-time behavior of the concentration in the thermodynamic limit, where $c(t) \simeq t^\alpha$. This is very useful for the determination of the "critical" exponent α in non-integrable models. In these cases, it is possible to examine finite systems (where the Hamiltonian can be diagonalized numerically) and to determine the finite-size scaling exponent x and therewith α by extrapolation.

The scaling relation can be understood from a more general point of view by looking at the scaling behavior of the concentration. In the

thermodynamic limit $L \rightarrow \infty$ with fixed t, z becomes small, so that the scaling function and the corrections can be expanded in powers of $1/z$ [cf. Eq. (6.9)]:

$$\begin{aligned} c(z, L) &= L^x F_0(z) + \dots = L^x \left(\frac{1}{z^\kappa} G + \dots \right) + \dots \\ &= \frac{L^{2\kappa+x}}{4^\kappa t^\kappa} (G + \dots) + \dots \end{aligned} \quad (6.12)$$

Since this has to be independent of L , it follows that $\kappa = -x/2$, so that

$$c(t) \simeq \frac{1}{t^{-x/2}} = \frac{1}{t^{1/2}} \quad (6.13)$$

This proves the relation $\alpha = x/2$.

6.2. The Coagulation Model with Open Boundary Conditions

The concentration is again calculated by means of Eq. (5.1). The expression for $\Omega(j, 1, t)$ needed for this calculation is obtained from the general expressions (5.57)–(5.60), using the same uncorrelated initial state as for periodic boundary conditions where the occupation probability p is equal for all sites:

$$\Omega_0(x, y) = (1-p)^{x-y} \quad (6.14)$$

Straightforward but rather laborious calculations show that the concentration is given by

$$\begin{aligned} c(t, L) &= \frac{1-\eta^{-2}}{1-\eta^{-2L}} [1 - (1-p)^L] \\ &+ \frac{4(1-\eta^{-2})}{L^2(\eta^L - \eta^{-L})} \sum_{k=1}^{L-1} [1 - (-1)^k (1-p)^L \eta^L] \\ &\times [\eta^L + \eta^{-L} - 2(-1)^k] \frac{\sin^2(\pi k/L)}{A_k} \left(\frac{1}{A_k} - \frac{1}{\bar{A}_k} \right) \exp(-A_k t) \\ &+ \frac{8}{L^3 \eta} \sum_{k=1}^{L-1} \sum_{\substack{l=k+1 \\ k+l \text{ odd}}}^{L-1} \left[\frac{1}{\cos(\pi k/L) - \cos(\pi l/L)} \left(\frac{1}{A_k} + \frac{1}{A_l} - \frac{1}{\bar{A}_k} - \frac{1}{\bar{A}_l} \right) \right. \\ &+ 2(-1)^k \eta^L (1-p)^L \left. \left(\frac{1}{A_k} - \frac{1}{\bar{A}_k} \right) \left(\frac{1}{A_l} - \frac{1}{\bar{A}_l} \right) - \frac{2}{A_k \bar{A}_l} + \frac{2}{A_l \bar{A}_k} \right] \\ &\times \frac{\sin^2(\pi k/L) \sin^2(\pi l/L)}{\cos(\pi k/L) - \cos(\pi l/L)} \exp[-(A_k + A_l) t] \end{aligned} \quad (6.15)$$

where $\bar{\lambda}_k$ is defined by

$$\bar{\lambda}_k = \eta \left[(1-p)\eta + (1-p)^{-1}\eta^{-1} - 2 \cos \frac{\pi k}{L} \right] \quad (6.16)$$

In the case $\eta = 1$ the concentration takes the form

$$\begin{aligned} c(t, L) = & \frac{1 - (1-p)^L}{L} \\ & + \frac{4}{L^3} \sum_{k=0}^{L-1} \sum_{\substack{l=1 \\ k+l \text{ odd}}}^{L-1} \left[\frac{1}{\cos(\pi k/L) - \cos(\pi l/L)} \left(\frac{1}{\lambda_k} + \frac{1}{\lambda_l} - \frac{1}{\bar{\lambda}_k} - \frac{1}{\bar{\lambda}_l} \right) \right. \\ & + 2(-1)^k (1-p)^L \left(\frac{1}{\lambda_k} - \frac{1}{\bar{\lambda}_k} \right) \left(\frac{1}{\lambda_l} - \frac{1}{\bar{\lambda}_l} \right) - \frac{2}{\lambda_k \bar{\lambda}_l} + \frac{2}{\lambda_l \bar{\lambda}_k} \left. \right] \\ & \times \frac{\sin^2(\pi k/L) \sin^2(\pi l/L)}{\cos(\pi k/L) - \cos(\pi l/L)} \exp[-(\lambda_k + \lambda_l)t] \end{aligned} \quad (6.17)$$

Performing now the finite-size scaling limit in Eq. (6.17), we find

$$\begin{aligned} Lc(z, L) = & 1 + \frac{16}{\pi^2} \sum_{k=0}^{\infty} \sum_{\substack{l=1 \\ k+l \text{ odd}}}^{\infty} \frac{k^2 + l^2}{(k^2 - l^2)^2} \exp \left[-\frac{z\pi^2}{4} (k^2 + l^2) \right] \\ & + \frac{1}{L^2} \sum_{k=0}^{\infty} \sum_{\substack{l=1 \\ k+l \text{ odd}}}^{\infty} \left[\frac{z}{3} \pi^2 \frac{(k^2 + l^2)(k^4 + l^4)}{(k^2 - l^2)^2} \right. \\ & \left. - \frac{8}{3} \frac{(1 + 6(1-p)/p^2)(k^4 + l^4) + k^2 l^2}{(k^2 - l^2)^2} \right] \exp \left[-\frac{z\pi^2}{4} (k^2 + l^2) \right] \\ & + O\left(\frac{1}{L^4}\right) \end{aligned} \quad (6.18)$$

and therefore we obtain the exponents $x = -1$ and $y = 2$. The functions F_0 and F can be written in a simpler form by rewriting the sums in Eq. (6.18) in terms of $\mu = (k + l - 1)/2$ and $\nu = (k - l - 1)/2$:

$$F_0(z) = 1 - \frac{1}{2} g_0(z) g_1(z) \quad (6.19)$$

$$\begin{aligned} F(z) = & -\frac{7z}{12} g_1(z) g_2(z) - \frac{z}{12} g_0(z) g_3(z) - \frac{1}{12} \{g_0(z) g_2(z) - [g_1(z)]^2\} \\ & - \left(1 + 6 \frac{1-p}{p^2} \right) \left\{ \frac{1}{6} g_0(z) g_2(z) + \frac{1}{2} [g_1(z)]^2 \right\} \end{aligned} \quad (6.20)$$

where the functions $g_i(z)$ are defined by

$$g_0(z) = \sum_{\mu=-\infty}^{\infty} \frac{-2}{\pi^2(\mu + 1/2)^2} \exp \left[-\frac{z\pi^2}{2} \left(\mu + \frac{1}{2} \right)^2 \right] \quad (6.21)$$

$$g_i(z) = \frac{\partial^i}{\partial z^i} g_0(z) \quad (i = 1, 2, 3) \quad (6.22)$$

In particular we have the identity

$$g_1(z) = \theta_2 \left(0, \frac{i\pi z}{2} \right) \quad (6.23)$$

where $\theta_2(u, \tau)$ is the Jacobi theta function defined by

$$\theta_2(u, \tau) = \sum_{l=-\infty}^{\infty} e^{i\pi\tau(l+1/2)^2} e^{2i\pi(l+1/2)u} \quad (6.24)$$

Now we are able to compare the finite-size scaling behavior for open and periodic boundary conditions. In both cases we find the scaling exponent $x = -1$ and the correction exponent $y = 2$. Thus the critical exponents are not influenced by the boundary conditions. The scaling function and the correction function, on the other hand, are different, as can be seen in Figs. 2 and 3. However, we find that in both cases the scaling functions and the correction functions are related to Jacobi theta functions. As in the case of

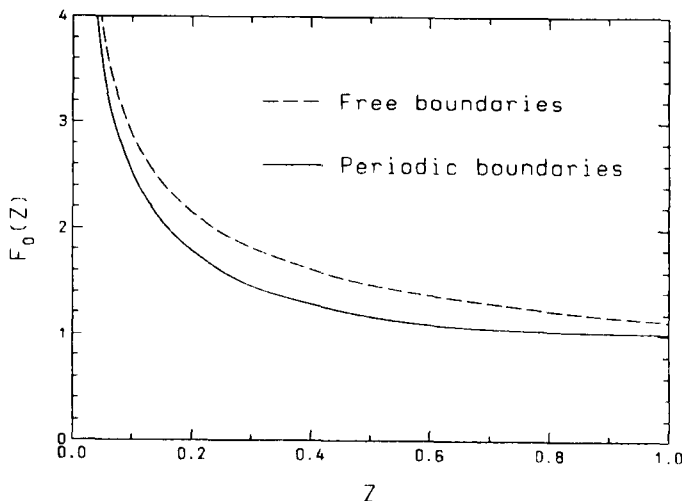


Fig. 2. Scaling functions for open and periodic boundary conditions.

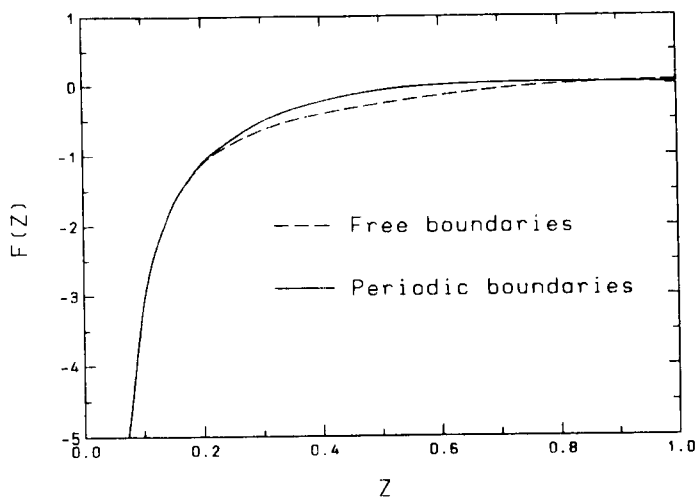


Fig. 3. Correction functions for open and periodic boundary conditions for initial occupation probability $p = 1$.

periodic boundary conditions, we observe that the scaling function (6.19) is independent of the initial probability p , whereas the correction function (6.20) is not.

6.3. Finite-Size Scaling of the Annihilation Model

In this section we will discuss the finite-size scaling behavior of the concentration of the annihilation model. The expression for the concentration simply follows from the one for the coagulation model using the similarity transformation described in Section 4. We consider only the case of periodic boundary conditions to illustrate the correspondence between the coagulation and the annihilation model.

We choose the rates in such a way that the similarity transformation can be applied:

$$\begin{aligned} \text{diffusion rate } D &= 1 \\ \text{annihilation rate } a &= 2 \end{aligned} \tag{6.25}$$

As initial condition we use a homogeneous initial occupation probability p . Then the relation between the concentration in the coagulation model and the annihilation model (4.12) reduces to

$$c_{\text{ann}}(p, t) = \frac{1}{2} c_{\text{coag}}(2p, t) \tag{6.26}$$

From the expression (6.6) for the concentration in the coagulation model we easily get

$$\begin{aligned}
 c_{\text{ann}}(t) &= \frac{1 - (1 - 2p)^L}{2L} \\
 &\quad - \frac{1}{2L} \sum_{k=1}^{L-1} \left[\frac{1 - (-1)^k (1 - 2p)^L}{[1 + (1 - 2p)^2]/2(1 - 2p) - \cos(\pi k/L)} \right. \\
 &\quad \left. - \frac{1 - (-1)^k (1 - 2p)^L}{1 - \cos(\pi k/L)} \right] \\
 &\quad \times \sin^2 \left(\frac{\pi k}{L} \right) \exp \left[-4t \left(1 - \cos \frac{\pi k}{L} \right) \right] \quad (6.27)
 \end{aligned}$$

If $0 < p < 1$, the term $(1 - 2p)^L$ can be neglected in the finite-size scaling limit where $L \rightarrow \infty$, whereas for an initially fully occupied lattice ($p = 1$) it has to be taken into account. The concentration then takes the form

$$c(t) = \frac{1 - (-1)^L}{2L} + \frac{2}{L} \sum_{k=1}^{L-1} \frac{1 - (-1)^{k+L}}{2} \exp \left[-4t \left(1 - \cos \frac{\pi k}{L} \right) \right] \quad (6.28)$$

For an even number of sites this result was first found by Lushnikov.⁽⁴⁴⁾ The reason for the special behavior of the concentration in the case $p = 1$ is the conservation of the charge $Q = (-1)^N$. Accordingly, the Hamiltonian splits up into two sectors describing the time evolution of states with an even or odd number of particles, respectively. The momenta q appearing in these sectors can be taken from the diagonalization in terms of free fermions. They are given by Eq. (3.16). For $p = 1$ we have $Q = (-1)^L$. As can be seen, the factor $1 - (-1)^{k+L}$ in Eq. (6.28) always selects the right values of the momenta q .

We now investigate the finite-size scaling behavior, again by taking the limit $L \rightarrow \infty$, $t \rightarrow \infty$ with $z = 4t/L^2$ fixed. For $0 \leq p < 1$ the calculations can be performed in complete analogy to those for the coagulation model. The finite-size scaling expansion for the concentration reads

$$\begin{aligned}
 Lc(z, L) &= \frac{1}{3} \theta_3 \left(0, \frac{i\pi z}{2} \right) \\
 &\quad + \frac{1}{L^2} \frac{1}{2} \left[\frac{z}{6} \frac{\partial^2}{\partial z^2} \theta_3 \left(0, \frac{i\pi z}{2} \right) + \frac{(1-p)^2}{2p^2} \frac{\partial}{\partial z} \theta_3 \left(0, \frac{i\pi z}{2} \right) \right] \\
 &\quad + O \left(\frac{1}{L^4} \right) \quad (6.29)
 \end{aligned}$$

As mentioned above, the case $p = 1$ needs special treatment. Here we have to discuss the finite-size scaling limit for L even and L odd separately.

- L even: In this case the concentration takes the form

$$c(t, L) = \frac{2}{L} \sum_{k=1}^{L/2} \exp \left[-4t \left(1 - \cos \frac{2k-1}{L} \pi \right) \right] \quad (6.30)$$

The calculation of the finite-size scaling limit yields

$$Lc(z, L) = \theta_2(0, 2i\pi z) + \frac{1}{L^2} \frac{z}{3!} \frac{\partial^2}{\partial z^2} \theta_2(0, 2i\pi z) + O\left(\frac{1}{L^4}\right) \quad (6.31)$$

where $\theta_2(u, \tau)$ is again the Jacobi theta function defined in Eq. (6.24). Up to the correction term this result was already obtained by Alcaraz *et al.*⁽¹⁴⁾

- L odd: Here we have

$$c(t, L) = \frac{1}{L} + \frac{2}{L} \sum_{k=1}^{(L-1)/2} \exp \left[-4t \left(1 - \cos \frac{2k}{L} \right) \right] \quad (6.32)$$

and the finite-size scaling limit yields

$$Lc(z, L) = \theta_3(0, 2i\pi z) + \frac{1}{L^2} \frac{z}{3!} \frac{\partial^2}{\partial z^2} \theta_3(0, 2i\pi z) + O\left(\frac{1}{L^4}\right) \quad (6.33)$$

Independently of the initial probability p we have the scaling exponent $x = -1$ and the correction exponent $y = 2$ similar to the coagulation model. This is not surprising, because these models are equivalent. The scaling function is again found to be independent of the initial probability p except for $p = 1$.

7. CONCLUSIONS

In this paper, we investigated two chemical models, the coagulation-decoagulation model and the annihilation model, both defined on a one-dimensional lattice. Mapping the master equation onto a Euclidean Schrödinger equation, it is possible to give a Hamilton formulation for nonequilibrium chemical systems. This formulation is essential to prove the complete equivalence of the Hamiltonians of both systems. The second subject of this paper was to investigate the applicability of a finite-size scaling theory for these systems in nonequilibrium.

Now we discuss the results in detail:

We were able to prove the equivalence of the two Hamiltonians. A sufficient condition for the existence of a similarity transformation mapping

one model onto the other is that the annihilation rate equals twice the coagulation rate. The consequences of this transformation, which is valid for periodic as well as for open boundary conditions, are various: Once having solved one model, one can easily find expectation values of the other model by application of the transformation. In particular we found a simple rule for all n -point functions [cf. Eq. (4.11)].

The study of the Hamiltonians revealed furthermore that for a special choice of the rates, both Hamiltonians are integrable in terms of free fermions whose energy levels have been calculated explicitly.

The key to an exact expression for the concentration in the coagulation model lies in having the empty interval probabilities $\Omega(j, n, t)$. Their time evolution is described by a system of coupled differential equations. For periodic boundary conditions a Fourier transformation decouples this system into L independent systems growing linearly with the lattice size L . This is no longer possible for open boundary conditions because of the lack of translational invariance. In this case, one obtains one system of $L(L+1)/2$ equations, i.e., a system that grows quadratically with lattice length L . Nevertheless a solution is possible and was derived explicitly. We computed the concentration for initial states where all sites are occupied with equal probability p .

The similarity transformation was applied to calculate the corresponding expression for the concentration in the annihilation model in the case of periodic boundary conditions.

It is very interesting that the energies determining the time evolution of the concentration can be identified as one- and two-fermionic excitations of the corresponding Hamiltonian. The question of whether and how a link between the Hamiltonian and the relevant energies for the concentration can be established still has to be answered.

A second point of major interest was to examine the applicability of a finite-size scaling theory for massless reaction-diffusion models. Starting from the exact expression for the concentration, we have shown that for the coagulation model with periodic and open boundary conditions and the annihilation model the concentration in the finite-size scaling limit can be written as $Lc(z, L) = F_0(z) + L^{-2}F(z)$, where $F_0(z)$ and $F(z)$ are functions depending only on the scaling variable $z = 4t/L^2$ and can be expressed in terms of Jacobi theta functions. The scaling exponent and the correction exponent are the same for both types of boundary conditions and the two models investigated here.

Since we were interested in the properties of the scaling function, we investigated its dependence on the initial conditions and the boundary conditions.

Concerning the dependence of the scaling functions on homogeneous uncorrelated initial conditions, we proved for the coagulation model and the annihilation model that the scaling functions are independent of the initial occupation probability. An exception is the case of an initially completely occupied lattice in the annihilation model, where we get different scaling functions for even and odd lattices. The reason is the Z_2 symmetry. Because the annihilation reaction reduces the number of particles by two, even and odd lattices decouple completely.

Another point of interest is the dependence of the scaling behavior on the boundary conditions. We demonstrated that the exponents in the case of open boundary conditions are still the same as in the case of periodic boundary conditions; the scaling functions, however, are different for periodic and for open boundary conditions. From this we conclude that in general, scaling functions in finite-size scaling studies of reaction-diffusion models depend on the geometry of the system.

Furthermore, we have shown that the same scaling function is obtained from the lattice and the continuous formulation of the coagulation model. Therefore the question arises whether it is at all necessary to study lattice models. In the present article, we only treated models where analytical calculations can be performed. Finite-size scaling allows for non-integrable models as well to extrapolate from finite to infinite systems. A numerical diagonalization of the Hamiltonian that can only be done on discrete lattices provides the input values for these extrapolations. Monte Carlo simulations as well can only be made on lattices. This will be the subject of our subsequent article, where several open questions will be investigated. Monte Carlo simulations will be used to study weakly correlated initial conditions as well as the dependence of the scaling behavior on the tuning of the rates. Here the cases will be studied where analytical methods cannot be applied easily. Furthermore, the question of whether extrapolations from small lattices can be used to determine scaling exponents and functions will be discussed.

A lot of work has still to be done in this field. The present article shows that the formulation of universality classes in nonequilibrium thermodynamics is not the same as in equilibrium statistical mechanics. The annihilation and coagulation models are equivalent although the annihilation model is Z_2 -symmetric and the coagulation model is not. A further interesting question arises upon looking at the scaling functions and the correction functions: Are they always related to Jacobi theta functions? The solutions of these problems will help us to gain deeper insight into the fascinating physics of the chemical models in nonequilibrium.

APPENDIX. DERIVATION OF THE SCALING FUNCTION IN THE CONTINUUM LIMIT

In this appendix, we present the continuum limit of the differential equations (5.12) for periodic boundary conditions, treating the coagulation-decoagulation model with diffusion rate = coagulation rate and decoagulation rate = 0 (i.e., $\eta = 1$). The continuum limit is obtained by replacing the discrete variable n , which denotes the length of an empty interval in Section 5, by a continuous variable $x \in [0, L]$. Because of periodic boundary conditions, the model is defined on a ring of circumference L . We define a new function $E(x, t)$ describing the probability that a chosen interval of length x is empty at time t . Since we are only interested in observables that are averaged over the whole system, we define $E(x, t)$ independently of the center point. So $E(x, t)$ corresponds to the continuum limit of $\Omega(0, n, t)$ [the Fourier transformation of the $\Omega(j, n, t)$ with zero momentum as defined in Section 5]. Following the derivation given in ref. 40, we obtain the differential equation for $E(x, t)$:

$$\frac{\partial E(x, t)}{\partial t} = 2 \frac{\partial^2 E(x, t)}{\partial x^2} \quad (\text{A.1})$$

This is the well-known heat equation. Before solving the differential equation, we first change the variable x to $y = x/L$ so that $y \in [0, 1]$. Denoting $E(x, t) = \tilde{E}(y, t)$ we obtain the differential equation

$$\frac{\partial \tilde{E}(y, t)}{\partial t} = \frac{2}{L^2} \frac{\partial^2 \tilde{E}(y, t)}{\partial y^2} \quad (\text{A.2})$$

with the boundary conditions

$$\tilde{E}(0, t) = 1, \quad \tilde{E}(1, t) = \tilde{E}(1, 0) \quad (\text{A.3})$$

The concentration can be calculated as a derivative of $\tilde{E}(y, t)$

$$c(t) = -\frac{1}{L} \left. \frac{\partial \tilde{E}(y, t)}{\partial y} \right|_{y=0} \quad (\text{A.4})$$

We now briefly present the solution of Eq. (A.2). As initial condition we choose

$$\tilde{E}(y, 0) = \exp(-c_0 L y) \quad (\text{A.5})$$

This probability distribution corresponds to an uncorrelated initial state with an initial concentration c_0 . A particular solution (steady state) satisfying the boundary conditions (A.3) is $\tilde{E}_s(y) = 1 - [1 - \exp(-c_0 L)] y$.

Solving the homogeneous problem, we observe that $\tilde{E}(y, t)$ can be expanded in terms of the eigenfunctions $\psi_k(y)$ of the eigenvalue problem:

$$-\lambda_k \psi_k(y) = \frac{2}{L^2} \frac{\partial^2 \psi_k(y)}{\partial y^2} \quad (\text{A.6})$$

with $\psi_k(0) = \psi_k(1) = 0$. Then $\tilde{E}(y, t)$ can be expressed in terms of the eigenfunctions as

$$\tilde{E}(y, t) = \sum_k B_k \psi_k(y) e^{-\lambda_k t} \quad (\text{A.7})$$

The solution of this problem is easily determined to be

$$\psi_k(y) = \sin(\pi k y), \quad \lambda_k = \frac{2\pi^2 k^2}{L^2} \quad (k = 1, 2, \dots) \quad (\text{A.8})$$

The complete solution of the differential equation (A.2) is now given by

$$\tilde{E}(y, t) = \tilde{E}_s(y) + \sum_{k=1}^{\infty} B_k \sqrt{2} \sin(\pi k y) e^{-2\pi^2 k^2 t / L^2} \quad (\text{A.9})$$

In this expression the coefficients B_k can be computed by using the orthogonality relation $2 \int_0^1 \sin(\pi k y) \sin(\pi l y) dy = \delta_{k,l}$:

$$B_k = \int_0^1 [\tilde{E}(y, 0) - \tilde{E}_s(y)] \sqrt{2} \sin(\pi k y) dy \quad (\text{A.10})$$

$$= \sqrt{2} \left[\frac{\exp(-c_0 L) \cos(\pi k) - 1}{\pi k (1 + (\pi k / c_0 L)^2)} \right] \quad (\text{A.11})$$

Now we are able to derive the concentration using Eq. (A.4)

$$c(t, L) = \frac{1 - \exp(-c_0 L)}{L} + \frac{2}{L} \sum_{k=1}^{\infty} \left[\frac{1 - \exp(-c_0 L) \cos(\pi k)}{1 + (\pi k / c_0 L)^2} \right] \exp\left(-\frac{2t\pi^2 k^2}{L^2}\right) \quad (\text{A.12})$$

This expression is exact for all lattice sizes L . If we consider the finite-size scaling limit $L \rightarrow \infty$, $t \rightarrow \infty$ with $z = 4t/L^2$ fixed, the above expression for the concentration becomes

$$c(z, L) = \frac{1}{L} + \frac{2}{L} \sum_{k=1}^{\infty} \exp\left(-\frac{z\pi^2 k^2}{2}\right) - \frac{2}{L^3 c_0^2} \sum_{k=1}^{\infty} \pi^2 k^2 \exp\left(-\frac{z\pi^2 k^2}{2}\right) + \dots \quad (\text{A.13})$$

$$= \frac{1}{L} \left[\theta_3\left(0, \frac{i\pi z}{2}\right) + \frac{2}{L^2 c_0^2} \frac{\partial}{\partial z} \theta_3\left(0, \frac{i\pi z}{2}\right) + \dots \right] \quad (\text{A.14})$$

From the expansion of this expression for small z we can calculate the long-time behavior in the thermodynamic limit:

$$c(t) = \frac{1}{(2\pi t)^{1/2}} \left(1 - \frac{1}{4tc_0^2} + \dots \right) \quad (\text{A.15})$$

Comparing Eqs. (A.14) and (A.15) with the corresponding expressions (6.7) and (6.11) for the lattice model, we observe that the leading terms are equal, but the corrections are different. In order to understand this, we take a closer look at the way the continuum limit of the lattice model has to be taken. Here we denote by N the number of sites, to distinguish it from the length L of the continuous model. If a is the lattice constant, i.e., the distance between two sites, taking the continuum limit means taking $N \rightarrow \infty$ and $a \rightarrow 0$ while keeping the length $L = Na$, the macroscopic diffusion constant $D = a^2 \Gamma_{01}^{10}$, and the initial concentration $c_0 = p/a$ constant. Therefore the transition from the lattice to the continuum is performed by replacing

$$c \rightarrow \frac{c}{a} = \frac{cc_0}{p}, \quad N \rightarrow \frac{L}{a} = \frac{Lc_0}{p}, \quad \Gamma_{01}^{10} \rightarrow \frac{D}{a^2} = \frac{Dc_0^2}{p^2} \quad (\text{A.16})$$

and then taking the limit $p \rightarrow 0$. It is clear that the value of the scaling variable z , which is $z = 4\Gamma_{01}^{10} t / N^2$ on the lattice and $z = 4Dt / L^2$ in the continuum, does not vary when p goes to zero.

If we apply the above procedure to Eqs. (6.7) and (6.11) for the lattice model, we obtain exactly Eqs. (A.14) and (A.15) for the continuous model. For open boundary conditions, it should also be possible to derive the scaling function from the continuous model. The resulting equations are much more complicated because of the lack of translation invariance. Instead of the simple heat equation, one obtains a two-dimensional system of differential equations corresponding to the one treated in Section 5.

To sum up, we have shown that it is possible to turn to the continuum limit of the coagulation model to study the scaling behavior. This should be possible for all models with reactions that can be described in the language of empty interval probabilities where the calculation of the

continuum limit is straightforward. The physics of the continuum model is the same as for the discrete model, but the differential equations are often much easier to solve.

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