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## Three-state model and chemical reactions

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**Abstract.** A three-state model is formulated in terms of raising and lowering operators. As an application, cyclic chemical reactions with three different species in the solid state are studied. The evolution equations for the densities and for the correlation functions can be derived starting from a master equation in a generalized Fock space representation on a lattice. Such a description guarantees the consideration of the excluded volume effect. In contrast to the classical kinetic behaviour, the system offers stable and unstable regimes depending on the averaged composition ratio.

### 1. Introduction

There is much effort in understanding the dynamical behaviour of classical stochastic systems under exclusion [1–11]. Physically, it means that the considered system is divided into small cells denoted by the index  $i$ . Every cell can be occupied only by a restricted number of particles, which are subjected to special dynamical rules depending on the situation in mind. Here, we consider the case where the occupation number per cell is restricted to two. The problem is to formulate the dynamics of the system in such a way that these restrictions are taken into account. In particular, such a situation can be described in a seemingly compact form starting from a master equation on a lattice [12, 13, 5].

From a quantum point of view two limiting cases exist: unrestricted occupation numbers (bosons) and, due to the Pauli principle, a restricted occupation number 0 and 1 which corresponds to an empty and to a single occupied cell in a lattice gas representation. Such a situation can be also described by a spin model with two orientations.

An obvious extension is given by a finite  $(p + 1)$ -state model, for instance a three-state model, i.e.  $p = 2$ , with empty, single and double occupied lattice cells, respectively. A possible application is given by a forest fire model [15–20] with burning and growing trees as well as empty sites. Further realizations are also defined for three-candidate voter models [21] or systems consisting of two different species with additional vacancies [23, 22].

The analysis of such finite state models requires additional strict constraints preventing an occupation number higher than  $p$ . The Fock space representation applied in this paper enables the formulation of the dynamics in terms of operators whose algebraic properties automatically contain these restrictions. Here we want to demonstrate that the mentioned situations of a  $p$ -fold occupation can be concisely described in terms of local raising and lowering operators,  $a_i$  and  $a_i^\dagger$ , which are characterized by the double commutator relation

$$[a_i, [a_j^\dagger, a_k]_-]_- = 2\delta_{ij}a_k. \quad (1)$$

A typical situation which can be treated using the Fock space method is chemical reactions in solid and glassy materials. Such systems are characterized by a low mobility manifested

by sufficient small diffusion coefficients, i.e. the particles are fixed over a time scale much longer than the effective reaction time. In these reaction-dominated processes a particle is surrounded by approximately the same environment. Therefore, the system should be described by the above-mentioned lattice. One cell is occupied at least only by one reactant (excluded volume effect). Hence, a chemical reaction is possible exclusively whenever the reactants are at adjacent lattice cells (nearest-neighbour interaction) such as



(compare also equation (16)). Obviously, the chemical reactions dominate the dynamics and yield the main contributions to the thermodynamical fluctuations in contrast to the diffusion controlled case, see [24]. To analyse the influence of such chemical fluctuations it is usual to start from master equations. The transformation of these equations into the Fock space representation allows both the consideration of the excluded volume effect via the algebraic properties of the Fock space operators and the application of well known quantum mechanical techniques.

After introducing the Fock space representation in terms of raising and lowering operators, satisfying equation (1) we have applied the method in studying an irreversible chemical ring reaction. It will be demonstrated that already in a lowest-order decoupling of the hierarchy of kinetic equations there appear regions of instability which are completely lacking in a conventional consideration without any fluctuations.

## 2. Fock space representation

The starting point is the master equation which can be derived on quite general grounds. It can be written in a symbolic form

$$\partial_t P(\mathbf{n}, t) = L' P(\mathbf{n}, t) \quad (2)$$

where  $P$  is the probability that a certain configuration characterized by the vector  $\mathbf{n}$  at time  $t$  is realized. The evolution operator  $L'$  has to be specified by the dynamics of the model. Following [12–14, 5, 9] the probability distribution  $P(\mathbf{n}, t)$  can be related to a state vector  $|F(t)\rangle$  in a Fock space according to  $P(\mathbf{n}, t) = \langle \mathbf{n} | F(t) \rangle$  with the basis vectors  $|\mathbf{n}\rangle \equiv |n_1 \dots n_i \dots\rangle = \prod_i |n_i\rangle$ . As a consequence, the master equation (2) is transformed to an equivalent equation in a Fock space

$$\partial_t |F(t)\rangle = \hat{L} |F(t)\rangle. \quad (3)$$

The operator  $L'$  in (2) is mapped onto the operator  $\hat{L}$  given in a second quantized form. Up to now the procedure is independent of the operators used. Usually  $\hat{L}$  is expressed in terms of creation and annihilation operators satisfying Bose commutation rules [12–14]. To avoid double occupancy, as for instance in a forest fire model [20] or a model simulating a traffic jam [25], the method had been extended to the case of restricted occupation numbers per lattice site [5, 6, 8, 2, 9] by introducing Pauli operators. These operators commute at different points and anticommute at the same lattice point.

In this paper we propose an extension to a statistics characterized by the twofold commutation relation (1). To be more specific, let us denote the local state of degree  $p$  at a lattice cell by  $|0\rangle, |1\rangle, \dots, |p\rangle$  indicating an empty, a single and a  $p$ -fold occupied cell. Later we will identify these states by different species reacting mutually upon a certain scheme.

Now we introduce local annihilation and creation operators which satisfy the relations

$$\begin{aligned} a_i | \dots n_i \dots \rangle &= \sqrt{n_i(p - n_i + 1)} | \dots n_i - 1 \dots \rangle \\ a_i^\dagger | \dots n_i \dots \rangle &= \sqrt{(p - n_i)(n_i + 1)} | \dots n_i + 1 \dots \rangle. \end{aligned} \tag{4}$$

It is convenient to expand the raising and lowering operators at lattice cell  $i$  in terms of usual local Pauli operators  $b_i^\alpha$  ( $SU(2)$   $b_i^\alpha$  operators)

$$a_i = \sum_{\alpha=1}^p b_i^\alpha \tag{5}$$

where  $p$  is the degree of the local state which corresponds to the quantum number of the total spin in the  $SU(2)$  algebra. A simple calculation confirms that the commutation rule (1) is fulfilled if the operators  $b_i^\alpha$  satisfy the following algebra:

$$\begin{aligned} [b_i^\alpha, b_i^{\alpha\dagger}]_+ &= 1 \\ [b_i^\alpha, b_j^{\beta\dagger}]_- &= 0 \quad \text{if } \alpha \neq \beta \quad \text{or } i \neq j \end{aligned} \tag{6}$$

where the ordinary Pauli operator has the property  $b_i^\alpha | \dots 1_i^\alpha \dots \rangle = | \dots 0_i^\alpha \dots \rangle$ . Hence the whole system consists of  $N \times p$  types of independent Pauli operators  $b_i^\alpha$  ( $\alpha = 1, \dots, p$ ;  $i = 1, \dots, N$ ,  $N$ : number of lattice cells). The anticommutation rule is valid only if the operators of the same class  $\alpha$  act at the same lattice cell  $i$ .

In a particle picture equation (5) means that a particle is composed of particles which exhibit the usual properties of Pauli operators. Another interpretation is that a particle offers  $p$  internal degrees of freedom. Here, we consider in detail the case  $p = 2$ , which is denoted as a three-state model.

The relation between the quantum formalism and the probability approach based on the master equation can be found by expanding the vector  $|F(t)\rangle$  with respect to the basis vectors of the Fock space

$$|F(t)\rangle = \sum_{\mathbf{n}_i} P(\mathbf{n}, t) |\mathbf{n}\rangle. \tag{7}$$

As was first shown by Doi [12] the average of an arbitrary physical quantity  $B(\mathbf{n})$  is given by the average of the corresponding operator  $\hat{B}(t)$

$$\langle \hat{B}(t) \rangle = \sum_{\{\mathbf{n}_i\}} P(\mathbf{n}, t) B(\mathbf{n}) = \langle s | \hat{B} | F(t) \rangle \tag{8}$$

with  $\langle s | = \sum_{\{\mathbf{n}_i\}} \langle \mathbf{n} |$ . This rule also remains valid as well as in the case of using Pauli operators [5] and the lowering and raising operators introduced in equation (4), respectively, but with a different meaning of the state vector  $|s\rangle$  used in the last equation. Generalizing the corresponding relation to that case we get for  $p = 2$

$$|s\rangle = \prod_i \left( 1 + \frac{1}{\sqrt{2}} a_i^\dagger + \frac{1}{2} (a_i^\dagger)^2 \right) |0\rangle. \tag{9}$$

Note that the normalization condition for the state function is manifested in the relation  $\langle s | F(t) \rangle = 1$ .

The evolution equation for an arbitrary operator  $\hat{B}$  can be written

$$\partial_t \langle \hat{B} \rangle = \langle s | [\hat{B}, \hat{L}] | F(t) \rangle. \tag{10}$$

To derive the last equation we have used the relation  $\langle s | \hat{L} = 0$ , which is a necessary condition for each  $\hat{L}$ . Note that dynamical equations for classical quantities are determined

by the commutation rules of the underlying operators and by the form of the evolution operator  $\hat{L}$ .

Because of the different algebraic properties of the lowering and raising operators, let us introduce two independent operators (indicators)

$$N_i = \frac{a_i^\dagger a_i}{2} \quad M_i = \frac{a_i^\dagger a_i^\dagger a_i a_i}{4}. \quad (11)$$

Using (5) and the algebra of the operators it follows that

$$\begin{aligned} N_i |\dots 0_i \dots\rangle &= 0 & N_i |\dots 1_i \dots\rangle &= |\dots 1_i \dots\rangle & N_i |\dots 2_i \dots\rangle &= |\dots 2_i \dots\rangle \\ M_i |\dots 0_i \dots\rangle &= 0 & M_i |\dots 1_i \dots\rangle &= 0 & M_i |\dots 2_i \dots\rangle &= |\dots 2_i \dots\rangle. \end{aligned} \quad (12)$$

Now the sum  $N_i + M_i$  corresponds to the particle number operator in terms of the lowering and raising operators. To simplify further analysis, one has to derive a lot of auxiliary relations like

$$N_i^2 = N_i \quad M_i^2 = M_i \quad a_i N_i = a_i \quad M_i a_i = 0 \quad M_i a_i^\dagger = a_i^\dagger N_i. \quad (13)$$

The following relations are also useful:

$$\langle s | a_i = \sqrt{2} \langle s | N_i \quad \langle s | a_i^\dagger = \sqrt{2} \langle s | (1 - M_i). \quad (14)$$

The annihilation and creation operators fulfil the relation (1) and, furthermore, we find for instance

$$[N_i, a_j^\dagger] = \delta_{ij} a_i^\dagger (1 - N_i) \quad [M_i, a_j^\dagger] = \delta_{ij} a_i^\dagger (N_i - M_i). \quad (15)$$

### 3. Model and evolution operator

The capability of our approach can be demonstrated for a system which consists of three different species denoted by  $A$ ,  $B$  and  $C$ . These substances react mutually due the the reaction scheme



Denoting the densities of the species by  $\rho_A$ ,  $\rho_B$  and  $\rho_C$ , respectively and the reaction rates by  $\tilde{k}_\beta$ ,  $\beta = 1, 2, 3$ , the mean-field equations for the processes introduced in (16) are immediately written in the form [26]

$$\begin{aligned} \partial_t \rho_A &= \tilde{k}_3 \rho_A \rho_C - \tilde{k}_1 \rho_A \rho_B \\ \partial_t \rho_B &= \tilde{k}_1 \rho_A \rho_B - \tilde{k}_2 \rho_B \rho_C \\ \partial_t \rho_C &= \tilde{k}_2 \rho_B \rho_C - \tilde{k}_3 \rho_A \rho_C. \end{aligned} \quad (17)$$

Such kinds of evolution equations can also be derived within the Fock space method in terms of three independent Bose operators, which was recently demonstrated in [27]. Note that the Bose approach is also appropriate to discuss in a convincing way the influence of fluctuations [24].

The above introduced equations (17) are equations on a mean-field level, as already stressed. The classical equations (17) do not take into account the fact that each lattice cell can only be occupied by a single species (excluded volume effect). Note that this effect remains relevant if the reaction processes dominate the diffusion processes. As a consequence, a local chemical reaction is only possible whenever the corresponding reactants

occupy adjacent cells, otherwise the reaction cannot be realized. In our approach these demands are obviously fulfilled by using a three-state model represented by the lowering and raising operators. The three states  $|0\rangle$ ,  $|1\rangle$ ,  $|2\rangle$  correspond to the  $A$ ,  $B$  and  $C$  particles. Using equations (11), (12) the particle operators at a lattice site  $i$  for the corresponding species are expressed by

$$\begin{aligned} A_i &= 1 - N_i \\ B_i &= N_i - M_i \\ C_i &= M_i. \end{aligned} \quad (18)$$

The evolution operator  $\hat{L}$  (3) can be derived using the properties of the lowering and raising operators. For instance it is simple to confirm the relation  $a^\dagger a^\dagger a|1\rangle = (2)^{3/2}|2\rangle$ , whereas  $a^\dagger a^\dagger a|0\rangle = 0$  and  $a^\dagger a^\dagger a|2\rangle = 0$ . Such a combination describes the reaction between a  $B$  and a  $C$  particle. Examining all possibilities we get  $\hat{L} = \sum_i L_i$  with the local evolution operator  $L_i$  at the cell  $i$

$$L_i = \frac{\tilde{k}_2^i}{2^{3/2}} a_i^\dagger a_i^\dagger a_i + \frac{\tilde{k}_1^i}{2^{3/2}} a_i a_i^\dagger a_i^\dagger + \frac{\tilde{k}_3^i}{2} a_i a_i + \frac{\tilde{k}_1^i - \tilde{k}_2^i}{2} a_i^\dagger a_i + \frac{\tilde{k}_3^i - \tilde{k}_2^i}{2} a_i a_i^\dagger + (\tilde{k}_2^i - \tilde{k}_1^i - \tilde{k}_3^i). \quad (19)$$

As mentioned above, we have to consider that the reaction is only possible when the reactants are available at neighbouring lattice sites simultaneously. To this end, the reaction rates are replaced in accordance with (18) by local operators:

$$\begin{aligned} \tilde{k}_1^i &= k_1 \sum_{j(i)} (N_j - M_j) \\ \tilde{k}_2^i &= k_2 \sum_{j(i)} M_j \\ \tilde{k}_3^i &= k_3 \sum_{j(i)} (1 - N_j). \end{aligned} \quad (20)$$

Here,  $j(i)$  means summation over all sites  $j$  adjacent to the site  $i$ . In view of equation (18) the interpretation of the last relation is obvious, for instance the rate for the reaction  $A + B \rightarrow B + B$  is only nonzero if a  $B$  particle is indeed present in the neighbourhood of an  $A$  particle. Both equations (19), (20) and the commutation rules of the operators used determine the dynamics of the model.

Although the operator  $\hat{L}$  is now given by a rather complicated expression (19), (20), one can find the evolution equations for the particle densities in a straightforward manner only by using the algebraic properties of the operators

$$\begin{aligned} \partial_t \langle A_i \rangle &= \sum_{j(i)} [k_3 \langle A_j C_i \rangle - k_1 \langle B_j A_i \rangle] \\ \partial_t \langle B_i \rangle &= \sum_{j(i)} [k_1 \langle B_j A_i \rangle - k_2 \langle C_j B_i \rangle] \\ \partial_t \langle C_i \rangle &= \sum_{j(i)} [k_2 \langle C_j B_i \rangle - k_3 \langle A_j C_i \rangle]. \end{aligned} \quad (21)$$

The result is a diffusive-like coupling to the neighbouring sites due to higher-order functions.

Our further aim is to study first the stationary case, and after that we discuss the equations for the higher-order terms appearing in (21).

Let us define three independent correlation functions

$$\begin{aligned}\langle A_i A_j \rangle &= \psi(R, t) \\ \langle A_i B_j \rangle &= \Phi(R, t) \\ \langle B_i B_j \rangle &= \chi(R, t).\end{aligned}\tag{22}$$

Here,  $R$  means the distance between the lattice points  $i$  and  $j$  which are not necessary nearest neighbours:  $R = |i - j|$ . If we consider neighbouring sites we denote this by  $R = 1$ .

Note that one can use instead of the defined function other independent combinations. In the stationary case we get using (21), (22)

$$\begin{aligned}\psi(1) &= \bar{A} - \left[ \frac{k}{q} + 1 \right] \Phi(1) \\ \chi(1) &= \bar{B} - [k + 1] \Phi(1)\end{aligned}\tag{23}$$

with the notation  $k = \frac{k_1}{k_2}$  and  $q = \frac{k_3}{k_2}$ . Furthermore,  $\bar{A}$  stands for the stationary expectation value of the density for the  $A$  particles.

To achieve further progress we need the evolution equations for the higher-order functions included in (21). After a tedious procedure we get

$$\begin{aligned}\partial_t \langle A_k A_l \rangle &= -k_1 \sum_j \{ (\Theta_{jk} + \Theta_{jl}) \langle A_k A_l B_j \rangle - \Theta_{jl} \delta_{kl} \langle A_k B_j \rangle \} \\ &\quad + k_3 \sum_j \{ (\Theta_{jk} + \Theta_{jl}) \langle A_k C_l A_j \rangle + \Theta_{jk} \delta_{kl} \langle C_k A_j \rangle \}.\end{aligned}\tag{24}$$

Here we have introduced  $\Theta_{jk}$ , which is only nonzero if  $j$  and  $k$  are nearest neighbour sites. The corresponding equation for  $\langle B_k B_l \rangle$  results after a cyclic permutation  $A_l \rightarrow B_l$ ,  $B_l \rightarrow C_l$ ,  $C_l \rightarrow A_l$ ,  $k_3 \rightarrow k_1$ ,  $k_1 \rightarrow k_2$ . As a third independent quantity we have chosen the correlation function  $\langle A_k B_l \rangle$ , which satisfies the dynamical equation

$$\begin{aligned}\partial_t \langle A_k B_l \rangle &= \sum_j \{ k_3 \Theta_{jk} \langle C_k B_l A_j \rangle - k_2 \Theta_{jl} \langle A_k B_l C_j \rangle \} \\ &\quad + k_1 \sum_j \{ \Theta_{jk} \langle A_k A_l B_j \rangle - \Theta_{jk} \langle A_k B_l B_j \rangle - \Theta_{jk} \delta_{kl} \langle A_k B_j \rangle \}.\end{aligned}\tag{25}$$

In the simplest approximation we decouple the third-order functions in (24), (25) to lower-order functions using the identity  $A^2 = A$ . Let us demonstrate the procedure for the following term:

$$\sum_j \Theta_{jk} \langle C_k A_l A_j \rangle \equiv \sum_j \Theta_{jk} (1 - \delta_{jl}) \langle C_k A_l A_j \rangle + \Theta_{kl} \langle C_k A_l \rangle.$$

Now we write

$$\langle C_k A_l A_j \rangle \equiv \frac{\langle C_k^2 A_l A_j \rangle}{\langle C_k^2 \rangle} \langle C_k^2 \rangle \approx \left( \frac{\langle C_k A_l \rangle \langle C_k A_j \rangle}{\langle C_k \rangle^2} \right) \langle C_k^2 \rangle = \frac{\langle C_k A_l \rangle \langle C_k A_j \rangle}{\langle C_k \rangle}.\tag{26}$$

The advantage of this decoupling procedure lies in a partial compensation of the failure occurring due to the approximation in the numerator and the denominator, respectively.

Using the approximation scheme proposed in (26) we get from (21), (24) and (25) the stationary solution for the nearest-neighbour functions (22)

$$\begin{aligned}\psi(1) &= \frac{(z-2)\bar{A}^2 + \bar{A}}{z-1} \\ \Phi(1) &= \frac{(z-2)\bar{A}\bar{B}}{z-1} \\ \chi(1) &= \frac{(z-2)\bar{B}^2 + \bar{B}}{z-1}\end{aligned}\tag{27}$$

with the coordination number  $z$  (e.g.  $z = 2d$  in a cubic lattice). Simultaneously, the stationary averaged particle concentrations are obtained:

$$\bar{A} = \frac{1}{1+k+q} \quad \bar{B} = q\bar{A} \quad \bar{C} = k\bar{A}\tag{28}$$

where the abbreviations were already introduced after equation (23). Furthermore, the complete stationary solution can be written in the form

$$\begin{aligned}\psi(R) &= \bar{A}^2 + \bar{A}(1-\bar{A})\delta_{kl} + \frac{\bar{A}(1-\bar{A})}{z-1}\Theta_{kl} \\ \Phi(R) &= \bar{A}\bar{B}(1-\delta_{kl}) - \frac{\bar{A}\bar{B}}{z-1}\Theta_{kl} \\ \chi(R) &= \bar{B}^2 + \bar{B}(1-\bar{B})\delta_{kl} + \frac{\bar{B}(1-\bar{B})}{z-1}\Theta_{kl}.\end{aligned}\tag{29}$$

Analysing the evolution equations (24) and (25) within the same approximation we find

$$\partial_t \psi(R > 1, t) = k_3 \frac{2z[\bar{A} - \psi(R) - \Phi(R)][\bar{A} - \psi(1) - \Phi(1)]}{1 - \bar{A} - \bar{B}} - k_1 \frac{2z\psi(R)\Phi(1)}{\bar{A}}.\tag{30}$$

Furthermore, the equation for  $\psi(1, t)$  reads

$$\begin{aligned}\partial_t \psi(1, t) &= 2k_3 \frac{(z-2)\bar{A} - \bar{B} + 1 - (z-1)(\psi(1) + \Phi(1))[\bar{A} - \psi(1) - \Phi(1)]}{1 - \bar{A} - \bar{B}} \\ &\quad - 2k_1 \frac{(z-1)\psi(1)\Phi(1)}{\bar{A}}.\end{aligned}\tag{31}$$

The corresponding equations for  $\chi(R)$  in the case of  $R > 1$  and  $R = 1$ , respectively, are found using the symmetry argument already applied above, equation (24). For completeness we present the equations for  $\Phi(R, t)$  and  $\Phi(1, t)$  explicitly:

$$\begin{aligned}\partial_t \Phi(R > 1, t) &= zk_3 \frac{[\bar{A} - \chi(1) - \psi(1)][\bar{B} - \chi(1) - \Phi(1)]}{\bar{C}} \\ &\quad - zk_2 \frac{[\bar{B} - \chi(1) - \Phi(1)]\Phi(R)}{\bar{B}} + zk_1 \frac{\Phi(1)[\psi(R) + \Phi(R)]}{\bar{A}}\end{aligned}\tag{32}$$

and

$$\begin{aligned}\partial_t \Phi(1, t) &= -k_1[\Phi(1) + \bar{A}] \frac{\Phi(1)}{\bar{A}} - k_2(z-1)[\bar{B} - \chi(1) - \Phi(1)] \frac{\Phi(1)}{\bar{B}} \\ &\quad + k_1(z-1) \frac{\Phi(1)\psi(1)}{\bar{A}} + k_3(z-1)[\bar{B} - \chi(1) - \Phi(1)] \frac{\bar{A} - \chi(1) - \Phi(1)}{1 - \bar{A} - \bar{B}}.\end{aligned}\tag{33}$$

As the result, a closed set of coupled equations like (21), (30) and (32) is obtained for the densities and for the correlation functions. In the next step let us analyse the dynamical stability of these coupled equations.



#### 4. Stability

Firstly we study the mean-field equations (17). The stationary solution is also given by (28) with  $k = \tilde{k}_1/\tilde{k}_2$  and  $q = \tilde{k}_3/\tilde{k}_2$ . A conventional linear stability analysis around the stationary point yields the eigenvalues of the corresponding  $3 \times 3$  matrix to be

$$\left\{ 0, \pm i\rho_0 \sqrt{\frac{\tilde{k}_1 \tilde{k}_2 \tilde{k}_3}{\tilde{k}_1 + \tilde{k}_2 + \tilde{k}_3}} \right\}$$

( $\rho_0$  is the total density) i.e. the stationary point is neither stable nor unstable. As a consequence of the two pure imaginary eigenvalues, an arbitrarily small initial deviation from the stationary solution leads to a periodic evolution in the phase space. The existence of such oscillations is independent of the classical reaction rates  $\tilde{k}_\beta$ . The eigenvalue 0 reflects the conservation of the total density  $\rho_0$ . Due to the conservation of the total density there exist only two relevant observables, for instance  $\rho_A$  and  $\rho_B$ .

The situation is completely different in the more refined approach used above, where excluded volume effects are considered explicitly. In the present approximation there appear five relevant functions:  $\langle A(t) \rangle$ ,  $\langle B(t) \rangle$ ,  $\psi(1, t)$ ,  $\Phi(1, t)$  and  $\chi(1, t)$ . They are determined by coupled nonlinear equations (21), (31) and (33) and the corresponding equation for  $\chi(1, t)$ . The evolution of all other quantities, e.g.  $\psi(R > 1, t)$ , depends on the time behaviour of these five basic observable.

To perform the stability analysis we make the ansatz

$$\begin{aligned} \langle A \rangle &= \bar{A} + a(t) & \langle B \rangle &= \bar{B} + b(t) \\ \psi(1, t) &= (z-1)\psi(1) + \psi_1(t) \\ \Phi(1, t) &= (z-1)\Phi(1) + \Phi_1(t) \\ \chi(1, t) &= (z-1)\chi(1) + \chi_1(t) \end{aligned} \quad (34)$$

where the five functions  $a$ ,  $b$ ,  $\psi_1$ ,  $\Phi_1$  and  $\chi_1$  are considered as small perturbative terms. Linearizing the evolution equations for the densities and the correlation functions there occurs a  $5 \times 5$  matrix whose eigenvalues determine the stability

$$\partial_t T_\alpha = S_{\alpha\beta} T_\beta$$

with  $T_\beta = (a, b, \psi_1, \chi_1, \phi_1)$ . The matrix  $S_{\alpha\beta}$  is given by

$$\begin{pmatrix} qz & 0 & -\frac{qz}{z-1} & 0 & -\frac{z(k+q)}{z-1} \\ 0 & -z & 0 & \frac{z}{z-1} & \frac{z(\bar{A}+\bar{B})}{z-1} \\ 2q[(z-1) & & & & \\ +2\bar{A}(z-1)(z-2) & & & & \\ +\bar{A}^2(z-2)^2] & 2q(z-2)^2\bar{A}^2 & -2q[1+2(z-1)\bar{A}] & 0 & -2q[1+2(z-1)\bar{A}] \\ 2k[1+(z-2)\bar{A}] & & -2k(z-2)\bar{B} & & -2k[1+(z-2)\bar{A}] \\ \times(z-2)\bar{B} & & & & \\ -2k(z-2)^2\bar{B}^2 & -2[1+(z-2)\bar{B}] & & & 2k[1+2(z-2)\bar{B}] \\ \times[z-1-(z-2)\bar{C}] & & 0 & 2(1+(z-2)(\bar{B}-\bar{C})) & +2[1+(z-2)\bar{B}] \\ -k(z-2)\bar{B} & -(z-2)\bar{A} & & & -k(z-2)(2\bar{B}-\bar{A}) \\ \times[1+(z-2)(\bar{A}-\bar{B})] & \times[z-1-(z-2)\bar{C}] & (z-2)(k-q)\bar{B} & (z-2)(1-q)\bar{A} & -(z-2)(\bar{C}-\bar{A}) \\ +q(z-2)\bar{B} & +q(z-2)\bar{A} & & & -q(z-2)(\bar{A}+\bar{B}) \\ \times[z-1+(z-2)\bar{A}] & \times[z-1+(z-2)\bar{B}] & & & \end{pmatrix}$$

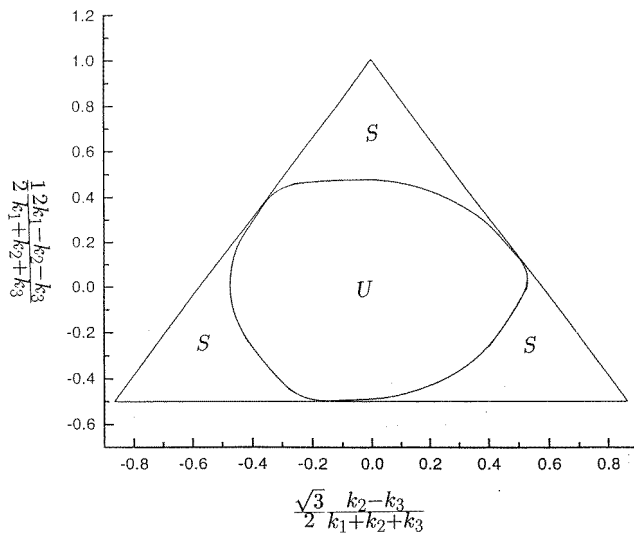
The three-dimensional case with  $z = 6$  for a simple cubic lattice is studied in detail. In particular, the eigenvalues of the  $5 \times 5$  matrix obey the secular equation

$\det |S - \lambda| = \sum_{i=0}^5 w_i \lambda^i = 0$  where the coefficients can be written in the form

$$\begin{aligned}
 w_0 &= -\frac{147456}{25} \alpha^3 \beta \\
 w_1 &= -\frac{3072}{25} \alpha^2 [4\alpha\beta^2 + \gamma + 12] \\
 w_2 &= -\frac{384}{10} \alpha [10\alpha\beta + 1] \\
 w_3 &= -\frac{16}{5} \alpha [10\alpha\beta^2 + \beta + \gamma + 21] \\
 w_4 &= -12\alpha\beta \\
 w_5 &= -1
 \end{aligned}
 \tag{35}$$

where we have introduced the abbreviations  $\alpha = \bar{A}\bar{B}\bar{C}$ ,  $\beta = \bar{A}^{-1} + \bar{B}^{-1} + \bar{C}^{-1}$  and  $\gamma = \bar{B}\bar{A}^{-1} + \bar{A}\bar{C}^{-1} + \bar{C}\bar{B}^{-1}$ .

This gives one real and two pairs of complex conjugated eigenvalues, where the real parts correspond to the Lyapunov exponents of the system. Furthermore, the sign of the real part is responsible for stability (negative real part) or instability (positive real part).



**Figure 1.** Stability regions—*S*: stable stationary solutions, *U*: unstable stationary solutions.

In figure 1 we present the stability regions of the underlying model depending on the reaction rates  $k_\beta$ . Note that the densities of the three species reacting mutually correspond to the three axes of an equilateral triangle. In the vicinity of a triangle corner the system is stable, i.e. the real part of all eigenvalues is negative. Due to the deficiency of one component, the remaining two react and a stable state can be realized.

The situation is completely different in the centre of the triangle, where all three components are present with approximately the same concentrations. In this region one gets at least one eigenvalue with a positive real part. There appears an extended region characterized by a marked unstable behaviour which is strongly different from the case based upon the mean-field equations (17).

Note that the peculiar representation in the figure reflects a  $\frac{2\pi}{3}$  symmetry which is related to the invariance of our basic model against cyclic permutation  $A \rightarrow B \rightarrow C \rightarrow A$ .

## 5. Conclusions

In this paper we have demonstrated that a three-state model can be described within a master equation mapping the corresponding equation into a Fock space representation. In contrast to the standard approach we have used operators which satisfy the algebraic properties of  $SU(2)$  lowering and raising operators, see equation (1). In particular, such a statistics seems appropriate in the case of an irreversible chemical ring reaction where three different species react mutually after a certain scheme introduced in the third section (16). Since we take into account the fact that the chemical reaction is only allowed if both reactants are available at adjacent sites, the reaction rates depend on the occupation numbers of the different species merged together within the reaction. In other words, we assume that the diffusive motion of the components is irrelevant, and the dynamics of the system is dominated by the reaction.

Although the underlying evolution operator is complicated due to the restrictions mentioned we are able to solve the coupled kinetic equations for the densities of the species and the corresponding density–density correlation functions. Using linear stability analysis gives a matrix whose eigenvalues determine the stability region. The reaction is stable whenever two species dominate the reaction. In the case when all three reactants are available in approximately the same amount, there appears an instability region not present within a simple mean-field approach based on Bose operators (see the classical equation (17)).

The advantage of the present method lies in the fact that like in quantum mechanics, an evolution operator combined with the algebraic properties of the applied operators essentially determine the dynamics. The method can be extended to other problems such as diffusion under exclusion in a  $p$ -state model [28], the analysis of phase separation in a model with two different species and vacancies [22] and some other problems like a three-voter model or a model describing the glass transition [23].

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