A Lotka-type model for oscillations in surface reactions

J Mai†, V N Kuzovkov‡§ and W von Niessen§

† Institut für Theoretische Polymerphysik, Universität Freiburg, Rheinstrasse 12, D-79104 Freiburg, Germany
‡ Institute of Theoretical Physics, University of Latvia, Rainis Boulevard 19, Riga, Latvia
§ Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D-38106 Braunschweig, Germany

Abstract. In this paper we introduce a reaction model on a lattice which leads to oscillations. The model consists of two monomolecular and one bimolecular reaction step and is related to the Lotka model. Despite the simple evolution rules, the model shows a complex behaviour (i.e. the appearance of oscillations). This offers us the opportunity to test different types of stochastic approximations and compare them with the results of a Monte Carlo simulation. The simulation is performed on a large lattice ($L = 1024$) in order to take long-range correlations into account. Comparing the results of this simulation with the stochastic approaches shows that only advanced numerical approximations are able to predict the system behaviour correctly. Simple approximations which do not account for long-range correlations (such as mean-field approximations) fail in the prediction of the system behaviour. The correlation analysis (an advanced stochastic description) is in overall good agreement with the results of the simulation and therefore is an alternative to computer simulation. Moreover, it is not restricted to using a finite lattice and does not need a large amount of computing time.

1. Introduction

Systems in which particles are created and annihilated are very interesting in many different areas of research. They play important roles in the description and understanding of energy transfer [1], Frenkel defect recombination and accumulation in solids [2, 3] and chemical reactions which may take place in a volume [4–7] or on a surface [8–10].

In this paper we want to study a stochastic model of a surface reaction system which can serve as a simplified model for a heterogeneously catalyzed reaction [11, 12, 8]. Such surface reaction models are characterized by the following properties.

(1) They are microscopic lattice models in which all interactions are defined by the state of the cell and by the states of its neighbours.

(2) These models may show a very complex behaviour (i.e. kinetic phase transitions or oscillations) despite their simple evolution rules.

(3) A theoretical description turns out to be very complicated. Due to segregation effects an approach which takes only global aspects (such as the global particle densities) into account fails in the prediction of the behaviour of such systems. Even simulations are problematic because the correlation length can be very large (larger than the lattice size used) or can diverge (see, for example [13]).

(4) An even more interesting behaviour may be observed if the lattice is disordered [12]. One observes a behaviour which is the result of chemical steps of the reaction system itself and of the lattice structure (percolation problem).

It is well known that the exact theoretical description of a system which shows kinetic phase transitions is nearly impossible [14], therefore approximations must be used. Standard approaches are the mean-field approximation, the cluster approximation and the correlation analysis.

The correlation analysis describes the reaction system on the lattice by stochastic differential equations. They are equations of motion for k-point probabilities. To this end one assumes that the system is a Markov process. For each cell of the lattice a variable defines the state of the cell (and in case of a disordered lattice, the state of the lattice [12]). The processes are described by matrices which contain the transition probabilities. The time evolution of the k-point probabilities leads to a hierarchy of master equations. This hierarchy is terminated at the 3-point level by using a superposition approximation [12, 13]. The direct use of such an approximation would be in conflict with the sum rules that the system has to fulfil. Therefore a function which corrects this should be introduced. This procedure leads to a set of nonlinear integrodifferential equations for the global densities and the pair correlation functions which are solved numerically. For details see [12, 13].

The cluster approximation [15] follows from the correlation analysis by neglecting the long-range correlations. This leads to a set of nonlinear equations for the global densities. Short-range correlations are taken into account.

The (site) mean-field approximation neglects all spatial correlations. This leads to simple expressions which may be calculated analytically in many cases.

For all these approximations the question of their relevance and applicability and in this case also of their accuracy is very important. In order to answer this question, one uses a test model. In the theory of equilibrium phase transitions the most important system is the Ising model. It would be very important to have such a reference system in the theory of stochastic surface reactions as well, but it turns out that such a system is not easy to find.

One possible model is the catalytic oxidation of CO [8]. This system shows two kinetic phase transitions under variation of the mole fraction of CO in the gas phase, y_{CO}. One phase transition of second order appears at $y_{CO} = y_1 = 0.395 \pm 0.005$. Another phase transition of first order appears at $y_2 > y_1$. The first order phase transition can easily be described by the mean-field approximation. But the phase transition of second order at y_1 is very difficult to describe correctly by a theoretical approach because long-range correlations are very important. Here the mean-field approximation leads to $y_1 = 0$ [10] which means that the phase transition does not exist at all. The cluster approximation gives the much better result of $y_1 = 0.258$ [15]. With the help of the correlation analysis one obtains perfect agreement with the simulation and obtains $y_1 = 0.395$ [13].

The cluster approximation has the advantage that it is much easier to formulate for a given system than the correlation analysis which is very complex. Moreover, the cluster approximation offers the possibility of a purely analytical solution. Therefore, it would be very important to know whether this approximation is useful for the description of surface reaction systems. The above-mentioned result of y_1 for the CO oxidation seems to indicate this. But it should be noticed that the coordination number z of the lattice is the only variable which describes the spatial structure of the system. It is well known from the theory of phase transitions that lattice models with the same z but different spatial dimensions lead to qualitative different results. This means that in principle the cluster approximation could lead to a wrong or incomplete description of the system. For example, it is not clear that this approximation allows a good description of the CO oxidation on a percolation cluster as the lattice. Therefore we want to introduce a test system which depends critically on spatial properties. These properties, which arise in the different approximation schemes (discussed above), will be compared with each other and with a simulation. The main question is:

Which approximation is required to obtain the spatial properties correctly?

The paper is organized as follows. First, in section 2, we introduce a lattice model which is well suited to test the different approximations. In section 3 we introduce the definitions of the formalism used and derive the evolution equations for the global densities. Sections 4 and 5 give the results obtained from the mean-field and cluster approximation, respectively. The main ideas of how to derive the correlation analysis approximation are given in section 6. Section 7 shows the result of the simulation and compares them with the approximations. A discussion and conclusion follow in sections 8 and 9 respectively.

2. The test model

As a test model we use a model of Lotka [16] which was introduced as a mean-field model. In this paper we will use a lattice representation of this model. The reaction scheme for the Lotka model reads as follows

$$E \longrightarrow A \qquad A + B \longrightarrow 2B \qquad B \longrightarrow F. \tag{1}$$
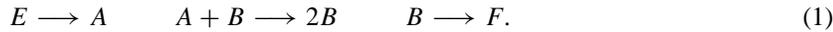
Here E is an infinite reservoir of matter. A linear transformation of E to A occurs, followed by an autocatalytic transformation of A into B and its decay. A biological interpretation might be the reproduction of animals B by division in a medium with a spontaneous production of food A for them. Other interpretations in the field of surface reactions (where autocatalytic reaction steps often occur) are possible. To this end the model must be extended.

For the lattice representation of the model of Lotka we have three possible states σ for each cell l: $\sigma_l \in \{0, A, B\}$, where 0 means the cell is empty. We define the dynamics of the system by two monomolecular steps

$$0 \xrightarrow{p_A} A \qquad B \xrightarrow{k_B} 0 \tag{2}$$

which represents the creation of A with the rate p_A and the annihilation of B with the rate k_B, respectively, and a bimolecular step

$$BA \xrightarrow{k} BB \tag{3}$$

which represents the transformation for nearest neighbours with the rate $k = R/z$. It is possible to introduce a time variable so that $p_A + k_B = 1$, $p_A = \zeta$, $k_B = 1 - \zeta$ and $0 < \zeta < 1$. Introducing $R \to \infty$ leads to a very simple model which depends only on ζ.

The main feature of the model is the possibility of transition chains: if an A particle which is part of an A cluster comes in contact with a B particle, all A particles in this cluster are changed into B particles (contagion).

3. Definitions

We introduce the necessary definitions which are used in the following. We denote by $\rho^{(k)} (k = 1, \ldots, \infty)$ the k-point densities. l, m and n are vectors which point to a cell on the lattice, $\sigma_l \in \{A, B, 0\}$ is the lattice variable which describes the state of the cell l. For $k = 1$, $\rho^{(1)}$ does not depend on the chosen lattice site l and we write $\rho^{(1)}(\sigma_l) = C_{\sigma_l}$ as an abbreviation. For the densities C the sum rule $C_A + C_B + C_0 = 1$ holds. For $k = 2$, $\rho^{(2)}(\sigma_l, \sigma_m)$ depends only on $|l - m|$ because of the translation invariance of the lattice. As a sum rule we obtain

$$\sum_{\sigma_m} \rho^{(2)}(\sigma_l \sigma_m) = \rho^{(1)}(\sigma_l). \tag{4}$$

The asymptotic condition

$$\lim_{|l-m|\to\infty} \rho^{(2)}(\sigma_l, \sigma_m) = \rho^{(1)}(\sigma_l)\rho^{(1)}(\sigma_m) \tag{5}$$

holds. We define the correlation functions $F_{\lambda\mu}(l - m)$, where $\lambda = \sigma_l$ and $\mu = \sigma_m$ by the equation

$$\rho^{(2)}(\sigma_l\sigma_m) = C_\lambda C_\mu F_{\lambda\mu}(l - m). \tag{6}$$

In the models discussed F depends only on the distance $r = l - m$. As an asymptotic case $|r| \to \infty$ the correlations between the particles vanish:

$$\lim_{|r|\to\infty} F_{\lambda\mu}(r) = 1. \tag{7}$$

Let us now write the temporal evolution of the A- and B-density:

$$\frac{\mathrm{d}}{\mathrm{d}t}C_A = p_A(1 - C_A - C_B) - KC_AC_B \tag{8}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}C_B = KC_AC_B - k_BC_B \tag{9}$$

where K is the reaction constant and is defined by $K = RF_{AB}(1)$.

In addition to the original model of Lotka [16] in which only two equations for the global densities exist, the lattice representation possess two new important properties.

(1) There exists a saturation for the particles which means that all densities are restricted by $\sum_\mu C_\mu = 1$. The original Lotka model [16] uses a continuous representation (without a limiting $C_0 = (1 - C_A - C_B)$ factor) and the densities are not restricted. As a result, the number of stationary solutions for our system increases from one (in the Lotka model) to two in our lattice representation.

(2) In the original Lotka model [16] K is truly a constant and therefore the system depends only on two parameters and can be solved analytically. In the lattice representation K depends on the correlation functions which means that K depends on the spatial structure of the system. To take this into account we must describe K in the form of an infinite chain of correlation functions (see for example [12, 13, 20]) in the cluster approximation and in the correlation analysis approximation.

4. The mean-field approximation

In this section we solve equations (8) and (9) in the mean-field approximation which means that K is a constant because all $F_{\lambda\mu}(1)$ are unity. For $p_A = \zeta$ and $k_B = 1 - \zeta$ one obtains two solutions.

(1) The trivial solution of A-poisoning:

$$C_A(\infty) = 1 \qquad C_B(\infty) = 0. \tag{10}$$

This solution is a stable knot for $K < 1 - \zeta$.

(2) The non-trivial solution

$$C_A(\infty) = \frac{1 - \zeta}{K} \qquad C_B(\infty) = \zeta\left(1 - \frac{1 - \zeta}{K}\right) \tag{11}$$

which is physically meaningful ($C_B(\infty) > 0$) only for $K > 1 - \zeta$. In this region the solution is stable (knot or vortex) and corresponds to the solution of the model of Lotka [16] without saturation.

From the synergetic point of view both solutions are not interesting because oscillations cannot occur [17, 18]. This is explained by a theorem of Hanusse [18] which states that the auto-oscillation regime cannot arise in a system with two intermediate products (A and B) if only the mono- and bimolecular reaction steps occur. In the mean-field approximation of this model only mono- and bimolecular reaction steps arise which do not lead to the cubic nonlinearities in the global densities which are necessary for the appearance of oscillations. It should be noted that this theorem is only valid for the mean-field approximation in which all spatial correlations are neglected ($F_{\lambda\mu}(r) = 1$ for all λ, μ). This leads to $K = R = $ constant. In the case of $R = \infty$ this would lead to the non-trivial solution

$$C_A(\infty) = 0 \qquad C_B = \zeta. \tag{12}$$

This solution is physically not meaningful: let $\zeta \ll 1$. This would represent a nearly empty lattice but despite this fact, A particles cannot be created.

A better mean-field approximation of this model would take into account the fact that for $R \to \infty$ the function $F_{AB}(1) \to 0$ (no AB pairs as nearest neighbours) but that the product $K = RF_{AB}(1)$ remains finite. This ansatz is not solvable.

Therefore the question to be answered remains: How large is the reaction constant K and which solutions are stable?

5. The cluster approximation

In this approximation the independent pair probabilities $\rho^{(2)}(\sigma_l\sigma_m)$ for the nearest neighbours are used. For details see [15]. In order to obtain the reaction constant K we write the equation for ρ_{AB} (from which we can obtain K by $\rho_{AB} = C_A C_B F_{AB}(1)$ and $K = RF_{AB}(1)$).

$$\frac{d\rho_{AB}}{dt} = \frac{d\rho^{(2)}(A_l B_m)}{dt} = p_A\rho^{(2)}(0_l B_l) - k_B\rho^{(2)}(A_l B_l) - \frac{R}{z}\rho^{(2)}(A_l B_m)$$
$$- \frac{R}{z}\sum_n \alpha_{l,n}\rho^{(3)}(A_l B_m B_n) + \frac{R}{z}\sum_n \alpha_{m,n}\rho^{(3)}(A_l A_m B_n). \tag{13}$$

The first term describes the creation of an AB pair by creation of an A in a vacant cell which has a neighbour cell occupied by a $B(0 \to A)$. The second term shows the annihilation of an AB pair by annihilation of a $B(B \to 0)$. The third term describes the annihilation of an AB pair by a direct transformation of an A to a $B(A \to B)$. The fourth and fifth terms show the annihilation of an AB pair by indirect transformations by a catalytic reaction over neighbours.

Within the cluster approximation [15] the three point densities $\rho^{(3)}$ are expressed by one and two point densities. Furthermore, the original sum rules should still be valid. We use the following ansatz:

$$\rho^{(3)}(\sigma_l\sigma_m\sigma_n) \Rightarrow \begin{cases} \rho_{\mu\lambda}\rho_{\lambda\nu}/C_\lambda = C_\lambda C_\mu C_\nu F_{\lambda\mu}(1)F_{\lambda\nu}(1) & \text{for } n \neq m \\ 0 & \text{for } n = m. \end{cases} \tag{14}$$

In this approximation the point l is the central point and C_λ represents the state of this point. The other points are the neighbours of point l. This approximation fulfils all required sum rules, i.e. $\sum_{\sigma_n} \rho^{(3)}(\sigma_l\sigma_m\sigma_n) = \rho^{(2)}(\sigma_l\sigma_m)$. One notes that for $R \to \infty$ the product $\hat\rho_{AB} = R\rho_{AB}$ remains finite. We can rewrite the last two equations in the form

$$\frac{1}{R}\frac{d\hat\rho_{AB}}{dt} = p_A\rho_{0B} - \hat\rho_{AB}\left(\frac{k_B}{R} + \frac{1}{z} + \frac{z-1}{zR}\frac{\hat\rho_{AB}}{C_A} - \frac{z-1}{z}\frac{\rho_{AA}}{C_A}\right). \tag{15}$$

The direct use of approximation equation (14) does not take the virtual configurations into account (an A particle between B particles). For the term $\hat{\rho}_{ABB} = \frac{R}{z}\sum_n \alpha_{l,n}\rho^{(3)}(A_l B_m B_n)$ we would obtain in the direct approximation $\hat{\rho}_{ABB} = \frac{z-1}{zR}\hat{\rho}_{AB}\frac{\hat{\rho}_{AB}}{C_A}$. In the limit $R \to \infty$ this term would be zero. We introduced a method to handle this problem [13]. With this ansatz we obtain for the three particle density $\hat{\rho}_{ABB}$:

$$\hat{\rho}_{ABB} = \frac{1}{z}p_A C_0(z\beta - 1 + (1-\beta)^z) \qquad \beta = \rho_{0B}/C_0. \tag{16}$$

For $R \to \infty$ we obtain the algebraic equation

$$\hat{\rho}_{AB} = \frac{p_A C_0[1 - (1-\beta)^z]}{1 - (z-1)\rho_{AA}/C_A}. \tag{17}$$

Without taking the three point density (equation (16)) into account we would obtain in the numerator of the last equation only the first term of a series of β expressions: $p_A C_0 z\beta = zp_A\rho_{0B}$. This result would be valid only for small C_B. From this we can derive the reaction constant which can be written in the form $K = \hat{\rho}_{AB}/C_A C_B$. The reaction constant in this approximation is not a constant but depends on the global densities and the pair probabilities.

For the global densities we obtain

$$\frac{dC_A}{dt} = p_A C_0 - \hat{\rho}_{AB} \qquad \text{and} \qquad \frac{dC_B}{dt} = \hat{\rho}_{AB} - k_B C_B. \tag{18}$$

With the sum rules $\rho_{AA} + \rho_{AB} + \rho_{A0} = C_A$ and $\rho_{BB} + \rho_{BA} + \rho_{B0} = C_B$ (with $\rho_{AB} = 0$) we only need the evolution equations for ρ_{AA} and ρ_{BB}:

$$\frac{d\rho_{AA}}{dt} = \frac{d\rho^{(2)}(A_l A_m)}{dt} = p_A(\rho^{(2)}(0_l A_m) + \rho^{(2)}(A_l 0_m)) - \frac{R}{z}\sum_n \alpha_{l,n}\rho^{(3)}(A_l A_m B_n)$$

$$-\frac{R}{z}\sum_n \alpha_{m,n}\rho^{(3)}(A_l A_m B_n) \tag{19}$$

$$\frac{d\rho_{BB}}{dt} = \frac{d\rho^{(2)}(B_l B_m)}{dt} = -2k_B\rho^{(2)}(B_l B_m) + \frac{R}{z}(\rho^{(2)}(A_l B_m) + \rho^{(2)}(B_l A_m))$$

$$+\frac{R}{z}\sum_n \alpha_{l,n}\rho^{(3)}(A_l B_m B_n) + \frac{R}{z}\sum_n \alpha_{m,n}\rho^{(3)}(B_l A_m B_n). \tag{20}$$

With the ansatz (14) and in the limit $R \to \infty$ we obtain:

$$\frac{d\rho_{AA}}{dt} = 2\left(p_A\rho_{0A} - \frac{z-1}{z}\hat{\rho}_{AB}\frac{\rho_{AA}}{C_A}\right) \tag{21}$$

$$\frac{d\rho_{BB}}{dt} = 2\left(\frac{1}{z}\hat{\rho}_{AB} + \hat{\rho}_{ABB} - k_B\rho_{BB}\right). \tag{22}$$

An analytical solution of the system (16)–(18), (21) and (22) is also obtainable. We obtain one stable stationary solution which can be expressed by a parameter. Let β be a solution of the nonlinear equation

$$\beta = \zeta(1 - (1-\beta)^z/z) \tag{23}$$

with $\beta/\zeta \leqslant 1$. It follows for the stationary densities

$$C_A(\infty) = a/x \qquad C_B(\infty) = b/x \qquad x = a + b + 1 \tag{24}$$

with

$$a = \frac{1 - \beta/\zeta}{[1 - \frac{z}{z-1}(1-\beta/\zeta)]} \qquad b = \frac{\zeta}{1-\zeta}. \tag{25}$$

Let us now compare this result with the result of the mean-field approximation. We notice that for $\zeta \rightarrow 1$ both results are nearly identical which means that in this region the mean-field approximation is sufficient. But for $\zeta \rightarrow 0$ we observe large differences. $C_B(\infty)$ in the cluster approximation is always smaller than the value obtained by the mean-field approximation. $C_A(\infty)$ is larger than zero (result of the mean-field ansatz).

One sees from the last three equations that the solution depends on the number of nearest neighbours z which means that we have at least partly taken the properties of the lattice into account. Also, this solution does not lead to oscillations.

6. The correlation analysis

The correlation analysis is presented in [20] in detail. In principle, very similar arguments as in the cluster approximation are used. The three point densities are expressed by two and one point densities. But in the correlation analysis these densities depend on the correlation functions $F_{\lambda\mu}(r)$ for $r \geqslant 1$. Here we use the Kirkwood approximation [21]:

$$\rho^{(3)}(\sigma_l\sigma_m\sigma_n) \Rightarrow C_\lambda C_\mu C_\nu F_{\lambda\mu}(l-m) F_{\mu\nu}(m-n) F_{\nu\lambda}(n-l). \tag{26}$$

The resulting equations are solved numerically on a lattice. Because the details of this approximation are very lengthy we do not want to repeat the steps here. We only present the results in the following.

7. Comparison of the results of the approximations with the simulation

In the following we will compare the different approximations with the results of the corresponding simulation.

First we want to study the stationary states of the model. This is presented in figure 1 in which the global densities are shown as a function of ζ. The small dots represent the results of the mean-field approximation, the broken curves represent the cluster approximation and the large dots represent the results of the simulation. Let us first study the behaviour of the
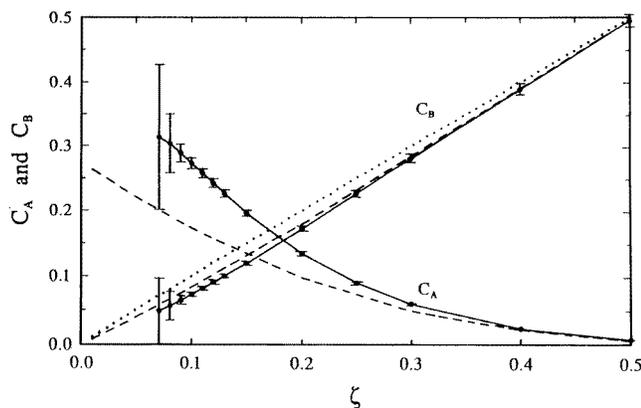
Figure 1. The stationary states of the global densities $C_A(\infty)$ and $C_B(\infty)$ in the Lotka model. The small dots represent the mean-field approximation (equation (12)) with $K \rightarrow \infty$, $C_A = 0$ and $C_B = \zeta$. The broken curves represent the results of the cluster approximation (equations (23)–(25)). The large dots represent the result of the simulation taking place on a lattice of size $L = 1024$. The mean deviations δC are also shown.

simulation: by increasing ζ, C_B increases nearly linearly and C_A decreases. This behaviour is understandable from the evolution rules. By increasing ζ, k_B decreases which leads to more B particles on the lattice. In this case A clusters can easily be transformed into B clusters, decreasing C_A and increasing C_B.

Also the mean squared deviations of the concentrations $\delta C^2 = \langle C^2 \rangle - \langle C \rangle^2$ are shown for the simulation in this figure. For $\zeta > 0.1$ the differences $\delta C / C$ are very small which means that the fluctuations produced by the system are small. For $\zeta < 0.1$ the difference increases strongly because of the appearance of oscillations (see below).

Let us now compare this result of the simulation with the stochastic approximations. One sees that the results of the mean-field approximation (dots) are not in agreement with the simulation: C_A is zero in the mean-field ansatz but the value for C_A in the simulation is much larger. The differences in C_B are smaller but still noticeable. The cluster approximation (broken curves) is in much better agreement with the simulation. For $\zeta > 0.3$ the differences are small but become larger for smaller values of ζ. Both approximations do not show oscillations (as discussed earlier) which is in contrast to the simulation. The result of the correlation analysis is for $\zeta \geqslant \zeta_0 = 0.120$ nearly identical to the one of the cluster analysis (differences are in the third digit) therefore it is not shown in the figure. For $\zeta < \zeta_0$ the correlation analysis leads to a qualitative change of the system behaviour. We obtain an instability in the correlation functions which corresponds to a spherical wave. As a result we obtain oscillations. The long-range correlations which are taken into account in the correlation analysis create new degrees of freedom in the system and lead to the appearance of oscillations. This aspect cannot be described by the simpler approximations (mean-field and cluster approximation).

In order to study the oscillations (obtained from the correlation analysis) we present the values of C_B as a function of time in figure 2. The points were collected for $\Delta t = 0.25$ for different values of ζ. One sees that the oscillations correspond to a limit cycle and we obtain a system driven by a pure periodic motion. For this type of motion we expect a series of lines (at $\omega = \omega_0, 2\omega_0, \ldots$) in the frequency spectrum. We in fact observe this behaviour which is shown in figure 3. The peaks have a certain width which may be explained by the occurrence of rounding errors in the numerical iteration. This additional noise cannot be avoided. This leads to the Lorentz-like curves shown in the figure.

The temporal behaviour of the simulation is of particular relevance and is thus studied in detail. In figure 4 the global density C_B is shown as a function of time for different values of ζ. For $\zeta = 0.07$ we observe the appearance of oscillations. They are not completely periodical due to the noise in the system. For smaller values of ζ we were not able to study the system behaviour properly due to the very large oscillations which appear. These oscillations can lead to the annihilation of all B particles and this therefore represents an instability of the system (especially for small lattice sizes). In figure 5 we present the frequency spectrum of the system. For $\zeta = 0.13, 0.11$ we obtain some kind of white noise in which all frequencies are present. Additionally, we observe a Lorentz-like curve. How can one explain this behaviour? For a lattice with L^2 cells we have L^2 stochastic variables (occupation numbers). From these we can define some macroscopic variables (i.e. the global densities C_A and C_B). All $L^2 - 2$ remaining variables are hidden in a macroscopic theory. Equations (8) and (9) describe the macroscopic motion of the system. The reaction constant K is a function of these hidden variables. We can express this in the form $K = K_0 + \delta K$ where K_0 is a constant and $\delta K = \delta K(t)$ is an arbitrary function of time with a mean value of zero. The behaviour of the system is strongly influenced by the value of K_0. As we have discussed in equation (11) the stationary solution of the system is a stable knot or a
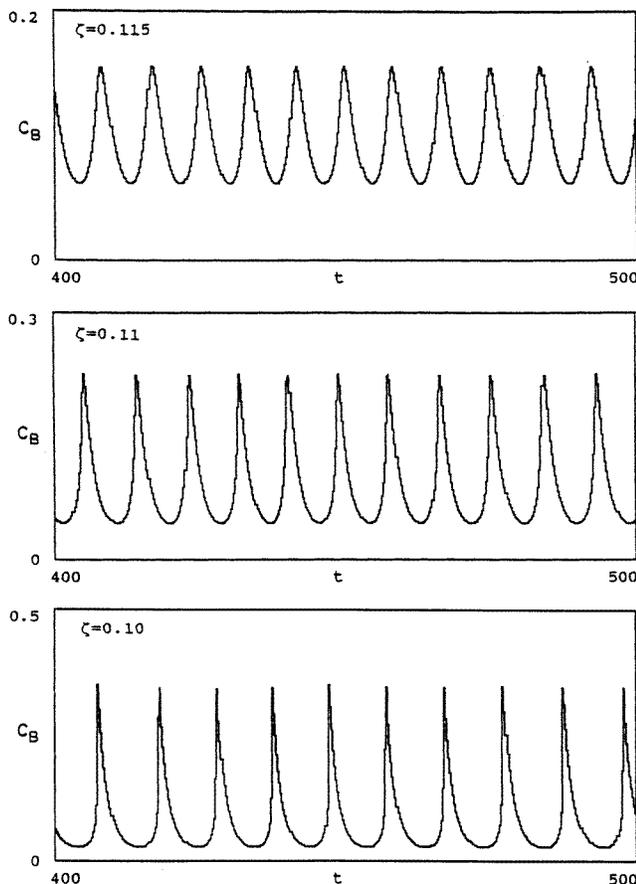
Figure 2. C_B is shown as a function of time for different values of ζ for the correlation analysis approximation. The points are sampled for every $\Delta t = 0.25$.

stable vortex. We obtain a vortex for $K_- < K < K_+$ with

$$K_{\mp} = \frac{2}{\zeta}\left(1 \mp \sqrt{1 - \zeta}\right) - \zeta. \tag{27}$$

We do not know exactly which value of K represents the simulation. From the cluster approximation we can numerically calculate K. This calculation indicates that K in fact lies between the border values of $K_{\mp}$. This means that the system (equations (8) and (9)) can be represented by a damped oscillator. This oscillator is influenced by the external noise δK which leads to the fluctuations in the global densities. Nevertheless, the system does not forget the properties of the basic system in which $K = $ constant. This seems to us to be the explanation for the Lorentz curve in the frequency spectrum.

For $\zeta = 0.09, 0.07$ the main frequency ω_0 can easily be seen. The noise is nearly the same as for the larger values of ζ. Here we observe a new force (with the frequency ω_0) which defines the motion of the global densities. The reaction constant is a periodical function of time.

Let us study now another aspect of our lattice version of the Lotka model. In the case where all B particles are annihilated by chance, the lattice will be completely covered by
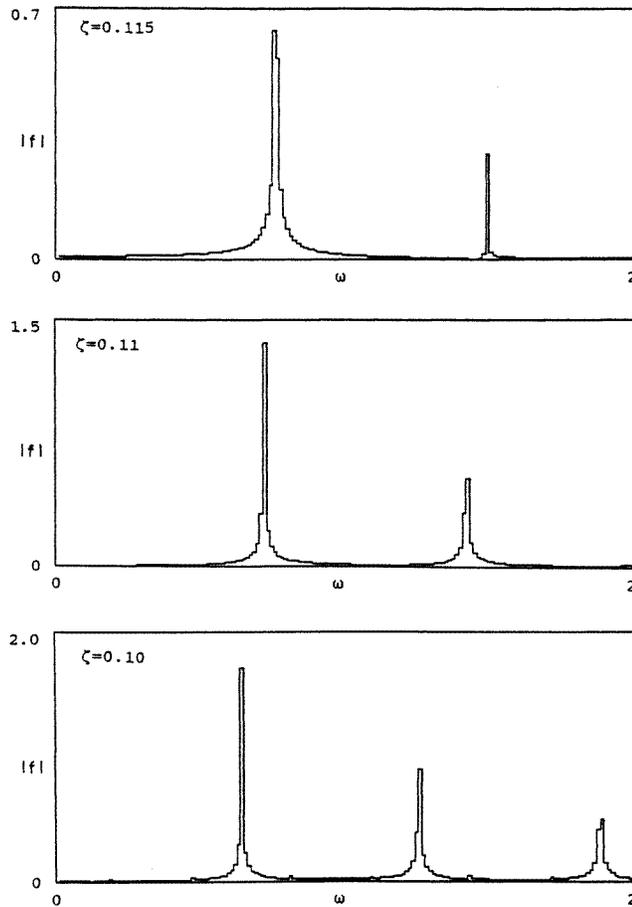
Figure 3. The frequency spectrum for figure 2. The number of sampled points is 2^{11} taken for $t < 512$ with $\Delta t = 0.25$.

A particles and the reaction comes to a stop. This is a specific instability of this system which has a larger probability to appear if the number of *B* particles is small. It means that the instability of the system is directly connected to the lattice size used in the simulation. Therefore it is very important to use a lattice which is large enough to avoid this instability. Let $C_B(\text{min})$ be the minimum density of *B* particles for a simulation on a lattice with L^2 cells. The condition $C_B(\text{min})L^2 = N_B(\text{min}) \gg 1$ should be fulfilled for the simulations. The minimum number of *B* particles can be determined from the simulation. In figure 6 the global density C_B is shown as a function of time for $\zeta = 0.08$ and for lattices of different length L. The frequency spectrum for the system is shown in figure 7. For a very small lattice with $L = 128$ we obtain large fluctuations in the densities because of the large noise in the system. The value of $C_B(\text{min})$ is of the order of 10^{-3} and $N_B(\text{min}) \approx 10$. With these small numbers the system can run easily into an instability and we obtain large fluctuations. With increasing lattice size the fluctuations become smaller. For $L = 1024$, $N_B(\text{min})$ is of the order of 10^4. These fluctuations are much smaller compared with the case of smaller lattices. At this lattice size we easily see the appearance of periodic oscillations. The noise cannot be completely avoided (even for $L \rightarrow \infty$) because it is an inherent quality of a
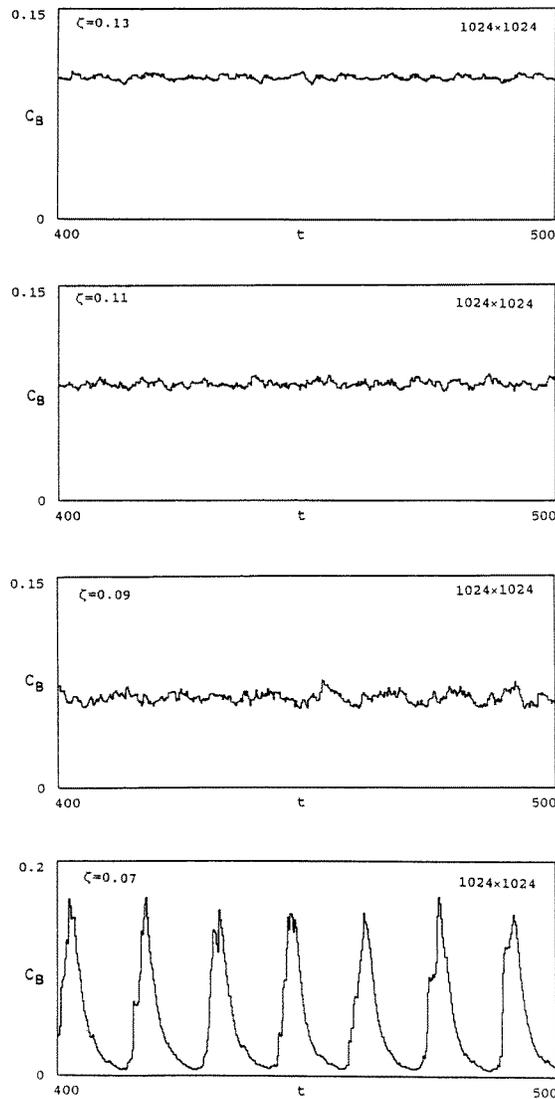
Figure 4. The global density C_B is shown as a function of time as the result of the simulation performed on a lattice with $L = 1024$. The other parameters are $\Delta t = 0.25$, $\zeta = 0.13, 0.11, 0.09, 0.07$.

system with many degrees of freedom. In the framework of the correlation analysis we study a thermodynamic limit with $L \to \infty$. Here C_B can reach very small values, but $N_B = C_B L^2 \to \infty$. This means that the instability (discussed above) cannot occur in the stochastic approximation.

The phase diagram for the simulation is shown in figure 8 for $\zeta = 0.07$ and in figure 9 for $\zeta = 0.08$. One clearly sees the limit cycle which the system approaches for $\zeta = 0.07$. For larger values of ζ the motion of the system is more chaotic which is a result of the increased noise.
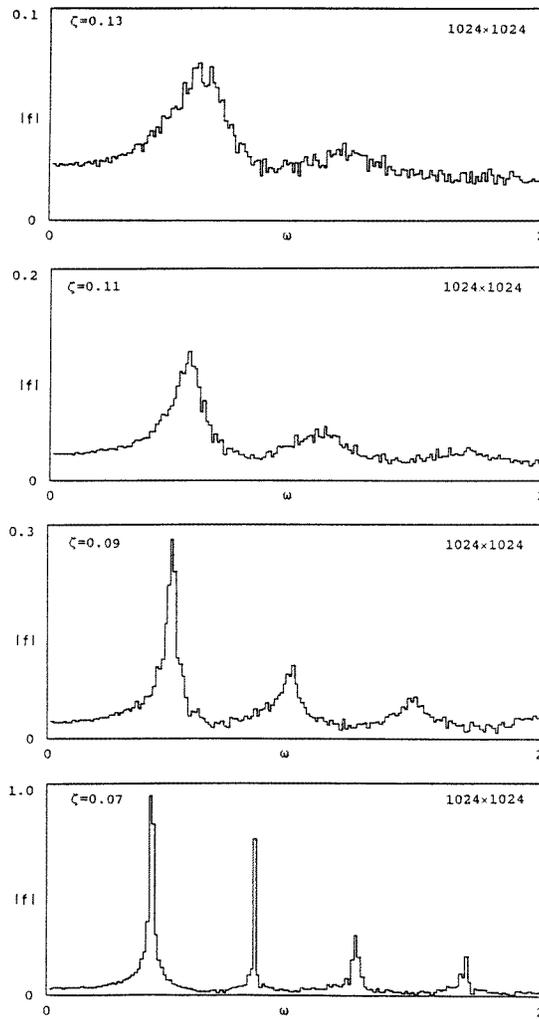
**Figure 5.** The frequency spectrum for figure 4. The number of sampled points is 2^{11} taken for $t < 512$ with $\Delta t = 0.25$.

8. Discussion

In this paper we have introduced a test model which is based on a model of Lotka [16]. This model is easy enough to handle with stochastic approximations of different complexities we introduced earlier [19, 12, 13]. On the other hand, it shows a complex behaviour (oscillations) which depends strongly on the spatial particle configuration. Therefore it is an ideal test model for our purpose.

For small values of a system parameter ζ, which is related to the creation rate of particles, we observe the appearance of oscillations in the simulation (on a large lattice). In this region the system depends critically on the spatial particle distribution. By using smaller lattices we do not see oscillations, only noise. Only the use of a lattice with $L = 1024$ reduces the noise to a level where the oscillations can be seen clearly. Therefore, it turns
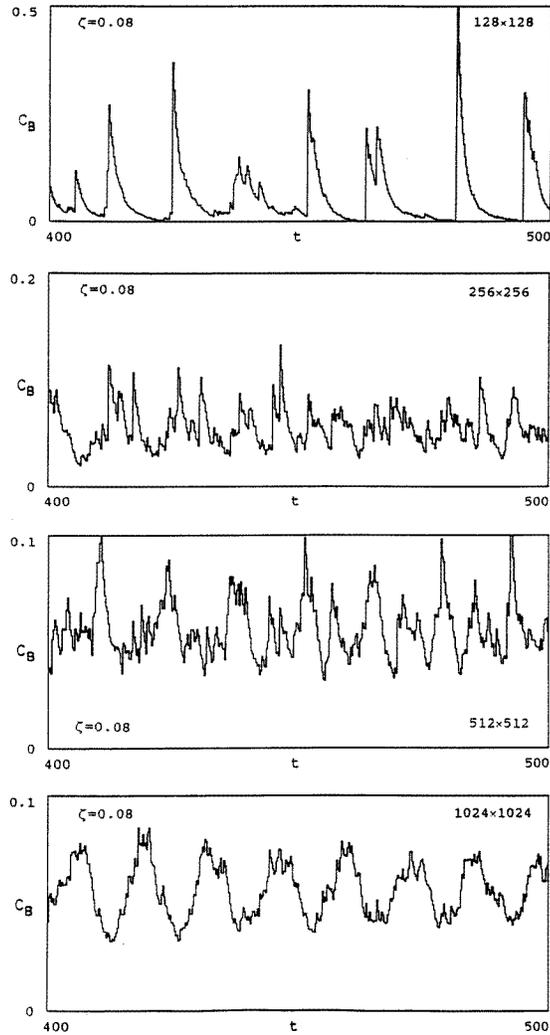
Figure 6. The global density C_B as a result of the simulation for $\zeta = 0.08$ on different lattices L^2 with $L = 128, 256, 512, 1024$.

out that a simulation of this system is not easy to achieve and requires large amount of computing time due to the minimum size of the lattice.

Let us now turn to the approximations. First they have the advantage that they are not restricted to a finite lattice. This rules out finite size effects. The calculations are straightforward and do not require a large amount of computing time.

The simplest approximation, the mean-field approximation, turns out to be unable to describe the system behaviour appropriately. C_A is always zero and the values of C_B are too large for all values of ζ.

The next step to a better description is the cluster approximation (only nearest-neighbour correlations). The global densities (see figure 1) obtained from this approximation are in much better agreement with the results of the simulation especially for large values of ζ.
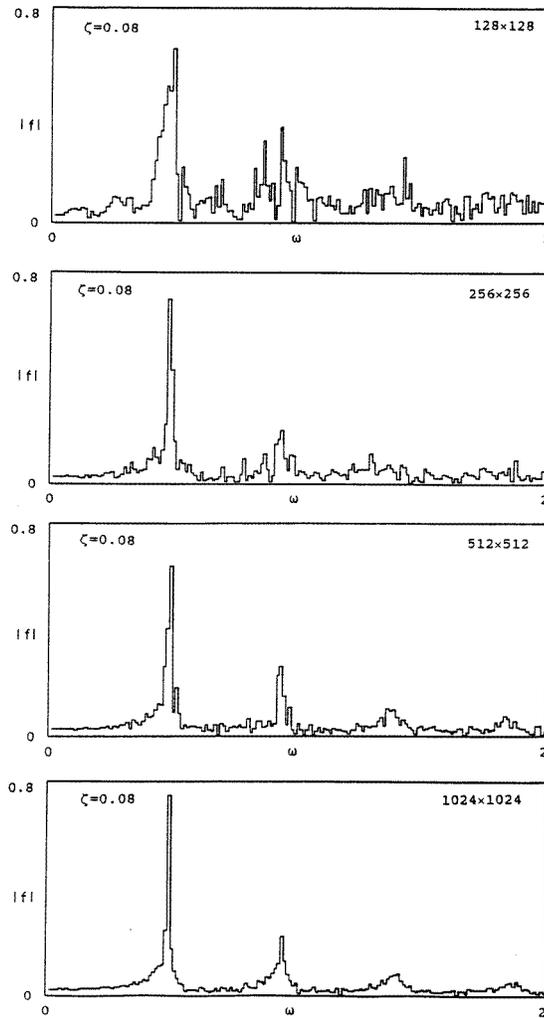
Figure 7. The frequency spectrum for figure 6. The number of sampled points is 2^{11} taken for $t < 512$ with $\Delta t = 0.25$.

For small values of ζ the system behaviour is dominated by oscillations. In this region the approximation must fail because it cannot account for the appearance of oscillations.

The correlation analysis leads to a qualitative change of the system behaviour. For $\zeta < \zeta_0$ this approximation is able to describe the appearance of oscillations correctly. For larger values of ζ this approximation is nearly identical to the cluster approximation. This means that a critical phenomenon-like oscillations can only be described by an advanced approximation such as the correlation analysis.

9. Conclusions

As a conclusion of this study we can state the following facts. The lattice representation of the Lotka model is well suited to act as a test model for stochastic approximations
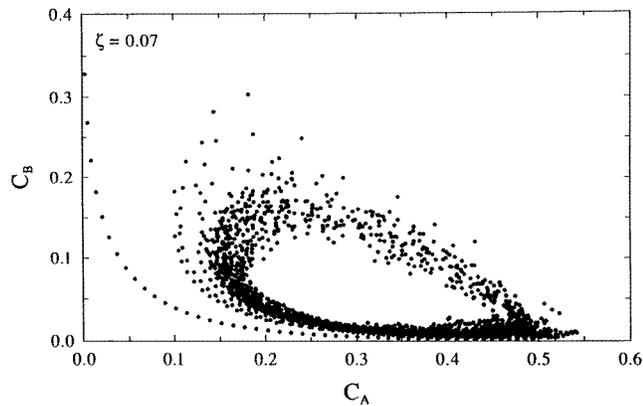
Figure 8. The phase diagram for the simulation on a lattice with $L = 1024$ for $\zeta = 0.07$ and $\Delta t = 0.25$.
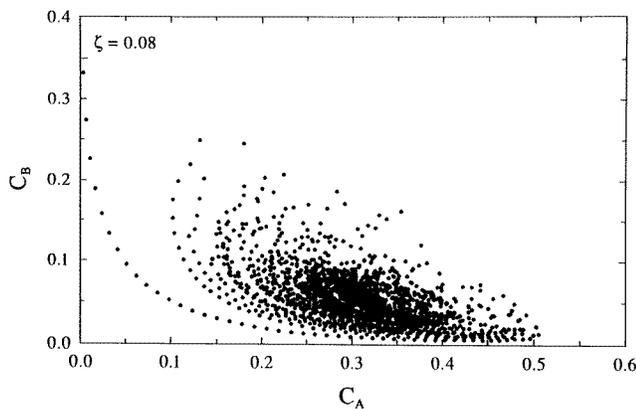
Figure 9. The phase diagram for the simulation on a lattice with $L = 1024$ for $\zeta = 0.08$ and $\Delta t = 0.25$.

because it depends strongly on the particle distribution and is complex enough to show a complicated temporal behaviour such as oscillations. On the other hand, it is easy enough to be handled by a theoretical stochastic approach. In order to test the approximation we used a simulation to obtain the behaviour of this model. The simulations turned out to be very complicated due to the requirement of using large lattices in order to avoid instabilities of the system. Let us turn now to the approximations. The simplest approximation (the mean-field approximation) fails in the prediction of the system behaviour. The cluster analysis is able to reproduce global properties (such as the global densities) to a certain degree. Nevertheless, it cannot account for the appearance of oscillations. This can only be done by the correlation analysis. This means that only this approximation is able to qualitatively predict the system behaviour completely. This shows that simple approximations (such as the mean-field approximation) are not useful to describe the complex reaction system. Using such methods leads to a qualitative false prediction of the system behaviour.

In a future paper we want to study this approximation in a more complex system which uses a disordered lattice.

Acknowledgments

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