Catalytic Surface Reactions: Monte Carlo Simulations of Systems with Creation, Annihilation and Diffusion of Interacting Reactants

Dissertation
Presented to the Department of Physics of Osnabrück University

by Guntars Zvejnieks
from Rīga, Latvia

Thesis Advisor: Prof. Dr. Gunnar Borstel

Osnabrück, March, 2001
Contents

Introduction 3

1 The resonance behavior in the Lotka-type model 5
  1.1 Introduction ........................................ 5
  1.2 Mathematical models ................................ 7
    1.2.1 The Lotka model .............................. 7
    1.2.2 The Lotka-Volterra model ................... 8
    1.2.3 The standard Lotka-type model .......... 10
    1.2.4 The generalized Lotka-type model ....... 13
  1.3 Simulation algorithm .............................. 13
  1.4 Mathematical methods ................................ 14
  1.5 Simulation results ................................ 15
  1.6 Conclusions ...................................... 28

2 The Lotka-type model with reactant surface diffusion and interaction 31
  2.1 Introduction ........................................ 31
  2.2 The generalized Lotka-type model .............. 33
  2.3 Simulation algorithm .............................. 34
  2.4 Simulation results ................................. 36
  2.5 Conclusions ...................................... 46

3 The $A + B \rightarrow 0$ model with surface reconstruction 49
  3.1 Introduction ........................................ 49
  3.2 Mathematical model ................................ 51
  3.3 Mean-Field formalism ............................. 54
  3.4 Monte Carlo results for the generalized $A + B \rightarrow 0$ model .... 64
3.4.1 The standard model with surface reconstruction 65
3.4.2 Surface poisoning 72
3.4.3 Asymmetric mobility 73
3.4.4 Reactant B adsorption on α phase 78
3.5 Discussion of the $A + B \rightarrow 0$ generalized model 79
3.6 Conclusions 79

General conclusions 81

Appendices 83

A Definition of transition rates 83

B The basis of the pair algorithm 87
   B.1 Master equation 88
   B.2 Monte Carlo 90
   B.3 The transition scheme from the master equation to the Monte Carlo 91

C Linear stability analysis 95

D The ZGB model 99

Bibliography 101
Introduction

During the last 30 years considerable attention was paid to open systems far from thermal equilibrium. Under certain conditions these dissipative systems show a qualitatively new behavior on macroscopic length scales, which are known as *spatiotemporal* structures. These new structures arise as a feature of collective behavior of a many-body systems.

One particular example of dissipative systems considered in the present Thesis is the systems with reactant birth and death. Such systems arise, e.g., in description of the population growth or the kinetics of chemical reactions.

To describe the systems with a large number of particles, one has to impose some restrictions. So, it is assumed that individual properties of particles are not important, only their interaction and interaction result (reaction) are taken into account. A number of rules, which describe the behavior of particles on the microscopic level, are known as a *mathematical model*.

There exist two methods to analyse properties of a mathematical model. The first is analysis based on the master equation. In general, this method fails to describe the properties of spatiotemporal structures. There are no analytical approximations taking into account the effect of long-range particle correlation, which is important for description of the changes on a macroscopic range. The second approach are Monte Carlo (MC) computer simulations, which actually is alternative to experiments. The MC method takes into account long-range reactant correlations. They arise as a result of microscopical model. MC has disadvantages typical for all numerical methods, e.g., a large simulation time.

In the present Thesis the Lotka-type and the $A + B \rightarrow 0$ models are considered in detail. These reactions are commonly found as one of a component in many chemical reactions. The emphasis is made on understanding the basic properties of these models. Further, several physically important modifications of the Lotka-type and the $A + B \rightarrow 0$ models are made. Firstly, in Chapter 1. the Lotka-type
model is extended to investigate the resonance properties. Secondly, the effect of reactant diffusion and interaction is incorporated into Lotka-type model in Chapter 2. Thirdly, the standard $A + B \rightarrow 0$ reaction is extended to the case of surface reconstruction in Chapter 3. General conclusion is presented at the end of the Thesis, which is ended by four Appendices.
Chapter 1

The resonance behavior in the Lotka-type model

1.1 Introduction

The heterogeneous catalysis belongs to a class of very complicated self-organizing phenomena, which is characterized by a formation of spatiotemporal structures in the reacting system [1, 2]. The recent attraction to the surface catalytic reactions was caused not only by the practical interest but also by a series of new experiments and methods [3], which resulted in a better understanding of the underlying microscopic processes. The most studied reaction is CO$_2$ catalysis on Pt(100) and Pt(110) monocrystal surfaces. It is found experimentally that the effective oxidation of CO on a Pt surface is accompanied by the formation of such spatiotemporal structures as periodical oscillations of the macroscopic CO$_2$ production rate and formation of waves of reacting particles (see for details [1] and references therein).

An important method for treating self-oscillating systems, in particular autocatalytic reactions, is a periodical modulation of an external parameter and analysis of the system’s response. This has been done experimentally in [4] for the autocatalytic CO+$\frac{1}{2}$O$_2$ reaction on Pt(110) surface in the low-pressure limit. In this study the external parameter, varied periodically in time, was the partial pressure of O$_2$ gas above the Pt(110) sample. It was experimentally detected that depending on the modulation frequencies, the self-oscillations in the system exhibit subharmonic and superharmonic resonances, phase locking, and quasiperiodic behavior. In a more general case, the periodic modulation of external parameter can lead a system to
To understand the mechanisms of spatiotemporal structure formation, the standard procedure is to define a mathematical model based on the experimentally observed microscopic processes. Such a mathematical model can then be analyzed either analytically, in terms of the corresponding master equation, or via Monte Carlo (MC) computer simulations. The first successful mathematical model of CO₂ catalysis on Pt(100) and Pt(110) surfaces, which took into account adsorption, desorption and reaction was presented by Ziff-Gulari-Barshad (hereafter ZGB model) [6]. This model leads to reactant concentration oscillations only via introduction of blocked sites (see [7] and Appendix D). Later, in terms of the ZGB model, the spatiotemporal pattern formation and oscillatory behavior were analyzed, incorporating particle diffusion and two different (reconstructed and non-reconstructed) surface phases [8, 9, 10, 11].

In this Chapter, we consider a simple Lotka-type model, which was first proposed by Mai et al. [12] for heterogeneous catalytic reactions on a crystalline surface. Using MC computer modeling, it was shown there that this model demonstrates macroscopic concentration oscillations [12, 13] within a certain parameter variation range, which are independent of the system’s size. The solution of the corresponding master equations in the mean-field (MF) approximation leads only to the stable solutions because this approximation does not take into account the long-range correlations [12]. The MC simulations of this model were extended for one- and three dimensions by Hovi et al. [13] (see also review articles [7, 14]). For the more complicated Lotka-Volterra model the MF approximation predicts the oscillatory behavior which indeed has been observed in MC computer simulations [15].

The standard Lotka-type model treats two species on a square lattice, referred hereafter as A and B. Reactants A (B) can be created (annihilated) with the probability ζ and (1−ζ), respectively. The autocatalytic reaction step A + B → 2B takes place instantly if reactants A and B are nearest neighbors. With an appropriate normalization, this model has only a single control parameter and reveals the spatiotemporal structures.

We employ the Lotka-type model and introduce therein a small periodically oscillating contribution to the parameter ζ, in order to determine which phenomena of the forced systems could be reproduced within this simple autocatalytic model.

Chapter 1 is organized in the following way: The mathematical models with detailed microscopical rules are described in Section 1.2. The simulation algorithm is given in Section 1.3. The analysis of data is performed using Fourier Transform
and All Poles methods which are introduced in Section 1.4. In Section 1.5 the simulation results are discussed.

1.2 Mathematical models

In the present Section the modifications of the Lotka model are discussed. Originally the Lotka model [16] has only stationary solutions. The first attempt to extend the Lotka model in order to find a temporal behavior was made by Lotka and Volterra. The extended model was called the Lotka-Volterra model [17, 18] and it shows concentration oscillatory behavior. However, this behavior has no preferred frequency of oscillations, therefore these oscillations are called a noise. The frequency of oscillations depends sensitively on initial conditions, which change from period to period and so does the frequency. More successful was the second attempt when the Lotka model was extended to the Lotka-type model by Mai et al. [12]. In this case as well, the analysis of the corresponding MF equations shows only stationary solutions. In its turn, computer simulations of the Lotka-type model reveal oscillatory behavior, which becomes more pronounced with larger lattice sizes. An increase of oscillatory behavior with lattice size is a unique phenomena. Usually it is harder to ensure the synchronization of local oscillations on large scales, which reflects as weakening of oscillations. Disagreement between MF analysis and computer simulations shows the inability of traditional MF approximations to describe the phenomena where long-range correlations are important.

1.2.1 The Lotka model

In 1910 Lotka [16] suggested the first mathematical model, which exhibits damped oscillations

\[ E \xrightarrow{k_1} A, \]  
\[ A + B \xrightarrow{k_2} 2B, \]  
\[ B \xrightarrow{k_3} P. \]

It is assumed that there exist an infinite reservoir of matter \( E \). Its concentration \( C_E \) is constant and \( E \) is linearly transformed into reactants \( A \) with rate \( k_1 \), Eq. (1.1). The reactants \( A \) are turned into \( B \) with the rate \( k_2 \), Eq. (1.2), if they are at the recombination distance. The product \( P \), which does not affect the reaction, is
obtained from $B$ with the rate $k_3$, Eq. (1.3). This model allows simple biological interpretation in terms of *prey animals* $A$ and *predators* $B$. The population of preys $A$ proliferates with a constant rate $k_1$, Eq. (1.1), since the amount of food $E$ is infinite. When a predator meets a prey, the prey perish and a new predator is created with the rate $k_2$, Eq. (1.2). The predators perish with a constant rate $k_3$, Eq. (1.3), due to natural reasons (death).

Let us analyze the MF equations of the Lotka model [19] Eqs. (1.1) to (1.2)

$$
\dot{C}_A(t) = p - k_2 C_A(t) C_B(t),
$$
(1.4)

$$
\dot{C}_B(t) = k_2 C_A(t) C_B(t) - k_3 C_B(t),
$$
(1.5)

where $p = k_1 E$ and $C_A(t)$ and $C_B(t)$ stay for reactant $A$ and $B$ concentration at time $t$, respectively. The system of Eqs. (1.4) and (1.5) has a single singular point, Eq. (C.2)

$$
C^0_A = \frac{k_3}{k_2}, C^0_B = \frac{p}{k_3}.
$$
(1.6)

The characteristic equation Eq. (C.7) is

$$
\lambda^2 + \frac{k_2 p}{k_3} \lambda + k_2 p = 0.
$$
(1.7)

It has two roots

$$
\lambda_{1,2} = -\frac{k_2 p}{2k_3} \pm \sqrt{\left(\frac{k_2 p}{2k_3}\right)^2 - k_2 p}.
$$
(1.8)

For $k_2 p > 4k_3^2$ the roots are real and $\lambda_{1,2} < 0$, which indicates that the singular point is a *stable node*. Classification of singular points in phase space is summarized in Appendix C. For the case $k_2 p < 4k_3^2$ the roots have a real part $\text{Re}\{\lambda_{1,2}\} < 0$ and imaginary part $\text{Im}\{\lambda_{1,2}\} \neq 0$, which classify the singular point as a *stable focus*. In this regime the system exhibits damped oscillations with frequency $\omega_0 = \sqrt{k_2 p - \left(\frac{k_2 p}{2k_3}\right)^2}$.

### 1.2.2 The Lotka-Volterra model

In 1920 Lotka and Volterra [17, 18] introduced the first theoretical model, which predicts sustained oscillations. It consists of two autocatalytic steps and one ami-
hilation reaction

\[
\begin{align*}
E + A \xrightarrow{k_1} 2A, \\
A + B \xrightarrow{k_2} 2B, \\
B \xrightarrow{k_3} P,
\end{align*}
\]

where concentrations \(C_E\) of reactants \(E\) is constant and uniform inside the reaction volume. Its biological interpretation is similar to the above discussed Lotka model. The pray animals \(A\) reproduce themselves if they have found food \(E\) with rate \(k_1\), Eq. (1.9). The amount of \(E\) is assumed to be infinite. A predator \(B\) reproduce itself if it has found a pray \(A\) with rate \(k_2\), Eq. (1.10). The population of predator animals decreases with rate \(k_3\), Eq. (1.11), due to natural reasons. The master equation for the Lotka-Volterra model, Eqs. (1.9) to (1.11), in the MF approximation leads to

\[
\begin{align*}
\dot{C}_A (t) &= pC_A (t) - k_2C_A (t) C_B (t), \\
\dot{C}_B (t) &= k_2C_A (t) C_B (t) - k_3C_B (t),
\end{align*}
\]

where \(p = k_1C_E\) and \(C_A (t)\) and \(C_B (t)\) are reactant \(A\) and \(B\) concentrations, respectively. There exist two singular points: a trivial solution

\[C_A^0 = C_B^0 = 0\]

and a nontrivial solution

\[C_A^0 = \frac{k_3}{k_2}, C_B^0 = \frac{p}{k_2}\]

Following the standard analysis procedure of singular points, see [20, 21] and Appendix C, let us write down the characteristic equation for the trivial solution

\[(p - \lambda)(-k_3 - \lambda) = 0.\]

It solution reads as follows

\[
\begin{align*}
\lambda_1 &= p, \\
\lambda_2 &= -k_3.
\end{align*}
\]

The roots are real and they have opposite signs, which indicates that the trivial solution is a saddle point (unstable). The characteristic equation for the nontrivial solution is

\[
\lambda^2 + pk_3 = 0.
\]

9
The characteristic exponents are

$$\lambda_{1,2} = \pm i\sqrt{pk_3}. \quad (1.20)$$

The characteristic exponents are imaginary, which shows that the nontrivial solution is a center. The system oscillates with a frequency $\omega_0 = \pm \sqrt{pk_3}$. In the last case the Lotka-Volterra model has a continuous spectrum of frequencies, which depend sensitively on the initial conditions. A small perturbation switches the system continuously from orbit to orbit with different frequencies, and there is no average, “preferred” orbit.

1.2.3 The standard Lotka-type model

Formally the Lotka-type model [12] is an extension of the Lotka model, Eqs. (1.1) to (1.3), with additional conditions. It consists of two kinds of reactants labeled hereafter as $A$ ($B$), which are situated on a discrete square lattice. The following rules are stated for reactants on the lattice: reactant $A$ can be adsorbed from a gas phase in an empty site $O$ with the adsorption rate $k_1$, Eq. (1.21):

$$A\text{(gas)} + O \stackrel{k_1}{\longrightarrow} A\text{(ads)}, \quad (1.21)$$

$$A\text{(ads)} + B\text{(ads)} \stackrel{k_2}{\longrightarrow} 2B\text{(ads)}, \quad (1.22)$$

$$B\text{(ads)} \stackrel{k_3}{\longrightarrow} B\text{(gas)} + O. \quad (1.23)$$

Contrary to Eq. (1.1), creation of reactants $A$ depends now on the amount of empty sites $O$. If reactant $A$ is located in the nearest neighbor (NN) position to an existing reactant $B$, an autocatalytic reproduction reaction takes place instantly $k_2 \to \infty$, Eq. (1.22). It is assumed that this step takes no time thus leading to the state where reactants $A$ and $B$ never occupy NN positions. Reactant $B$ can be desorbed with the rate $k_3$, Eq. (1.23). In the limiting case $k_2 \to \infty$, and with a time normalization the Lotka-type model depends on a single parameter $\zeta$

$$k_1 = \zeta,$$

$$k_3 = 1 - \zeta.$$

The mathematical model has a number of realistic interpretations in two-dimensional space. Bacterial growth in the presence of nutrient is treated within this model [22], if $B$ states for a bacteria and $A$ for spontaneously created nutrient, Eq. (1.21). Bacteria reproduce themselves if they have found a nutrient Eq. (1.22). The
population of bacteria decreases due to natural reasons, Eq. (1.23). Next, in the forest fire model [13] particularly for small $\zeta$ values, $A$ states for slowly growing tree Eq. (1.21) that could be ignited by the neighboring burning tree $B$, Eq. (1.22). Then trees $B$ burn very fast leaving empty space, Eq. (1.23). The other application of the model is the description of the spread of an infection, where $A$ states for a non-infected cell and $B$ for an infected one. Non-infected cells are created randomly, when they meet an infected cell $B$, $A$ is infected immediately, Eq. (1.22). Infected cells $B$ die leaving empty space, Eq. (1.23). This model also allows a few more chemical interpretations [13]. For example, $A$ stays for adsorbed reactant on a reconstructed site and $B$ stays for a reactant on a non-reconstructed site. If they are in NN sites, the reactant on non-reconstructed site $B$ induces the lifting of reconstruction and $A$ is turned into $B$. One more model’s realization could be the following. Reactant $A$ stays for reactant $B$ with an additional ligand. When these two reactants come into contact, the ligand could desorb immediately leaving two reactants $B$.

Let us analyze the Lotka-type model in MF approximation. The model, Eqs. (1.21) to (1.23), is described by the following MF equations

$$
\dot{C}_A(t) = \zeta (1 - C_A(t) - C_B(t)) - k_2 C_A(t) C_B(t),
$$

$$
\dot{C}_B(t) = k_2 C_A(t) C_B(t) - (1 - \zeta) C_B(t).
$$

This system of equations has two singular points

$$
C^o_A = 1, C^o_B = 0,
$$

$$
C^o_A = \frac{1 - \zeta}{k_2}, C^o_B = \zeta \left(1 - \frac{1 - \zeta}{k_2}\right).
$$

The characteristic equation for the singular point Eq. (1.26) is

$$
(-\zeta - \lambda) (k_2 - 1 + \zeta - \lambda) = 0.
$$

Its solutions are

$$
\lambda_1 = -\zeta,
$$

$$
\lambda_2 = k_2 - 1 + \zeta.
$$

Both roots are real and they lead to a stable node if $k_2 < 1 - \zeta$, i.e., both roots are negative. In the case $k_2 \to \infty$, the singular point Eq. (1.26) is an unstable saddle point, since the root Eq. (1.30) is positive.
The characteristic equation for the singular point Eq. (1.27)
\[ \lambda^2 + \zeta (k_2 + \zeta) \lambda + \zeta (k_2 - 1 + \zeta) = 0 \] (1.31)
leads to two roots
\[ \lambda_{1,2} = -\frac{\zeta (k_2 + \zeta)}{2} \left[ 1 \pm \sqrt{1 - \frac{4(k_2 - 1 + \zeta)}{\zeta (k_2 + \zeta)^2}} \right]. \] (1.32)
In the case of \( k_2 < 1 - \zeta \), the singular point Eq. (1.27) is an unstable saddle point, since roots \( \lambda_1 \) and \( \lambda_2 \) are real and have different signs. Oscillatory behavior with decaying amplitude (stable focus) is possible if the term under the square root in Eq. (1.32) is negative. In this case the reaction rate \( k_2 \) has to satisfy the condition
\[ k_2^2 - 2k_2 \left( \frac{2}{\zeta} - \zeta \right) + \zeta^2 + \frac{4}{\zeta} - 4 < 0. \] (1.33)
The condition Eq. (1.33) is fulfilled if the reaction rate \( k_2 \) lies between two values of \((k_2)_-\) and \((k_2)_+\)
\[ (k_2)_{-+} = \frac{2}{\zeta} \left( 1 \mp \sqrt{1 - \frac{4}{\zeta}} \right) - \zeta. \] (1.34)

Two limiting cases can be considered. Firstly, in the limit of small \( \zeta \) values one obtains
\[ (k_2)_- (\zeta \to 0) = \lim_{\zeta \to 0} (k_2)_- = 1, \] (1.35)
\[ (k_2)_+ (\zeta \to 0) = \frac{4}{\zeta}. \] (1.36)
Then the type of the singular point, Eq. (1.27), depends on the reaction rate \( k_2 \): For \( k_2 < 1 \) the singular point is a saddle point. In the case of \( k_2 > 1 \) the singular point is a stable focus. For \( k_2 > 4/\zeta \) the singular point is stable node, since both roots of Eq. (1.32) are negative.
Secondly, in the limiting case of large \( \zeta \to 1 \) values the stable focus is obtained only, when \( k_2 = 1 \) (i.e., \((k_2)_- (\zeta \to 1) = (k_2)_+ (\zeta \to 1) = 1 \)). The singular point Eq. (1.32) is a stable node for \( 0 < k_2 < 1 \) and \( k_2 > 1 \).

In contrast to the predictions of the standard MF analysis, the MC simulations show, that the Lotka-type model reveals an oscillatory behavior [12]. The oscillations become more pronounced, i.e., the noise level decreases with increase of lattice size. The failure of the MF approximations to describe oscillations is due to the fact, that the MF approximation does not take into account the long-range correlations between reactants. Therefore one has to use, e.g., MC computer simulations to analyze such systems.
1.2.4 The generalized Lotka-type model

In order to study the resonance properties of the oscillatory systems, the standard procedure is to introduce a small periodic modulation of a control parameter. The system has a resonance behavior, when for some particular modulation frequency the amplitude of oscillations increase. It is easy to introduce the periodic modulations in the Lotka-type model, since it has a single control parameter

\[ \zeta(t) = \zeta_0 + \Delta \zeta \sin(\omega_{mod} t), \] (1.37)

where \( \Delta \zeta \ll \zeta_0 \) is the modulation amplitude, \( \omega_{mod} \) the modulation frequency and \( t \) the time. Its physical realization is the following: In the case of chemical interpretation, the \( \zeta(t) \) correspond to the pressure of a gas above the catalytic surface. The gas pressure can be periodically changed in time, Eq. (1.37). In the biological interpretation, \( \zeta(t) \) corresponds to the amount of available food, which changes periodically in time.

1.3 Simulation algorithm

In the MC computer simulations a discrete square lattice \( L \times L \) with periodic boundary conditions is used. Let us denote the concentration of \( A \) and \( B \) reactants on the lattice as \( C_A \) and \( C_B \), respectively. Then the initial conditions are \( C_A(0) = 0 \) and \( C_B(0) = 0.5 \), where \( B \) reactants initially are distributed randomly on the lattice. The initial conditions in this model are not important, the only stipulation is that initially \( B \) reactants should be present somewhere on the lattice. The simulation loop consists of the following steps:

1) time is set to \( t = 0 \);
2) \( \zeta \) is calculated from Eq. (1.37),
3) a time step is determined as the time which is necessary for the quickest process, \( dt = \min(1/\zeta, 1/(1 - \zeta)) \);
4) time is updated \( t = t + dt/L^2 \);
5) a site is chosen randomly;
6) for this site the following cases are distinguished:

   i) if the site is empty, \( A \) is created there with the probability \( \zeta dt \). Then the four nearest-neighbor sites are checked for \( B \) reactants. If one was found, the just-created \( A \) transforms into \( B \). The four nearest-neighbor sites of newly-created \( B \) then are checked for the presence of \( A \) reactants, if any \( A \) is found, it transforms
into $B$. This continues, as long as no $A$ reactants anymore are connected to the $B$ cluster.

ii) if a site is occupied by $B$, then $B$ is annihilated with probability $(1 - \zeta)\, dt$;

7) the loop returns to the second step, if $t$ is less than a given simulation time.

1.4 Mathematical methods

The concentration of species obtained from computer simulations is recorded with the sampling frequency $f_{\text{scan}}$. To analyze the oscillating quantities, we calculate the power spectral density (PSD) [23]. In this Thesis two methods are used. The first one is straightforward and based on the calculation of the discrete Fourier transform coefficients from a discrete set of $N$ data $c_j$,

$$C_k = \sum_{j=0}^{N-1} c_j e^{2\pi ijk/N} \quad k = 0, \ldots, N - 1 \quad (1.38)$$

with the following calculation of PSD coefficients

$$P^{FT}(\omega_k) = \frac{|C_k|^2}{N^2}, \quad k = 0, N/2, \quad (1.39)$$

$$P^{FT}(\omega_k) = \frac{2|C_k|^2}{N^2}, \quad k = 1, \ldots, N/2 - 1 \quad (1.40)$$

at frequencies $\omega_k$, where $\omega_k$ is defined as

$$\omega_k = 2\pi \frac{k}{N f_{\text{scan}}}, \quad k = 0, \ldots, N/2. \quad (1.41)$$

From here one can find the increase step for frequency $\Delta\omega = 2\pi/(N f_{\text{scan}})$ and the maximal frequency $\omega_{N/2} = \pi/ f_{\text{scan}}$. The scanning frequency determines the maximal frequency of PSD, but the number of data $N$ determines the frequency resolution. PSD is normalized in such a way that the sum over all $N/2 + 1$ values of $P^{FT}(\omega_k)$ is equal to the mean-squared amplitude $c_j$. PSD values can be calculated only at discrete frequencies. But if one assumes that the system oscillates with some frequency in-between two of such discrete quantities, one gets at least two non-zero PSD values at the neighboring frequencies. The trick to get a clear spectrum function is based on the variation of the length of the sampled data $N$ in such a way that one of $\omega_k$ coincides with the systems’ oscillation frequency. It allows us to determine the corresponding PSD value as well.
Another method is the all-poles method (AP) [23] based on the Wiener-Khinchin theorem. The latter states that the Fourier transform of autocorrelation is equal to the PSD. The oscillation frequency range \( \omega_k \) is extended to the complex \( \omega \)-plane and then this plane is transformed to the \( z \)-plane by the transformation \( z = e^{\omega / \omega_{\text{osc}}} \). The PSD is approximated with the Laurent series

\[
P_{\text{AP}}(\omega) \approx \frac{a_0}{\left| 1 + \sum_{k=1}^{M} a_k z^k \right|^2},
\]

where \( M \) is the number of poles. To determine the coefficients \( a_k \) of the Laurent series, the Laurent series is mapped on the Fourier transform of the autocorrelation

\[
\frac{a_0}{\left| 1 + \sum_{k=1}^{M} a_k z^k \right|^2} \approx \sum_{j=-M}^{M} \Phi_j z^j,
\]

where the autocorrelation \( \Phi \) at lag \( j \) is defined as

\[
\Phi_j = \Phi_{-j} \approx \frac{1}{N + 1 - k} \sum_{k=0}^{N-k} c_k c_{k+j}, \quad k = 0, 1, \ldots, N.
\]

The coefficients \( a_k \) can be found iteratively [23], e.g., at the first approximation \( a_{0}^{(0)} = \Phi_0 \), then at the next step \( a_{1}^{(0)} = -\Phi_1 / \Phi_0 \) and \( a_{0}^{(1)} = \Phi_0 \left( 1 - (\Phi_1 / \Phi_0)^2 \right) \). This method can resolve very close oscillation frequencies, but its disadvantage is that it cannot be used for signals of a sinusoidal shape, in this case the AP method gives a singularity at the corresponding frequency.

### 1.5 Simulation results

The MC computer simulation is performed on a square lattice with the side length \( L = 1024 \) (\( L \) is given in the units of the lattice constant). For smaller system sizes oscillations are not clearly observable because of a high noise level. Although at lattice size \( L = 1024 \) oscillation parameters still depend on the lattice size \( L \), it is already possible to reproduce all the qualitative properties of the system and it is a good compromise between system’s size and simulation time.

To describe the oscillations quantitatively, the PSD is used. It is directly connected to the amplitude of the oscillations, e.g., it tends to zero if there are no oscillations.

First, let us consider the standard Lotka-type model. MC computer simulations reveal the concentration oscillations for small \( \zeta \) values, Fig. 1.1-a). In this regime
Figure 1.1: The reactant A (thin line) and B (thick line) concentration time dependence. The parameter $\zeta$ has the value 0.06 a), 0.08 b) and 0.12 c).
oscillations have well-defined frequency and they do not decay with time. A slight increase of $\zeta$ leads to the loose of a well-defined frequency, which then changes randomly in a certain interval of frequencies. As a result, the amplitude of oscillations is smaller and frequency is not well defined, see Fig. 1.1-b). A further increase of $\zeta$ eliminates any oscillatory behavior, Fig. 1.1-c), and the concentrations show small fluctuations without any well-defined frequency.

The oscillatory behavior depends on the lattice size as follows. For $\zeta < 0.7$ the amplitude of oscillations stays constant with increase of lattice size, Fig. 1.2-a). The larger lattices ensure the smaller noise level, which results in smaller amplitude fluctuations, compare thin and thick lines in Fig. 1.2-a). The oscillatory behavior disappears for $\zeta \geq 0.7$, see Fig. 1.2-b) and c).

The parameter’s $\zeta$ variation could be approximately divided into two regions separated by the value of $\zeta \approx 0.07$. Particle concentration oscillations are observed for an $A$ particle creation probability $\zeta < \zeta_c$, see Fig. 1.3. The transition to the oscillatory regime occurs within a narrow interval of $\zeta$ around $\zeta_c$. The system still exhibits an oscillatory behavior for $\zeta$ slightly larger than $\zeta_c$. In this region the height of the PSD peak at the system’s self-oscillation frequency decreases for larger data interval in the PSD calculations, since this determines the higher frequency resolution in the Fourier Transform. As far as the system does not oscillate with one particular self-oscillation frequency, the PSD function peak at the system’s self-oscillation frequency in high frequency resolution limit distributes over a range of frequencies, which are close to the system’s self-oscillation frequency. In the spectrum this is seen as the broadening and lowering of the peak at the self-oscillation frequency. Below $\zeta < \zeta_c$ where the concentration oscillations are more stable, the lowering of the PSD peak at the self-oscillation frequency is not pronounced. To obtain stable PSD values, one has to find a compromise between the precision of determining the oscillation frequency and amplitude (e.g., the uncertainty in the frequency determination is 10% of the system’s self-oscillation frequency). Both of them could not be calculated simultaneously with an arbitrarily high precision (a kind of uncertainty relation holds here).

The frequency of the self-oscillation decreases nearly linearly with $\zeta$, as seen in Fig. 1.3. This relation and the fact that the PSD values increase at small $\zeta$ could be easily illustrated by the following example. Let us start with a situation, when there are a minimum concentration of the reactants $A$ on the lattice, see state (a) in the Fig. 1.4. At the same time there are a few $B$ present on the lattice. This is illustrated in the snapshot of the lattice Fig. 1.5-a). As time goes on, reactants $A$
Figure 1.2: The reactant $B$ concentration time dependence for lattice size $1024 \times 1024$ (thin line) and $8192 \times 8192$ (thick line). The parameter $\zeta$ has the value 0.065 a), 0.075 b) and 0.080 c).
Figure 1.3: The PSD (Fourier Transform) at the system’s self-oscillation frequency $\omega_{sys}$ vs A particle creation probability $\zeta$ (squares), and the self-oscillation frequency $\omega_{sys}$ vs A particle creation probability (circles).
are created in empty sites; see state (b) in Fig. 1.4 and the corresponding snapshot (b) in Fig. 1.5. The probability of $A$ to survive is larger if they are organized in clusters, which reduces the probability of reaction with $B$. In this stage reactants $B$ generally are annihilated. If cluster of $A$ meets some $B$ then the gain of reactants $B$ is small, since in this stage the average radius of $A$ clusters (connected as a NNs reactants $A$) is small Fig. 1.5-b). In this regime the adsorption of $A$ prevails the reaction, which is reflected in the increase of concentration of $A$ and decrease of $B$, see Fig. 1.4-b). The situation changes, when there are enough reactants $A$ to create a percolating cluster, see state (c) in Fig. 1.4 and snapshot (c) in Fig. 1.5. As soon as it grows up, eventually it touches a reactant $B$ that survived till then. If this happens, the autocatalytic reaction $A + B \rightarrow 2B$ takes place immediately and a whole $A$ cluster turns into a $B$, see snapshot (d) in Fig. 1.5. This corresponds to the instant where concentration of $A$ decreases, but that of $B$ correspondingly increases, see state (d) in Fig. 1.4. At this stage the reactants $B$ are picked up very often and they are annihilated very quickly, leaving empty space for the creation of reactants $A$, that will form a new cluster. Concentration oscillations arise in the system only if creation of $A$ and annihilation of $B$ fall into a certain range of parameters. The lattice still should have a few reactants $B$ at the end of time which
Figure 1.5: The snapshots of the lattice during concentration oscillations. Reactants $A$ and $B$ are shown separately on the left and right hand side, respectively. Shown are $256 \times 256$ sections of $1024 \times 1024$ lattice.
is necessary to create percolating cluster of $A$. This interpretation explains decrease of the oscillation frequency with the decrease of $\zeta$ seen in Fig. 1.3. The period of oscillations increases (frequency decreases), because reactants $A$ are created slower, which allows more $B$ to be annihilated and thus $A$ have more space to create a larger percolating cluster. It takes longer time for this cluster to meet some reactant $B$. Simultaneously, the oscillation amplitude increases due to the fact that more $A$ are accumulated in the lattice. It is reflected by an increase of PSD values for small $\zeta$ values.

Decrease of $\zeta$ below 0.055 leads to the $A$ poisoning. Reactants $A$ are created so slowly that all $B$ are annihilated before any catalytic reaction takes place. To treat this model for small $\zeta$ values one can use, for example, the method proposed in [13]. For our study this is irrelevant as far as our simulations are not performed for $\zeta < 0.055$.

Let us choose now the parameter $\zeta = 0.08$ in the region $\zeta > \zeta_c$, where oscillations are not pronounced. In this case the system’s self-oscillation frequency is found to be $\omega_{sys} = 0.465$ s$^{-1}$. The small amplitude of reactant $B$ oscillations allows us to clearly detect the influence of external modulation. For $\zeta < \zeta_c$, the effect of external modulation is weakly expressed, since the concentrations of reactants already oscillate with a large amplitude.

Now we assume that a periodical external force, Eq. (1.37), is switched on at some moment, Fig. 1.6, with a small modulation amplitude $\Delta \zeta = 0.01$ and frequency $\omega_{mod} = \omega_{sys}$. In this case the system is forced with the frequency close to its self-oscillation frequency and one can see that the oscillations frequency becomes locked to the external frequency and PSD increases, indicating an increase in the oscillations amplitude.

Changing $\omega_{mod}$ and keeping $\Delta \zeta = 0.01$ constant, one can scan all the spectrum of possible modulation frequencies. It is found that in PSD, besides the maximum at the system’s self-oscillation frequency $\omega_{sys}$, now there appears the maximum corresponding to the frequency $\omega_{mod}$ of an external modulation. The height of this maximum increases monotonously as $\omega_{mod}$ approaches the oscillation frequency $\omega_{sys}$, or doubled frequency $2\omega_{sys}$, see Fig. 1.7. The external force is damped at small frequencies, but with an increase of the external modulation frequency the damping decreases. There is a peculiarity in the region around frequency $\omega_{sys}/2$ where a small window exists in which damping decrease is more pronounced. This is more clearly shown in an insert of Fig. 1.7. Further damping again decreases monotonously, until the frequency of external modulation reaches the system’s oscillation frequency.
Figure 1.6: The concentrations of $A$ (thin line) and $B$ (thick line). The modulation of parameter $\zeta = 0.08$ with amplitude $\Delta \zeta = 0.01$ and frequency $\omega_{\text{mod}} = 0.465$ is turned on at $t = 2000$.

Figure 1.7: The PSD (Fourier Transform) at the modulation frequency $\omega_{\text{mod}}$ vs ratio $\omega_{\text{mod}}/\omega_{\text{sys}}$. Parameter $\zeta_0 = 0.08$ and modulation amplitude $\Delta \zeta = 0.01$. 

23
where damping starts to grow.

Let us compare the PSD changes at the system's oscillation frequency $\omega_{sys}$, Fig. 1.8, with the PSD changes at the modulation frequency $\omega_{mod}$, Fig. 1.7. It is easy to notice that both PSDs have maxima at the same modulation frequencies, namely at $\omega_{mod} = 1/2$, 1 and 2 of $\omega_{sys}$. When $\omega_{mod}$ approaches one of these frequencies, $\omega_{sys}$ becomes locked to the modulation frequency $\omega_{mod}$, i.e., the system oscillates with $2\omega_{mod}$, $\omega_{mod}$ or $\omega_{mod}/2$, respectively. The $\omega_{sys}$ locking to modulation frequency depends on the modulation amplitude $\Delta \zeta$. If $\Delta \zeta$ increases, $\omega_{sys}$ locks to the modulation frequency, even if $\omega_{mod}$ is far from the resonance ratios of 1/2, 1 or 2.

As an example of the PSD spectrum in the $\omega_{mod}$ resonance regions, one can consider Fig. 1.9. In Fig. 1.9-a), two maxima are observed for the modulation frequency: $\omega_{mod} = 0.23 \text{ s}^{-1}$, i.e., close to $\omega_{sys}/2$, and $\omega_{sys}$ frequency, which is locked now to frequency $2\omega_{mod}$. To relate these observations to the previous figures, let us consider two points, one at the modulation frequency $M_{1/2}$ and another at the system's oscillation frequency $S_{1/2}$ when the modulation frequency is half of the self-oscillation frequency. Now it is seen that the height of the PSD maximum at $\omega_{mod} = 0.23 \text{ s}^{-1}$ (point $M_{1/2}$) corresponds to the point $M_{1/2}$ in Fig. 1.7, which is a local maximum. The PSD value (point $S_{1/2}$) at $\omega_{sys}$ frequency corresponds to point $S_{1/2}$ in Fig. 1.8-a), which is also a local maximum. In Fig. 1.9-b) the modulation frequency $\omega_{mod} = 0.46 \text{ s}^{-1}$ is chosen to be close to the system's oscillation frequency, which in its turn, is captured by the external modulation frequency, leading to just one maximum $M_1 = S_1$ in the oscillation spectrum. This maximum corresponds to the points $M_1$ in Fig. 1.7 and $S_1$ in Fig. 1.8, which coincide in the locking region. This is the global maximum point, provided the system is forced with the modulation frequency close to its self-oscillation frequency.

The AP method gives clear illustration of phase locking, occurring for example, when $\omega_{mod}$ approaches $\omega_{sys}/2$ frequency, and starting at $\omega_{mod}/\omega_{sys} \approx 0.46$. Then in the PSD curves in Fig. 1.10 one can find a maximum corresponding to the self-oscillation frequency at $\omega/\omega_{sys} = 1$ and a small maximum corresponding to frequency $2\omega_{mod}$ at $\omega/\omega_{sys} \approx 0.9$. As $\omega_{mod}$ is increased, this small maximum approaches the $\omega_{sys}$ frequency and becomes more pronounced. At the ratio $\omega_{mod}/\omega_{sys} \approx 0.49$ the modulation frequency captures the self-oscillation frequency and forces the system to oscillate with $\omega_{sys} = 2\omega_{mod}$ (but not with the self-oscillation frequency of unmodulated system).

To determine the resonance behavior, one can use a visual observation method as well. For example, forcing the system at frequencies close to ratio $\omega_{mod}/\omega_{sys} = 1/3$
Figure 1.8: The PSD (Fourier Transform) at system’s self-oscillation frequency $\omega_{sys}$ vs ratio $\omega_{mod}/\omega_{sys}$. Parameter $\zeta_0 = 0.08$, modulation amplitude $\Delta \zeta = 0.01$. 

Figure a) $S_{1/2}$, Figure b) $S_1$. 

$10^3 P_{FT}$ vs $\omega_{mod}/\omega_{sys}$.
Figure 1.9: The PSD (Fourier Transform) for parameter $\zeta_0 = 0.08$, modulation amplitude $\Delta \zeta = 0.01$ and the modulation frequencies: $\omega_{mod} = 0.23 \text{ s}^{-1}$ a), $0.46 \text{ s}^{-1}$ b).
Figure 1.10: The PSD (All Poles method) vs the modulation frequency $\omega_{\text{mod}}$, approaching the resonance frequency $1/2$ (scaled with respect to self-oscillation frequency $\omega_{\text{sys}}$). Parameter $\zeta_0 = 0.08$ and modulation amplitude $\Delta \zeta = 0.01$. 
with the forcing amplitude $\Delta \zeta = 0.02$ shows a resonance behavior, see Fig. 1.11. During one oscillation period of $\zeta(t)$, the $B$ particle concentration reveals three oscillations, that implies the resonance behavior at frequency ratio $\omega_{\text{mod}} / \omega_{\text{sys}} = 1/3$. In the case of $\Delta \zeta = 0.01$ when visually observing the concentration oscillations, the maxima are not well distinguishable, but already as $\Delta \zeta = 0.02$ the maxima are well pronounced. This method can be used as the first estimate of the resonance behavior and as the only real method for more complicated cases when the system continuously exhibits transitions between two or more resonance regimes.

### 1.6 Conclusions

The periodically-forced Lotka-type autocatalytic reaction model has been studied here by means of the MC computer simulations. Two mathematical methods were employed for analyzing simulations results. The first one is based on the power spectral density (PSD) calculation, using the Fourier Transform. Using this method, the oscillations are analyzed in the unperturbed system and in the resonance regions of the modulated system. The second approach used to calculate the PSD is the All-Poles method, which is employed for detecting the frequency locking processes.
One can use additionally a visual observation method to determine the resonance behavior.

Considered Lotka-type model is a remarkable simplification of theoretical models available for describing the oscillatory systems. It differs strongly from the real catalytic reactions (e.g., CO catalytic transformation on Pt surface) in the following respects: (i) concentration oscillations are not connected to surface reconstructions; (ii) diffusion of reactants (quick and very important process in the real systems) are not taken into account; (iii) our model has an original mechanism of oscillations’ synchronization (obviously different from that in real systems), which ensures macroscopic oscillations of reactant concentrations independently on the lattice size without implicating any additional mechanisms of synchronization, like reactant diffusion.

We have clearly detected the existence of the resonance behavior when the frequency ratio (external modulation frequency vs system’s self-oscillation frequency) is one of the three: 1 : 2, 1 : 1 or 2 : 1 at forcing amplitude Δζ ≥ 0.01. The resonance behavior at the ratio 1 : 3 with forcing amplitude Δζ ≥ 0.02 is observed, but its full demonstration is limited in the MC simulations due to a large noise level. Frequency locking is observed at the resonance frequencies and in their neighborhood. The region of observed frequency locking depends on the amplitude of modulation force Δζ: the frequency locked region is the larger, the larger is the amplitude of the modulation force.

The resonance behavior at frequency ratios 1 : 3, 1 : 2, 1 : 1 and 2 : 1 is similar to the experimentally obtained results for the forced CO catalysis on Pt surface [4]. In-between the resonance frequencies, our simulations show a quasiperiodic behavior, similarly to the real experiment. However, in contrast to this experiment, MC computer simulations do not show resonance behavior for some frequency ratios, e.g., 1 : 4, 3 : 5 or 2 : 3. An increase of the modulation amplitude in the resonance regions does not lead to a quasiperiodic behavior, like it is observed in the experiments for frequency ratios 3 : 5 or 2 : 3. The transition to chaos has not been detected. One should note that these discrepancies could arise by the two reasons: (i) the Lotka-type model suggests quite simplified treatment of a real autocatalytic reactions. Refining the model will lead to the better agreement with the experimental data, and more effects will be reproduced. But this step increases the number of parameters in the model and thus an origin of the resonance behavior will be harder to trace. (ii) The specific feature of the MC method is a large noise level thus complicating a detection of resonance phenomena. Most probably due to this particular fact we
were unable to detect the resonance behavior at other ratios (e.g., 1 : 4, 3 : 5 or 2 : 3).

A comparison of experimental data with our simulation results shows that the resonance phenomena (like frequency locking, quasiperiodic and resonance behavior) are not connected to a specific surface reaction, e.g., CO catalytic oxidation, but they reflect very general aspects of oscillatory processes. The abstemiousness of the formulated Lotka-type model and a large number of observed oscillatory and resonance phenomena could nominate the Lotka-type model to serve as the kinetic analog of the Ising model, which is well-known in statistical physics.
Chapter 2

The Lotka-type model with reactant surface diffusion and interaction

2.1 Introduction

In the last decade along with studies of dissipative structures in homogeneous catalytic reactions of the Belousov-Zhabotinskii-type, considerable attention was attracted to the heterogeneous catalytic reactions. They reveal a whole spectrum of synergetic effects, e.g., rate oscillations, concentration waves, spirals and chaos [1]. The heterogeneous systems are simpler than the homogeneous ones. Therefore, one can use for their study a number of powerful experimental and theoretical methods, which allow to determine the origin of spatiotemporal structures.

In particular, the oscillatory kinetics were observed in heterogeneous catalysis on many metal surfaces as well as on oxide catalysts [1]. The actual mechanism of oscillations is different for various catalysts [24]. The more so, for the same catalyst the origin of oscillations is also different in the high and low gas pressure limits. However, independently on the type of a catalyst, the global synchronization of oscillations is observed [1]. This fact implies the existence of very universal rules in the behavior of oscillatory systems, which exist independently on both type of catalyst and mechanism of a particular catalytic reaction.

One of the theoretical methods used to attack the problem of catalysis is a MC
computer simulation (see [25, 26] and references therein). Its role considerably increased during the last years due to increase of computational facilities. The idea of the MC method is to define a mathematical model, which accounts for basic experimentally detected reaction steps. The reactants are assumed to be classical particles (usually denoted as \( A, B, \) etc.), which can occupy sites on a discrete crystalline lattice. This allows easily to describe adsorption, desorption, diffusion and reaction of reactants as one- or two-site processes with the corresponding rates. Both reconstructed and non-reconstructed surfaces can be modeled by assigning different sticking coefficients of reactants to the lattice sites. Some models consist of more than ten-step reactions. A detailed mathematical model often complicates an analysis of simulation results and thus prevents from understanding of basic driving mechanisms, e.g., the origin of synchronization of oscillations.

To study the very basic properties of catalytic systems, mathematical models, which are less detailed, are of particular importance. One of such models is the Lotka-type model introduced for a simplified description of the autocatalytic surface reactions by Mai et al. [12] and further employed in a series of papers [7, 13, 14], see Chapter 1. This is a single-parameter model, with two kinds of reactants. It was shown that reactant concentrations exhibit here stable oscillations independently of lattice size. Self-sustained oscillations of the model allow to apply standard methods used for a treatment of oscillatory systems. For example, the resonance properties of the Lotka-type model were analyzed recently [27] by periodically varying in time the control parameter. Another model which, however, show unstable oscillations is the Lotka-Volterra model. The effects of the spatial constraints on the dynamics of this model was studied recently [15].

Diffusion of reactants in real catalytic surface reactions is a very quick and important process, which can lead to a formation of reactant aggregates, clusters and spatial structures. This is why of particular interest are those mathematical models which take into account diffusion of reactants. The studies of chemical reaction kinetics with mobile reactants have a long history [26]. The diffusion is implemented usually as random walks on the lattice with and without energetic interaction between reactants. For example, the coagulation effects as diffusion-controlled processes were studied for \( A + B \rightarrow \) inert reactions by Silverberg and Ben-Shaul [28]. The Ziff-Gularly-Barshad (ZGB) model, which mimics the catalytic \( \text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2 \) reaction, had been also extended for diffusion of reactants on a regular surface [29, 30, 31], diffusion on a reconstructing surface [8] and for diffusion and energetic interaction between reactants on a regular surface [32].
reactions with mobile and energetically interacting reactants on a reconstructing catalytic surface were studied by Zhdanov (see [33] and references therein). However, almost in all papers which deal with reactant energetic interactions, the kinetic model is not defined uniquely. For the same system different authors use transition rates of elementary processes (e.g., adsorption, desorption etc.), which could have or have not energetic (and temperature) dependence. It makes a comparison of the results practically impossible. The more so, the simulation algorithms are not always adequate to the problem. For example, in simulations [33] of non-equilibrium processes in the kinetic model the method of Metropolis was used. However, this method is defined only for equilibrium systems, where the kinetic aspects of the model are neglected.

In the present Thesis, we extend the standard Lotka-type model [12] via introduction of reactant diffusion. This step automatically leads to energetically-dependent reaction rates. In particular, we are interested in determining and understanding the impact of mobile and interacting reactants on the temporal structures in the Lotka-type model.

The Chapter 2 is organized in the following way. In the next Section 2.2 we generalize the standard Lotka-type model by an incorporation of diffusion and energetic interaction of reactants. The algorithm and details of simulations are described in Section 2.3. The simulation results and discussion are presented in Section 2.4. Lastly, conclusions are given in Section 2.5. Taking into account the above-mentioned problems arising from incorporation of diffusion into the mathematical model, we give in Appendix A a detailed description of this procedure. The suggested standard model defines uniquely the transition rates dependence on the interaction energy for all elementary process rates. The formalism can be applied to every kinetic lattice model. The relation between the “pair algorithm”, which is used in our MC simulations, and Master Equation is given in Appendix B.

2.2 The generalized Lotka-type model

The standard Lotka-type model, Eqs. (1.21) to (1.23), can be easily generalized by an incorporation of reactant diffusion. Reactant \( A \) (\( B \)) can jump to its NN site if it is empty:

\[
A{}_{\text{(ads)}} + O \xrightarrow{\nu^A} O + A{}_{\text{(ads)}}, \tag{2.1}
\]

\[
B{}_{\text{(ads)}} + O \xrightarrow{\nu^B} O + B{}_{\text{(ads)}}, \tag{2.2}
\]
with the jump rate $\nu_J$, where $J=A, B$. (The diffusion coefficient $D_J$ is related to a jump rate by the following equation: $D_J = (1/2) a^2 \nu_J$, where $z$ is a site coordination number and $a$ is a lattice constant.) The jump rate for isolated reactant depends only on the activation energy $e_{\text{act}, J}$ (in units of $kT$): $\nu_J = \nu_J^0 = \nu_{0,J} \exp(-e_{\text{act}, J})$, where $\nu_{0,J}$ is a pre-exponential factor and $\nu_J^0$ denotes the jump rate of non-interacting reactants. Lastly, we take into account an energetic interaction between reactants, see Appendix A. To do so, we introduce the energetic characteristics of the reactant configuration. If the two reactants are in the NN positions, their interaction energy equals to $e_{AA}$, $e_{BB}$ and $e_{AB}$ (in units of $kT$) depending on the type of reactants, $AA$, $BB$, $AB$ respectively. Since we are interested in determining the role of energetic interaction on temporal structures, it is assumed that temperature $T$ is constant, which allows us to consider energy terms $e_{J,J'}$ and $e_{\text{act}, J}$ independently. The jump rate is weighted according to the reactant local configuration. The interaction energy at initial $e_\alpha$ and final $e_\beta$ reactant state is calculated as:

$$e_{\alpha,\beta} = e_{AA}n_A + e_{BB}n_B + e_{AB}n_{AB},$$

(2.3)

where $n_A$ ($n_B$) is the number of nearest reactants $A$ ($B$) around the considered reactant and $n_{AB}$ is the number of $AB$ pairs, respectively. Finally, the jump rate for interacting reactants reads as follows:

$$\nu_J = 2\nu_J^0 \frac{1}{1 + \exp(e_\beta - e_\alpha)},$$

(2.4)

(see Appendix A for more details). If energetic interaction between reactants is neglected, then $e_\alpha = e_\beta = 0$ and we obtain from Eq. (2.4) the jump rate of isolated reactant $\nu_J = \nu_J^0$.

2.3 Simulation algorithm

Unlike the standard MC, in our computer simulations we consider pairs of NN lattice sites. That makes a simulation procedure more transparent and its extension to two-site processes, such as diffusion, becomes straightforward. Relation between our simulation algorithm and the corresponding master equation is given in Appendix B. The considered algorithm has been used earlier in a series of papers (see, e.g., [10, 34] and references therein). We want to stress here that on the basis of this algorithm it was proposed in [10, 34] to use a very quick method of cellular automaton (CA) instead of usual MC. These methods coincide if the two conditions are fulfilled: The

34
diffusion of reactants is very quick, and all transition rates are finite. Since these conditions are not fulfilled in the Lotka-type model, we have to use a standard MC procedure. Our simulation loop consists of the following steps:

1) The time update is determined as following: All possible initial distributions $i$ of reactants $A (B)$ in the two lattice sites are considered. For each such a configuration all possible independent reactions, Eqs. (1.21) to (1.23) and (2.1) to (2.2), are summed, which allows to determine the transition rate $p_i$ of changing the initial configuration:

$$B_1B_2 : \text{desorption of } B_1 + \text{desorption of } B_2,$$

$$p_1 = 2 \left(1 - \zeta \right),$$

$$B_iO_2 : \text{desorption of } B_i + \text{adsorption in } O_2 +$$

$$+ \text{jump of } B_i,$$

$$p_2 = 1 + 2\nu_B^0,$$

$$A_1O_2 : \text{adsorption in } O_2 + \text{jump of } A_1,$$

$$p_3 = \zeta + 2\nu_A^0,$$

$$O_1O_2 : \text{adsorption in } O_1 + \text{adsorption in } O_2,$$

$$p_4 = 2\zeta,$$

$$A_1A_2 : \text{configuration does not change},$$

$$p_5 = 0,$$

where lower indices at $X_iY_j$ denote the first and the second site of a pair. The step for an optimal time update is chosen to be proportional to an inverse of the maximal transition rate, $dt = 1 / \max(p_i)$. Time update cannot be chosen larger because the probabilities $p_i$ are normalized to unity, i.e., $p_i dt < 1$ for all $i$. Time update can be chosen smaller, but then the computer code would not be very effective due to many empty loops.

2) The simulation time is updated, $t \rightarrow t + 2dt/L^2$, where $L$ is the lattice size.

3) A random number (RN) is generated, in order to choose between horizontal or vertical orientations for a pair.

4) Two RNs are generated to chose the coordinates of the pair.

5) The state of chosen sites is determined. Depending on it, see Eqs. (2.5) to (2.9), one of independent reactions can be chosen randomly according to the standard MC simulation algorithm. E.g., in the case of a pair $A_1O_2$ (Eq. (2.7)): First, a RN is generated. Then reactant A adsorption step in $O_2$ is started if
RN< $\zeta dt$, else if $\zeta dt \leq RN< p_3 dt$ the jump step of $A_i$ is started. Nothing happens if $RN \geq p_3 dt$.

a) In a reactant $A$ adsorption step, reactant $A$ is created in the corresponding empty site. Then the system is checked for all $AB$ pairs, which could be in the NN lattice sites. If such a pair is found, the autocatalytic reaction, Eq. (1.22), takes place instantly. The checking and autocatalytic steps are repeated until there are no $AB$ pairs left in the lattice.

b) In a reactant $B$ desorption step, the corresponding $B$ is removed from a lattice leaving empty site $O$.

c) If the jump step is started, it does not necessarily mean that a reactant will really jump. The energy for initial and final configuration is calculated according to Eq. (2.3). A new RN is generated. A reactant jumps to the empty site only if condition $RN < 1/[1 + \exp (e_\beta - e_\alpha)]$ is fulfilled.

6) Loop returns to the step 2) if $t$ is less than a given simulation time.

2.4 Simulation results

The lattice size effect on oscillations amplitude in the Lotka-type model was analyzed by Mai et al. [12]. They found that there is a large noise level for small lattices. Only for 1024x1024 lattices and larger the noise is reduced to the level where oscillations are clearly seen. In our simulations we use a square discrete lattice of 1024x1024 sites with the periodic boundary conditions.

There is certain relaxation time in our simulations, which depends on the initial concentration and distribution of reactants $B$. The requirement for initial conditions is the following: reactants $B$ should be present in the lattice and their concentration should be nonzero after the relaxation time. Reactants $A$ initially are not required, but they can be added in free sites, which do not contain reactants $B$ as NN. After the relaxation time simulation results are independent on initial conditions. The following initial conditions are used: There are no reactants $A$ at the beginning and half of the lattice is randomly filled with reactants $B$.

From the MC computer simulations for every set of external parameters (adsorption rate $\zeta$, jump rate $\nu_j$ and interaction energy $e_{j,\nu}$) we obtain the time dependence of concentrations of reactants $A$ and $B$. The PSD analysis is performed on concentration of reactants $B$ as a function of time (see Section 1.4 and [27, 35] for details). Starting from this Chapter the amplitude is used instead of PSD function. The fol-
The following relation holds: \( \text{amplitude} = \sqrt{PSD} \). As a result, both oscillation frequency \( \omega_0 \) and amplitude at this frequency are determined for various diffusion regimes.

(i) First, a standard Lotka-type model is analyzed in terms of the reactant \( A \) adsorption rate \( \zeta \). The oscillatory behavior is found for small \( \zeta \) values, Fig. 2.1. It arises as an interplay between the two processes, which to a first approximation could be considered separately: Firstly, reactants \( A \) are created in lattice and they form statistically a percolating cluster. Secondly, at the same time, reactants \( B \) are mainly desorbed whereas the percolating cluster of \( A \) extends. At some moment the percolating \( A \) cluster meets one of survived reactants \( B \) and thus it is transformed from a cluster of \( A \)'s to a cluster of \( B \)'s. The cycle then repeats once again, reactants \( B \) desorb and reactants \( A \) form a new percolating cluster.

To distinguish between oscillatory and non-oscillatory behavior, we postulate that non-oscillatory regime occurs, when visually one can see no longer oscillations. The corresponding PSD amplitude, which separates these two cases, is \( Amp_{\text{crit}} = 0.007 \) - see a dashed line in Fig. 2.1. The amplitude in non-oscillatory regime (below the dashed line) is approximately seven times less than the maximal amplitude obtained in the oscillatory regime. Besides the shape of concentration oscillations has lost the clear sinusoidal behavior, which now is distorted by a large noise level. The PSD method is so sensitive, that it can determine an oscillation frequency and
amplitude even in the non-oscillatory regime, since the peak at oscillation frequency is distinguishable from the background. The critical adsorption rate for a given lattice size, which separate oscillatory and non-oscillatory regimes, can be found readily from Fig. 2.1 to be $\zeta_{\text{crit}} = 0.075$. The PSD amplitude's excess above $Amp_{\text{crit}}$ observed for $\zeta < \zeta_{\text{crit}}$ reflects an increase of amplitude of concentration oscillations. Further decrease of $\zeta$ is accompanied by a catastrophe in the Lotka-type model: Reactants $A$ are created so slowly that all existing reactants $B$ are desorbed before any autocatalytic reaction begins to take place. Under these conditions the system is poisoned by reactants $A$.

To extend definition of oscillatory and non-oscillatory regions to other lattice sizes one should note that postulated $Amp_{\text{crit}}$ is used instead of signal-to-noise ratio, SNR. Since the noise level in our simulations (lattice size 1024x1024) turns out to be a constant, the $Amp_{\text{crit}}$ is proportional to the critical SNR and we use only the PSD criterium. To relate this criterium to other lattice sizes, it is necessary to introduce the critical SNR, which is independent of the lattice size. The corresponding critical value $\zeta_{\text{crit}}$ depends on lattice size. For larger lattices $\zeta_{\text{crit}}$ value increases, if we use the SNR criterium. Both PSD amplitude and noise level decrease with respect to the results obtained for smaller lattices, but their ratio SNR increases, due to very effective noise level reduction for large lattices. Reactant $A$ poisoning threshold shifts to smaller $\zeta$ values with an increase of lattice size.

(ii) Next, we considered $A$ ($B$) diffusion without energetic interactions between reactants. In a general case of non-oscillating reactions, diffusion can lead to a segregation of reactants [19]. In a case of oscillating reactions one of the important questions is synchronization of local oscillations [9, 10]. In the Lotka-type model the synchronization of oscillations is possible even without diffusion of reactants, therefore the role of diffusion is not so obvious.

We have observed that diffusion of reactants decreases the PSD amplitude of oscillations. Besides, reactant $B$ diffusion is more effective in suppressing concentration oscillations than that of reactants $A$, see Fig. 2.2. Mobile reactants $A$ form clusters thus screening the inner reactants $A$ and preventing them from moving. Only surface reactants can diffuse, which makes reactant $A$ diffusion less effective in damping oscillations. The frequency of oscillations in this case is only slightly affected by mobile $A$, due to already discussed screening effect. In its turn, reactants $B$ have more empty neighbor positions due to a random $B$ desorption, Eq. (1.23). This makes reactant $B$ diffusion more effective in the damping oscillatory behavior. The frequency of oscillations increases with an increase of jump rate, Fig. 2.2. It
reflects the fact, that, e.g., mobile reactants $B$ find existing clusters of reactants $A$ in a shorter time, which determines the higher oscillation frequency. Besides if some reactant $B$ reaches a cluster of $A$ quicker, the cluster of $A$ does not have enough time to grow to a percolating size. As a result, we observe desynchronization of oscillations when the system splits into autonomously oscillating regions with different phases. This situation is similar to the case of the standard Lotka-type model without diffusion but at large parameter $\zeta$ values, Fig. 2.1.

As it was shown, the reactant diffusion modifies the amplitude of oscillations, which in turn affects the critical adsorption rate $\zeta_{\text{crit}}$ dividing oscillatory and non-oscillatory regions. The diffusion of $B$ suppresses the oscillations and thereby decreases the $\zeta_{\text{crit}}$ value in a larger extent than diffusion of $A$, Fig. 2.3, due to already discussed reactant $A$ screening effect. The dependence of critical adsorption rate on diffusion is nonlinear, e.g., in order to decrease the $\zeta_{\text{crit}}$ by $\approx 20\%$ one needs to increase the jump rate $\nu_A$ from 0 to 1 s$^{-1}$. Further to get the same decrease, one needs to change $\nu_A$ from 1 to 3 s$^{-1}$. The reactant $A$ poisoning region below the dashed lines, see Fig. 2.3, is defined as follows: The system is poisoned at a value $\zeta$ if the poisoning occurs during the relaxation time, which for the considered cases is $\approx 100$ s. This definition does not include cases when poisoning may occur.
Figure 2.3: The critical adsorption rate dependence on the jump rate $v_J$ of (i) reactants $A$, $J=A$ (solid squares) and (ii) reactants $B$, $J=B$ (open squares), respectively. The border of the poisoning region is depicted as dashed line with solid (open) circles in the case of reactant $A$ ($B$) diffusion.

at a later time due to statistical fluctuations of reactant $B$ concentration. Thus the oscillatory behavior takes place for $\zeta$ values between the lines with solid (open) squares and solid (open) circles in the case of reactant $A$ ($B$) diffusion, see Fig. 2.3, respectively. Above the lines with squares (solid and open) the amplitude of oscillations is smaller than $\zeta_{\text{crit}}$ and thus this is non-oscillatory region, according to our postulate. Below the lines with circles (solid and open) the reactant $A$ poisoning occurs.

(iii) Lastly, the energetic interaction of reactants can considerably affect the oscillatory behavior. For example, an attraction between reactants promotes the formation of larger clusters. We consider the interaction between reactants only in NN sites, which determines the finite impact of interaction. For example, one could chose the interaction energy to be very large, but due to a short-range interaction, the effect will be still limited.

Let us now consider several limiting cases of energetic interactions. In a standard model the energetic interaction of reactants is taken into account only through diffusion of reactants, which is governed by three NN interaction energies: $e_{AA}$, $e_{AB}$ and $e_{BB}$. In the limiting case, when one type of reactants is immobile, e.g., reactants $A$,
Figure 2.4: The amplitude (squares) and frequency (circles) dependence on the dimensionless energetic interaction $e_{BB}$ between similar reactants $BB$. There are no interactions between $AA$ and $AB$: $e_{AA} = e_{AB} = 0$. Parameters $\nu_B = 0.10$ s$^{-1}$ and $\zeta = 0.065$.

the energetic parameter $e_{AA}$ plays no role. Thus, we obtain a two-parameter model, where diffusion is governed only by $e_{AB}$ and $e_{BB}$. Further, one can study separately the impact of each of these energetic parameters. In more complex situations when both energetic parameters are non-zero, usually some interference of corresponding limiting cases occurs.

First, let us consider the interaction effects in the case of mobile reactants $B$ and immobile $A$. Mutual attraction between similar reactants $B$ ($e_{BB} < 0$) increases the amplitude of oscillations, see Fig. 2.4. This leads to a formation of clusters of $B$’s, which reduces the reactivity of a single reactant $B$. This allows more reactants $A$ to be accumulated in the system during an oscillation period and results in an increase of amplitude in Fig. 2.4. Repulsion between reactants $B$ ($e_{BB} > 0$) promotes dissolving of clusters of $B$’s. It makes every single reactant $B$ to be even more effective in autocatalysis, Eq. (1.23). The frequency of oscillations decreases/increases slightly for $e_{BB} < 0$ and $e_{BB} > 0$, respectively. This reflects the fact that for attracting/repelling reactants $B$ it takes longer/shorter time to find a percolating cluster of $A$. The variation of amplitude with the energetic interaction saturates already at $|e_{BB}| > 2$, due to a short-range interaction nature used in our model.

Secondly, let us consider now the case of mobile reactants $B$ with interaction
Figure 2.5: The amplitude (squares) and frequency (circles) dependence on the dimensionless energetic interaction $e_{AB}$ between dissimilar reactants $AB$. There are no interactions between similar reactants, $e_{AA} = e_{BB} = 0$. Parameters $\nu_B = 0.10$ s$^{-1}$ and $\zeta = 0.065$.

between dissimilar reactants $A$ and $B$. Repulsion between reactants $A$ and $B$, $e_{AB} > 0$, makes it harder for $B$ to make a jump to an empty position, which has a reactant $A$ in its nearest neighborhood. It promotes formation of large clusters of $A$'s, which is reflected in an increase of PSD amplitude, Fig. 2.5. Oscillation frequency decreases slightly thus indicating that the time needed for a creation of percolating cluster of $A$ has increased too. Contrary, an attraction between reactants $A$ and $B$, $e_{AB} < 0$, leads to a decrease of the PSD amplitude, see Fig. 2.5. The period of oscillations is slightly decreased, which implies that mobile $B$ finds quicker clusters of $A$. This prevents a creation of large clusters of $A$'s and thus the PSD amplitude decreases.

The large amplitude dispersion observed in Fig. 2.5 is due to the following reasons. To reduce the simulation time, we have assumed that concentration oscillations have no memory effect. Thus, we used a single long simulation run, i.e., we neglected the relaxation time only once. We considered various parts from a simulation as independent simulations, in order to get an average of PSD amplitude. This method works fine in many cases. However, for the case of attraction between $AB$ the system obviously has memory effects. We have chosen this method as a compromise between the accuracy of the results and large simulation time.

Thirdly, we consider now the case when reactants $A$ are mobile but $B$ are immo-
Figure 2.6: The amplitude (squares) and frequency (circles) dependence on the dimensionless energetic interaction $e_{AB}$ between dissimilar reactants $AB$. There are no interactions between similar reactants: $e_{AA} = e_{BB} = 0$. Parameters $\nu_A = 0.14$ s$^{-1}$ and $\zeta = 0.065$.

Bile. An incorporation of interaction between reactants $A$ and $B$ gives results similar to the case of mobile reactants $B$, Fig. 2.6. Repulsion between reactants $A$ and $B$ allows accumulation of more reactants $A$ per period, which increases the amplitude. Contrary to the mobile $B$ case, the frequency of oscillations is not changed at all.

Fourthly, an interesting case occurs if only reactants $A$ are mobile and we consider the energetic interaction only between $AA$, Fig. 2.7. Since the Lotka-type model is asymmetric with respect to $A$ and $B$ reactants, this behavior differs from the case of interacting and mobile reactants $B$. Now, if we consider an attraction between reactants $AA$ ($e_{AA} < 0$), the percolating cluster of $A$’s is created quicker than in the non-interacting case, Fig. 2.7. An attraction between reactants $A$ ensures the formation of connected $A$ cluster with smaller $C_A(t)$ concentration, see Figs. 2.8 and 2.9-c). This process occurs quicker and, as a result, the amplitude and the period of oscillations decrease (the frequency increases), as observed from simulations in Fig. 2.7. In the case of repulsion between reactants $AA$, the critical concentration of reactants $A$ has to be larger, in order to create a percolating cluster of $A$’s, see Figs. 2.10 and 2.11-c). In the later case reactants $A$, which sit on the surfaces of clusters, repel from reactants $A$ in their NN positions. Thus, a loose structure is formed, which can accumulate additional reactants $A$, compare Figs. 2.9 and 2.11.
Figure 2.7: The amplitude (squares) and frequency (circles) dependence on the dimensionless energetic interaction $e_{AA}$ between similar reactants $AA$. There are no interactions between $AB$ and $BB$: $e_{AB} = e_{BB} = 0$. Parameters $\nu_A = 0.14 \text{ s}^{-1}$ and $\zeta = 0.065$.

Figure 2.8: The concentrations of reactants $A$ (thin line) and $B$ (thick line). Snapshots of the lattice are taken at the points marked by letters. Parameters $\zeta = 0.065$, $\nu_A = 0.14 \text{ (s}^{-1})$ and $e_{AA} = -2$. 
Figure 2.9: The snapshots of lattice during oscillation period. Reactants $A$ are to the left, reactants $B$ - to the right. Shown are $256 \times 256$ region of $1024 \times 1024$ lattice. Parameters $\zeta = 0.065$, $\nu_A = 0.14$ (s$^{-1}$) and $\epsilon_{AA} = -2$. 
Figure 2.10: The concentrations of reactants $A$ (thin line) and $B$ (thick line). Snapshots of the lattice are taken at the points marked by letters. Parameters $\zeta = 0.065$, $\nu_A = 0.14 \text{ (s}^{-1})$ and $e_{AA} = 2$.

a) and b) and corresponding concentrations Figs. 2.8 and 2.10. This process is more time-consuming which is well seen from a decrease of the frequency for $e_{AA} > 0$, see Fig. 2.7. In this case, if a cluster of $A$ is formed in the time interval between (a) and (b), see Fig. 2.10, of each period, it has a small size. And if it is transformed into the state $B$, it changes no global state of the lattice. In its turn, when the percolating cluster of $A$ is transformed into $B$, it change the state of all lattice from $A$ to $B$, Fig. 2.11-d).

2.5 Conclusions

It is well known that the standard Lotka-type model has a self-sustained oscillatory behavior [12]. Therefore, we were able to expand this standard model by an incorporation of diffusion of reactants and to analyze the impact of diffusion on the temporal structures. Since diffusion is a reversible process, which leads the system to equilibrium, we introduced the energetic (and temperature) dependence into the model. In Appendix A a detailed description of this procedure is given, which is not unique, unless we define the standard model.

Usually diffusion gives rise to the spatiotemporal structures, like running waves or
Figure 2.11: The snapshots of lattice during oscillation period. Reactants $A$ are to the left, reactants $B$ - to the right. Shown are $256 \times 256$ region of $1024 \times 1024$ lattice. Parameters $\zeta = 0.065$, $\nu_A = 0.14 \text{ (s}^{-1})$ and $c_{AA} = 2$. 
spiral. In our computer simulations the spatial structures were not found, because of a peculiarity of the Lotka-type model. Namely, an infinite reaction rate $A + B \to 2B$ determines, that configurations with reactants $A$ and $B$ in the NN sites do not exist. In other words, the front of reaction goes with an infinite speed and all clusters of $A$'s are transformed into clusters of $B$'s instantly, without any reaction front.

We have observed that diffusion results only in desynchronization of concentration oscillations. The amplitude of oscillations decreases with an increase of diffusion. Particularly, diffusion of reactants $A$ is less effective in destroying the oscillatory behavior, because reactants $A$ form clusters and only a small portion of reactants at cluster surfaces can diffuse, whereas most of inner reactants $A$ are screened. In contrast, clusters of reactants $B$ are more loose due to reactant $B$ desorption. Thus, reactants $B$ turn out to be more mobile, which results in more pronounced mobility effects.

Lastly, a nontrivial behavior has been observed in the case of mobile and interacting reactants $A$. For example, repulsion between reactants $AA$ leads to the reactant distribution, which accumulates more reactants $A$ before the percolation cluster of reactants $A$ occurs. This results in an increase of the amplitude and decrease of the oscillation frequency.

To understand the impact of diffusion, we used here a simple mathematical model. More detailed models could better reproduce experimentally observed structures. However, the understanding of the mechanisms of these phenomena is often problematic or even impossible. Therefore, models such as the Lotka-type are of great importance, since they allow to study and understand individual processes, e.g., diffusion or energetic interaction, independently of other factors.
Chapter 3

The $A + B \rightarrow 0$ model with surface reconstruction

3.1 Introduction

One of the simplest bimolecular reaction $A + B \rightarrow 0$ has a long history. It received a considerable attention, see, e.g., review papers [36, 37], when the Frenkel defect accumulation in solids under irradiation was observed experimentally [38, 39]. In this case the model allows the following interpretation: Radiation produces two types of complementary defects - interstitial atoms $A$ and vacancies $B$. When defects $A$ and $B$ are within the recombination radius, the perfect crystalline structure is restored. The two characteristics of the model are of particular interest[19]: Firstly, it is defect decay law without irradiation and kinetics of defect accumulation and corresponding saturation concentration if such exists under irradiation. Secondly, it is spatial distribution of reactants.

The spatial structure formation in $A + B \rightarrow 0$ reaction takes place even without particle source. In this case it is assumed that initially a certain concentration of reactants is distributed in the system and then the reaction (and diffusion) is turned on. It was demonstrated first analytically by Zeldovich and Ovchinnikov [40] and then by Toussaint and Wilczek [41] using computer simulations, that dissimilar reactant segregation and similar reactant aggregation take place for ”symmetric” diffusion, when both $A$ and $B$ are mobile. Immobile reactants show aggregation if there exist a long range tunneling recombination, which depend exponentially on the distance between reactants [42, 43]. It was pointed out that reactant density
fluctuations leads to deviations from decay law predicted by standard chemical kinetics [41, 44]. So in the limit of large times $t \to \infty$ the standard decay law of reactant concentrations $n(t) \propto t^{-1}$ (both concentrations are equal) is replaced by a slower decay $n(t) \propto (Dt)^{-3/4}$, where $D$ is diffusion coefficient [19], due to reactant screening effect. Several analytical methods were examined in [19] to describe the decay law in case of equal reactant concentrations. The Kirkwood superposition approximation turns out to be the best estimate for one and two dimensional systems with and without reactant diffusion.

The continuous irradiation is implemented in the $A + B \to 0$ model as a permanent particle source or reversible reaction. In this case reactants $A$ and $B$ are created continuously and randomly in the lattice with equal probability. If creation of one type of reactants, e.g. $A$, prevails, it will lead to extinction of other type, e.g. $B$. As a result the system arrives at the state when there are only reactants $A$, which is known as $A$ poisoning. The model with immobile reactants and permanent particle source was considered, e.g., in Refs. [45, 46, 47, 48] by the means of computer simulations. The analytical calculation were made, in order to estimate the saturation concentration of immobile defects (see [48] and references therein) and to determine the accumulation kinetics of mobile and immobile defects [19]. The predictions of analytical methods for immobile reactants with irradiation were tested by computer simulations [42, 43, 49, 50, 51, 52].

The theoretical studies of defect accumulation kinetics in the $A + B \to 0$ model with irradiation shows the infinite power and logarithmic growth in one and two dimensional systems [53], respectively. The real saturation of reactant concentrations is predicted for three dimensional systems. The analysis of correlation functions shows the formation of spatial-structures, e.g., defect segregation, but temporal-structures, like concentration oscillations, were not detected.

In the present Chapter 3 the two dimensional $A + B \to 0$ model is extended to the case of surface reconstruction. Formally, the model turns out to be similar to the ZGB model (see Appendix D) with surface reconstruction. As it is known adsorption of molecules on reconstructed surfaces can promote the surface backward reconstruction. In its turn, the lack of the molecules results in a surface reconstruction. This is an essential step in many catalytic surface reactions, which leads to spatiotemporal structures. It is demonstrated in [10, 54] that extension of the ZGB model to include the surface reconstruction gives rise to oscillatory behavior.

The difference between the ZGB and the $A + B \to 0$ models is the following: the first treats adsorption of a dimer molecule, while the last one considers adsorption
of a monomer. The role of dimer adsorption in the ZGB model is questioned. The qualitative behavior of the system often turns out to be independent of particular details of reaction. The properties of the extended model are analyzed in the limit of fast reactant diffusion.

Two methods are used to analyse the generalized model. The first is MF approximation used as cutoff for the infinite chain of nonlinear differential equations obtained from master equation. The second method is MC computer simulations (see, e.g., [26]) which is extensively applied as an independent method and as a test for several analytical approximations.

Chapter 3 is organized in the following way. The generalized \( A + B \rightarrow 0 \) model is introduced in the next Section 3.2. MF approximation is examined in the Section 3.3. The Sections 3.4 and 3.5 presents the results of MC computer simulations and discussion, respectively. The conclusions are summarized in the Section 3.6.

### 3.2 Mathematical model

One of the simplest monomer-monomer annihilation reaction is \( A + B \rightarrow 0 \). The standard rules for this surface reaction are: Adsorption of reactants \( A \) (\( B \)) in empty sites \( O \) with the rate \( \zeta \) (\( [1 - \zeta] \)), Eqs. (3.1) and (3.2), respectively,

\[
A \text{ (gas)} + O \xrightarrow{\zeta} A \text{ (ads)}, \tag{3.1}
\]

\[
B \text{ (gas)} + O \xrightarrow{[1 - \zeta]} B \text{ (ads)}, \tag{3.2}
\]

\[
A \text{ (ads)} + B \text{ (ads)} \xrightarrow{R} O. \tag{3.3}
\]

Annihilation reaction, Eq. (3.3), of reactant \( A \) and \( B \) takes place with rate \( R \) only for a pair of \( A \) and \( B \), which are NNs. The annihilating pair is chosen randomly, when the same reactant \( A \) (\( B \)) has several \( B \) (\( A \)) as NNs.

To complement these basic rules with new reactions, one has to relate the standard model with some real process. The new reaction steps then arise, naturally reflecting experimentally detected microscopical processes. Here the \( A + B \rightarrow 0 \) model is used as a simplified description of the CO catalytic oxidation on Pt surfaces. The model is a simplification of the ZGB model, where reactants \( A \) stay for CO molecules and \( B \) for O atoms. The reaction between \( A \) and \( B \) occurs only on the surface of catalyst since a CO cannot brake the chemical bonding of \( O_2 \) molecule in the gas phase. In the \( A + B \rightarrow 0 \) model the geometrical aspect of oxygen molecule chemisorption into two sites is neglected.
It is detected experimentally that the following processes are significant for the CO catalytic oxidation reaction. Firstly, diffusion of CO molecules is known to be a fast and important process, which can lead to a formation of spatiotemporal structures [1]. Secondly, it is the surface reconstruction, which is a driving force of oscillatory behavior. It is shown that in the absence of adsorbates only the reconstructed surfaces of Pt(100) and Pt(110) are stable [1]. On such reconstructed surfaces adsorption of oxygen is hindered. Adsorbed CO molecules is known to change the surface energy, which results in surface backward reconstruction (non-reconstructed state) which takes place above some critical CO adsorbate concentration. It is known that $O_2$ adsorption on non-reconstructed surfaces is effective. In this regime the CO oxidation takes place. When the amount of CO becomes less than critical, the surface reconstruction takes place and adsorption of $O_2$ becomes hindered.

Let us generalize the standard model to include these effects. The first, diffusion of both reactants $A$ and $B$ is assumed as jumps to the NN empty sites with a jump rate $\nu_X$ (where $X \in \{A, B\}$) Eqs. (3.4) and (3.5)

\[
A(ads) + O \xrightarrow{\nu_A} O + A(ads), \quad (3.4)
\]

\[
B(ads) + O \xrightarrow{\nu_B} O + B(ads). \quad (3.5)
\]

Secondly, two different surfaces (phases) denoted hereafter as $\alpha$ and $\beta$ are introduced. The phase $\alpha$ stays for reconstructed phase and $\beta$ for non-reconstructed, respectively. This allows both (i) to model some processes (such as adsorption, diffusion) to proceed differently in each phase and (ii) implement the surface reconstruction mechanism, which transfers one phase into another.

i) Reflecting the experimentally detected differences between CO and $O_2$ adsorption, it is assumed that reactant $A$ and $B$ adsorption proceeds differently on each phase. Adsorption of reactants $A$ ($O_2$) allowed in all empty lattice sites irrespective of phase, see Eq. (3.1), which is valid for both $\alpha$ and $\beta$ phases

\[
A(gas) + O^\chi \xrightarrow{\zeta} A^\chi(ads), \quad \text{where} \quad \chi = \alpha, \beta. \quad (3.6)
\]

The adsorption of reactants $B$ ($O_2$) with probability $1 - \zeta$, see Eq. (3.2), is allowed only on the $\beta$ phase

\[
B(gas) + O^\beta \frac{1}{1-\zeta} \xrightarrow{\zeta} B^\beta(ads). \quad (3.7)
\]

Adsorption of $B$ on the $\alpha$ phase is determined by the law

\[
B(gas) + O^\alpha \frac{s(1-\zeta)}{(1-\zeta)} \xrightarrow{\zeta} B^\alpha(ads), \quad (3.8)
\]
where the sticking coefficient $s$ is chosen in the interval between 0 and 1. The limiting case of $s = 0$ corresponds to reactant $B$ adsorption exclusively on $\beta$ phase. In its turn, the opposite limit $s = 1$ leads to uniform reactant $B$ adsorption on the lattice irrespective of phase.

The different values of parameter $s$ correspond to different crystallographic orientations of a crystal. To this end, let us consider the $O_2$ adsorption on Pt surface in more details. On Pt(100) surface the ratio of $O_2$ adsorption on non-reconstructed ($\beta$ phase) vs reconstructed phase ($\alpha$ phase) is $\sim 10^{-3}$ while on Pt(110) this ratio is $\sim 1$, see [1]. It means that on Pt(100) surface there are practically no $O_2$ ($B$) adsorption on a reconstructed phase ($s = 0$) while on Pt(110) surface $O_2$ can be adsorbed on a reconstructed surface ($s > 0$).

Besides the reactant adsorption, the diffusion of reactants depends on the phase properties as well. It is assumed that reconstructed and non-reconstructed phases do not change the diffusion coefficient significantly and it remains the same in each phase. In its turn, the experimentally detected different reactant concentrations on different phases [1, 55, 56, 57, 58] can be explained by asymmetric diffusion when reactants cross the phase border [59, 60]. For example, jumps from $\alpha$ to $\beta$ phase are promoted, while the back jumps are suppressed. This will result in reactant accumulation in $\beta$ phase. Let us define the asymmetric jump rate $\kappa$ as follows

$$\nu_{\alpha\beta} = \nu (1 + \kappa),$$  \hspace{1cm} \text{(3.9)}

$$\nu_{\beta\alpha} = \nu (1 - \kappa),$$  \hspace{1cm} \text{(3.10)}

where $\nu_{\alpha\beta}$ and $\nu_{\beta\alpha}$ are jump rates from $\alpha$ to $\beta$ and $\beta$ to $\alpha$ phases, respectively. Mathematically parameter $\kappa$ changes in the interval $[-1, 1]$, while the physically interesting case is $[0, 1]$. The physical basis for asymmetric diffusion is a higher CO adsorption energy on the $\beta$ phase [55, 56], which leads to promoted CO diffusion in direction from $\alpha$ to $\beta$ phase.

One can express the asymmetric jump rate from Eqs. (3.9) and (3.10) as a dimensionless parameter

$$\kappa = \frac{\nu_{\alpha\beta} - \nu_{\beta\alpha}}{\nu_{\alpha\beta} + \nu_{\beta\alpha}},$$  \hspace{1cm} \text{(3.11)}

ii) It is known that surface reconstruction mechanism on Pt monocrystals is associated with adsorbed CO molecules [1]. Therefore the following reconstruction model was proposed [10]: Let us assume the phase boundary, i.e., two NN sites which are in state $\alpha\beta$. If reactants $A$ (CO) is present on one of these sites, it induces the
\( \alpha \) phase growth with the rate \( V \). The eventual surface state then reads as \( \alpha \alpha \), Eqs. (3.12) and (3.13),

\[
A^\alpha + X^\beta \xrightarrow{V} A^\alpha + X^\alpha, \quad (3.12)
\]
\[
A^\beta + X^\alpha \xrightarrow{V} A^\alpha + X^\alpha, \quad (3.13)
\]

where \( X \in \{0, A, B\} \). In its turn, when there are no reactant \( A \) on the phase boundary, the \( \beta \) phase grows with the rate \( V \). In this case the eventual state is \( \beta \beta \), Eq. (3.14),

\[
X^\alpha + Y^\beta \xrightarrow{V} X^\beta + Y^\beta, \quad (3.14)
\]

where \( X, Y \in \{0, B\} \).

The model allows extension to the case of spontaneous phase nucleation as well. It is assumed that a single surface site can change its phase spontaneously. This process is independent on the phase of the neighboring sites and reactant adsorbed on the site, Eqs. (3.15) and (3.16),

\[
X^\alpha \xrightarrow{\gamma} X^\beta, \quad (3.15)
\]
\[
X^\beta \xrightarrow{\gamma} X^\alpha, \quad (3.16)
\]

where \( X \in \{0, A, B\} \). This process is modeled as a weak noise, which produces phase defects. Its rate \( \gamma \) is several magnitudes of order less than rates of other processes.

### 3.3 Mean-Field formalism

Let us consider the generalized \( A + B \rightarrow 0 \) model with surface reconstruction. The corresponding MF equations for the generalized model, Eqs. (3.1) to (3.14), with
parameters \( s = 0 \) and \( \kappa = 0 \) follow from Eqs. (B.14) and (B.15)

\[
\frac{d}{dt} c_A^\alpha = \zeta c_0^\alpha - R c_A^\alpha (c_B^\alpha + c_B^\beta) - V c_A^\alpha (c_0^\alpha + c_A^\beta + c_B^\beta) + \nu_A (c_0^\alpha c_A^\beta - c_A^\alpha c_0^\beta),
\]

(3.17)

\[
\frac{d}{dt} c_A^\beta = \zeta c_0^\beta - R c_A^\beta (c_B^\alpha + c_B^\beta) + V c_A^\alpha (c_0^\alpha + c_A^\beta + c_B^\beta) - \nu_A (c_0^\alpha c_A^\beta - c_A^\alpha c_0^\beta),
\]

(3.18)

\[
\frac{d}{dt} c_B^\alpha = -R c_A^\alpha (c_0^\alpha + c_A^\beta) - V c_B^\alpha (c_0^\alpha + c_B^\beta) + \nu_B (c_0^\alpha c_B^\beta - c_B^\alpha c_0^\beta),
\]

(3.19)

\[
\frac{d}{dt} c_B^\beta = (1 - \zeta) c_0^\beta - R c_B^\beta (c_A^\alpha + c_B^\beta) + V c_B^\beta (c_0^\alpha + c_B^\beta) - \nu_B (c_0^\alpha c_B^\beta - c_B^\alpha c_0^\beta),
\]

(3.20)

\[
\frac{d}{dt} c_0^\alpha = R (2 c_A^\alpha c_B^\alpha + c_A^\beta c_B^\alpha + c_B^\alpha c_A^\beta) + V c_0^\alpha (c_A^\beta - c_B^\beta) - \nu_A (c_0^\alpha c_A^\beta - c_A^\alpha c_0^\beta) + \nu_B (c_0^\alpha c_B^\beta - c_B^\alpha c_0^\beta),
\]

(3.21)

\[
1 = c_0^\alpha + c_A^\alpha + c_A^\beta + c_0^\beta + c_B^\beta,
\]

(3.22)

where \( c_X^\chi \) is the concentration of reactants \( X \) in \( \chi \)-phase. All concentrations \( c_X^\chi \) depend on time which is omitted in abbreviation. The last equation expresses the normalization condition for concentrations.

The set of Eqs. (3.17) to (3.22) can be solved numerically. The solutions show the oscillatory behavior for \( \zeta < 0.5 \) values, irrespectively of the type of mobile reactants. In the interval \( 0.5 \leq \zeta \leq 0.501 \) the solutions are constant in time and depend linearly on \( \zeta \) as follows: Concentration of \( A \) increase from 0.86 to 1. Concentration of \( B \) decrease from \( 8 \times 10^{-1} \) to 0, but \( \Theta_B = 1 \). The solutions are independent on \( \zeta \) for \( \zeta > 0.501 \) and they are \( C_A = 1 \), \( C_B = 0 \) and \( \Theta_B = 1 \).

As an example of oscillatory behavior, the two limiting cases are considered. Firstly, the reactants \( A \) and \( B \) are mobile and immobile, respectively, Fig. 3.1. The oscillation amplitude of reactants \( A \) increase slightly with \( \zeta \), but its average value remains constant. The amplitude of \( B \) oscillations increases linearly with \( \zeta \). Oscillations of \( \Theta_B \) show a complex behavior, the amplitude of oscillations and the average value increase with \( \zeta \).

The relations among concentrations are easy to interpret. Let us start with a situation, when concentration of \( A \) has a minimum. It means that amount of \( \beta \) phase decreases, since there are no \( A \) to maintain \( \beta \) phase. One can see, that minimums of \( C_A \) are followed by minimums of \( \Theta_B \). The minimal area of \( \beta \) phase determines the minimal adsorption of \( B \), since \( B \) can be adsorbed exclusively on \( \beta \) phase. Two minimums of \( C_B \) and \( \Theta_B \) coincide in time. In this situation adsorption of \( A \) prevails and concentration of \( A \) increases. The \( \beta \) phase increases with an increase of \( C_A \),
Figure 3.1: Concentrations of reactants $A$ (line), $B$ (short dashed) and $\Theta_\beta$ (long dashed) lines. The adsorption rate $\zeta$ is $0.15$ a), $0.30$ b), $0.45$ c). Reactants $A$ are mobile, $\nu_A = 100$ (s$^{-1}$), and $V = 1$ (s$^{-1}$), $R = 100$ (s$^{-1}$). Reactants $B$ are immobile $\nu_B = 0$. MF approximation.
which in its turn, enhances the adsorption of $B$. Adsorption of reactants $B$ first stops the growth of $C_A$ and then ensures its decrease due to reaction. At that stage there is still a large $\beta$ phase area and adsorption of $B$ continues, which corresponds to the maximum of $C_B$ and minimum of $C_A$. This process ends, when the lack of $A$ decreases the area of $\beta$ phase and the period starts from the beginning. The adsorption rate $\zeta$ determines the speed of $A$ adsorption. The larger $\zeta$, the larger on the average is the area of $\beta$ phase, which allows to adsorb more $B$.

Secondly, let us consider the case when both reactants $A$ and $B$ are mobile, Fig. 3.2. In this case the oscillations of concentrations have reached the maximally possible amplitude, which shows almost no dependence on the adsorption rate $\zeta$. In its turn, the period of oscillations depends nonlinearly on $\zeta$; e.g., for $\zeta = 0.15$ the period is large, it decreases for $\zeta = 0.30$, but then increases again for $\zeta = 0.45$, see Fig. 3.2. In this case the interpretation of the origin of oscillations is similar to the previous case. There is a difference as well that the adsorption of $B$ is not limited by the amount of $\beta$ phase. The $\beta$ phase acts as a gate, which allows adsorption of $B$. Once $B$ reactants are adsorbed, they can freely diffuse, e.g., to $\alpha$ phase. Thus sites of $\beta$ phase are cleaned and new $B$ can be adsorbed. Once $B$ are not limited by the area of $\beta$ phase, they can both: (i) be adsorbed in a larger amount and (ii) find effectively reactants $A$ on all lattice, which is reflected by a decreased $C_A$ global concentration during the oscillation period.

The limit of fast reactant $A$ and $B$ diffusion allows us to perform the analytical analysis of stability. To this end, let us introduce the global densities of reactants $A$ - $C_A$, reactants $B$ - $C_B$ and $\beta$ phase - $\Theta_\beta$ and functions $\psi$ and $\varphi$, which reflect the fraction of reactants $A$ and $B$ in $\beta$ phase, respectively,

$$
c^\alpha_A = (1 - \psi) C_A, \quad (3.23) \\
c^\beta_A = \psi C_A, \quad (3.24) \\
c^\alpha_B = (1 - \varphi) C_B, \quad (3.25) \\
c^\beta_B = \varphi C_B, \quad (3.26) \\
c^\beta_\Theta = \Theta_\beta - \psi C_A - \varphi C_B, \quad (3.27)
$$

where the normalization condition, Eq. (3.22), is used. Applying the coordinate transformations, Eqs. (3.23) to (3.27), to the system of Eqs. (3.17) to (3.22), one
Figure 3.2: Concentrations of reactants $A$ (line), $B$ (short dashed) and $\Theta_\beta$ (long dashed) lines. The adsorption rate $\zeta$ is 0.15 a), 0.30 b), 0.45 c). Reactants $A$ and $B$ are mobile, $\nu_A = \nu_B = 100$ (s$^{-1}$), and $V = 1$ (s$^{-1}$), $R = 100$ (s$^{-1}$). MF approximation.
readily obtains MF equations for global concentrations and their fractions in β phase

\[
\frac{d}{dt} C_A = \zeta (1 - C_A - C_B) - RC_A C_B, \quad (3.28)
\]

\[
C_A \frac{d}{dt} \psi = \zeta (\Theta_\beta - \psi + C_B (\psi - \varphi)) + V C_A \Theta_\beta (1 - \psi) \\
\quad + \nu_A C_A (\Theta_\beta - \psi + C_B (\psi - \varphi)), \quad (3.29)
\]

\[
\frac{d}{dt} C_B = (1 - \zeta) (\Theta_\beta - \psi C_A - \varphi C_B) - RC_A C_B, \quad (3.30)
\]

\[
C_B \frac{d}{dt} \varphi = (1 - \zeta) (\Theta_\beta - \psi C_A - \varphi C_B) (1 - \varphi) \\
\quad - V C_B (\varphi (1 - \Theta_\beta) + \varphi C_A (2\psi - 1) - \psi C_A) \\
\quad + \nu_B C_B (\Theta_\beta - \varphi - C_A (\psi - \varphi)), \quad (3.31)
\]

\[
\frac{d}{dt} \Theta_\beta = V (2\Theta_\beta C_A (1 - 2\psi) + 2\psi C_A (1 - C_A (1 - \psi)) - \Theta_\beta (1 - \Theta_\beta)). \quad (3.32)
\]

In the limit of a fast reactant A and B diffusion (\(\nu_X \to \infty\), where \(X \in \{A, B\}\)) the Eqs. (3.28) to (3.32) can be rewritten as

\[
\frac{d}{dt} C_A = \zeta (1 - C_A - C_B) - RC_A C_B, \quad (3.33)
\]

\[
0 = \Theta_\beta - \psi + C_B [\psi - \varphi], \quad (3.34)
\]

\[
\frac{d}{dt} C_B = (1 - \zeta) (\Theta_\beta - \psi C_A - \varphi C_B) - RC_A C_B, \quad (3.35)
\]

\[
0 = \Theta_\beta - \varphi - C_A [\psi - \varphi], \quad (3.36)
\]

\[
\frac{d}{dt} \Theta_\beta = V (2\Theta_\beta C_A (1 - 2\psi) + 2\psi C_A (1 - C_A [1 - \psi]) \\
\quad - \Theta_\beta [1 - \Theta_\beta]). \quad (3.37)
\]

The solution of Eqs. (3.34) and (3.36) is trivial, \(\Theta_\beta = \psi = \varphi\). Taking the trivial solution into account, the system of Eqs. (3.33) to (3.37) can be reduced to three equations

\[
\frac{d}{dt} C_A = \zeta (1 - C_A - C_B) - RC_A C_B, \quad (3.38)
\]

\[
\frac{d}{dt} C_B = \Theta_\beta (1 - \zeta) (1 - C_A - C_B) - RC_A C_B, \quad (3.39)
\]

\[
\frac{d}{dt} \Theta_\beta = V \Theta_\beta (1 - \Theta_\beta) [1 - 2 (1 - C_A)^2]. \quad (3.40)
\]

The system of Eqs. (3.38) to (3.40) can be analyzed by means of the linear stability method (see Appendix C). According to the standard procedure, one finds the corresponding singular points:

59
1. \[ C_A^0 = 1 - \frac{1}{\sqrt{2}}, \quad \frac{C_B^0}{R} = \frac{R \zeta (1 + \sqrt{2}) + \zeta^2 \sqrt{2}}{(R + 2 \zeta)^2 - 2 \zeta^2}, \quad \Theta^0_\beta = \frac{\zeta}{1 - \zeta}, \quad (3.41) \]
2. \[ C_A^0 = 0, \quad C_B^0 = 1, \quad \Theta^0_\beta = 0, \quad (3.42) \]
3. \[ C_A^0 = 0, \quad C_B^0 = 1, \quad \Theta^0_\beta = 1, \quad (3.43) \]
4. \[ C_A^0 = 1, \quad C_B^0 = 0, \quad \Theta^0_\beta = 0, \quad (3.44) \]
5. \[ C_A^0 = 1, \quad C_B^0 = 0, \quad \Theta^0_\beta = 1. \quad (3.45) \]

To check the stability of the singular points, Eqs. (3.38) to (3.40) need to be linearized, see Eq. (C.4) and (C.5),
\[
\frac{d}{dt} C_A(t) = - (\zeta + R C_B^0) C_A(t) - (\zeta + R C_A^0) C_B(t), \quad (3.46) \]
\[
\frac{d}{dt} C_B(t) = - \left[ (1 - \zeta) \Theta^0_\beta + R C_B^0 \right] C_A(t) - \left[ (1 - \zeta) \Theta^0_\beta + R C_A^0 \right] C_B(t) + (1 - \zeta) \left( 1 - C_A^0 - C_B^0 \right) \Theta_\beta(t), \quad (3.47) \]
\[
\frac{d}{dt} \Theta_\beta(t) = 4V \Theta_\beta^0 \left( 1 - \Theta_\beta^0 \right) \left[ 1 - C_A^0 \right] C_A(t) + V \left( 1 - 2 \Theta_\beta^0 \right) \left[ 1 - 2 \left( 1 - C_A^0 \right)^2 \right] \Theta_\beta(t), \quad (3.48) \]
where the time dependence of functions is now explicitly stated and constants \( C_A^0, \)
\( C_B^0 \) and \( \Theta_\beta^0 \) refer to the values of the corresponding singular points. According to
the standard procedure, one can search the unknown functions in the exponential form, Eq. (C.6), thus arriving at Eq. (C.7). In the considered case the characteristic exponents are found as roots of the 3rd order polynomial. The characteristic equation for the first singular point reads as follows
\[
-\lambda^3 - \lambda^2 \left( 2 + 16 \sqrt{2} \right) \frac{R^2 + (22 + 16 \sqrt{2}) R \zeta + (28 + 20 \sqrt{2}) \zeta^2}{(4 + 3 \sqrt{2}) \frac{R + 2 \left( 7 + 5 \sqrt{2} \right) \zeta}{\left( 2 + \sqrt{2} \right) \left( 1 - 2 \zeta \right) \frac{R \zeta}{1 - \zeta}} = 0. \quad (3.49) \]

In the case of large reaction rate \( R \gg 1 \) Eq. (3.49) has a simple solutions
\[
\lambda_1 = - \frac{\sqrt{2}}{2} R + O \left( \frac{1}{R} \right), \quad (3.50) \]
\[
\lambda_{2,3} = \pm \sqrt{\frac{2 \zeta (1 - 2 \zeta)}{1 - \zeta}} + O \left( \frac{1}{R} \right). \quad (3.51) \]

The fast reaction rate limit \( R \to \infty \) and condition \( \zeta < 0.5 \) indicate that the singular
point, Eq. (3.41), is a stable torus \((-, 0, 0\)). The second and third root leads to oscillation frequency, which depends on reactant creation rate \(\zeta\). It is found to be 
\[ \omega_0 = \sqrt{2\zeta(1 - 2\zeta) / (1 - \zeta)} \] and it has a maximum at \(\zeta = 1 - 1 / \sqrt{2} \approx 0.293\). The corresponding maximal frequency \(\omega_{0,\text{max}} = \sqrt{6 - 4\sqrt{2}} \approx 0.59\). For \(\zeta > 0.5\) the roots Eqs. (3.50) and (3.51) are real with different signs \((-, +, +\)), which indicate that the singular point Eq. (3.41) is an unstable point.

One obtains the following characteristic equation for the second singular, point Eq. (3.42)

\[- (1 + \lambda) \left( \lambda^2 + (R + \zeta) \lambda - R\zeta \right) = 0. \tag{3.52} \]

It has the following solutions

\[ \lambda_1 = -1, \tag{3.53} \]

\[ \lambda_{2,3} = -\frac{R + \zeta}{2} \left( 1 \mp \sqrt{1 + \frac{4R\zeta}{(R + \zeta)^2}} \right). \tag{3.54} \]

The characteristic exponent \(\lambda_2\) is positive, which makes the second singular point Eq. (3.42) unstable. In the limit of fast reaction rate \(R \to \infty\), \(\lambda_2 = 0\) and the singular point is a stable limit cycle \((- , 0, -\)), see Appendix C.

The characteristic equation for the third singular point Eq. (3.43) is the following

\[- (-1 + \lambda) \left( \lambda^2 + (R + 1) \lambda + R(1 - 2\zeta) \right) = 0. \tag{3.55} \]

It has the solutions

\[ \lambda_1 = 1, \tag{3.56} \]

\[ \lambda_{2,3} = -\frac{R + 1}{2} \left( 1 \mp \sqrt{1 - \frac{4R(1 - 2\zeta)}{(R + 1)^2}} \right). \tag{3.57} \]

In the limit of fast reaction rate \(R \to \infty\), the characteristic exponents have the following signs: \((+, 0, -\)). The singular point then is classified as a chaotic attractor.

The characteristic equation for the singular point Eq. (3.44) reads as

\[(1 - \lambda) (R + \lambda) (\zeta + \lambda) = 0. \tag{3.58} \]

It indicates that the singular point Eq. (3.44) is unstable since one of the roots

\[ \lambda_1 = 1, \tag{3.59} \]

\[ \lambda_2 = -R, \tag{3.60} \]

\[ \lambda_3 = -\zeta, \tag{3.61} \]

61
is positive.

The fifth singular point Eq. (3.45) leads to a characteristic equation

\[(1 + \lambda) \left( \lambda^2 + (R + 1) \lambda - R(1 - 2\zeta) \right) = 0. \tag{3.62}\]

Equation (3.62) has the solutions

\[\lambda_1 = -1, \tag{3.63}\]

\[\lambda_{2,3} = -\frac{R+1}{2} \left[ 1 + \sqrt{1 + \frac{4R(1-2\zeta)}{(R+1)^2}} \right]. \tag{3.64}\]

In the limit of fast reaction rate \(R \to \infty\), the characteristic exponents have the following signs \((- , 0, -)\). It indicates, that the singular point is a stable limit cycle.

The linear stability analysis predicts the concentration oscillatory behavior for the first singular point Eq. (3.41). The concentration oscillations are observed in numerical solutions Fig. 3.2 as well. Let us study the limit of a fast reactant \(A\) and \(B\) diffusion in more details. It is easy to notice that during oscillation period there is only one type of reactants \(A\) or \(B\) present, see Fig. 3.2, irrespective of \(\zeta\). The more so, each such case of reactants \(A\) and \(B\) can be assumed to exist exclusively on a single phase \(\alpha\) or \(\beta\). These assumptions lead to oscillation period division into four stages. (i) Concentration of \(A\) grows on empty lattice, which is in \(\alpha\) phase. The concentration of reactants \(B\) is small since they cannot be adsorbed. The MF equation for this case follows from Eq. (3.38) with \(C_B(t) \ll C_A(t)\)

\[\frac{d}{dt} C_A(t) = \zeta \left( 1 - C_A(t) \right).\]

Its solution reads

\[C_A(t) = 1 - (1 - C_{A0}) \exp \left(-\zeta t\right),\]

where \(C_{A0}\) is concentration of \(A\) at the beginning of stage (i). The growth follows this rule while it reaches the maximum \(A\) concentration \(C_{A1}\). Reactant \(A\) growth time \(\tau_1\) is obtained from

\[\tau_1 = \frac{1}{\zeta} \ln \frac{1 - C_{A0}}{1 - C_{A1}}. \tag{3.65}\]

The lattice is in \(\beta\) phase in the stage (ii), i.e., \(\Theta = 1\). Reactants \(B\) are adsorbed but their concentration is constant and remains small \(C_B(t) \ll C_A(t)\) while concentration of \(A\) is decreasing due to the annihilation reaction. It follows from Eqs. (3.38)
\[
\frac{d}{dt} C_A(t) = \zeta (1 - C_A(t)) - R C_A(t) C_B(t),
\]
\[
0 = (1 - \zeta) (1 - C_A(t)) - R C_A(t) C_B(t).
\]

From these equations one can exclude \( C_B \) and then find the reactant \( A \) decay law
\[
C_A(t) = 1 - (1 - C_{A1}) \exp \left( \frac{1 - 2\zeta}{1 - C_{A1}} \right),
\]
where \( C_{A1} \) is the maximum \( A \) concentration at the beginning of stage (ii). The decay time \( \tau_2 \) is defined as concentration of \( A \) reaches \( C_{A0} \)
\[
\tau_2 = \frac{1}{1 - 2\zeta} \ln \frac{1 - C_{A0}}{1 - C_{A1}}. \tag{3.66}
\]
During the stages (iii) and (iv) it is assumed that reactant \( A \) concentration \( C_A(t) = C_{A0} \ll C_B(t) \). Reactant \( B \) growth time \( \tau_3 \) in the stage (iii) and decay time \( \tau_4 \) in the stage (iv) is found using similar arguments as in the stages (i) and (ii)
\[
\tau_3 = \frac{1}{1 - 2\zeta} \ln \frac{1 - C_{B0}}{1 - C_{B1}}, \tag{3.67}
\]
\[
\tau_4 = \frac{1}{\zeta} \ln \frac{1 - C_{B0}}{1 - C_{B1}}, \tag{3.68}
\]
where \( C_{B0} \) and \( C_{B1} \) is reactant \( B \) minimum and maximum concentrations, respectively.

The total length of the period \( \tau \) reads as a sum of all four stages
\[
\tau = \tau_1 + \tau_2 + \tau_3 + \tau_4 = \frac{1 - \zeta}{\zeta (1 - 2\zeta)} \ln \frac{(1 - C_{A0})(1 - C_{B0})}{(1 - C_{A1})(1 - C_{B1})}. \tag{3.69}
\]
The extreme period length with respect to the creation rate \( \zeta \) can be found from the condition \( d\tau/d\zeta = 0 \). It leads to the second-order equation
\[
-2\zeta^2 + 4\zeta - 1 = 0, \tag{3.70}
\]
with the following two conditions \( \zeta \neq 0 \) and \( \zeta \neq 1/2 \). One of the roots of Eq. (3.70)
\[
\zeta = 1 - \frac{1}{\sqrt{2}} \tag{3.71}
\]
correspond to an extreme period value while the other root \( \zeta = 1 + 1/\sqrt{2} \) is meaningless in our mathematical model, where \( \zeta \leq 1 \).

63
Let us calculate the \( \frac{d^2\tau}{d\zeta^2} \) to determine the type of extreme point

\[
\frac{d^2\tau}{d\zeta^2} = \left( \frac{2}{\zeta^3} + \frac{8}{(1 - 2\zeta)^3} \right) \ln \frac{(1 - C_{A_0})(1 - C_{B_0})}{(1 - C_{A_1})(1 - C_{B_1})}.
\]

The logarithm is positive since minimal concentration values \( C_{A_0} \) and \( C_{B_0} \) are smaller than maximum values \( C_{A_1} \) and \( C_{B_1} \). The first term in brackets is positive for \( \zeta < 1/2 \) and negative for \( \zeta > 1/2 \). The second derivative \( d^2\tau/d\zeta^2 \) is positive in the interval \( 0 < \zeta < 1/2 \), which indicates that the critical \( \zeta \) corresponds to the minimum oscillation period. The critical \( \zeta \) value coincides with the predictions of linear stability analysis for the singular point, Eq. (3.41).

The derived Eqs. (3.23) to (3.26) allow to compare the growth and decay time of oscillations. The minimal oscillation period correspond to the case when growth of reactant A concentration is \( \sqrt{2} \) times longer than its decay

\[
\frac{\tau_1}{\tau_2} = \sqrt{2}.
\]

The case when growth and decay time of one type of reactants are equal \( \tau_1 = \tau_2 \) corresponds to the A creation rate

\[
\zeta_{q_0} = \frac{1}{3}.
\]

One can also consider the case when growth times of both type reactants are the same \( \tau_1 = \tau_3 \). The corresponding creation rate

\[
\zeta = \left( 2 + \frac{\ln \frac{1 - C_{B_0}}{1 - C_{B_M}}}{\ln \frac{1 - C_{A_0}}{1 - C_{A_M}}} \right)^{-1}
\]

depends on minimum and maximum concentrations of reactants A and B. Another situation can be imagined, when both decay times coincide \( \tau_2 = \tau_4 \). The corresponding critical adsorption rate is

\[
\zeta = \left( 2 + \frac{\ln \frac{1 - C_{A_0}}{1 - C_{A_M}}}{\ln \frac{1 - C_{B_0}}{1 - C_{B_M}}} \right)^{-1}.
\]

### 3.4 Monte Carlo results for the generalized \( A + B \to 0 \) model

It is well known that MF approximation assumes a homogeneous random distribution of reactants. The concentration oscillations in MF approximation arise as
a result of nonlinear differential equations. However, reactants are not distributed homogeneously in many real cases, e.g., when spatiotemporal structures are formed. Aggregation of reactants change a behavior of a system considerably, which in general makes MF results incorrect. In these cases, the direct MC computer simulations should be used instead of MF method. In the present Section the MC computer simulations are based on the pair algorithm, see Appendix B and Chapter 2.3 for more details.

3.4.1 The standard model with surface reconstruction

Let us consider the limiting case of asymmetrical diffusion, with mobile reactants $A$ and immobile $B$. Diffusion of $A$ over the $\alpha\beta$ phase boundaries is symmetric, irrespective of the phase type from which the boundary is approached. The phase reconstruction is allowed. A spontaneous creation of an opposite phase is not allowed, $\gamma = 0$. The following parameter values are chosen $\nu_A = 100 \text{ (s}^{-1}\text{)}$ and $V = 1 \text{ (s}^{-1}\text{)}$. As it is shown in the limit of constant $A$ coverage [10], the amount of $\beta$ phase area has saturation for these parameter values. The Fig. 3.3 shows concentration oscillations for three different $\zeta$ values. Oscillatory behavior is irregular and it proceeds as pulses, which are characterized by the change of oscillation amplitude in time. The oscillation amplitude depends on the adsorption rate $\zeta$. The origin of difference between MF and MC results can be explained from the following two figures. Let us look at snapshots of a lattice during one period of oscillations, Fig. 3.4. Both reactants and the $\beta$ phase distribution are not homogeneous during the period, Fig. 3.5, which already contradicts the basic MF assumption. One can start with a case when concentration of $A$ is maximum, see state a) in Fig. 3.4 and Fig. 3.5-a). In this stage reactants $A$ ensure the increase of $\beta$ phase. It is shown in the next Fig. 3.5-b), that reactants $A$ have created an excess of $\beta$ phase in the bottom right area. The corresponding state b) in Fig. 3.4 indicates that concentration of $\beta$ phase has reached its maximum. The excess of $\beta$ phase allows to adsorb additional reactants $B$, see excess of $B$ in Fig. 3.5-b). The reaction between $A$ and $B$ effectively depletes the amount of $A$ in the considered region, see Fig. 3.5-b). The concentrations of $A$ and $B$ reach the minimum and maximum, respectively, in the state c), Figs. 3.4 and 3.5. The $\beta$ phase becomes unstable without $A$ and its concentration reaches a minimum, see state d) in Figs. 3.4 and 3.5. The amount of $\beta$ phase has been depleted in the same area where it has an excess, compare Fig. 3.5-b) and d). In this region the $A$ are adsorbed intensively, but $B$ in less extend. One can think of
Figure 3.3: The concentrations of $A$ (thin line above the break) $B$ (thin line below the break) and $\beta$ phase (thick line). The adsorption rate $\zeta$ is 0.15 a), 0.30 b) and 0.45 c).
Figure 3.4: The concentrations of \( A \) (thin line above the break) \( B \) (thin line below the break) and \( \beta \) phase (thick line). The snapshots of lattice are taken at \( a) \), \( b) \), \( c) \) and \( d) \). Adsorption rate \( \zeta = 0.375, \nu_A = 100 \text{ (s}^{-1}) \).

these processes as waves of concentrations in the direction from the bottom right to the top left corner.

Let us analyze now the system qualitatively. It is readily seen from Fig. (3.6), that the mean concentrations reveal four qualitatively different types of behavior depending on the reactant \( A \) adsorption rate \( \zeta \). (i) The first region corresponds to small \( \zeta \) values and it is characterized by reactant \( A \) poisoning on \( \alpha \) phase. The system arrives in this state because the number of adsorbed and mobile reactants \( A \) are insufficient to maintain the \( \beta \) phase. Once the lattice is in the \( \alpha \) phase, reactants \( B \) cannot be adsorbed any more. Existing \( B \) vanishes due to an annihilation reaction with adsorbed \( A \) and soon all lattice is covered only by adsorbed \( A \). (ii) The reaction region is characterized by the non-zero \( AB \) production \( R_{AB} \). There are detected concentration oscillations, which amplitudes depend on both reactant \( A \) creation rate \( \zeta \) and lattice size \( L \). First, let us review the case of oscillation dependence on \( \zeta \) for the fixed lattice size \( L = 256 \). The MC simulations show that there exist a frequency maximum at \( \zeta = 0.3 \) and oscillation amplitude maximum at \( \zeta = 0.375 \), Fig. (3.7). However, these \( \zeta \) values do not coincide. The simplified explanation of the origin of these \( \zeta \) values can be obtained from the MF analysis, see Sections 3.3 and 3.5.
Figure 3.5: The snapshots of lattice during oscillation period. Reactants $A$ are in the left column, reactants $B$ - in the middle column and $\beta$ phase - in the right column. Shown are $160 \times 160$ region of $256 \times 256$ lattice. The adsorption rate $\zeta$ is 0.375, $\nu_A = 100$ (s$^{-1}$).
Figure 3.6: Mean concentration of reactants $A$ (squares), reactants $B$ (circles) shifted for 0.2, $\beta$-phase (up triangles) shifted for 0.4 and $AB$ production rate (down triangles) shifted for 0.6 dependence on creation rate.

Figure 3.7: The amplitude (squares) and frequency (circles) dependence on reactant $A$ creation rate $\zeta$. Parameter $\nu_A = 100 \text{ (s}^{-1})$. 
Figure 3.8: The SNR dependence on the linear lattice size. The jump rate $\nu_A$ is 100 (squares), 150 (down triangles) and 200 (up triangles) (s$^{-1}$). Parameter $\zeta = 0.35$.

Secondly, the oscillation amplitude depends on the lattice size. In order to show this dependence, the signal-to-noise ratio (SNR) [61, 62, 63, 64, 65, 66, 67, 68] is exploited. SNR was used there to detect the stochastic resonance phenomena, see [69], which was defined as an amplification of the output signal with an increase of the noise level.

Here the SNR is defined as the ratio of the PSD peak at the systems oscillation frequency to the average amplitude of the background noise level in the vicinity of PSD peak [67]. The SNR has a maximum for certain lattice sizes, Fig. (3.8), (note the logarithmic scale). It indicates that nature of observed oscillations is the stochastic resonance. The lattice size determines a noise level; the larger lattice, the smaller the noise level. The amplitude of oscillations decrease with lattice size as well. In its turn, the SNR, which is the ratio of the above mentioned values, increases for a certain noise level, which is characteristic for the stochastic resonance. The more so, it is detected that diffusion is a synchronization mechanism of oscillations in the stochastic resonance, see Fig. (3.8). Larger jump rates result in both the SNR increases and oscillations are synchronized for larger lattice sizes. (iii) The feature of the third region is the reactant $B$ poisoned $\beta$ phase, see Fig. (3.6). The system evolves to this state gradually. The first adsorbed reactants $A$ promote the formation of $\beta$ phase, while the $\alpha$ phase is eliminated completely. Now the $\beta$
phase is stable even without reactants $A$. It cannot be transformed back to the $\alpha$ phase, since there is no $\alpha$ phase area left to trigger this reaction. This situation corresponds to the adsorption of reactants $A$ and $B$ uniformly on a whole lattice. Since the adsorption rate of $A$ is less than that of $B$, it is only the question of time when the system comes to the $B$-poisoned state. (iv) The forth region can classified as the reactant $A$-poisoned $\beta$ phase. It is observed for adsorption rates $\zeta \geq 0.5$. The transition to uniform $\beta$ phase is the same as in the case (iii). The reactant $A$ adsorption rate prevails for $\zeta > 0.5$ over that for $B$ and thus the final state is $A$-poisoning. Now the question is: to which case does the boundary value $\zeta = 0.5$ belong? It is important to remember, that concentration of reactants $A$ exceeds the concentration of $B$ at the moment, when uniform $\beta$ phase is created. Since that moment both type of reactants are created with equal probabilities and uniformly in the lattice. Their concentrations drift due to statistical fluctuations up and down the "initial" concentration values (when $\beta$ phase was created). One of such drifts usually ends up with $A$ poisoning since reactant $A$ concentration initially was larger.

An inclusion of reactant $B$ diffusion brings no qualitatively new effects to the oscillatory behavior in comparison with immobile $B$. The frequency of oscillations increases but only slightly, Fig. 3.9. The amplitude of oscillations increases as well and it shows qualitatively the same dependence on $\zeta$ as in the limit of immobile $B$, Fig. 3.9.
Figure 3.10: Mean concentrations of reactant $A$ (squares), reactant $B$ (circles) shifted for 0.2, $\beta$-phase (up triangles) shifted for 0.4 and $AB$ production rate (down triangles) shifted for 0.6 dependence on creation rate. The spontaneous phase creation $\gamma = 10^{-4}$. Parameter $\nu_A = 100$ (s$^{-1}$).

3.4.2 Surface poisoning

Let us analyze the reasons of surface poisoning observed in regions (i) and (iii). The main problem lies in the fact that once one of the existing phases is eliminated completely, it cannot be created any more. Development of any phase needs its seed but it can happen that such seed no longer is present in the lattice. This is a finite-lattice size effect since for infinite lattices such a seed should exist. For instance, for the adsorption rate $\zeta = 0.05$ the $\alpha$ phase poisoning, which occurs for lattices of size $L = 256$, changes to a reactive regime (ii) for $L = 1024$ when both phases coexist. Similarly for $\zeta = 0.482$ the $\beta$ phase poisoning occurs for lattices of size $L = 256$, but an increase the size up to $L = 4048$, brings the system into reactive regime (ii). An increase of lattice size extends the borders of reactive region (ii), however it greatly increases the computational time as well. An effective way to overcome this finite lattice size effect is to introduce a spontaneous transition reaction from one phase to another with a very small rate, say $\gamma = 10^{-5}$. This reaction was included here in the model in reactive region (ii), in order to determine its impact on system’s behavior but no changes were found. An incorporation of this reaction in the regions (i) and (iii), Fig. (3.10), instead of phase poisoned regions, gives only a single extended reaction region (ii), which transfers to $\beta$ poisoned state (region (iv)) for $\zeta \geq 0.5$. 

72
Figure 3.11: The concentration of A (squares), B (circles) and $\beta$-phase (triangles) dependence on time. Parameters $\zeta = 0.375$, $\kappa = 0.9$ and $\nu_A = 100$ (s$^{-1}$).

One can assume that there are only two regions for infinitely large lattices: reactive and stationary, which are separated by marginal value of $\zeta = 0.5$.

### 3.4.3 Asymmetric mobility

Let us assume that diffusion of reactants A is asymmetric on the two sides of the phase boundary. For example, for $\kappa > 0$ jumps from $\alpha$ to $\beta$ phase are promoted while reverse jumps are hindered. In other words, $\beta$ phase acts as an effective trap of reactants A. Once reactants A find themselves in $\beta$ phase, they jump with the same rate as before. The only difference is that now A diffusion is restricted by the size of $\beta$ phase and the height of activation barrier, when reactants A try to leave the $\beta$ phase. As an example, let us consider the limit of A diffusion with a strong asymmetry, $\kappa = 0.9$. The period of oscillation is shown in Fig. 3.11, whereas the snapshots of the lattice are taken in Fig. 3.12 at the time moments marked by letters. The diffusion asymmetry results in an increase of the oscillation amplitude, compare Figs. 3.4 and 3.11. The interpretation of the origin of oscillations is similar to the case of $\kappa = 0$. The maximum amount of reactants A promote the growth of $\beta$ phase, Fig. 3.12-a). When $\beta$ phase reaches its maximum, see b) in Figs. 3.11 and 3.12, it results in two effects: first, it traps A and they are bounded by the $\beta$ phase.
Figure 3.12: The snapshots of the lattice during oscillation period. Reactants $A$ are in the left column, reactants $B$ - in the middle column and $\beta$ phase - in the right column. Shown are $160 \times 160$ region of $256 \times 256$ lattice. Parameters $\zeta = 0.375$, $\kappa = 0.9$ and $\nu_A = 100 \,(s^{-1})$. 
Secondly, reactants $B$ are intensively adsorbed on $\beta$ phase. It results in decrease of $A$ concentration in the $\beta$ phase region and excess of $B$'s, which have no $A$ partners for reaction. At the time c), in Figs. 3.11 and 3.12, reactants $A$'s have created $\beta$ phase everywhere except those regions, where it already was created at the time a) in Fig. 3.12.

The $\beta$ phase is created in local regions asynchronously, due to a finite speed of reactant diffusion. One can estimate approximately the mean squared path of reactants $A$ during the two successive snapshots at times b) and c) in Fig. 3.11. The average distance, which is traveled by $A$ in the units of lattice constant is $\sqrt{\nu_A t} = \sqrt{100 \times 4} = 20$. The side length of the snapshot is 160 units of lattice constant. It indicates, that $A$ travels the distance approximately equal to 1/8 of the picture length during the two successive pictures.

The minimum of $A$ concentration at time c) Fig. 3.11 means that $\beta$ phase will decreased, see Fig. 3.11-d). At this stage reactants $A$ are adsorbed but $B$ adsorption is minimal. The reactants $B$, which were accumulated during the maximum of $\beta$ phase, readily react with adsorbing $A$. Thus the concentration of $B$ is decreasing, but that of $A$ is increasing, see state e) in Figs. 3.11 and 3.12.

The trapping of reactants $A$ obviously makes $\beta$ phase more stable and promotes the oscillatory behavior seen in Fig. 3.13. This asymmetry has three results. Firstly, a strong oscillation amplitude increase is observed under the asymmetry (with respect to non-asymmetric case, $\kappa = 0$) for $\zeta = 0.20$. Frequency of oscillations remains constant in the interval $0.1 \leq \kappa \leq 0.9$, while at the limiting $\kappa$ values 0 and 1 the frequency slightly decreases and increases, respectively. Secondly, the oscillation amplitude increases with the asymmetry at $\zeta = 0.35$. Its increase is maximal when $\kappa = 1$, i.e., reactants $A$ once trapped by $\beta$ phase stay there forever. Thirdly, the amplitude of oscillations remains constant for $\zeta = 0.45$ up till $\kappa < 0.8$. It means high concentration of reactants $A$ and their trapping into $\beta$ phase does not affect the oscillatory behavior. In this regime an increase of $\kappa$ up to unity leads to the stationary state, when $\beta$ phase has covered all the lattice and there is no chance for $\alpha$ phase to develop. No oscillatory behavior is possible in this case. To overcome the problem of the $\beta$ poisoning, the point at $\zeta = 0.45$ and $\kappa = 1$ in Fig. 3.13 is calculated with spontaneous phase creation $\gamma = 10^{-5}$ s$^{-1}$. In this case the decrease of oscillation amplitude is observed, Fig. 3.13. The frequency of oscillations decreases linearly with $\kappa$ but with different slopes in the last two cases. The larger is $\zeta$, the steeper is the slope. The decrease of frequency indicates that a period between two successive maximums of concentration increases due to the time needed for promoted lattice
reconstruction processes.

Let us fix diffusion asymmetry at \( \kappa = 0.95 \) and vary the adsorption rate \( \zeta \), Fig. 3.14. The \( \beta \) phase acts now as a trap of reactants \( A \). The oscillatory behavior is better pronounced at \( \zeta = 0.35 \), which is similar to symmetric case, Fig. 3.7. The difference lies in the amplitude of oscillations, which increases in the asymmetrical case. The asymmetry stabilizes the oscillations for small \( \zeta \) values, e.g., the oscillations with \( \kappa = 0.95 \) are observed for \( \zeta \geq 0.04 \), while in the symmetric case the poisoning occurred at \( \zeta \leq 0.05 \). The frequency of oscillations depends on \( \zeta \) as well. Unlike the symmetric case, the frequency maximum is shifted to the lower values, \( \zeta = 0.20 \), instead of \( \zeta = 0.30 \). Comparing the values of frequencies in Figs. 3.7 and 3.14, one can see that diffusion asymmetry has no effect on the oscillation frequency at \( \zeta \) values slightly above 0.20. Diffusion asymmetry results in frequency increase for smaller \( \zeta \), see, e.g., \( \zeta = 0.20 \) case in Fig. 3.13, or linear decrease for larger \( \zeta \) values.

From the mathematical point of view, the diffusion asymmetry can be also chosen negative, Fig. 3.15. The oscillation frequency remains constant, while its amplitude decreases. It reaches minimum at \( \kappa = -0.5 \), when it starts to grow. The oscillation amplitude at \( \kappa = -1 \) is almost the same as for \( \kappa = 0 \).
Figure 3.14: The amplitude (squares) and frequency (circles) dependence on the adsorption rate $\zeta$. Parameters $\kappa = 0.95$ and $\nu_A = 100$ (s$^{-1}$).

Figure 3.15: The amplitude (squares) and frequency (circles) dependence on diffusion asymmetry. Parameters $\zeta = 0.375$, $\nu_A = 100$ (s$^{-1}$), $V = 1$ (s$^{-1}$), $R = 100$ (s$^{-1}$).
Figure 3.16: The amplitude (squares) and frequency (circles) dependence on parameter $s$. Parameters $\zeta = 0.35$, $\nu_A = 100$ (s$^{-1}$), $V = 1$ (s$^{-1}$) and $R = 100$ (s$^{-1}$).

### 3.4.4 Reactant $B$ adsorption on $\alpha$ phase

As the next limiting case, let us consider the adsorption of reactants $B$ on $\alpha$ phase, i.e., the non-zero $s$ values. In the limiting case $s = 1$ the reconstruction has no effect and the model coincides with the standard $A + B \rightarrow 0$ annihilation reaction. It is known, that the later has $B$ and $A$ poisoning for $\zeta < 0.5$ and $\zeta > 0.5$, respectively. Only for the case $\zeta = 0.5$, when both types of reactants are created with absolutely equal probability, the system shows the reaction regime. MC simulations show that poisoning states are reached already for $s < 1$. Firstly, an increase of $s$ slightly increases the oscillation amplitude, see Fig. 3.16, but then amplitude decreases while the $B$ poisoning is reached, e.g., for $\zeta = 0.35$, the poisoning starts at $s > 0.4$. The frequency only decreases with $s$ increase. As an example, the limiting case with $s = 0.1$ is studied for various $\zeta$ in Fig. 3.17. The amplitude is slightly increased in the region of a maximum ($\zeta$ varies in the interval $0.350 - 0.425$), while the frequency has slightly decreased in comparison with the case of no $B$ adsorption on $\alpha$ phase, see Fig. 3.7. The $B$ poisoning occurs at the adsorption rates of $\zeta < 0.15$. 78
Figure 3.17: The amplitude (squares) and frequency (circles) dependence on adsorption rate. Parameters \( s = 0.1, \nu_A = 100 \text{ (s}^{-1} \text{)}, \text{ } V = 1 \text{ (s}^{-1} \text{)} \) and \( R = 100 \text{ (s}^{-1} \text{)} \).

### 3.5 Discussion of the \( A+B \rightarrow 0 \) generalized model

The MC computer simulations show the existence of frequency and amplitude maximum for adsorption rates \( \zeta \approx 0.29 \) and \( \zeta \approx 0.375 \), respectively, see Fig. 3.7. The origin of frequency maximum and the corresponding adsorption rate can be explained using MF analysis, see Section 3.3. The critical adsorption rate \( \zeta = 1 - 1/\sqrt{2} \) follows from both the linear stability analysis of the singular point Eq. (3.41) and from the qualitative considerations, Eq. (3.71). It follows from the latest that in the case of critical adsorption rate, the growth time of reactant \( A \) concentration is \( \sqrt{2} \) times larger than the decay time. However, MC simulations show no such behavior.

Interpretation of oscillation amplitude maximum obtained in MC simulations is more complicated problem. MF equations solved numerically show almost constant amplitude of oscillations depending on adsorption rate, see Fig. 3.2.

### 3.6 Conclusions

The ZGB model \( A + 1/2B_2 \rightarrow 0 \) with surface reconstruction is known to describe adequately the catalytic \( \text{CO}_2 \) formation on Pt(110) and Pt(100) surfaces. In the
present Chapter 3 the ZGB model is reduced to the $A + B \to 0$ model with surface reconstruction. It is shown that such a model has qualitatively the same properties as the original ZGB model.

The $A + B \to 0$ model was analyzed using two methods: MF analysis and MC computer simulations. The MF approximation leads to analytical estimates in the limit of fast diffusion of reactants $A$ and $B$. In this limit MF predicts stable oscillatory behavior. However, the MC simulations reveal only local oscillatory behavior, which is not synchronized over a whole lattice. The disagreement between these two methods is due to the fact that MF assumes homogeneous distribution of reactants, while MC simulations show cluster formation. Both methods predict the maximum of oscillation frequency at the same adsorption rate. The dependence of oscillation amplitude on the reactant adsorption rate is detected only in MC.

Several physically interesting limiting cases were studied. Firstly, the geometrical aspect of oxygen molecule dissociation into two sites was neglected. Nevertheless, the model shows the oscillatory behavior, which qualitatively agrees with more elaborated models, e.g., the ZGB model with the surface reconstruction. It drives us to the conclusion that dimer adsorption is important in physical interpretation, but it gives no significant contribution to the origin of oscillatory behavior.

Secondly, the asymmetric reactant diffusion over a phase boundary is considered. The amplitude of oscillations increases, if the diffusion of $A$'s over a phase boundary is promoted towards $\beta$ phase. In this case $\beta$ phase acts in fact as a trap for reactants $A$.

Thirdly, different crystalline surface orientations, e.g., (110) are modeled introducing $B$ adsorption on $\alpha$ phase. Increase of $B$ adsorption rate on $\alpha$ surface the first promotes oscillatory behavior for small $s \leq 0.1$ and then suppresses it for $s > 0.1$. Indeed, it is detected experimentally that CO$_2$ oscillatory behavior on Pt(110) surfaces is more pronounced than on Pt(100) [1].

Real experimental situations can be assumed as interference of the limiting cases considered in the present Chapter. So, the generalized $A + B \to 0$ model predicts an increase of oscillatory behavior in the limit of asymmetric diffusion and $B$ creation on $\alpha$ phase (e.g., $s = 0.1$), which coincides with experimental studies of CO catalysis on Pt(110) surfaces. The oscillatory behavior is less pronounced in the case of no $B$ adsorption on $\alpha$ phase, which again agrees with the results obtained for Pt(100) surfaces.
General conclusions

The real catalytic surface reactions usually reveal a very complex behavior which is characterized by formation of the spatiotemporal structures. The theoretical description of reactions involves a number of elementary reaction steps. Simultaneous analysis of all reaction steps is as complicated as interpretation of experiment. Therefore, of particular interest are simplifications of reactions, in order to study the origins of spatiotemporal structures.

In the present Thesis two elementary models were considered: the Lotka-type and the \( A + B \rightarrow 0 \) model. The standard definitions of these models are extended to several physically interesting limits. Firstly, the oscillatory behavior of Lotka-type model was studied. The amplitude and frequency dependence on the single parameter were explained in a simple way.

Secondly, the Lotka-type model was exploited to demonstrate the resonance properties. To this end, the control parameter was periodically modulated in time with a small amplitude. The resonance behavior was detected for several modulation frequencies, which is characterized by both, the systems frequency locking to the modulation frequency and an increase of oscillation amplitude.

Thirdly, the Lotka-type model was generalized to the case of mobile and interacting reactants. It was shown that diffusion of reactants decreases the oscillation amplitude. The interaction between reactants results in a more complicated behavior. Due to asymmetry of the Lotka-type model with respect to the reactants \( A \) and \( B \), the repulsion or attraction inside \( AA \) and \( BB \) reactant pairs have different results. For example, in the limit of mobile and repulsing reactants \( AA \) the oscillation amplitude increases. However, in the limit of mobile and repelling \( BB \) the amplitude of oscillations decreases. The impact of reactant diffusion and interactions on oscillation amplitude and frequency was interpreted in a simple way.

Fourthly, the standard \( A + B \rightarrow 0 \) model is generalized to the case of surface reconstruction. It shows qualitatively the same behavior as the more complicated ZGB
model with the surface reconstruction. The conclusion was drawn that the dimer
\((O_2)\) adsorption in the ZGB model is irrelevant for the qualitative interpretation.
An increase or decrease of the oscillatory behavior is associated with other factors,
e.g., the adsorption rate, asymmetric diffusion and different adsorption probabilities
on both reconstructed and non-reconstructed phases.
Appendix A

Definition of transition rates

The kinetic model is uniquely defined by a set of possible states of a stochastic system and the transition rates between these states. To extend the mathematical model by an incorporation of the energetic interaction between reactants, one has to define the transition rate dependence on the energy and temperature. However, this procedure is not unique.

Let us consider for the illustration an elementary transition of a system from the state $\alpha$ to the state $\beta$. Examples are: (i) process of diffusion, considered as a jump from one lattice site to another; (ii) adsorption/desorption of a reactant from a gas phase on a randomly chosen empty lattice site. In the first case the system is closed and a number of reactants is preserved (a single mobile reactant), but the total systems energy changes after diffusion jump due to different configurations of surrounding reactants. In the second case, the system is open. The state $\alpha$ corresponds to an absent reactant (empty site), whereas the state $\beta$ corresponds to an adsorbed reactant (occupied site), which interacts with its neighborhood.

Now, let us fix the configuration of reactants and allow one of the following events: in the case of (i) reactant either can jump to the NN empty site thus leaving the initial configuration, or jump from NN occupied site to empty site (two-site process). In the case (ii) reactant can be adsorbed/desorbed on a single site (one-site process). The kinetics of these extremely simplified processes is described by the kinetic equation

$$\frac{dW(\beta)}{dt} = -\frac{dW(\alpha)}{dt} =$$

$$= K(\alpha \rightarrow \beta) W(\alpha) - K(\beta \rightarrow \alpha) W(\beta).$$  \hspace{1cm} (A.1)
Here $W(\alpha)$ and $W(\beta)$, $W(\alpha) + W(\beta) = 1$, are probabilities to find the system in the state $\alpha$ and $\beta$, $K(\alpha \to \beta)$ and $K(\beta \to \alpha)$ are transition rates from one state to another, respectively. As a result of such processes, the local equilibrium should be reached in the limit $t \to \infty$

$$W^{eq}(\beta) = f(\varepsilon, \mu), W^{eq}(\alpha) = 1 - f(\varepsilon, \mu), \quad (A.2)$$

where $\mu = 0$ in the case (i) and $\mu \neq 0$ in the case (ii). The function

$$f(\varepsilon, \mu) = \frac{1}{1 + \exp((\varepsilon - \mu)/k_B T)}, \quad (A.3)$$

where $\mu$ denotes chemical potential and $\varepsilon = E_\beta - E_\alpha$. The Eq. (A.3) might look similar to the Fermi-Dirac distribution. However, this is not a case. The fermionic shape of distribution is determined by the following fact: We have considered one reactant in the two possible states. If one would like to consider the adsorption-desorption of not a monomer but a dimer (still two possible states, but now for a pair of reactants) the Eq. (A.3) should be correspondingly modified, see [70] for details. The unknown chemical potential $\mu$ is usually determined from the given average number of particles in a system. Quite different assumption is used in the kinetic models: The chemical potential is determined by the corresponding direct and backward transition rates from an initial state to a final one, see below for details. The unique definition of the transition rates is impossible, because the equilibrium condition of Eq. (A.1) gives only the ratio of transition rates but not the rates themselves:

$$\frac{K(\alpha \to \beta)}{K(\beta \to \alpha)} = \frac{W^{eq}(\beta)}{W^{eq}(\alpha)}. \quad (A.4)$$

In other words, the kinetic model with reactant energetic interaction is not defined uniquely by the analysis of the limiting case, where one can use the Gibbs statistics. The same equilibrium distribution (if it takes place) could be reached with different transition rates.

To solve this problem, it was suggested [70] to use a so-called standard model for describing the chemical reactions. We note that ideas of the standard model applied for the simpler systems like the kinetic Ising model, gives already known definition of individual transition rates suggested by Glauber [71] (see also Refs. [72, 73, 74, 75]).

It is defined in the standard model that

$$K(\alpha \to \beta) = QW^{eq}(\beta), \quad K(\beta \to \alpha) = QW^{eq}(\alpha), \quad (A.5)$$

84
where $Q$ is a co-factor independent of $\alpha$ and $\beta$, which value is defined by the procedure described below. This ansatz, Eq. (A.5), fulfills the requirements of Eq. (A.4).

To find the co-factor $Q$, let us consider the limiting case of a surface, where there are no other reactants in the neighborhood of a given reactant. Formally this limit corresponds to the value $\varepsilon = 0$ in Eq. (A.5). So, in the case of diffusion, the parameter $\mu = 0$ and $f(0, 0) = 1/2$, then the right hand sides of Eq. (A.5) in this limit give $Q/2$. These relations determine the jump rate on an empty surface. If we denote it by $\nu^0$, then we arrive at the relation $Q = 2\nu^0$.

Now we consider the case when the number of reactants changes. According to our interpretation, in the case (ii), the limit $\varepsilon = 0$ for the transition rate $K(\alpha \rightarrow \beta)$ should give an adsorption rate $p$ on an empty surface, $Q f(0, \mu) = p$. For the reverse process (desorption from an empty surface, $k$) we get $Q(1 - f(0, \mu)) = k$, correspondingly. As a result, we have two equations for two unknown values, $Q$ and $\mu$. This allows us to determine uniquely the transition rates in the general case. We arrive at the relations

$$Q = p + k, \quad \frac{p}{k} = \frac{f(0, \mu)}{1 - f(0, \mu)}.$$

(A.6)

The last equations establish an important property of the standard model. Namely, they allow to define the energetic dependence for the transition rates.

For example, let us consider the irreversible adsorption in the Lotka-type model: Reactant $A$ could be adsorbed with $p \neq 0$, but the desorption is forbidden $k = 0$. The irreversible process then is defined as a limiting case, when the transition rate $k$ tends to zero. It follows from Eq. (A.6) that $Q = p$ and $f(0, \mu) = 1$ (or $\mu \rightarrow \infty$). Taking this into account and considering the case $\varepsilon \neq 0$, we obtain the adsorption rate to follow $p f(\varepsilon, \mu) = p$ for every neighboring configuration of reactants. In other words, we have to use a constant adsorption rate, which is independent of energetic interactions. The described methodology applied to other irreversible processes leads to energetically independent transition rates.

In summary, we wish to note, that three irreversible processes in the Lotka-type model are: adsorption of $A$, desorption of $B$ and the reaction $A+B \rightarrow 2B$. It means that energetic interactions in these processes are trivial by definition, i.e., transition rates are energetically independent constants. We should take energetic interaction into account in the only reversible process, namely diffusion.

The standard model defines uniquely the energetic dependence of every transition rate. The formulation of the standard model eliminates the ambiguity in the
previous definitions of mathematical models, when energetic dependence could be freely attributed to some parameters.
Appendix B

The basis of the pair algorithm

Below we give the formal foundations of our algorithm. It was already used without detailed description in a series of papers [9, 10, 54, 59, 76], where it was applied to different problems of the surface reaction kinetics. The main advantages of the proposed algorithm are: (i) Its universality (adding of a new process does not demand rewriting a whole code). (ii) It is very quick (the code mainly generates random numbers and compares these numbers with predefined limits of processes). We do not consider here the energetic interaction between reactants, in order to keep the explanation transparent. The corresponding generalization can be easily done.

The suggested algorithm "translates" the master equations of the defined class of kinetic lattice models to the language of MC simulation. We consider the lattice with equivalent sites (the coordination number is $z$). The state of each site $l$ is determined by a variable $\sigma_l$, which can have different values: 0 (empty site), $A$ (site occupied by a reactant $A$) etc. The kinetic model is characterized by a set of elementary events and transition rates. The change of elementary events determine the change of the state of a whole system $\sigma = (\sigma_1, \sigma_2, \ldots)$. In the development of algorithm, we have chosen one important class of lattice models: namely, we allow for only monomolecular and bimolecular processes (the terminology and abbreviation follows [10, 34]). The bimolecular processes are allowed only for reactants in the NN positions. The monomolecular processes are defined as processes, which result in a change of only one site of a lattice. Examples are adsorption ($0\rightarrow A$) and desorption ($B\rightarrow 0$) of a monomer. The bimolecular processes describe diffusion ($A0\rightarrow 0A$), ($B0\rightarrow 0B$) and reaction (annihilation) of the nearest two reactants ($AB\rightarrow 00$). In this case the state of two sites changes simultaneously.
B.1 Master equation

Let us consider only monomolecular and bimolecular reaction steps. The master equation for such a model looks quite simple

$$\frac{d}{dt} \rho(\sigma) = \frac{d}{dt} \rho(\sigma)|_{\text{in}} - \frac{d}{dt} \rho(\sigma)|_{\text{out}},$$  

(B.1)

where the terms “in” and “out” describe the creation and annihilation of state $\sigma$, respectively, and are given by

$$\frac{d}{dt} \rho(\sigma)|_{\text{in}} = \sum_{i} \sum_{i'} P(\sigma_i' \to \sigma_i) \rho(\sigma_i'),$$

$$+ \frac{1}{z} \sum_{\sigma_i' \sigma_m} Q(\sigma_i' \sigma_m \to \sigma_i \sigma_m) \rho(\sigma_{im}),$$  

(B.2)

$$\frac{d}{dt} \rho(\sigma)|_{\text{out}} = \sum_{i} \sum_{i'} P(\sigma_i \to \sigma_i') \rho(\sigma_i') +$$

$$+ \frac{1}{z} \sum_{\sigma_i' \sigma_m} \sum_{\sigma_i} Q(\sigma_i \sigma_m \to \sigma_i' \sigma_m) \rho(\sigma_{im}).$$  

(B.3)

Here we use the following notations $\sigma_i = (\sigma_1, ..., \sigma_i, ...)$, $\sigma_i' = (\sigma_1, ..., \sigma_i', ...)$, $\sigma_{im} = (\sigma_1, ..., \sigma_i, \sigma_m, ...)$, $\sigma_{im}' = (\sigma_1, ..., \sigma_i', \sigma_m', ...)$, $\sigma_{lm}$ denotes as $P(\sigma_i \to \sigma_i')$, those for bimolecular processes as $Q(\sigma_i \sigma_m \to \sigma_i' \sigma_m')$. The symbol $\langle l, m \rangle$ stands for a summation of pairs, which are NNs. The co-factor $1/z$ has been used for the convenience in the further transformations (see [10, 54]).

If transition rates for mono- and bimolecular processes are described using abbreviation

$$w(\lambda \mu \to \lambda' \mu') =$$

$$= \frac{1}{z} [Q(\lambda \mu \to \lambda' \mu') + P(\lambda \to \lambda') \delta_{\mu \mu'} + P(\mu \to \mu') \delta_{\lambda \lambda'}],$$  

(B.4)

where $\delta_{\lambda \mu}$ stands for Kronecker delta symbol then Eqs. (B.2) and (B.3) obtain a very compact form

$$\frac{d}{dt} \rho(\sigma)|_{\text{in}} = \sum_{\langle l, m \rangle} \sum_{\sigma_i' \sigma_m} w(\sigma_i' \sigma_m \to \sigma_i \sigma_m) \rho(\sigma_{im}).$$  

(B.5)
\[
\frac{d}{dt} \rho(\sigma) \bigg|_{\text{out}} = \sum_{\lambda} \sum_{\sigma_i, \sigma_m} w(\sigma_i \sigma_m \rightarrow \sigma'_i \sigma'_m) \rho(\sigma_{im}). \tag{B.6}
\]

The transition rates introduced in Eq. (B.4) describe general pseudo-bimolecular transitions in two NN sites. The transition $\sigma_i \sigma_m \rightarrow \sigma'_i \sigma'_m$ is considered as both: a real bimolecular transition (the state of two sites changes instantly) and pseudo-transition (the state of one of the sites does not change). The goal of the transformation is to demonstrate that the kinetics of the given class of problems formally can be described using only pair pseudo-elementary processes.

By summing over local states one can introduce the reduced $i$-point probabilities $\rho^{(i)}(\sigma_i)$ instead of a complete set $\rho(\sigma)$. The one-point probability with $i=1$

\[
\rho^{(1)}(\sigma_i) \equiv c_\lambda \quad \text{with} \quad \lambda = \sigma_i = X^\chi \tag{B.7}
\]

is independent of the lattice vector 1 due to translation symmetry in the lattice. In general case the abbreviation $c_\lambda = c_X^\chi$ stands for concentration of reactants $X$ on surface phase $\chi$, where $X \in \{0, A, B\}$ and $\chi \in \{\alpha, \beta\}$. The macroscopic reactant densities are normalized to unity

\[
\sum_\lambda c_\lambda = 1 \quad \text{or} \quad \sum_{\chi=\alpha,\beta} \sum_{X=0,A,B} c_X^\chi = 1. \tag{B.8}
\]

The global densities of either the reactants $C_X$ or the surface phase $\Theta_\chi$ are defined by

\[
C_X = \sum_{\chi} c_X^\chi \quad \text{with} \quad C_0 + C_A + C_B = 1 \tag{B.9}
\]

and

\[
\Theta_\chi = \sum_{\chi} c_X^\chi \quad \text{with} \quad \Theta_\alpha + \Theta_\beta = 1. \tag{B.10}
\]

The two-point probability $\rho^{(2)}(\sigma_i \sigma_m)$ express the probability to find the site 1 in state $\lambda = \sigma_i$ and site $m$ in state $\mu = \sigma_m$ at time $t$. Due to translation symmetry this probability depends only on the distance $r = 1 - m$ between these sites. Therefore one can introduce correlation function $F_{\lambda \mu}(r)$

\[
\rho^{(2)}(\sigma_i \sigma_m) = c_\lambda c_\mu F_{\lambda \mu}(r), \tag{B.11}
\]

with condition that correlations between reactants vanish in asymptotic limit $|r| \rightarrow \infty$

\[
\lim_{|r| \rightarrow \infty} F_{\lambda \mu}(r) = 1. \tag{B.12}
\]
The following sum rule holds for one- and two-point probabilities

$$\sum_{\sigma_m} \rho^{(2)}(\sigma_i \sigma_m) = \rho^{(1)}(\sigma_i). \quad (B.13)$$

Let us sum both sides of Eqs. (B.2) and (B.3) over all local states except one. Then one-point probabilities can be expressed as a function of one- and two-point probabilities

$$\frac{d}{dt} c_{\lambda}|_{in} = \frac{d}{dt} \rho^{(1)}(\sigma_i)|_{in} = \sum_{\sigma'_i} P(\sigma'_i \rightarrow \sigma_i) \rho^{(1)}(\sigma'_i) +$$

$$\frac{1}{z} \sum_{m} \sum_{\sigma'_i, \sigma'_m} Q(\sigma'_i \sigma'_m \rightarrow \sigma_i \sigma_m) \rho^{(2)}(\sigma'_i \sigma'_m), \quad (B.14)$$

$$\frac{d}{dt} c_{\lambda}|_{out} = \frac{d}{dt} \rho^{(1)}(\sigma_i)|_{out} = \sum_{\sigma'_i} P(\sigma_i \rightarrow \sigma'_i) \rho^{(1)}(\sigma'_i) +$$

$$\frac{1}{z} \sum_{m} \sum_{\sigma'_i, \sigma'_m} Q(\sigma_i \sigma_m \rightarrow \sigma'_i \sigma'_m) \rho^{(2)}(\sigma_i \sigma_m), \quad (B.15)$$

where unknown functions are two point probabilities $\rho^{(2)}(\sigma_i \sigma_m)$. The differential equations for two point probabilities are obtained by summation of Eqs. (B.2) and (B.3) over all local states except two and they now contain the unknown three point probabilities.

## B.2 Monte Carlo

Formally the MC simulations are equivalent to the problem of random walks in multidimensional space $\sigma$ (the state of a whole system). For the given class of kinetic problems, in every step only two projections of the vector $\sigma$ can be changed simultaneously.

The random walks are described by a set of equations

$$\rho_{n+1}(\sigma) = \sum_{\sigma'} U(\sigma' \rightarrow \sigma) \rho_n(\sigma'), \quad (B.16)$$

which for the kinetic applications should be accompanied by an additional relation, which determines the time

$$t_{n+1} = t_n + \delta t_n. \quad (B.17)$$
Here $\rho_n(\sigma)$ is the probability to find the system in a state $\sigma$ at the $n$ th microscopical step, $t_n$ the corresponding time, $\delta t_n$ the time increment, $U(\sigma' \to \sigma)$ the transition probability from state $(\sigma')$ to state $(\sigma)$.

We use the following normalization condition for the transitions

$$\sum_{\sigma'} U(\sigma \to \sigma') = 1, \quad (B.18)$$

which determines the normalization of probabilities $\rho_n(\sigma)$ to

$$\sum_{\sigma} \rho_n(\sigma) = 1. \quad (B.19)$$

For the models of a given class with pseudo-bimolecular transitions

$$\rho_{n+1}(\sigma) = \sum_{<l,m>} \frac{1}{M} \sum_{\sigma'_m} u(\sigma'_m \to \sigma_l) \rho_n(\sigma_{lm}) \quad (B.20)$$

the transition probabilities in a random pair $u(\lambda \mu \to \lambda' \mu')$ are normalized to unity

$$\sum_{\lambda' \mu'} u(\lambda \mu \to \lambda' \mu') = 1. \quad (B.21)$$

Eq. (B.20) has a clear mathematical structure and corresponds to the following MC algorithm:

A pair of NN sites is chosen randomly from a number of pairs $M = \frac{1}{2}L^2$ available on a lattice of size $L$ (the co-factor $1/M$ in Eq. (B.20) stands for the probability to choose the corresponding pair).

One of the possible events in the pair is chosen randomly (with the help of a random number $\varsigma \in [0, 1]$ according to the weight $u(\lambda' \mu' \to \lambda \mu)$). As a result, two variables of the state of sites are changed correspondingly, $\sigma'_m \to \sigma_l \sigma_m$.

### B.3 The transition scheme from the master equation to the Monte Carlo

Now we have to establish the relation between the master equation and the random walks (and MC). In other words, we have to relate the language of the transition rates (and time) and language of the transition probabilities (and MC steps). We use here the differential transition scheme, where we exploit the analogy between the Eq. (B.1) and Eq. (B.20) and we choose the algorithm with $\delta t_n = const$. Several
transition schemes were suggested in [8], where the time step $\delta t_n$ is a random variable and its value is determined from the corresponding distribution. The methods described in [8] are related to the previously considered algorithm in the same manner as continuous-time random walks (CTRW) introduced by Montroll and Weiss [77] is related to the problem of random walks. Both approaches are practically identical, if the average value $\langle \delta t_n \rangle$ in CTRW coincides with $\delta t$ in the random walks problem. The CTRW schemes require more random numbers. A comparison of these two methods has revealed that our algorithm is a very economic one.

To connect the formalism of the random walks and the master equation, let us first construct the differential analog of a derivative from Eq. (B.16)

$$\frac{\rho_{n+1}(\sigma) - \rho_n(\sigma)}{\delta t_n} =$$

$$= \frac{1}{\delta t_n} \left[ \sum_{\sigma'} U(\sigma' \rightarrow \sigma) \rho_n(\sigma') - \sum_{\sigma'} U(\sigma \rightarrow \sigma') \rho_n(\sigma) \right], \quad (B.22)$$

where the normalization condition of Eq. (B.18) is used on the right hand side. The differential equation is obtained using the correspondences

$$\frac{\rho_{n+1}(\sigma) - \rho_n(\sigma)}{\delta t_n} \rightarrow \frac{d}{dt} \rho(\sigma), \quad \rho_n(\sigma) \rightarrow \rho(\sigma), \quad (B.23)$$

with $t$ instead of $t_n$, and $\rho(\sigma)$ instead of $\rho_n(\sigma)$. Secondly, the time increment can be chosen constant $\delta t_n = \delta t = \text{const}$ (the method is easily generalized to the problems, where the transition rates depend on time) in the simplest MC algorithm

$$\delta t = \frac{z \tau}{M}, \quad (B.24)$$

where parameter $\tau$ has a dimension of time. Then the master equation follows from the system of Eqs. (B.20) and (B.22) to (B.24) with

$$\frac{d}{dt} \rho(\sigma)|_{in} = \sum_{<1,m> \sigma' \sigma_m} \frac{1}{z \tau} u(\sigma' \sigma_m \rightarrow \sigma \sigma_m) \rho(\sigma_{1m}), \quad (B.25)$$

$$\frac{d}{dt} \rho(\sigma)|_{out} = \sum_{<1,m> \sigma' \sigma_m} \frac{1}{z \tau} u(\sigma \sigma_m \rightarrow \sigma' \sigma_m') \rho(\sigma_{1m}). \quad (B.26)$$

The main difference lies in the terms of transition probabilities $\frac{1}{z \tau} u(\lambda \mu \rightarrow \lambda' \mu')$ of Eqs. (B.25) and (B.26) instead of $w(\lambda \mu \rightarrow \lambda' \mu')$, see Eqs. (B.5) and (B.6).
The transition rates \( w(\lambda \mu \rightarrow \lambda' \mu') \) of the Master Equation as defined consider only nontrivial transitions \( \lambda \mu \neq \lambda' \mu' \). In contrary, the transition probabilities \( u(\lambda \mu \rightarrow \lambda' \mu') \) form a complete set due to the normalization Eq. (B.21) and thus contain trivial (empty) transitions \( \lambda \mu = \lambda' \mu' \). Additional terms in Eqs.(B.25) and (B.26) mutually vanish, since the trivial transitions does not change a state of a system.

Let us define now

\[
W_{\lambda \mu} = z \sum_{\lambda' \neq \lambda \mu' \neq \mu} w(\lambda \mu \rightarrow \lambda' \mu').
\]  

(B.27)

Using Eq. (B.4) one arrives at

\[
W_{\lambda \mu} = \sum_{\lambda' \mu'} Q(\lambda \mu \rightarrow \lambda' \mu') +
\]

\[
+ \sum_{\lambda'} P(\lambda \rightarrow \lambda') + \sum_{\mu'} P(\mu \rightarrow \mu').
\]  

(B.28)

If we choose \( W_0 = \max [W_{\lambda \mu}] \) and define \( \tau = W_0^{-1} \) then transition probabilities read as follows

\[
u(\lambda \mu \rightarrow \lambda' \mu') = \frac{z}{W_0} w(\lambda \mu \rightarrow \lambda' \mu').
\]  

(B.29)

Since a sum

\[
\sum_{\lambda' \neq \lambda \mu' \neq \mu} u(\lambda \mu \rightarrow \lambda' \mu') \leq 1
\]  

(B.30)

is always restricted, the trivial transitions obtain a unique definition as terms, which complement the sum to unity

\[
\sum_{\lambda'} \sum_{\mu'} u(\lambda \mu \rightarrow \lambda' \mu') \equiv 1.
\]  

(B.31)

Thus, MC simulations become a uniquely defined problem, which coincide with the initial kinetic problem described by the master equation. These relations could look rather formal, however, they allow us a very simple and effective realization in a computer code. We note, that the state of a pair of sites \( \lambda \mu \) is denoted in the code by a single number, thus the transition probability \( u(\lambda \mu \rightarrow \lambda' \mu') \) can be written as a two dimensional matrix. The elements of the matrix are predefined, therefore during MC simulations they are not calculated. The efficiency of the code is characterized by the fact that the speed is determined by the random number generator, which is not characteristic for other algorithms.
Appendix C

Linear stability analysis

Let us start with an autonomous system of nonlinear differential equations

\[ \dot{q}(t) = N(q(t)). \quad (C.1) \]

It is assumed that a stable solution \( q_0 \) (singular point), which satisfies Eq. \( (C.2) \)

\[ N(q_0) = 0, \quad (C.2) \]

exists for this system. In order to analyze the stability of the singular point, we make the hypothesis

\[ q(t) = q_0 + \delta q(t), \quad (C.3) \]

where deviation \( \delta q(t) \) is assumed to be small. Inserting Eq. \( (C.3) \) into Eq. \( (C.1) \)
and keeping only linear terms in \( \delta q(t) \), we arrive at the following equation

\[ \dot{\delta q}(t) = L \delta q(t), \quad (C.4) \]

where the matrix \( L \) is defined by \( L = (L_{kl}) \),

\[ L_{kl} = \frac{\partial N_k(q(t))}{\partial q_l(t)}|_{q(t)=q_0}. \quad (C.5) \]

The solution of Eq. \( (C.4) \) is searched in the form

\[ \delta q(t) = \delta q(0) \exp(\lambda t), \quad (C.6) \]

which transforms Eq. \( (C.4) \) into a system of linear algebraic equations for the constant vector \( \delta q(0) \) and eigenvalue \( \lambda \)

\[ L \delta q(0) = \lambda \delta q(0). \]
The unknown eigenvalue $\lambda$ for independent solutions are determined as roots of the characteristic equation

$$
\det |L_{kl} - \lambda \delta_{kl}| = 0,
$$

(C.7)

where $\delta_{kl}$ stays for Kronecker delta symbol. There are at most $n$ different eigenvalues $\lambda_j$, if a matrix $L$ is of finite dimension $n$. Further we exploit two definitions [78]:

**Definition 1.** We say that $\delta q(t)$ is Lyapunov stable if given $\varepsilon > 0$ and $t = t_0$, there exists and $\eta = \eta(\varepsilon, t_0)$ such that any solution $\delta \tilde{q}(t)$ for which $|\delta q(t_0) - \delta \tilde{q}(t_0)| < \eta$ satisfies also $|\delta q(t) - \delta \tilde{q}(t)| < \varepsilon$ for $t \geq t_0$. If no such $\eta$ exists, the solution is unstable.

**Definition 2.** If $\delta q(t)$ is stable, and if

$$
\lim_{t \to \infty} |\delta q(t) - \delta \tilde{q}(t)| = 0
$$

we say that $\delta q(t)$ is asymptotically stable.

For $t > 0$ the asymptotic behavior of Eq. (C.6) is governed by the sign of $\text{Re}\{\lambda_j\}$. For all roots $\text{Re}\{\lambda_j\} < 0$, $\delta q(t)$ is exponentially damped (the singular point is asymptotically stable). If for at least one of the roots $\text{Re}\{\lambda_j\} > 0$, $\delta q(t)$ grows exponentially (the singular point is unstable). If for at least one of the roots $\text{Re}\{\lambda_j\} = 0$ while the others remain negative, the system is stable in the sense of Lyapunov, but not asymptotically stable. This situation is called marginal stability. Here the exponents $\lambda_j$ are called the characteristic exponents.

The singular point $q_0$ then can be classified as follows, depending on the sign of characteristic exponents $\text{Re}\{\lambda_j\}$:

**1D case**

$$(\lambda) = (-)$$ stable fixed point,

$$(\lambda) = (+)$$ unstable fixed point.

**2D case**

$$(\lambda_1, \lambda_2) = (-, -)$$ stable fixed point (focus),

$$(\lambda_1, \lambda_2) = (-, 0)$$ stable limit cycle.

One can make even more refine analysis distinguishing real and imaginary parts of characteristic exponents:

<table>
<thead>
<tr>
<th>$\text{Im}(\lambda) = 0$</th>
<th>$\text{Im}(\lambda) \neq 0$, $\text{Re}(\lambda) \neq 0$</th>
<th>$\text{Re}(\lambda) = 0$, $\text{Im}(\lambda) \neq 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_1, \lambda_2 = (-, -)$ stable node,</td>
<td>$\lambda_1, \lambda_2 = (+, +)$ unstable node,</td>
<td>$\lambda_1, \lambda_2 = (+, -)$ saddle point,</td>
</tr>
<tr>
<td>$\lambda_1, \lambda_2 = (-, +)$ stable focus,</td>
<td>$\lambda_1, \lambda_2 = (-, +)$ unstable focus,</td>
<td>$\text{center}$</td>
</tr>
</tbody>
</table>
3D case

$(\lambda_1, \lambda_2, \lambda_3)=(-, -, -)$ stable fixed point (focus),

$(\lambda_1, \lambda_2, \lambda_3)=(-, -, 0)$ stable limit cycle,

$(\lambda_1, \lambda_2, \lambda_3)=(-, 0, 0)$ stable torus,

$(\lambda_1, \lambda_2, \lambda_3)=(+, 0, 0)$ unstable torus,

$(\lambda_1, \lambda_2, \lambda_3)=(+, 0, -)$ chaotic attractor,

$(\lambda_1, \lambda_2, \lambda_3)=(+, +, 0)$ unstable limit cycle,

where $+$ ($-$) stays for positive (negative) characteristic exponents $\lambda_j$ respectively.
Appendix D

The ZGB model

Originally the Ziff-Gulari-Brashard (ZGB) [6] model was introduced as a lattice gas version of CO$+\frac{1}{2}O_2$ reaction on catalytic surface. It consists of three reactions

\[ A\text{ (gas)} + O \xrightarrow{\zeta} A\text{ (ads)}, \]
\[ 2B\text{ (gas)} + 2O \xrightarrow{1-\zeta} 2B\text{ (ads)}, \]
\[ A\text{ (ads)} + B\text{ (ads)} \rightarrow O, \]

which mimic the reactant $A = CO$ and $2B = O_2$ adsorption in empty sites $O$ and reaction. The model was intensively investigated by various theoretical methods, e.g., MC computer simulations and master equation formalism (e.g., MF analysis). By the MC method it was found that two stationary states exist in the limit $t \rightarrow \infty$, which depend exclusively on the parameter $\zeta$ value. The irreversible reactant $B$ ($A$) poisoning occurs if $\zeta \leq \zeta_1 \cong 0.3874$ ($\zeta \geq \zeta_2 \cong 0.5250$) [26], respectively. It is shown, that these critical points can be associated with the phase transitions. For the intermediate case, $\zeta_1 < \zeta < \zeta_2$, the system shows a reactive steady state in which, however, the stable oscillatory behavior is not detected.

The effect of reactant $A$ and $B$ diffusion on the values of critical points was studied by Jensen and Fogedby [30]. They found that the first critical point $\zeta_1$ is governed only by $B$ diffusion. With infinitely fast $A$ and $B$ diffusion $\zeta_1 \rightarrow 0$, while the second critical point increases only slightly $\zeta_2 = 0.59$ [30]. In the limiting case of $A$ diffusion Mai et al. have found $\zeta_2 = 0.65$ [29].

The corresponding Master Equation was analyzed by Mai et al. [79] using the modified Kirkwood approximation. For original ZGB model they have found the following critical values $\zeta_1 = 0.395$ and $\zeta_2 = 0.565$. The first critical point value
is in good agreement with simulation data, while the MC simulations give smaller estimate of the second point. Mai et al. showed that this discrepancy can be attributed to the finite size effect. Simulations on finite lattices leads to incorrect results for reactant long range correlations in the vicinity of the critical point $\xi_2$. The critical point value is lowered since $B$ poisoning occurs, when the cluster of $B$ reaches the size of lattice, i.e., for larger lattices the critical point can be larger.

As a next the ZGB model was generalized to the case of surface reconstruction, which reflected the experimentally detected fact that reactants $B$ adsorb with different rates on different surfaces. In the first models surface reconstruction was introduced phenomenologically, e.g., when concentration of reactants $A$ reaches some critical value $0.3$, the surface is assumed to undergo the reconstruction globally in all lattice. More elaborated model was suggested by Kuzovkov et al. [9, 10], where the surface reconstruction is caused by adsorbed reactants $A$. Within this model was reproduced the experimentally detected different oscillatory behavior on Pt(100) and Pt(110) surfaces. It was shown that globally synchronized oscillations on Pt(110) surfaces is a result of spontaneous phase nucleation [54]. The more so, the phenomenological critical value $0.3$ used hitherto was obtained $(0.293)$ as a result of the model [59].
Bibliography


[35] V. Kashcheyeys, (private communication).


Acknowledgements

The author is greatly indebted to G. Borstel, V. N. Kuzovkov, E. A. Kotomin, D. Fuks and M. Neumann for many stimulating discussions.

He thanks also all members of the Department of Physics of University of Osnabrück for a great time and nice hospitality during his stay in Osnabrück.
Erklärung

Hiermit erkläre ich, die vorliegende Arbeit selbständig angefertigt und außer der angegebenen Literatur keine weiteren Hilfsmittel verwendet zu haben.


Guntars Zvejnieks