A stochastic approach to surface reactions including energetic interactions: I. Theory

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Abstract. A stochastic model to describe surface reaction systems is introduced. The reactions may include mono- and bimolecular steps (i.e. adsorption, desorption, reaction and diffusion steps). Furthermore, energetic interactions between the adsorbed particles are allowed. The temporal evolution of the system is described by master equations using the Markovian behaviour of these systems. The resulting infinite chain of equations is truncated at a certain level by using an improved superposition approximation. The equations are solved in a small lattice region exactly and their solution is connected to continuous functions which represent the behaviour of the system for large distances. We define a standard model which can be used to model various surface reaction systems in a unique manner. This gives the possibility for a better and easier comparison between different models.

1. Introduction

Surface reaction systems are in general not well understood, even today. Due to their importance in theoretical and applied research, much effort has been undertaken to obtain more insight. One can use different approaches to get a better understanding. Experimental observations are certainly of paramount importance. But it turns out that information on the individual reaction steps is very difficult to obtain and that interpretation of the data is, in general, not easy. A second possibility is the use of computer simulations. For the so-called $A+A \to 0$, $A+B \to 0$, $A+\frac{1}{2}B_2 \to 0$ reaction systems, Monte Carlo and cellular automata simulations were introduced. Lattices are used to represent the surface. Particles (A and/or B) can adsorb onto the lattice from a gas phase. Some of these simulations are in good agreement with some experimental observations [1]. The most prominent systems which have been studied are the CO oxidation on a Pt catalyst (see e.g. [2, 3]) and the formation of NH_3 [4]. The computer simulations have the disadvantage that the reaction steps should not be too complicated, because of the large amount of computer time which is needed. Therefore, purely theoretical approaches are very interesting for the description of these lattice models. But it has turned out that only very simple systems such as the $A + A \to 0$ reaction can be solved analytically (in one dimension) [5]. More complex systems which are able to model real systems cannot be solved via purely analytical methods. For this reason we want to introduce a combined analytical and numerical approach which is also

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able to handle more complex systems, and which takes explicitly structural and energetic aspects into account.

In order to describe real surface reactions it is necessary to include the aspect of energetic interactions between the particles, and consequently all processes should depend on temperature. Methods introduced so far [6–10] are incomplete and tend to contradict each other. For example, some authors consider parameters as energetically dependent on the neighbourhood which are treated by other authors as independent of it. Moreover, in an irreversible model (e.g. setting the desorption rate to zero) an equilibrium state cannot be obtained. In this case the transition probability for the processes cannot be modelled with the help of a Gibbs distribution. But information about other distributions is not available. Thus we conclude that the work introduced so far does not lead to a consistent and physically reasonable model for surface reactions in the case of energetic interactions.

We want to introduce a systematical approach to describe surface reactions including energetic interactions. This work is based on a stochastic model introduced in [11]. We will present the main ideas of the method here. Readers interested in the details are referred to the paper cited above. This model takes correlations explicitly into account, but it neglects the aspect of energetic interactions between the adsorbed particles and between a particle and the metal surface. The sequence of reaction steps is formulated by master equations on the assumption that they are of the Markovian type. An infinite chain of master equations for the distribution functions of the state of the surface and of pairs of surface sites (and so on) arises. This chain of equations cannot be solved analytically. To treat this problem in practice, this hierarchy is truncated at a certain level. The resulting equations can be solved numerically exactly in a small region and can be connected to a mean-field solution for large distances from a reference point. Therefore the model avoids three main difficulties: (i) the large amount of computer time which is normally needed for the simulations (this ansatz is about 100 times faster than comparable MC simulations), (ii) the finite (and rather small) lattice size used in MC simulations and (iii) the loss of structural information which occurs in simple theoretical models (site mean-field models) which do not take structural aspects of the adsorbate layer into account. Site mean-field models fail in the prediction of phase transition points due to long-range correlations. More sophisticated mean-field models (i.e. pair mean-field models) lead to a better quantitative agreement with MC simulations [12, 13].

The model [11] has been applied to the $A + \frac{1}{2}B_2 \rightarrow 0$ reaction and the results were compared with computer simulations [14]. The results are in very good agreement with each other. Disordered surfaces were treated within the stochastic approach in [15]. In the present paper we want to introduce energetic interactions into the model defined in [11]. We define a standard model in order to compare different surface reaction systems which are modelled by using this theoretical ansatz. In the absence of energetic interactions, the model reduces to the previous one of [11].

The paper is structured as follows. In section 2 we introduce the stochastic model. The i-point probabilities are defined in section 3. The resulting lattice equations which represent the temporal evolution (master equations) are represented in section 4. The superposition approximation is discussed in section 5. Section 6 deals with the numerical procedure which we use to solve the lattice equations. In section 7 the standard model is defined, and in section 8 an example is discussed which shows the equivalence to a previously introduced model in the limiting case of no energetic interactions.

2. The model

2.1. Definitions

We use a lattice with coordination number z. Each lattice site is given a lattice vector l. The state of the site l is represented by the lattice variable σ_l which may depend on the state of the catalyst site (e.g. promoted or not) and on the coverage with a particle. Here we deal only with the simple case in which all sites are equal and therefore σ depends only on its coverage (the other case is studied in [15]). Therefore $\sigma \in \{0, A, B, \ldots\}$ where 0 represents a vacant site, A a site which is occupied by an A particle and so on. Sometimes we will use the abbreviation $\sigma_l = \lambda$, $\sigma'_l = \lambda'$, $\sigma_n = \nu$ and $\sigma'_n = \nu'$. The states of the neighbourhood (z sites) of site l are denoted by $\{\sigma\}_l^z$.

2.2. Monomolecular steps

The simplest processes depend only on one lattice site. Examples are the creation of a particle ($0 \rightarrow A$), the annihilation ($A \rightarrow 0$) or the transformation ($A \rightarrow B$). These steps can be described by

$$\sigma_l \overset{p}{\Rightarrow} \sigma'_l \qquad \text{with } p \equiv \tilde{P}(\sigma_l \rightarrow \sigma'_l | \{\sigma\}_l^z) \tag{1}$$
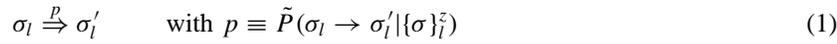
where p is the transition rate from state σ_l to σ'_l and $\{\sigma\}_l^z$ represents the set of states of the z neighbours of site l. For the square lattice $z = 4$. All these transition rates are listed in the matrix $\tilde{P}$. The transition probabilities do not depend on the chosen site l (i.e. we have spatial homogeneity) but they depend on the neighbourhood of site l. This is different from the model without energetic interactions.

2.3. Bimolecular steps

A more complicated situation arises if the step depends on two lattice sites l and n. Examples are reaction processes ($A + B \rightarrow 0 + 0$), diffusion processes ($A + 0 \rightarrow 0 + A$) or a pair creation ($0 + 0 \rightarrow B + B$), the latter being useful for the description of dissociative adsorption events. All these processes can be formulated by

$$\sigma_l \sigma_n \overset{k}{\Rightarrow} \sigma'_l \sigma'_n \tag{2a}$$

$$k \equiv \tilde{K}(\sigma_l \sigma_n \rightarrow \sigma'_l \sigma'_n | \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1})/z. \tag{2b}$$

The neighbourhood in the case of these processes is given by the $(z - 1)$ nearest neighbour sites of site l (with the exception of site n) and by the $(z - 1)$ neighbours of site n (with the exception of site l). We want to study only such lattices where $\{\sigma\}_l^{z-1}$ is not equal to $\{\sigma\}_n^{z-1}$. This holds for the square but not for the triangular lattice. We have introduced a factor $1/z$ in order to simplify the equations which will arise.

3. i-point probabilities

We introduce the probabilities $\rho^{(i)}$ which depend on i lattice sites. For $i = 1$ we have the simple density of particles on the lattice. For these probabilities the condition

$$\sum_{\sigma_l} \rho^{(1)}(\sigma_l) = 1 \tag{3}$$

holds. We use the abbreviation

$$C_\lambda = \rho^{(1)}(\sigma_l) \qquad \text{with } \lambda = \sigma_l \tag{4}$$

yielding $\sum_\lambda C_\lambda = 1$.

The two-point probabilities $\rho^{(2)}$ depend on two states (σ_l and σ_m) and on the distance $k = l - m$ of the lattice sites. For these probabilities the following sum rule holds:

$$\sum_{\sigma_m} \rho^{(2)}(\sigma_l \sigma_m) = \rho^{(1)}(\sigma_l). \tag{5}$$

The correlation functions $F_{\lambda\mu}(l - m)$, where $\lambda = \sigma_l$ and $\mu = \sigma_m$, are defined with the help of $\rho^{(2)}$:

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

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

$$\lim_{|k|\to\infty} F_{\lambda\mu}(k) = \frac{1}{C_\lambda C_\mu} \lim_{|k|\to\infty} \rho^{(2)}(\sigma_l \sigma_m) = 1. \tag{7}$$

In order to obtain a physical interpretation of the correlation functions let us define $c_\mu = C_\mu F_{\mu\lambda}(k)$. It is a mean density at the distance k from a central site which is in the state λ. c_μ represents structural information about the particle distribution on the lattice. As a normalization condition we get

$$\sum_\mu C_\mu F_{\lambda\mu}(k) = 1. \tag{8}$$

4. Master equations

The master equations are written in the form of an infinite chain of equations for the many-point probabilities. To this end we have to calculate *all* one-point densities and *all* pair correlation functions. These calculations and the results are presented in detail in the appendix. One ends up with a system of nonlinear equations for the densities, C_λ, and the pair correlation functions, $F_{\lambda\mu}$. The general form of the temporal evolution of the densities can be written as

$$\frac{dC_\lambda}{dt} = A_\lambda(C, F) - B_\lambda(C, F)C_\lambda. \tag{9}$$

For the pair correlation functions we obtain

$$\frac{dF_{\lambda\mu}}{dt} = A_{\lambda\mu}(C, F) - B_{\lambda\mu}(C, F)F_{\lambda\mu} \tag{10}$$

where $A(C, F)$ and $B(C, F)$ are simple positive functions (polynomials) of the densities C and the correlation functions F.

5. The superposition approximation

The temporal evolution equations for the densities $\rho^{(i)}$ form an infinite hierarchy of equations. This chain must be truncated to obtain a finite system of nonlinear equations. There are various possibilities to do this. The simplest model neglects all spatial correlations between the particles by setting all correlation functions to unity: one obtains a site mean-field model. Taking correlation functions for nearest neighbours into account, the model is of a pair mean-field type. We have studied this model in [16] using the Mamada–Takano approximation [17]. In a model which takes long-range correlations into account, one uses the idea of the superpositions approximation of Kirkwood [18]. We have studied this approximation for a model without energetic interactions in [11].

In this paper we study a more general model which includes energetic interactions between nearest neighbour particles. In spite of this definition of the interactions (short range) we observe the appearance of long-range spatial correlations. In contrast to the model without energetic interactions, high-order densities are essential. For example, the temporal evolution of the one-point densities $\rho^{(1)}$ depends on $\rho^{(1+z)}$ and $\rho^{(2z)}$, where z is the coordination number of the lattice. This means that compared to the case without energetic interactions, where we have only one- and two-point densities, very high point densities appear. In order to break these densities we use the Mamada–Takano approximation for terms of type $\rho^{(1+z)}$ and $\rho^{(2z)}$ in the temporal evolution equations for one point densities (see equations (A9) and (A16)). Terms of the type $\rho^{(2+z)}$ which appear in the temporal evolution of two-point densities are decomposed into two parts (see equation (A30)): a term $\rho^{(3)}$ and a cofactor. For the three-point density the Kirkwood approximation is used. The cofactor is approximated using the idea of Mamada and Takano. This leads to an expression containing only two-point densities.

The Mamada–Takano and Kirkwood approximations are purely mathematical concepts which have been very sucessfully used in various models. Both approximations are mathematically very similar. Therefore we focus our discussion on the Kirkwood approximation.

In the Kirkwood approximation the three-point probability is expressed as

$$\rho^{(3)}(\sigma_l \sigma_n \sigma_m) \Rightarrow C_\lambda C_\nu C_\mu F_{\lambda\nu}(l-n) F_{\nu\mu}(n-m) F_{\mu\lambda}(m-l). \tag{11}$$

This approximation fulfils all necessary conditions:

(i) It is a function of C and F.

(ii) If the lattice sites l, n, m are far away from each other, their states should be independent, which means

$$\rho^{(3)}(\sigma_l \sigma_n \sigma_m) \approx \rho^{(1)}(\sigma_l) \rho^{(1)}(\sigma_n) \rho^{(1)}(\sigma_m) = C_\lambda C_\nu C_\mu.$$

This holds because of equation (7).

(iii) If two sites are near each other (e.g. l and n) and m is far away, the state σ_m should be independent of the others. This means

$$\rho^{(3)}(\sigma_l \sigma_n \sigma_m) \approx \rho^{(2)}(\sigma_l \sigma_n) \rho^{(1)}(\sigma_m) = C_\lambda C_\nu C_\mu F_{\lambda\nu}(l-n).$$

The accuracy of the Kirkwood approximation decreases if all three points are near each other. Nevertheless, this approximation has been very successfully used [19].

We also use an improvement of the Kirkwood approximation which allows us to treat all correlation functions as independent ones [11]. We do not want to discuss this rather technical detail in this paper.

6. Method of solution

The main problem in solving the obtained equation system is connected with the solution of an infinite system of nonlinear differential equations for a chosen type of lattice. To solve this problem in practice the following approximation is used. A threshold value m_0 is introduced. For $|k| < m_0$ the lattice equations are solved exactly (here we use $m_0 = 5$). This first area determines several coordination spheres in which the lattice aspect of the problem is important. In the second area all properties change quasi-continuously with the distance $|k|$. Therefore we can use a continuum approximation by introduction of the coordinates $r = |k|$ and substitution of the correlation function $F(k)$ by the radial one $F(r)$. By this substitution, the equations transform into nonlinear equations in partial derivatives.

As the left (or inner) boundary condition (circumference of the circle with radius m_0), the solution within the first area at $|k| = m_0$ is used. Because of the weakness of the correlation we can use $F(\infty) = 1$ as the right (or external) boundary condition.

7. Definition of a standard model

In the past several simulation models for surface reaction systems including energetic interactions have been introduced [6–10]. These approaches are problematic in certain aspects because they contradict each other in the definition of the transition probabilities. Furthermore, steps which are considered to be independent of energetic interactions in one paper show a dependency in another. The main point of critique is that in the case of an irreversible reaction these models cannot lead to a Gibbs distribution. Therefore it is necessary and useful to introduce a standard model in order to compare different models in the future. Moreover, we will systematically use the Gibbs distribution in order to introduce a temperature. It is then possible to define the transition probabilities in such a way that an equilibrium state can be reached.

The definition of the transition rates for our stochastic model follows an ansatz of Kawasaki [20, 21]. We use the abbreviation X for an initial state (σ_l for mono- and $\sigma_l\sigma_n$ for bimolecular steps), Y for a final state (σ_l' for mono- and $\sigma_l'\sigma_n'$ for bimolecular steps) and Z for the states of the neighbourhood ($\{\sigma\}_l^z$ for mono-and ($\{\sigma\}_l^{z-1}$; $\{\sigma\}_n^{z-1}$) for bimolecular steps). If we study the system in which the neighbourhood is fixed we can see a relaxation process in a very small area. We introduce the normalized probability $W(X)$ and the corresponding rates $\tilde{K}(X \to Y|Z)$. For this (reversible) process we write the Markovian master equation

$$\frac{dW(X)}{dt} = \tilde{K}(Y \to X|Z)W(Y) - \tilde{K}(X \to Y|Z)W(X). \tag{12}$$

For $t \to \infty$ we expect to get an equilibrium state

$$W(X) = W_{eq}(X|Z) = \exp(-H(X|Z)/k_BT)$$
$$\times (\exp(-H(X|Z)/k_BT) + \exp(-H(Y|Z)/k_BT))^{-1} \tag{13}$$

where $H(X|Z)$ is the corresponding energy of the system in the state X. (For an open system we must also take the chemical potential into account.)

For the reversible processes (irreversible processes are discussed in section 8 of this paper) we can define the ratio of the transition rates using equation (12):

$$\tilde{K}(X \to Y|Z)/\tilde{K}(Y \to X|Z) = \exp(-\delta H/k_BT) \tag{14a}$$
$$\delta H = H(Y|Z) - H(X|Z). \tag{14b}$$

In order to define the rates, we use as a condition of our model a *symmetric* form for the rates:

$$\tilde{K}(X \to Y|Z) = Q(X|Y)W_{eq}(Y|Z) \tag{15a}$$
$$Q(X|Y) = Q(Y|X) \tag{15b}$$

where $Q(X|Y)$ is a factor which is independent of the neighbourhood Z. The neighbourhood is only taken into account by $W_{eq}(Y|Z)$. Normally one writes this in the form [21]

$$\tilde{K}(X \to Y|Z) = \frac{1}{2\tau}\left[1 - \tanh\left(\frac{\delta H}{2k_BT}\right)\right] \tag{16}$$

which is identical to our representation with $1/2\tau = Q(X|Y)$. The choice of the standard form (15) offers two advantages. First, the rates are bounded by $Q(X|Y)$ and second, we can use the normalizable probability $W_{eq}(Y|Z)$.

In principle the non-symmetric ansatz

$$\tilde{K}(X \to Y|Z) = Q(X|Y)\exp(-\delta H/k_B T) \tag{17a}$$

$$\tilde{K}(Y \to X|Z) = Q(X|Y) \tag{17b}$$

can be used, but then one would encounter the problem that the transition rate is not bounded. Furthermore, steps such as the diffusion should be symmetric which is not possible with the non-symmetric ansatz.

Let us study the energetic aspect in detail. For the monomolecular steps we obtain

$$H(X|Z) \equiv H(\sigma_l|\{\sigma\}_l^z) = (\epsilon(\sigma_l) - \chi(\sigma_l; T)) + \sum_{i=1}^{z} E_{\sigma_l \sigma_i} \tag{18}$$

where $E_{\lambda\nu}$ is the matrix which contains the interaction energies, $\epsilon(\lambda)$ is the particle energy and $\chi(\lambda; T)$ is the chemical potential which depends on the temperature T. For vacant sites $(\sigma_l = 0)$, $\epsilon(0) = \chi(0; T) = E_{\lambda 0} \equiv 0$.

In the standard model we obtain for the one-point transition rates (using equation (15))

$$\tilde{P}(\sigma_l \to \sigma_l'|\{\sigma\}_l^z) \equiv Q(\sigma_l|\sigma_l')\exp(-H(\sigma_l'|\{\sigma\}_l^z)/k_B T)$$
$$\times (\exp(-H(\sigma_l|\{\sigma\}_l^z)/k_B T) + \exp(-H(\sigma_l'|\{\sigma\}_l^z)/k_B T))^{-1}. \tag{19}$$

For the bimolecular steps we obtain (analogously to equation (18))

$$H(\sigma_l \sigma_n|\{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}) = (\epsilon(\sigma_l) - \chi(\sigma_l; T)) + (\epsilon(\sigma_n) - \chi(\sigma_n; T))$$
$$+ E_{\sigma_l \sigma_n} + \sum_{i=1}^{z-1} E_{\sigma_l \sigma_i} + \sum_{j=1}^{z-1} E_{\sigma n \sigma j}. \tag{20}$$

For the two-point transition rates we get (using equation (15))

$$\tilde{K}(\sigma_l \sigma_n \to \sigma_l' \sigma_n'|\{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}) = Q(\sigma_l \sigma_n|\sigma_l' \sigma_n')W_{eq}(\sigma_l' \sigma_n'|\{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}). \tag{21}$$

8. Examples for the standard model

Some examples serve to demonstrate the flexibility of the standard model. We introduce a model which includes mono- and bimolecular steps as discussed in [14]. The previous model had no energetic interactions. Applying the model described in this paper to an empty lattice we must obtain the previous model. This will be shown below.

The monomolecular steps such as the creation of a particle A with the rate $P(0 \to A) = p_A = p_A(T)$ and an annihilation process $P(A \to 0) = k_A = k_A(T)$ are normally written in the form $k_A = k_A^0 \exp(-E_A/k_B T)$ with an activation energy E_A and a frequency factor k_A^0. In the following we use the abbreviation $\{0\}_l^z$ for the empty neighbourhood of site l. We obtain

$$H(A|\{0\}_l^z) = \epsilon(A) - \chi(A; T) \qquad H(0|\{0\}_l^z) = 0. \tag{22}$$

From equation (19) follows

$$\tilde{P}(0 \to A|\{0\}_l^z) \equiv Q(A|0)\frac{\omega}{1+\omega} = p_A \tag{23a}$$

$$\tilde{P}(A \to 0|\{0\}_l^z) \equiv Q(A|0)\frac{1}{1+\omega} = k_A \tag{23b}$$

with

$$\omega = \exp(-[\epsilon(A) - \chi(A; T)]/k_B T). \tag{24}$$

Hence $\omega = p_A/k_A$ and $Q(A|0) = (p_A + k_A)$. For the difference $[\epsilon(A) - \chi(A; T)]$ the physical interpretation

$$\epsilon(A) - \chi(A; T) = k_B T \ln(k_A/p_A) = k_B T \ln(k_A^0/p_A) - E_A \tag{25}$$

is obtained. The last equality holds for $p_A = $ constant. Therefore our model can take into account the adsorption energy and also the frequency factor.

In our previous model without energetic interactions [14] we have for a bimolecular step the two-point transition rates $\tilde{K}(\sigma_l \sigma_n \to \sigma_l' \sigma_n')$. Let us study the processes $K(BB \to 00) = \beta_B$ (desorption) and $K(00 \to BB) = p_B$ (adsorption). In the new model we get for an empty surface

$$H(BB|\{0\}_l^{z-1}; \{0\}_n^{z-1}) = 2(\epsilon(B) - \chi(B; T)) + E_{BB} \tag{26a}$$
$$H(00|\{0\}_l^{z-1}; \{0\}_n^{z-1}) = 0. \tag{26b}$$

The transition rates are given by

$$\tilde{K}(00 \to BB|\{0\}_l^{z-1}; \{0\}_n^{z-1}) = Q(00|BB)\frac{\omega}{1+\omega} \tag{27a}$$

$$\tilde{K}(BB \to 00|\{0\}_l^{z-1}; \{0\}_n^{z-1}) = Q(00|BB)\frac{1}{1+\omega} \tag{27b}$$

with

$$\omega = \exp(-2[\epsilon(B) - \chi(B; T)]/k_B T - E_{BB}/k_B T). \tag{28}$$

We obtain that $\omega = p_B/\beta_B$, $Q(00|BB) = (p_B + \beta_B)$ and

$$\epsilon(B) - \chi(B; T) = \{k_B T ln(\beta_B/p_B) - E_{BB}\}/2 = \{k_B T ln(\beta_B^0/p_B) - E_B - E_{BB}\}/2 \tag{29}$$

for the case that $\beta_B = \beta_B^0 \exp(-E_B/k_B T)$ and $p_B = $ constant.

For a diffusion process on an empty surface we obtain

$$\tilde{K}(A0 \to 0A|\{0\}_l^{z-1}; \{0\}_n^{z-1}) \equiv Q(A0|0A)/2 = D = D_0 \exp(-E_{diff}/k_B T) \tag{30}$$

and $Q(A0|0A) = 2D$, where D is the transition rate for this process for the case without energetic interactions.

This proposed standard model has some important features. If in the case of a reversible process on an empty surface one of the rates goes to zero, the rate for the case of the occupied surface (taking interactions with the neighbourhood into account) would also go to zero. In this limit, the rate for the reverse process would become independent of the neighbourhood. To show this property, let us discuss an example for the adsorption/desorption process. The process taking place on an empty surface is defined by equation (23). For an occupied surface we obtain for the transition rates

$$\tilde{P}(0 \to A|\{\sigma\}_l^z) = Q(A|0)\frac{w}{1+w} \tag{31a}$$

$$\tilde{P}(A \to 0|\{\sigma\}_l^z) = Q(A|0)\frac{1}{1+w} \tag{31b}$$

with $w = v\omega$. v describes the interactions with the neighbourhood and clearly depends on the values of $E_{\lambda\mu}$. The role of ω is very interesting. We have already obtained $Q(A|0) = (p_A + k_A)$ and $\omega = p_A/k_A$. We discuss the following two cases.

(i) $p_A \to 0, k_A = $ constant. We obtain $\omega \to 0, \tilde{P}(0 \to A|\{\sigma\}_l^z) \to 0$ and $\tilde{P}(A \to 0|\{\sigma\}_l^z) \to k_A = \tilde{P}(A \to 0|\{0\}_l^z)$.

(ii) $k_A \to 0, p_A = $ constant. We obtain $\omega \to \infty, \tilde{P}(0 \to A|\{\sigma\}_l^z) \to p_A = \tilde{P}(0 \to A|\{0\}_l^z)$ and $\tilde{P}(A \to 0|\{\sigma\}_l^z) \to 0$.

We see that if a rate goes to zero, the corresponding rate for the reverse process will be independent of the neighbourhood. Furthermore, for such an irreversible process (one rate goes to zero) the Gibbs distribution cannot be used, and we are not able to say anything about the energetics of the system. Therefore, we must describe irreversible processes with rates which are independent of the neighbourhood (which means independent of Z in equation (14)).

There is another interesting point in the standard model which has to be explained. Applied to normal reaction systems we always have the reaction step $AB \rightarrow 00$, which is irreversible and therefore has to be described as independent of the neighbourhood. But the effective reaction rate depends clearly on the correlation functions, which means that it depends finally on the neighbourhood, but we are not allowed to write it in a neighbourhood-dependent form from the beginning.

9. Conclusions

The stochastic ansatz is useful to describe surface reaction systems which include mono- and bimolecular steps such as adsorption, desorption, diffusion and reaction in the presence of energetic interactions. The equations of motion are written as master equations for the one- and two-point probabilities. The appearance of high-order correlation functions in the equations of motion is avoided by making use of a generalized superposition approximation, and by suitable averaging procedures which are guided by a correspondence principle. According to this principle, the equations should reduce to the previously developed model [11, 14] in the absence of energetic interactions. Because the model takes correlations of the particles on the lattice into account explicitly, the results are in good agreement with computer simulations in the absence of energetic interactions. The same is expected to be the case if they are present.

At a first glance the equations seem to be very complex, but the numerical solution of the equations is a process which can be done with a computer program.

The model offers several advantages compared to simulations. The theoretical ansatz needs only a small amount of computing time. Therefore more complex systems can be studied. Moreover, our models are not restricted to small lattices which are normally used in computer simulations. This is of particular interest at phase transition points of first and second order or in the case of strong energetic interactions where large correlations appear. All these advantages hold for the present model. In the following paper we will apply this model to a real model of a surface reaction system including energetic interactions.

Appendix. Equations for the many-point probabilities

A1. Equation of motion for the one-point probabilities

For the one-point probabilities we obtain

$$\frac{d\rho^{(1)}(\sigma_l)}{dt} \equiv \frac{dC_\lambda}{dt} = \frac{dC_\lambda}{dt}\bigg|_{in} - \frac{dC_\lambda}{dt}\bigg|_{out} \tag{A1}$$

where the term with the index *in* describes the creation of a state σ_l and the term with the index *out* the annihilation of a state σ_l. The terms of equation (A1) are separated into mono- and bimolecular steps:

$$\frac{dC_\lambda}{dt}\bigg|_{in} = \frac{dC_\lambda}{dt}\bigg|_{in}^{mono} + \frac{dC_\lambda}{dt}\bigg|_{in}^{bi}. \tag{A2}$$

We define a variable $\alpha_{l,n}$ which is unity for the case that l and n are nearest neighbour sites on the lattice and zero otherwise. With this definition we obtain

$$\frac{dC_\lambda}{dt}\bigg|_{in}^{mono} = \sum_{\{\sigma\}_{l}^{z}} \sum_{\sigma_l'} \tilde{P}(\sigma_l' \to \sigma_l | \{\sigma\}_l^z) \rho^{(1+z)}(\sigma_l'; \{\sigma\}_l^z) \tag{A3}$$

$$\frac{dC_\lambda}{dt}\bigg|_{in}^{bi} = \sum_{n} \frac{\alpha_{l,n}}{z} \sum_{\{\sigma\}_l^{z-1}} \sum_{\{\sigma\}_n^{z-1}} \sum_{\sigma_l'\sigma_n'\sigma_n} \tilde{K}(\sigma_l'\sigma_n' \to \sigma_l\sigma_n | \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1})$$
$$\times \rho^{(2z)}(\sigma_l'\sigma_n'; \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}) \tag{A4}$$

and

$$\frac{dC_\lambda}{dt}\bigg|_{out} = \frac{dC_\lambda}{dt}\bigg|_{out}^{mono} + \frac{dC_\lambda}{dt}\bigg|_{out}^{bi} \tag{A5}$$

with

$$\frac{dC_\lambda}{dt}\bigg|_{out}^{mono} = \sum_{\{\sigma\}_l^z} \sum_{\sigma_l'} \tilde{P}(\sigma_l \to \sigma_l' | \{\sigma\}_l^z) \rho^{(1+z)}(\sigma_l; \{\sigma\}_l^z) \tag{A6}$$

$$\frac{dC_\lambda}{dt}\bigg|_{out}^{bi} = \sum_{n} \frac{\alpha_{l,n}}{z} \sum_{\{\sigma\}_l^{z-1}} \sum_{\{\sigma\}_n^{z-1}} \sum_{\sigma_l'\sigma_n'\sigma_n} \tilde{K}(\sigma_l\sigma_n \to \sigma_l'\sigma_n' | \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1})$$
$$\times \rho^{(2z)}(\sigma_l\sigma_n; \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}). \tag{A7}$$

Here monomolecular steps need $(1 + z)$-point probabilities and bimolecular steps need $(2 + 2(z - 1) = 2z)$-point probabilities for their description.

In principle many different approaches can be used to treat an equation such as (A5) which we take as an example. We want to use a correspondence principle: in the absence of energetic interactions this model should be equivalent to the model discussed in [11]. This results in the condition

$$\sum_{\{\sigma\}_l^z} \rho^{(1+z)}(\sigma_l; \{\sigma\}_l^z) = \rho^{(1)}(\sigma_l) \tag{A8}$$

where we used equation (10) from [11]. In order to avoid the explicit appearance of high-order correlation functions one uses the Mamada–Takano approximation [17]

$$\rho^{(1+z)}(\sigma_l; \{\sigma\}_l^z) \Rightarrow \rho^{(1)}(\sigma_l) \prod_{i=1}^{z} \frac{\rho^{(2)}(\sigma_l\sigma_i)}{\rho^{(1)}(\sigma_l)} \tag{A9}$$

which gives the condition (A8) automatically. For the square lattice with $z = 4$ we can rewrite this equation in the form

$$\rho^{(1+z)}(\sigma_l; \{\sigma\}_l^z) \Rightarrow C_\lambda \prod_{i=1}^{4} (C_{\nu_i} F_{\lambda\nu_i}(1)). \tag{A10}$$

From this follows for the monomolecular steps

$$\frac{dC_\lambda}{dt}\bigg|_{out}^{mono} = \sum_{\sigma_l'} P(\sigma_l \to \sigma_l') \rho^{(1)}(\sigma_l) \tag{A11}$$

which is formally identical to the model without energetic interactions. Here P (which replaces $\tilde{P}$) is defined as the mean value over the nearest neighbourhood

$$P(\sigma_l \to \sigma_l') = \sum_{\{\sigma\}_l^z} \tilde{P}(\sigma_l \to \sigma_l' | \{\sigma\}_l^z) \prod_{i=1}^{z} \frac{\rho^{(2)}(\sigma_l \sigma_i)}{\rho^{(1)}(\sigma_l)}. \tag{A12}$$

We thus do not take into account the explicit configuration of the neighbours, which is certainly a sensible approximation. By doing this we obtain for the first term in equation (A5)

$$\left.\frac{\mathrm{d}C_\lambda}{\mathrm{d}t}\right|_{out}^{mono} = \sum_{\lambda'} P(\lambda \to \lambda')C_\lambda \tag{A13}$$

where the mean value $P(\lambda \to \lambda')$ is a homogeneous polynomial function of order z in C_μ and in $F_{\lambda\mu}(1)$.

The monomolecular *in* term has a very similar form.

$$\left.\frac{\mathrm{d}C_\lambda}{\mathrm{d}t}\right|_{in}^{mono} = \sum_{\lambda'} P(\lambda' \to \lambda)C_{\lambda'}. \tag{A14}$$

For the bimolecular steps (A7), we proceed in a similar way as follows. Here we use the sum rule

$$\sum_{\{\sigma\}_l^{z-1}} \sum_{\{\sigma\}_n^{z-1}} \rho^{(2z)}(\sigma_l \sigma_n; \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}) = \rho^{(2)}(\sigma_l \sigma_n). \tag{A15}$$

With the Mamada–Takano [17] approximation we get

$$\rho^{(2z)}(\sigma_l \sigma_n; \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}) \Rightarrow \rho^{(2)}(\sigma_l \sigma_n) \prod_{i=1}^{z-1} \frac{\rho^{(2)}(\sigma_l \sigma_i)}{\rho^{(1)}(\sigma_l)} \prod_{j=1}^{z-1} \frac{\rho^{(2)}(\sigma_n \sigma_j)}{\rho^{(1)}(\sigma_n)}. \tag{A16}$$

Using the last expression we obtain

$$\left.\frac{\mathrm{d}C_\lambda}{\mathrm{d}t}\right|_{out}^{bi} = \sum_n \frac{\alpha_{l,n}}{z} \sum_{\sigma_l' \sigma_n' \sigma_n} K(\sigma_l \sigma_n \to \sigma_l' \sigma_n')\rho^{(2)}(\sigma_l \sigma_n) \tag{A17}$$

which is identical to the model without energetic interactions. We have used as a mean value over the neighbourhood

$$K(\sigma_l \sigma_n \to \sigma_l' \sigma_n') = \sum_{\{\sigma\}_l^{z-1}} \sum_{\{\sigma\}_n^{z-1}} \tilde{K}(\sigma_l \sigma_n \to \sigma_l' \sigma_n' | \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1})$$

$$\times \prod_{i=1}^{z-1} \frac{\rho^{(2)}(\sigma_l \sigma_i)}{\rho^{(1)}(\sigma_l)} \prod_{j=1}^{z-1} \frac{\rho^{(2)}(\sigma_n \sigma_j)}{\rho^{(1)}(\sigma_n)}. \tag{A18}$$

We can rewrite this result in the form

$$\left.\frac{\mathrm{d}C_\lambda}{\mathrm{d}t}\right|_{out}^{bi} = \sum_{\lambda'\nu'\nu} K(\lambda\nu \to \lambda'\nu')C_\lambda C_\nu F_{\lambda\nu}(1). \tag{A19}$$

Here the effective transition rate $K(\lambda\nu \to \lambda'\nu')$ is a function of the density C_μ and the pair correlation functions $F_{\lambda\mu}(1)$ and $F_{\nu\mu}(1)$.

For the *in* term of the bimolecular step we obtain

$$\left.\frac{\mathrm{d}C_\lambda}{\mathrm{d}t}\right|_{in}^{bi} = \sum_{\lambda'\nu'\nu} K(\lambda'\nu' \to \lambda\nu)C_{\lambda'} C_{\nu'} F_{\lambda'\nu'}(1). \tag{A20}$$

A2. Equation of motion for the two-point probabilities

We turn to the processes which take place on two different lattice sites l and m. The following processes are possible.

(1) l and m are not nearest neighbours on the lattice.

(a) The state σ_l can be created or annihilated independently of m. Only the neighbourhood of l is important.

(b) The state σ_m can be created or annihilated independently of l. Only the neighbourhood of m is important.

(2) If l and m are nearest neighbours on the lattice, additional terms must be taken into account which represent the bimolecular steps.

We want to introduce a diagrammatic description for these processes:

$$\frac{d\rho^{(2)}(\sigma_l\sigma_m)}{dt} = \underset{l \quad m}{\bullet\!-\!\!\!-\!\circ} + \underset{l \quad m}{\circ\!-\!\!\!-\!\bullet} + \alpha_{l,m}\{\bullet\bullet\}. \tag{A21}$$

On the site ($\bullet$) a process takes place. The symbol ($\circ$) means that this site plays no role in the determination of the state of the other site. Therefore the first two terms correspond to the cases (1a) and (1b) and the third term represents the bimolecular step for l and m being nearest neighbours. The diagrams of type (1a) and (1b) are of the form

$$\underset{l \quad m}{\bullet\!-\!\!\!-\!\circ} = \left(\underset{l \quad m}{\bullet_{in}\!-\!\!\!-\!\circ} - \underset{l \quad m}{\bullet_{out}\!-\!\!\!-\!\circ} \right). \tag{A22}$$

The first term on the right-hand side represents all processes which create the state σ_l. The difference from equation (A1) lies in the additional condition that the site m is in the state σ_m. Therefore we can write (compare equations (A6), (A7))

$$\frac{d\rho^{(2)}(\sigma_l\sigma_m)}{dt}\bigg|_l^{out} = \frac{d\rho^{(2)}(\sigma_l\sigma_m)}{dt}\bigg|_l^{mono,out} + \frac{d\rho^{(2)}(\sigma_l\sigma_m)}{dt}\bigg|_l^{bi,out} \tag{A23}$$

with

$$\frac{d\rho^{(2)}(\sigma_l\sigma_m)}{dt}\bigg|_l^{mono,out} = \sum_{\{\sigma\}_l^z}\sum_{\sigma_l'} \tilde{P}(\sigma_l \to \sigma_l'|\{\sigma\}_l^z)\rho^{(2+z)}(\sigma_l\sigma_m; \{\sigma\}_l^z) \tag{A24}$$

$$\frac{d\rho^{(2)}(\sigma_l\sigma_m)}{dt}\bigg|_l^{bi,out} = \sum_n \frac{\alpha_{l,n}}{z} \sum_{\{\sigma\}_l^{z-1}}\sum_{\{\sigma\}_n^{z-1}}\sum_{\sigma_l'\sigma_n'\sigma_n} \tilde{K}(\sigma_l\sigma_n \to \sigma_l'\sigma_n'|\{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1})$$
$$\times \rho^{(2z+1)}(\sigma_l\sigma_n\sigma_m; \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}). \tag{A25}$$

This equation is only valid for $|l - m| > 1$. The corresponding case where m and l are nearest neighbours will be treated below. Let us first discuss the monomolecular step in the case $|l - m| > 1$. Using equation (A10) we obtain

$$\rho^{(2+z)}(\sigma_l\sigma_m; \{\sigma\}_l^z) \Rightarrow \rho^{(2)}(\sigma_l\sigma_m) \prod_{i=1}^z \frac{\rho^{(2)}(\sigma_l\sigma_i)}{\rho^{(1)}(\sigma_l)}. \tag{A26}$$

From this equation follows

$$\frac{d[C_\lambda C_\mu F_{\lambda\mu}(l - m)]}{dt}\bigg|_l^{mono,out} = \frac{d\rho^{(2)}(\sigma_l\sigma_m)}{dt}\bigg|_l^{mono,out} = \sum_{\lambda'} P(\lambda \to \lambda')C_\lambda C_\mu F_{\lambda\mu}(l - m). \tag{A27}$$

For the *in* term a similar expression can be derived in the same way.

We have still to treat the terms where a process on site l occurs without m being affected, but l and m are nearest neighbours. For $|l - m| = 1$ (nearest neighbours) we must change the expression for ρ to

$$\rho^{(1+z)}(\sigma_l \sigma_m; \{\sigma\}_l^{z-1})$$

and

$$\rho^{(2z)}(\sigma_l \sigma_n \sigma_m; \{\sigma\}_l^{z-2}; \{\sigma\}_n^{z-1})$$

respectively. Again we use equation (A9). But now we get a non-complete mean value because one site must be in the state σ_m. Therefore we introduce the definition

$$P(\sigma_l \to \sigma_l' | \sigma_m) = \sum_{\{\sigma\}_l^{z-1}} \tilde{P}(\sigma_l \to \sigma_l' | \{\sigma\}_l^z) \prod_{i=1}^{z-1} \frac{\rho^{(2)}(\sigma_l \sigma_i)}{\rho^{(1)}(\sigma_l)} \tag{A28}$$

$$\{\sigma\}_l^z = \{\sigma\}_l^{z-1}, \sigma_m.$$

For the nearest neighbours follows

$$\frac{d[C_\lambda C_\mu F_{\lambda\mu}(1)]}{dt}\Big|_l^{mono,out} = \sum_{\lambda'} P(\lambda \to \lambda' | \mu) C_\lambda C_\mu F_{\lambda\mu}(1). \tag{A29}$$

If no energetic interactions are present $P(\lambda \to \lambda' | \mu)$ reduces to $P(\lambda \to \lambda')$. The *in* term is analogous.

For the true bimolecular steps (the triple (lmn)) we make the ansatz

$$\rho^{(2z+1)}(\sigma_l \sigma_n \sigma_m; \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1}) \Rightarrow \rho^{(3)}(\sigma_l \sigma_n \sigma_m) \prod_{i=1}^{z-1} \frac{\rho^{(2)}(\sigma_l \sigma_i)}{\rho^{(1)}(\sigma_l)} \prod_{j=1}^{z-1} \frac{\rho^{(2)}(\sigma_n \sigma_j)}{\rho^{(1)}(\sigma_n)}. \tag{A30}$$

Let l and n be nearest neighbours in this triple on which the bimolecular step takes place. We must distinguish between the two cases in which m is or is not a nearest neighbour of site l. Using this expression we get for the case that l and m are not nearest neighbours

$$\frac{d[C_\lambda C_\mu F_{\lambda\mu}(l-m)]}{dt}\Big|_l^{bi,out} = \sum_n \frac{\alpha_{l,n}}{z} \sum_{\sigma_l' \sigma_n' \sigma_n} K(\sigma_l \sigma_n \to \sigma_l' \sigma_n') \rho^{(3)}(\sigma_l \sigma_n \sigma_m). \tag{A31}$$

Otherwise we get (for $m \neq n$)

$$\frac{d[C_\lambda C_\mu F_{\lambda\mu}(1)]}{dt}\Big|_l^{bi,out} = \sum_n \frac{\alpha_{l,n}}{z} \sum_{\sigma_l' \sigma_n' \sigma_n} K(\sigma_l \sigma_n \to \sigma_l' \sigma_n' | \{\sigma_m\}_l) \rho^{(3)}(\sigma_l \sigma_n \sigma_m) \tag{A32}$$

where

$$K(\sigma_l \sigma_n \to \sigma_l' \sigma_n' | \{\sigma_m\}_l) = \sum_{\{\sigma\}_l^{z-2}} \sum_{\{\sigma\}_n^{z-1}} \tilde{K}(\sigma_l \sigma_n \to \sigma_l' \sigma_n' | \{\sigma\}_l^{z-1}; \{\sigma\}_n^{z-1})$$

$$\times \prod_{i=1}^{z-2} \frac{\rho^{(2)}(\sigma_l \sigma_i)}{\rho^{(1)}(\sigma_l)} \prod_{j=1}^{z-1} \frac{\rho^{(2)}(\sigma_n \sigma_j)}{\rho^{(1)}(\sigma_n)} \tag{A33}$$

and $\{\sigma_m\}_l$ means that the state of one neighbour of site l is fixed in the state σ_m.

Therefore we can write for the *out* terms of the bimolecular steps of equation (A21) (in the notation given there)

$$\{\bullet\bullet\}_{out} = \frac{1}{z} \sum_{\{\sigma\}_l^{z-1}} \sum_{\{\sigma\}_m^{z-1}} \sum_{\sigma_l' \sigma_m'} \tilde{K}(\sigma_l \sigma_m \to \sigma_l' \sigma_m' | \{\sigma\}_l^{z-1}; \{\sigma\}_m^{z-1}) \rho^{(2z)}(\sigma_l \sigma_m; \{\sigma\}_l^{z-1}; \{\sigma\}_m^{z-1}).$$

$$\tag{A34}$$

The approximation (A16) simplifies the $2z$-point probabilities. The *in* terms can be obtained in an analogous manner to the *out* terms.

Finally we get

$$\alpha_{l,m}\{\bullet\bullet\} = \frac{\alpha_{l,m}}{z} \sum_{\lambda'\mu'} K(\lambda'\mu' \to \lambda\mu) C_{\lambda'} C_{\mu'} F_{\lambda'\mu'}(1) - \frac{\alpha_{l,m}}{z} \sum_{\lambda'\mu'} K(\lambda\mu \to \lambda'\mu') C_{\lambda} C_{\mu} F_{\lambda\mu}(1).$$

$$(A35)$$

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