A stochastic approach to surface reactions including energetic interactions: II. Application to the $A + \frac{1}{2}B_2 \to 0$ reaction

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Abstract. We study a stochastic model for the $A + \frac{1}{2}B_2 \to 0$ reaction with energetic interactions between the particles. The reaction system includes adsorption, desorption, reaction and diffusion steps which depend on energetic interactions. The temporal evolution of the system is described by master equations using the Markovian behaviour of the system. We study the system behaviour at different values of the energetic parameters and at varying diffusion and desorption rates. The location and the character of the phase transition points will be discussed in detail. The role of the constants used *in situ* mean field theories such as kinetic constants etc are discussed in view of the new theories. All such constants, if they are at all meaningful, are functions of correlation functions and not constants. This has important implications for the analysis of experiments.

1. Introduction

In chemical kinetics involving many particles (i.e. reactions where, not the individual steps dictate the system behaviour, but the statistical effects arising from the large number of particles, e.g. reactions on surfaces) one has two main approaches at hand: mean-field type approaches (the classical chemical kinetics) or Monte Carlo (MC) type approaches. Site mean-field approaches are sometimes transferred directly from gas-phase kinetics to surface reactions without worrying much about the extreme limitations arising from the absence of homogeneity, from segregation effects etc. These approaches, by definition, neglect all correlations, but they have proven very useful for analysing experimental data and extracting activation energies, reaction and diffusion constants, etc from experimental measurements. This is not without substantial problems which may arise if the mean-field type equations just do not describe the processes correctly. We shall come back to this problem below in more detail.

In the MC approaches the correlations are included. These methods have become very fashionable starting with the work of Ziff, Gulari and Barshad (ZGB model) [1] for the oxidation of CO on a metal surface. Although the models used to date are still somewhat simplistic and ignore many experimental details of the reaction steps they have proven to be very useful and they are capable of describing certain aspects of the reaction if experiment

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and the 'MC reaction' are performed in a way corresponding to each other [2]. Many MC simulations for different aspects have been performed on the CO oxidation reaction [3–18].

Energetics is rarely included in the MC simulations so far, with the exception of approaches in [19–21]. There are two reasons for the rareness of such investigations. First, the experimental data for energetic interactions are, at least on metal surfaces, in general not available and if data exist they frequently refer to surfaces at high coverages, i.e. these data already contain the effect of energetic interactions among the particles, which is inappropriate. Secondly, the inclusion of energetic interactions is difficult and computationally costly. The investigations in [19–21] demonstrate the strong influence of interactions on the system behaviour for the case of the CO oxidation. But these approaches have also to be criticized. They include the energetic effect of the environment on irreversible reactions, which, from statistical mechanics, is incorrect (see the preceding paper [22], referred to as paper I in the following). Also, for no apparent reason, some individual steps are included and related ones left out. In one approach adsorption is made dependent on energetic interactions but not desorption, in the other it is vice versa, but no argument is given for either.

We have presented in paper I [22] a general stochastic theory for surface reactions including energetic interactions among the particles. This theory consists of the equation of motion for the i-point probabilities and the truncation of this hierarchy of equations via the Mamada–Takano [23] and the Kirkwood [24] superposition approximation and of a standard statistical mechanical model following the work of Kawasaki [25]. An important directive emerges automatically from this standard model. An irreversible reaction cannot depend on energetic interactions with the neighbourhood. In other words, if one reaction depends on the neighbourhood (e.g. adsorption), then so does the reverse reaction as well (desorption in this case). This is also the reason why in the present paper we shall not deal with the activation energy of the CO_2 formation. The reaction is conducted irreversibly—CO_2 leaves the surface.

This stochastic theory is an extension of previous work dealing with surface reactions [26–29]. We have compared the results of the stochastic ansatz with the MC simulation of the ZGB model (see table 1). Even for a phase transition point of second order (y_1) we found good agreement with MC simulations [27].

Table 1. Second-order phase-transition points of the ZGB model without energetic interactions obtained by different methods.

Method	y_1
MC simulation [1]	0.395
Correlation analysis [27]	0.395
Cluster approximation [29]	0.258
Pair mean field [32]	0.250
Site mean field [8]	0.000

In the present article the $A + \frac{1}{2}B_2 \rightarrow 0$ (or $CO + \frac{1}{2}O_2 \rightarrow CO_2$) reaction will be studied by the new stochastic theory including energetic interactions. The ZGB model takes the following steps into account:

$$A + S \rightarrow A - S \tag{1}$$

$$B_2 + 2S \rightarrow 2B - S \tag{2}$$

$$A - S + B - S \rightarrow 2S \tag{3}$$

where S denotes a free lattice site and A and B are the reactant particles of interest. Many studies of this system have been performed because of its similarity to surface reaction systems. It has been shown [2] that some aspects of the behaviour of this system are in agreement with the heterogeneously catalysed oxidation of CO. In this case A stands for a CO molecule, B_2 for an O_2 molecule and S for a free-metal site which represents the catalyst. Equation (1) then shows the event of a CO-adsorption on a free-surface site, (2) the dissociative adsorption of O_2 which requires two adjacent vacant sites and (3) the instantaneous reaction of adsorbed CO and O to CO_2 which desorbs immediately from the surface.

The most prominent feature of the original ZGB model is the existence of kinetic phase transitions. Denoting the mole fraction of CO in the gas phase by y_{CO} (and therefore $y_{O_2} = 1 - y_{CO}$), one finds a reactive interval $0.395 = y_1 < y_{CO} < y_2 = 0.525$ [1] in which both particle types are co-existing on the surface. For $y_{CO} < y_1$ and for $y_{CO} > y_2$ the surface is completely covered by O_2 or CO, respectively. The phase transitions are found to be of second order at y_1 and of first order at y_2; see table 1.

By the effect of CO-diffusion (a very common process at the normal temperatures of the CO oxidation) the value of y_2 is increased and reaches the stochiometric value of $\frac{2}{3}$ in the limit of an infinite diffusion rate [8, 10]; see, however, [30]. Because of the irreversible character of the model (1)–(3) a completely covered surface (by one species) means that the system cannot escape from this state (absorbing state) and therefore no further reactions can take place. In terms of the catalytic CO oxidation this is a state which describes a poisoned catalyst. The value of $y_2 = \frac{2}{3}$ is in agreement with experimental observations [31].

In order to get a more realistic model, additional aspects have been taken into account. The CO-desorption can be modelled by

$$A - S \rightarrow A + S. \tag{4}$$

The additional aspect of CO desorption (equation (4)) leads to the disappearance of the CO-poisoned state [9, 15] because at every value of y_{CO} adsorbed CO molecules are able to leave the surface.

Many other investigations under various conditions have been performed [3–18], and also energetic interactions have been studied [19–21].

In the stochastic method we have to treat the $A + \frac{1}{2}B_2 \rightarrow 0$ (or $CO + \frac{1}{2}O_2 \rightarrow CO_2$) reaction as a model system for studying the effects of energetic interactions because the 'true experimental' energetic interaction parameters referring to a surface at very low coverage are not available. We shall study the effects of the particle interactions on the position and character of the poisoning phase transitions, the reaction constant, reaction rate, etc. We shall consider repulsive and attractive interactions, diffusion, A adsorption and desorption, B_2 adsorption, but also B_2 desorption in some detail.

The paper also serves another purpose, however. There are, as mentioned above, basic conceptual problems in the interpretation of experimental data. We are going to raise the question, what is the reaction constant in the new theory, does such a quantity exist? The answer will be simply, no. The reaction 'constant' is a function of the local configuration and thus of time. Another question deals with the sticking coefficient, which is frequently introduced into the adsorption terms of the kinetic equations and which is useful in analysing experimental data. Obviously a sticking coefficient is a quantity to be evaluated from scattering theory. Can it appear in a proper way in kinetic equations or stochastic equations? The answer is again, no. A third question deals with the diffusion constant. Diffusion is the fastest process in the present case, yet a diffusion term does not exist in the kinetic equations (but in the stochastic equations). Also it can be shown under certain premises

that the surface reaction is entirely diffusion controlled, but this finds no expression in the equations. These three points (and some other ones) point to severe conceptual problems of the site mean field equations. Actually the inclusion of energetic interactions leads to even more severe problems than is the case in their absence.

The paper is structured as follows. In section 2 we give the necessary definitions of the model and discuss some conceptual problems; for details see [22, 26]. The results are discussed in section 3.

2. The model

We use a square lattice with coordination number $z = 4$. The model can be described by

$$\frac{dC_A}{dt} = p_A C_0 - k_A C_A - K C_A C_B \tag{5}$$

$$\frac{dC_B}{dt} = p_B C_0^2 - k_B C_B^2 - K C_A C_B \tag{6}$$

where C_λ is the density (concentration) of particles of type λ on the surface ($\lambda = A, B, 0$). The sum rule $C_A + C_B + C_0 = 1$ holds. p_A and p_B are the adsorption and k_A and k_B are the desorption rates for the A and B particles, respectively, and K is the reaction constant. In the equations written above the first terms describe the creation of particles, the second ones represent the desorption and the last terms describe the reaction between an A and a B particle. In a site mean-field model k, p and K are constants which do not depend on the particle distributions. In the case that spatial correlations are taken into account (but without energetic effects), some of the parameters become dependent on the particle distributions:

$$p_A = p_A^0 \qquad k_A = k_A^0 \qquad p_B = p_B^0 F_{00}(1) \tag{7}$$

$$k_B = k_B^0 F_{BB}(1) \qquad K = R^0 F_{AB}(1) \tag{8}$$

where the variables with superscript 0 do not depend on the particle distributions. $F_{\lambda\mu}(1)$ with $\lambda, \mu \in \{A, B, 0\}$ is the correlation function between nearest neighbours, $\rho_{\lambda\mu} = C_\lambda C_\mu F_{\lambda\mu}(1)$. In the extended ZGB model $p_A^0 = y_A = y_{CO}$, $p_B^0 = 2(1 - y_A) = 2(1 - y_{CO})$ and $K = R^0 F_{AB}(1)$ with $R^0 \to \infty$. In the ZGB model R^0 is infinite for nearest neighbours but the macroscopic reaction constant K is finite because $F_{AB}(1)$ goes to zero. This is a simple example for the fact that between true constants (with superscript 0) and effective variables (without superscript 0) there may be a vast difference if these quantities are configuration dependent. The variable K, e.g. is not a constant but a structure and thus time-dependent variable (see below for an example). For the case of energetic interactions all parameters appearing in equations (5) and (6) depend on the particle distributions and therefore on the correlation functions. In order to solve these equations for the temporal evolution of the system we use the *standard model* discussed in [22] and an improvement of the Kirkwood approximation [24] (discussed in [27]) to handle the problem which is necessitated by the fact that R^0 goes to infinity.

Let us discuss a few examples. It is known from previous work [27] that without the correlation function $F_{00}(1)$ it is impossible to describe a second-order phase transition in the ZGB model. It is commonly assumed that in p_A and p_B a sticking coefficient appears, e.g. $p_B = P_{B_2} ks$, where P_{B_2} is the partial pressure of B_2 in the gase phase, k is a flux constant and s a sticking coefficient. The sticking coefficient is certainly a useful concept, but one should not forget that it stems from scattering. A sticking coefficient can in principle depend on the densities. Thus one may suggest $s \propto F_{00}(1)$. But we know already that at the second order phase transition at y_1 $F_{00}(1) \to \infty$. This would mean that a sticking coefficient could

be infinite, which is certainly not meaningful. A sticking coefficient cannot be defined properly in a stochastic nor in a mean field approach, it is a concept from scattering.

As the next example let us turn to diffusion. Where is the diffusion in equations (5) and (6)? The equations know of no diffusion! But the diffusion constant is the largest parameter of all which occur in the $CO + O_2$ reaction. It should play a very prominent role and the stochastic theory needs this parameter and makes use of it, whereas site mean-field approaches simply ignore it because diffusion enters only via two (and more) point distribution functions. Yet there is another aspect to it. Let us assume that the assumption of the ZGB model that $R^0 \to \infty$ is valid also in reality (which is nearly true). Then we can calculate the reaction constant analytically. Formally it is given by

$$K = \frac{\tilde{\rho}_{AB}}{C_A C_B}. \tag{9}$$

Here

$$\tilde{\rho}_{AB} = \lim_{R^0 \to \infty} R^0 \rho_{AB} = C_A C_B \lim_{R^0 \to \infty} R^0 F_{AB}(1) = C_A C_B K. \tag{10}$$

The quantity $\tilde{\rho}_{AB}$ was calculated in a previous article [27] (equations (28) and (35))

$$\tilde{\rho}_{AB} = p_A^0 C^0 g(\beta) + p_B^0 \rho_{00} h(\alpha) + D \rho_{A0} h(\beta) \tag{11}$$

where D is the frequency factor of diffusion and g and h are polynomials

$$h(x) = 1 - (1 - x)^3 \qquad g(x) = 1 - (1 - x)^4 \tag{12}$$

with $\alpha = \rho_{A0}/C_0$, $\beta = \rho_{B0}/C_0$. This variable $\tilde{\rho}_{AB}$ describes not only the reaction of particles, when they are on the surface (the third term), but also the formation of nearest neighbour AB-pairs via adsorption (the first two terms). Only the third term is proportional to a product of C_A and C_B (the bimolecular reaction, see section 2 of [27]). The first two terms change the effective adsorption rates. Let us take K as the value of the reaction constant on an empty surface ($C_A, C_B \to 0, C_0 \to 1$) without correlations between the particles ($F_{\lambda\mu}(1) = 1$) and without the additional creation of particles ($p_A^0 = p_B^0 = 0$). Via the reaction $F_{AB}(1) = 0$, but (11) does not make use of it. From (9) and (11) one obtains $K = 3D$, i.e. we have a totally diffusion-controlled reaction. K is proportional to D. To explain the difference we need to take into account the energetic interaction of the particles. If we do this we obtain (see section 7 of [22])

$$K = 6D \frac{\omega}{1 + \omega} \qquad \text{with } \omega = \exp(-E_{AB}/k_B T). \tag{13}$$

In the case without energetic interactions ($E_{AB} = 0$) we obtain $\omega = 1$ and therefore the result $K = 3D$ as discussed above.

The derivation of the last equation is straight forward: consider a $0B$ configuration in which the central site is empty. In order to form an AB pair an A particle has to jump to the central site. There are three different sites from which the A can jump to the central site. Therefore $K = 3Q W_{eq}$ with $Q = Q(0A|A0) = 2D$ (for the definition of W_{eq} see section 7 of [22]). Furthermore the start configuration has the energy $E = 0$ because there is no particle interaction. After forming the AB pair (but before reaction) it has the energy $E = E_{AB}$. This explains the form of ω. The factor $\omega/(1 + \omega)$ follows from the Gibbs distribution for the diffusion process.

If $E_{AB}/k_B T \gg 1$ we obtain $\omega \ll 1$ and $K \approx 6D \exp(-E_{AB}/k_B T)$. In this way a stochastic theory with energetics explains a difference in the activation energy.

Next let us illustrate this and the 'constancy' of the reaction 'constant' and some other parameters by an example. We choose $E_{AB}/k_B T = 5$, $E_{AA} = E_{BB} = 0$ and D to be very
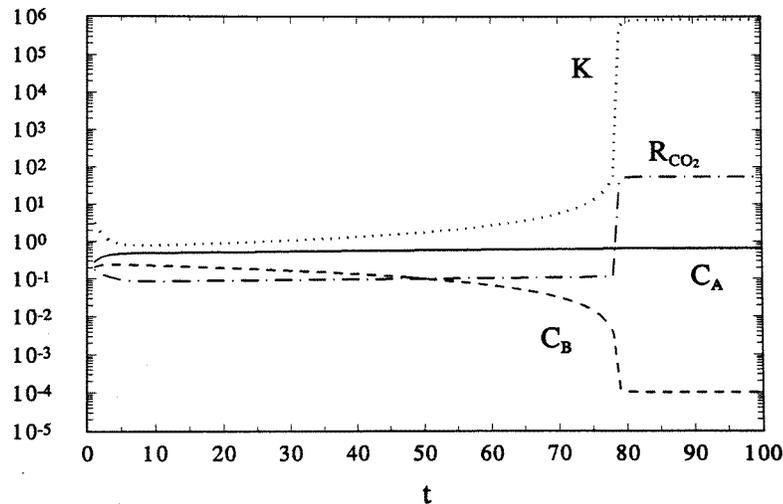
Figure 1. The reaction constant, the production rate $R_{AB} = R_{CO_2}$ and the densities C_A, C_B as a function of time for very fast diffusion and strong A–B repulsion.

large. The temporal behaviour of the system is illustrated in figure 1. The B particles first form islands as usually observed for this reaction and then fight against the fast diffusing and thus very reactive A particles. Because of the strong repulsion the reaction rate (defined as $R_{AB} = R_{CO_2} = KC_AC_B$) is exceedingly small. But the B particles finally become loose and almost suddenly all islands, which in the meantime have become very small, disappear from the surface. The reaction constant increases by a factor of 10^5 and the production rate R_{AB} by a factor of 10^3.

There is one more point which should be mentioned—a complication arising in the case of energetic interactions between the particles. In the mean field approach one usually assumes that a generalization could be that the 'true' constants be replaced by functions of densities, interaction energies and temperatures, i.e they become effective parameters. For example

$$p_A = p_A^0 S(C, E, T). \tag{14}$$

The stochastic theory says that this is not correct. The effective parameters can only be calculated approximately, and the defining equation is totally different

$$p_A = Q S(C, F, E, T). \tag{15}$$

S depends on the correlation functions. It is also important to realize that the frequencies p_A^0 or k_A^0 (for an empty surface) do not, as in mean-field theories, appear as prefactors. Q and S are now the functions (see section 8 of paper I)

$$Q = p_A^0 + k_A^0 \qquad S = S\left(\frac{k_A^0}{p_A^0}\right) \tag{16}$$

i.e. the adsorption rate is also a function of the desorption frequency.

3. Results

3.1. Repulsive interactions

First we study the system without the effect of B desorption ($k_B^0 = 0$). This case is realistic for the oxidation of CO because the O atoms (B particles) are strongly bound to the metal surface and desorption is a process which does not occur at the normal temperatures used for this reaction. In this case the parameter E_{BB} does not play a role because the transition probabilities for the A and B particles depend on k_A^0/p_A^0 and on k_B^0/p_B^0, respectively. Therefore we have reduced the number of energetic parameters to two (E_{AA} and E_{AB}). In the following we give all values of E in $k_B T$ units.
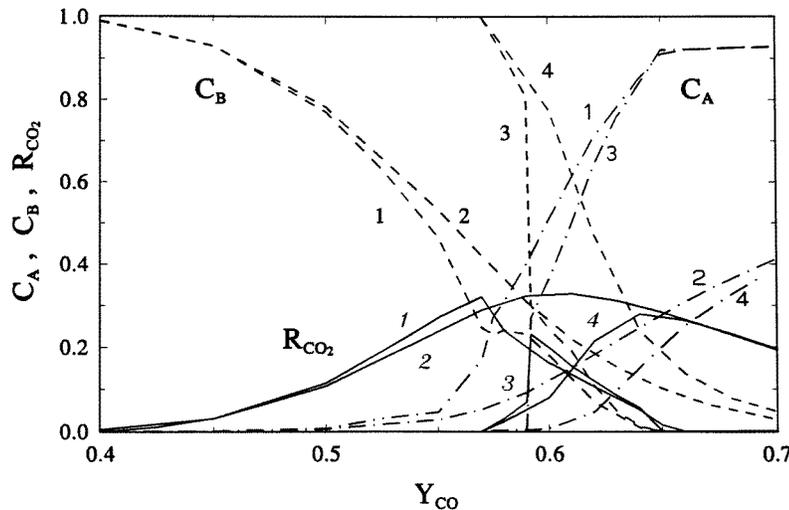
Figure 2. The densities C_A, C_B and the production rate $R_{AB} = R_{CO_2}$ are shown as a function of $y_A = y_{CO}$ for $k_A^0 = 0.05$ and $D = 0$. The energetic parameters are: $E_{AA} = E_{AB} = 0$ (curve 1), $E_{AA} = 1$, $E_{AB} = 0$ (curve 2), $E_{AA} = 0$, $E_{AB} = 1$ (curve 3) and $E_{AA} = E_{AB} = 1$ (curve 4).

In figure 2 the coverages of A and B and the production rate R_{AB} are shown as a function of y_A. We use a large desorption rate and no diffusion. For curve 1 we have $E_{AA} = E_{AB} = 0$. This corresponds to the case of the ZGB model with A desorption. The value of y_1 is not shifted by the desorption because at this point too few A particles are present. Complete occupation of the lattice by A does not occur because at every time step A particles have the chance to desorb from the surface. Both facts are in agreement with the corresponding MC simulation [9].

In curve 2 we switch on the A–A repulsion. Due to the repulsion the phase transition at y_2 nearly disappears and we obtain a very smooth transition. The coverages are not influenced by E_{AA} for small values of y_A which arises from the small number of A particles in this region.

Curve 3 shows the diagram for $E_{AA} = 0$ and for $E_{AB} = 1$. The parameter E_{AB} shifts the critical point y_1 dramatically to larger values of y_A which means that the complete occupation of the lattice by B can take place more easily. This is understandable from the fact that the A-adsorption probability is decreased by the repulsion with the B particles, which are the dominant species on the lattice. Therefore the tendency of the B particles to
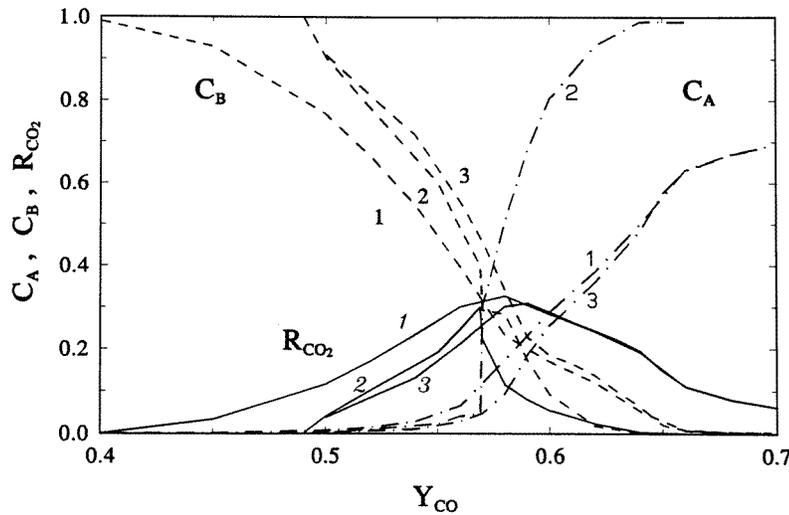
Figure 3. The densities C_A, C_B and the production rate $R_{AB} = R_{CO_2}$ are shown as a function of $y_A = y_{CO}$ for $k_A^0 = 0.01$ and $D = 0$. The energetic parameters are: $E_{AA} = 1$, $E_{AB} = 0$ (curve 1), $E_{AA} = 0$, $E_{AB} = 1$ (curve 2) and $E_{AA} = E_{AB} = 1$ (curve 3).

form large clusters is enhanced. This can be seen from R_{AB} which is for $y_A < y_2$ nearly zero and rises sharply at $y_A \approx y_2$.

In curve 4 we have $E_{AA} = E_{AB} = 1$. This results in a smooth transition at y_2 for the A density (caused by E_{AA}) and a phase transition at y_1 at large values of y_A (caused by E_{AB}). The parameter E_{AA} is important for large values of C_A (i.e. for large values of y_A) and E_{AB} dominates the system behaviour at large values of C_B (i.e. for small values of y_A).

In figure 3 we study the system for the case of a small desorption rate of A particles and no diffusion. The system behaviour is strongly influenced by the desorption. Due to the smaller desorption rate (compared to the previous figure) the phase transition point y_2 is shifted to lower values of y_A and the transition appears to be sharper. Also the phase transition point y_1 is shifted to lower values of y_1 in the cases of curves 2 and 3 which means that B poisoning is more difficult to achieve due to the reaction with A particles sitting on the surface. This effect is particularly important in the case of curve 3 (compare with curve 4 from the previous figure, where the critical point y_1 is located at larger values of y_A). Here more A particles are present and the desorption plays a significant role.

How does the system behaviour change under the influence of diffusion together with A–A repulsion (see figure 4)? The diagram is plotted for larger values of y_A because for smaller values the diffusion plays no role. Under the influence of diffusion, the phase transition point y_2 is shifted to larger values of y_A because the fast moving A particles remove small B clusters via reaction from the lattice. On the lattice cleared in this way the B_2 particles have a larger probability to find two adjacent free sites to adsorb and build large clusters (the density of B particles increases). Therefore the complete occupation with A takes place at larger values of y_A compared to the case without diffusion. This result is in agreement with MC simulations [8]. The maximum value of the production rate is also shifted to larger values of y_A in accordance with the shift of the A density to larger values of y_A. In the limited case of a well-stirred system we would obtain that the maximum rate is located at the stoichiometric gas phase composition ($y_A = \frac{2}{3}$) [8]. The parameter E_{AA} acts in the same way as discussed for the previous figure.
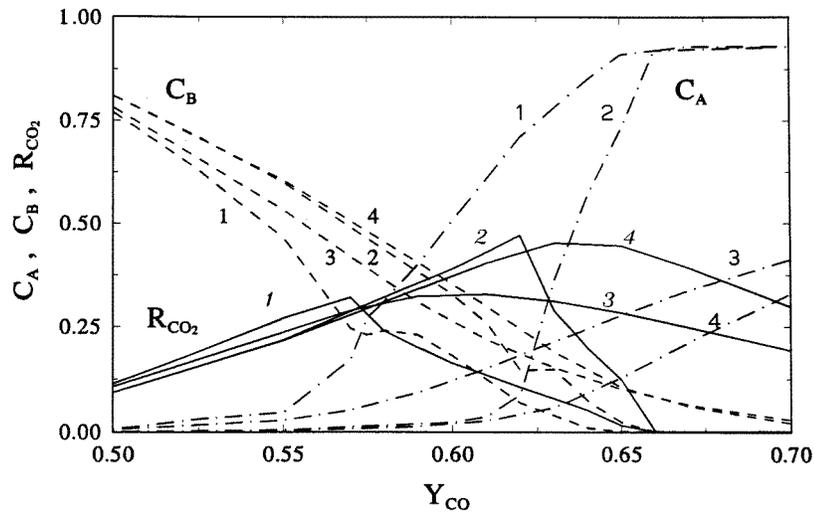
Figure 4. The densities C_A, C_B and the production rate $R_{AB} = R_{CO_2}$ are shown as a function of $y_A = y_{CO}$ for $k_A^0 = 0.05$ and $E_{AB} = 0$. The parameters are: $E_{AA} = 0$, $D = 0$ (curve 1), $E_{AA} = 0$, $D = 10$ (curve 2), $E_{AA} = 1$, $D = 0$ (curve 3) and $E_{AA} = 1$, $D = 10$ (curve 4).
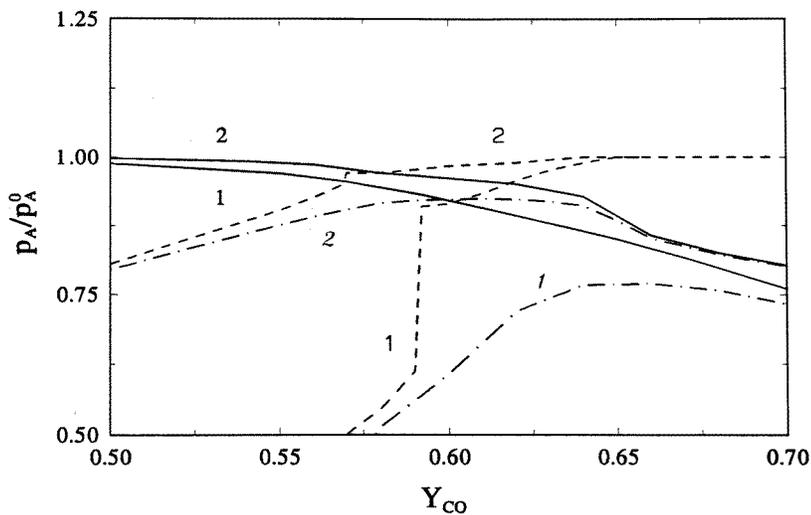

Figure 5. The effective sticking coefficient p_A/p_A^0 as a function of $y_A = y_{CO}$ for $k_A^0 = 0.05$ (curve 1) and for $k_A^0 = 0.01$ (curve 2). The energetic parameters are $E_{AA} = 1$, $E_{AB} = 0$ (full curve); $E_{AA} = 0$, $E_{AB} = 1$ (broken curve) and $E_{AA} = E_{AB} = 1$ (chain curve).

Next we turn to the details of the reaction and study the effective sticking coefficient, the effective desorption rate and the reaction constant. We denote by full curves the energetic parameters $E_{AA} = 1$, $E_{AB} = 0$; by broken curves $E_{AA} = 0$, $E_{AB} = 1$ and by chain curves $E_{AA} = E_{AB} = 1$.

In figure 5 the ratio p_A/p_A^0 (which represents an effective sticking coefficient for the A particles) is shown as a function of y_A for a large and a small desorption rate. We see that for $y_A < y_2$ only a small number of A particles is on the lattice (see above). From

the full curves we therefore conclude that the effect of blocking and the repulsion with other A particles plays no role and the sticking coefficient is nearly unity. For increasing y_A the sticking coefficient decreases due to the larger number of A particles on the lattice. A larger desorption rate increases this effect because A particles located in unfavourable configurations desorb immediately. The repulsion between A and B particles (broken curves) is only important in the region where many B particles are present (at lower values of y_A) resulting in a dramatic decrease of the sticking coefficient at lower values of y_A.

For the case that the A–A and the A–B interactions are both repulsive we obtain a composite system behaviour resulting from the behaviour discussed above.
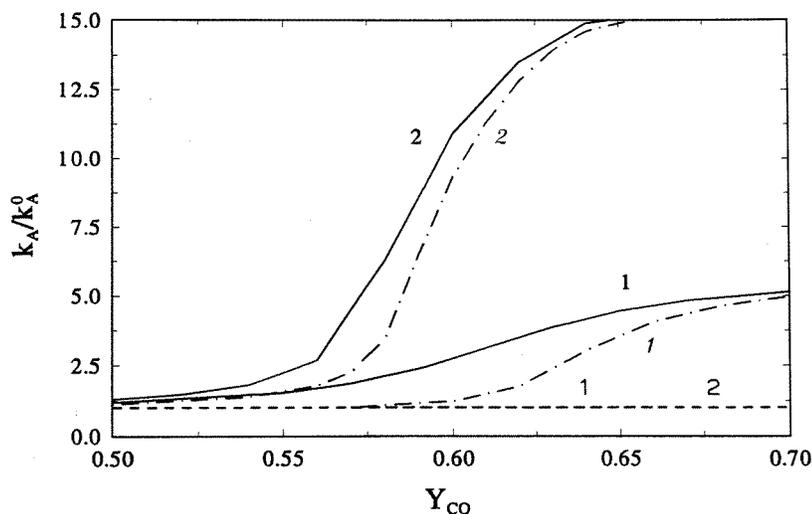

Figure 6. The effective desorption rate k_A/k_A^0 as a function of $y_A = y_{CO}$ for $k_A^0 = 0.05$ (curve 1) and $k_A^0 = 0.01$ (curve 2). The energetic parameters are $E_{AA} = 1$, $E_{AB} = 0$ (full curve); $E_{AA} = 0$, $E_{AB} = 1$ (broken curve) and $E_{AA} = E_{AB} = 1$ (chain curve).

In figure 6 the effective desorption rate k_A/k_A^0 is shown as a function of y_A. The A–A repulsion is important for large values of y_A resulting in an increase of the desorption rate. The smaller k_A^0 the more effective is the desorption rate influenced by the A–A repulsion. The A–B interaction plays no role in the A desorption because in our model AB pairs cannot exist on the lattice due to the infinite reaction rate. The chain curve shows the intermediate situation of the two cases discussed above.

The reaction constant K is shown in figure 7. It is small in the parameter region where large clusters are formed because reaction can only occur at the border of the particle islands. This is the case below about $y_A < 0.64$. The diffusion increases the reaction rate due to the fact that the A particles are much more reactive. There is an interesting effect of the desorption rate in the absence of diffusion. Below about $y_A = 0.64$, where large clusters occur a smaller desorption rate reduces the reaction constant K probably because a larger desorption rate enhances the adsorption which among others exchanges non-reactive A particles with reactive ones. Above $y_A = 0.64$ a small desorption rate enhances K compared to a larger desorption rate because the stoichiometric particle composition on the lattice is reached at lower values of y_A for the smaller desorption rate.

One sees easily that K is not a constant. This quantity changes by a factor of 100 in the present case.
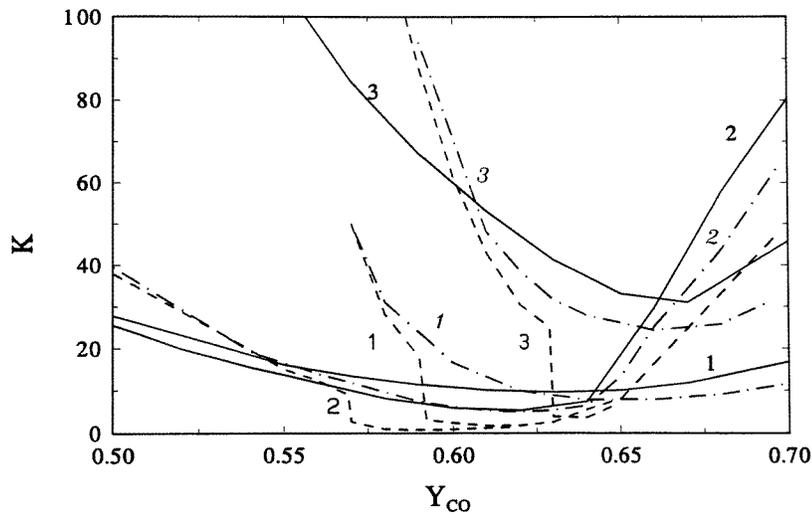
Figure 7. The reaction constant K as a function of $y_A = y_{CO}$ for $k_A^0 = 0.05$, $D = 0$ (curve 1); $k_A^0 = 0.01$, $D = 0$ (curve 2) and for $k_A^0 = 0.05$, $D = 10$ (curve 3). The energetic parameters are $E_{AA} = 1$, $E_{AB} = 0$ (full curve); $E_{AA} = 0$, $E_{AB} = 1$ (broken curve) and $E_{AA} = E_{AB} = 1$ (chain curve).
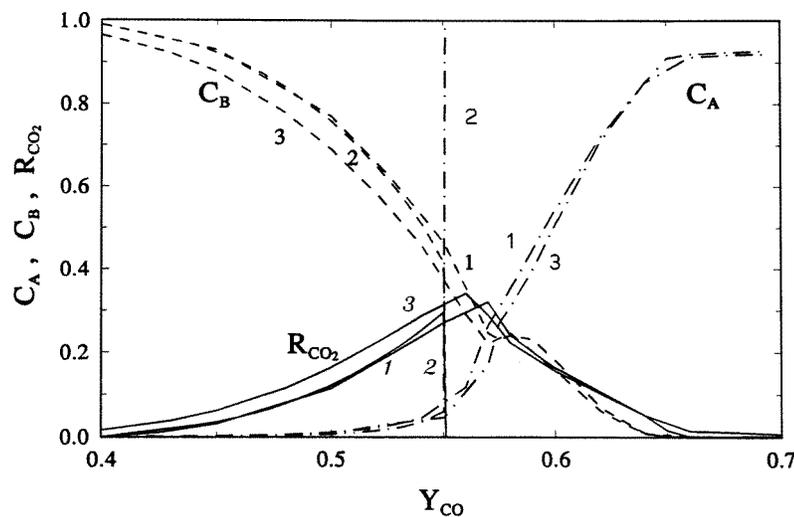

Figure 8. The particle densities and the production rate are shown as a function of $y_A = y_{CO}$ for $D = 0$ and $k_A^0 = 0.05$. The energetic parameters are: $E_{AA} = E_{AB} = 0$ (curve 1); $E_{AA} = -1$, $E_{AB} = 0$ (curve 2) and $E_{AA} = 0$, $E_{AB} = -1$ (curve 3).

3.2. Attractive interactions

So far we have treated repulsive interactions. We now turn to the investigation of systems with attractive interactions ($E_{\lambda\mu} < 0$). In figure 8 the particle densities and the production rate are shown as a function of y_A for $D = 0$ and $k_A^0 = 0.05$. Due to the attractive interaction between A particles (curve 2) the phase transition at y_2 changes its character to first order and the value of y_2 is significantly lowered. At lower values of y_A this interaction plays

no role due to the small number of A particles. An attractive interaction between A and B particles (curve 3) smoothes the transition again and the resulting system behaviour is very similar to the case without energetic interactions for larger values of y_A. The difference is a small decrease in C_A (for larger values of y_A) and a small decrease in C_B (for smaller values of y_A). This results from the attraction of A and B particles which enlarges the probability of reactive events.
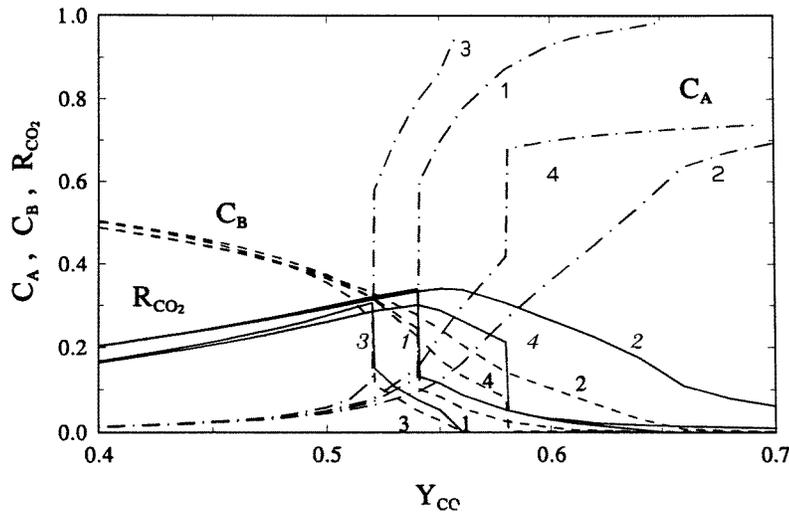

Figure 9. The particle densities and the production rate are shown as a function of $y_A = y_{CO}$ for $D = 0$, $E_{BB} = 1$ and $k_A^0 = k_B^0 = 0.01$. The remaining energetic parameters are: $E_{AA} = E_{AB} = 0$ (curve 1); $E_{AA} = 1, E_{AB} = 0$ (curve 2); $E_{AA} = 0, E_{AB} = 1$ (curve 3) and $E_{AA} = E_{AB} = 1$ (curve 4).

3.3. The influence of B desorption

We now take the additional aspect of B_2 desorption into account. In figure 9 the particle densities and the production rate are shown as a function of y_A. The phase transition at y_1 disappears due to the effect of B desorption (which is equivalent to the effect of A-desorption at y_2). The repulsive interaction of A particles (curve 2) smoothes the phase transition at y_2. $E_{AB} = 1$ (curve 3) shifts y_2 to lower values of y_A. This comes from the fact that the A particles can easily adsorb on the free sites created by B desorption. The increased number of A particles on the lattice leads to an increased B desorption due to the repulsive A–B interaction. In curve 4 the repulsion between the A particles leads to a shift of y_2 to larger values of y_A. A smoothing of the phase transition (cf curve 2) can only be observed at the beginning of the phase transition point region. At larger values of y_A, C_A increases abruptly. This can be explained by the fact that at this point the B particles nearly all have left the lattice which leads to a decrease of the repulsion on the A particles.

With the variation of the energetic parameters the value of y_2 can be shifted over a very large range of y_A. The system behaviour at small values of y_A is much more stable against changes of the energetic parameters.

The effective adsorption and desorption rate for B particles are much more difficult to interpret than for the A particles because they are strongly influenced by structural correlations. Even without energetic interactions they are of the form $p_B = p_B^0 F_{00}(1)$ and

$k_B = k_B^0 F_{BB}(1)$, respectively.

Therefore one sees only a product of the adsorption (or desorption) rate and correlation functions and in which the correlation may be very large (see [27]).

4. Conclusions

We have studied a stochastic approach including energetic interactions for an extended ZGB model with diffusion and desorption as additional steps. We have used different values for the diffusion and the desorption rate and different values for the energetic parameters. In the case of repulsive interactions the system behaviour is strongly influenced by E_{AA} for large values of y_A and by E_{AB} for small values of y_A. The former parameter leads to a smooth phase transition at y_2 and the latter to a sharp transition at y_1. The sharpness and the location of the phase transitions depend also on the diffusion and desorption rate of the A particles. The A diffusion leads to an increase of the value of y_2 due to the higher reactivity of the A particles. At lower values of y_A the system behaviour is hardly influenced by the diffusion. The A desorption increases the values of the critical points and smoothes the phase transition at y_2. This effect becomes very important if C_A is large.

Attractive interactions between A particles change significantly the system behaviour at y_2, resulting in a decrease of the value of y_2 and the change of the character of the phase transition to first order (second order for the case of no energetic interactions and with desorption). We have a case similar to a condensation. This is mainly the effect of the reduced desorption rate of the A particles which leads to the same character of the phase transition at y_2 as without the effect of desorption. The parameter E_{AB} enlarges the effective diffusion rate but the system behaviour is not significantly influenced by this change.

The effect of B desorption leads to the disappearance of the phase transition at y_1 which is equivalent to the effect of the A desorption at y_2. The dependence of the system behaviour on the energetic parameters is very complex. Interpretation of the results is difficult due to the complicated adsorption and desorption rules for the B_2 particles. The value of the phase transition point y_2 can be shifted over a large range of y_A by different model parameters.

The model we presented here is well suited for the description of surface-reaction systems including energetic interactions. The use of realistic parameters for the energetic interactions (which are not available today) should lead to a more realistic description of surface-reaction systems.

Acknowledgments

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