

A theoretical stochastic model for the $A + \frac{1}{2}B_2 \rightarrow 0$ reaction

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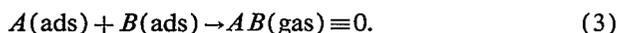
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A surface reaction model for the $A + \frac{1}{2}B_2 \rightarrow 0$ reaction is studied by a theoretical approach. To this end, we introduce a stochastic ansatz which describes the system behavior by master equations. These equations are solved numerically in the superposition approximation. The results of the theoretical description are in good agreement with the corresponding computer simulations of the system. We focus our interest on the study of oscillations. The correlation functions and the parameter ranges in which oscillations are possible are studied in detail. This model as well as the computer simulations describe some aspects of the heterogeneously catalyzed oxidation of CO on a Pt surface.

I. INTRODUCTION

The understanding of the behavior of surface reaction systems is extremely challenging. Computer simulations are a very powerful tool to get more insight into the behavior and the dynamics of such systems. A further step which follows after the simulations is the theoretical description of the reaction system. Normally, mean-field or stochastic methods are used for this purpose. In this paper, we present a stochastic ansatz to describe such a model of a surface reaction system.

In this paper, the system of interest is the $A + \frac{1}{2}B_2 \rightarrow 0$ reaction. The elementary steps are



Step one shows the adsorption of A from the gas phase. The adsorption of B_2 is a dissociative process (step two). The third step shows the reaction which follows the Langmuir-Hinshelwood mechanism. The reaction product (AB) desorbs immediately after formation.

For this reaction system, Ziff *et al.*¹ introduced a Monte Carlo simulation (the ZGB model). In this simulation, the metal surface is represented by a two-dimensional square lattice with periodic boundary conditions. A gas phase containing A and B_2 with the mole fraction of y_A and $y_B = 1 - y_A$, respectively, sits above this surface. Adsorption can occur if a randomly selected site on the surface is vacant. Because the adsorption of B_2 is dissociative, a B_2 molecule requires two adjacent vacant sites and an A molecule only one. If an A molecule is a nearest neighbor of a B atom, reaction occurs via the Langmuir-Hinshelwood (LH) process with the probability one and the product molecule AB desorbs immediately after formation.

Ziff *et al.*¹ found two kinetic phase transitions. For $y_A < y_1 = 0.395$, the surface is completely covered by B , and for $y_A > y_2 = 0.525$, the same holds for the coverage of A . These two regimes represent poisoned states because no further reaction is possible. A reactive interval exists only in the parameter range $y_1 < y_A < y_2$. The character of the phase transitions points is found to be of second order at y_1 and of first order at y_2 .

This model has been proposed in the literature as a simple model of the heterogeneously catalyzed oxidation of CO. The A particles represent the CO molecules and the B_2 particles the O_2 molecules. This model shows some aspects of the real surface reaction system.² Therefore we want to use the terms of *adsorption*, *oxidation*, etc., if we are speaking about the reaction steps.

In Ref. 3, we have extended this system by the additional effect of A diffusion because the A (CO) particles are mobile at normal temperatures. The B particles (O atoms) which are stronger bound to the surface remain immobile. For this model, we have obtained in the case of fast A diffusion two critical values for the mole fraction of A in the gas phase. At $y_1 = 0.395$, we obtained a second order phase transition (B poisoning) and a first order phase transition at $y_2 = 0.650$ (A poisoning).

In order to describe the system theoretically, we introduced a site mean-field ansatz.³ We obtained $y_1 = 0$ and $y_2 = 2/3$. The value of y_1 is not in agreement with the result of the simulation because in the neighborhood of this point, long range correlations appear which cannot be described by a simple mean-field ansatz which neglects spatial correlations. The value of y_2 is in good agreement with the simulation. No long range correlations do appear. In the case of an infinite diffusion rate, the values of y_2 become identical for the mean-field ansatz and the simulation.

Dickman⁴ introduced a pair mean-field ansatz which takes more correlations into account than our site ansatz. He obtained $y_1 = 0.2497$ and $y_2 = 0.524$.

Another interesting aspect of surface reaction systems is the appearance of oscillations in which the coverages of particles fluctuate. Spatial and temporal oscillations were observed in real catalyst systems for a wide range of parameters (pressure and temperature)⁵ (and references there). Waves propagate across the surface and lead to the formation of spatial and temporal structures⁶ (and references there). Such oscillations were also observed in computer simulations by Möller *et al.*⁷ and Eiswirth *et al.*⁸ These authors introduced a model which takes surface reconstructions into account. In the model of Ziff *et al.*,¹ oscillations were not found. In a mean-field approximation to the model of Ziff *et al.*, we have shown that oscillations cannot appear.³ It seems necessary that a third parameter (such as a surface state, subsurface oxide formation, etc.) must be introduced to obtain oscillations. We are going to see that the present stochastic model leads to the appearance of oscillations. Several other authors have studied the model of Ziff *et al.* For details and additional references, see Refs. 3 and 9–11.

In this paper, we want to introduce a stochastic model for the *A* oxidation which is based on the ZGB model. We add to this model the aspect of *A* diffusion (one of the most important additional steps). This system is able to show certain aspects of a real system (e.g., phase transitions and oscillations). An extension of our ansatz to the description of a more realistic model which takes interactions between adsorbed particles and the step of *A* desorption into account is also possible.

The main elements of the present stochastic model are the following: We use master equations for the distribution functions of *A*, *B* and pairs of particles whose hierarchy is truncated at a certain level. The resulting equations are solved exactly in a small region and connected to a mean-field solution for large distances from a reference point. As the correlations in a small neighborhood should be dominant for the presently studied reaction (except close to the phase transition points), there should be good agreement with the model of Ziff *et al.* when we include the diffusional motion of the particles, but we are also going to see the appearance of new phenomena, e.g., oscillations, which arise from a finite reaction rate. Their study may contribute to the understanding of oscillations in real systems.

The paper is structured as follows: In Sec. II, we represent the general theory which will be used here. In Sec. III, the theory will be applied to the specific model of the $A + \frac{1}{2}B_2$ reaction. The used master equations and the superposition approximation will be introduced. Section IV deals with the method for the solution of the proposed model. The results are presented in Sec. V.

II. DISTRIBUTION FUNCTIONS

In this section, we want to study the *k*-point distribution functions $\rho^{(k)}$ ($k=1, \dots, \infty$) for the particles on the lattice. We use the following notations: **l**, **m**, and **n** are vectors which point to a cell on the lattice. $\sigma_l \in A, B, 0$ is the lattice variable which describes the state of the cell **l** on the lattice. Here *A* means an *A* molecule, *B* a *B* atom, and 0 an empty cell. The short notation $a_l, b_l, 0_l$ will also be used.

For $k=1$, $\rho^{(k)}$ does not depend on **l** and we can write $\rho^{(1)}(a_l) = c_a$, $\rho^{(1)}(b_l) = c_b$, and $\rho^{(1)}(0_l) = 1 - c_a - c_b$, where c_i is the concentration of particles of type *i* on the lattice.

For $k=2$, $\rho^{(k)} = \rho^{(2)}(\sigma_l, \sigma_m)$ depends only on $|\mathbf{l}-\mathbf{m}|$ because of the translation invariance of the lattice. As an asymptotic condition, we obtain

$$\lim_{|\mathbf{l}-\mathbf{m}| \rightarrow \infty} \rho^{(2)}(\sigma_l, \sigma_m) = \rho^{(1)}(\sigma_l) \rho^{(1)}(\sigma_m). \quad (4)$$

Next we define the correlation function as

$$F_{\sigma_l \sigma_m}(\mathbf{l}-\mathbf{m}) = \frac{\rho^{(2)}(\sigma_l, \sigma_m)}{\rho^{(1)}(\sigma_l) \rho^{(1)}(\sigma_m)}, \quad (5)$$

where $\rho^{(2)}$ obeys the sum rule

$$\sum_{\sigma_m} \rho^{(2)}(\sigma_l, \sigma_m) = \rho^{(1)}(\sigma_l). \quad (6)$$

We choose as independent pair-correlation functions

$$X_a(\mathbf{l}-\mathbf{m}) = F_{aa}(\mathbf{l}-\mathbf{m}), \quad X_b(\mathbf{l}-\mathbf{m}) = F_{bb}(\mathbf{l}-\mathbf{m}), \quad (7)$$

$$Y(\mathbf{l}-\mathbf{m}) = F_{ab}(\mathbf{l}-\mathbf{m}) = F_{ba}(\mathbf{l}-\mathbf{m}) \quad (8)$$

and as dependent pair-correlation functions

$$\begin{aligned} f_a(\mathbf{l}-\mathbf{m}) &= F_{a0}(\mathbf{l}-\mathbf{m}) = F_{0a}(\mathbf{l}-\mathbf{m}) \\ &= 1 - c_a X_a(\mathbf{l}-\mathbf{m}) - c_b Y(\mathbf{l}-\mathbf{m}), \end{aligned}$$

$$\begin{aligned} f_b(\mathbf{l}-\mathbf{m}) &= F_{b0}(\mathbf{l}-\mathbf{m}) = F_{0b}(\mathbf{l}-\mathbf{m}) \\ &= 1 - c_b X_b(\mathbf{l}-\mathbf{m}) - c_a Y(\mathbf{l}-\mathbf{m}), \end{aligned}$$

$$f_0(\mathbf{l}-\mathbf{m}) = F_{00}(\mathbf{l}-\mathbf{m}) = 1 - c_a f_a(\mathbf{l}-\mathbf{m}) - c_b f_b(\mathbf{l}-\mathbf{m}) \quad (9)$$

for $\mathbf{l} \neq \mathbf{m}$. For $\mathbf{l} = \mathbf{m}$, we define $F = 0$.

Also higher correlation functions can be studied. For $k=3$, we obtain the sum rule

$$\sum_{\sigma_n} \rho^{(3)}(\sigma_l, \sigma_m, \sigma_n) = \rho^{(2)}(\sigma_l, \sigma_m). \quad (10)$$

Frequently the superposition approximation (Kirkwood approximation) is used to express $\rho^{(3)}$,

$$\begin{aligned} \rho^{(3)}(\sigma_l, \sigma_m, \sigma_n) &\Rightarrow \rho^{(1)}(\sigma_l) \rho^{(1)}(\sigma_m) \rho^{(1)}(\sigma_n) F_{\sigma_l \sigma_m}(\mathbf{l}-\mathbf{m}) \\ &\quad \times F_{\sigma_m \sigma_n}(\mathbf{m}-\mathbf{n}) F_{\sigma_n \sigma_l}(\mathbf{n}-\mathbf{l}). \end{aligned} \quad (11)$$

It should be noted that this approximation contradicts the sum rule. As a consequence, different formulas for the dependent correlation functions can be constructed.

III. THE MODEL

We next have to introduce the adsorption rates p_a for the *A* and p_b for the *B* particles. These rates depend on the mole fraction of *A* and B_2 in the gas phase (y_A and $y_B = 1 - y_A$) and on the concentration of vacant cells on the lattice (p_0). We get $p_a = p_A = p_0 y_A$ for the *A* particles which require for the adsorption one vacant cell on the lattice. For the *B* particles, we obtain $p_b = 2p_{B_2} = 2p_0 y_B$. The *A* diffusion is introduced via a random walk model. The rate

in a unit time interval is D/z , where D is the diffusion coefficient and z the coordination number of the lattice. For small concentrations of A , we obtain $D_0 = Da_0^2$, where a_0 is the lattice constant. The reaction between adsorbed A and B is introduced by the reaction probability R which is also normalized to the number of nearest neighbor sites of the lattice (R/z).

A. Master equations

We model the evolution of the system as a Markov process. This can be formulated by a system of master equations. Using the definitions made above, we get for the temporal evolution of the A density in cell l ,

$$\begin{aligned} \frac{\partial \rho^{(1)}(a_l)}{\partial t} = & p_a \rho^{(1)}(0_l) + \frac{D}{z} \sum_n \alpha_{n,l} [\rho^{(2)}(0_l, a_n) \\ & - \rho^{(2)}(a_l, 0_n)] - \frac{R}{z} \sum_n \alpha_{n,l} \rho^{(2)}(a_l, b_n). \end{aligned} \quad (12)$$

Three terms appear in the equation. The first one describes the adsorption of A from the gas phase which depends on the number of vacant empty sites on the lattice and on the mole fraction of A in the gas phase. The second term accounts for possible diffusion events of the A particles. The first term in the bracket represents the flux of A from cell n (which is a nearest neighbor of cell l) to cell l . The flux in the opposite direction has a negative sign because the density of cell l is reduced by this event. The third term describes a reactive event in which an A particle which is located at cell l reacts with a B particle which is located in a neighboring cell n . $\alpha_{n,l}$ are coefficients which are zero if n and l are not nearest neighbors and unity if they are.

From the last equation, we derive the temporal evolution of the concentration of A ,

$$\frac{\partial c_a(t)}{\partial t} = p_a c - R c_a c_b Y(1) \equiv \mu_a c_a, \quad (13)$$

where $Y(1)$ is the pair correlation function for different particles.

The evolution equation for the density of B particles can be derived by the same considerations as for the A particles

$$\frac{\partial \rho^{(1)}(b_l)}{\partial t} = \frac{p_b}{z} \sum_n \alpha_{n,l} \rho^{(2)}(0_l, 0_n) - \frac{R}{z} \sum_n \alpha_{n,l} \rho^{(2)}(b_l, a_n) \quad (14)$$

and

$$\frac{\partial c_b(t)}{\partial t} = p_b c^2 f_0(1) - R c_a c_b Y(1) \equiv \mu_b c_b. \quad (15)$$

B. The superposition approximation

We also need to introduce the distribution functions of higher order. Because of the invariance of the correlation functions to a translation of the lattice, which means that cell l is equivalent to cell m , we can write for the temporal evolution of $\rho^{(2)}(a_m, a_l)$,

$$\begin{aligned} \frac{\partial \rho^{(2)}(a_m, a_l)}{\partial t} = & 2p_a \rho^{(2)}(a_m, 0_l) - \frac{2R}{z} \sum_n \alpha_{n,l} \rho^{(3)}(a_m, a_l, b_n) \\ & + \frac{2D}{z} \sum_n \alpha_{n,l} [\rho^{(3)}(a_m, 0_l, a_n) \\ & - \rho^{(3)}(a_m, a_l, 0_n)]. \end{aligned} \quad (16)$$

The different configurations of cell m and l are accounted by the factor two in each term. Before applying the superpositional approximation (11), it is reasonable to transform the diffusion terms to extract in explicit form the corresponding difference operators. To this end, we write Eq. (10) in the form

$$\begin{aligned} \rho^{(3)}(a_m, a_l, 0_n) = & \rho^{(2)}(a_m, a_l) - \rho^{(3)}(a_m, a_l, a_n) \\ & - \rho^{(3)}(a_m, a_l, b_n). \end{aligned} \quad (17)$$

Next we introduce a definition of the operation of space averaging of the correlation function

$$\hat{F}_{\sigma\sigma'}(\mathbf{l}) = \frac{1}{z} \sum_n \alpha_{n,l} F_{\sigma\sigma'}(\mathbf{n}). \quad (18)$$

With these definitions, we rewrite Eq. (16) in the form

$$\begin{aligned} \frac{\partial X_a(\mathbf{m})}{\partial t} = & 2p_a \frac{c}{c_a} f_a(\mathbf{m}) + 2D \Delta X_a(\mathbf{m}) \\ & - 2D c_b Y(1) Y(\mathbf{m}) \hat{X}_a(\mathbf{m}) - 2 \left[\mu_a - \frac{D}{z} \alpha_{0,\mathbf{m}} \right. \\ & \left. + (R - D) c_b Y(1) \hat{Y}(\mathbf{m}) \right] X_a(\mathbf{m}). \end{aligned} \quad (19)$$

All the sums in this equation which are influenced by the superposition approximation have as a factor the correlation function $Y(1)$. $\Delta X_a(\mathbf{m})$ is given by

$$\Delta X_a(\mathbf{m}) = \hat{X}_a(\mathbf{m}) - X_a(\mathbf{m}) = \frac{1}{z} \sum_n \alpha_{n,l} [X_a(\mathbf{n}) - X_a(\mathbf{m})]. \quad (20)$$

It is easy to recognize in this definition the discrete Laplace operator. The equivalent approach for the second independent pair distribution function leads to

$$\begin{aligned} \frac{\partial \rho^{(2)}(b_m, b_l)}{\partial t} = & \frac{p_b}{z} \alpha_{m,l} \rho^{(2)}(0_m, 0_l) + 2 \frac{p_b}{z} \sum_n \alpha_{n,l} \\ & \times \rho^{(3)}(b_m, 0_l, 0_n) - \frac{2R}{z} \sum_n \alpha_{n,l} \\ & \times \rho^{(3)}(b_m, b_l, a_n). \end{aligned} \quad (21)$$

The first term describes the creation of BB pairs on free nearest neighbor cells. The second sum (without the factor 2) corresponds to the adsorption of a B_2 molecule on cells l and n under the condition that the cell m is already occupied by a particle B . The superposition approximation leads to

$$\frac{\partial X_b(\mathbf{m})}{\partial t} = \frac{p_b c^2 f_0(1)}{z c_b^2} \alpha_{0,\mathbf{m}} + 2p_b \frac{c^2 f_0(1)}{c_b} f_b(\mathbf{m}) \hat{f}_b(\mathbf{m}) - 2[\mu_b + R c_a Y(1) \hat{Y}(\mathbf{m})] X_b(\mathbf{m}). \quad (22)$$

The remaining third pair distribution function reads

$$\begin{aligned} \frac{\partial \rho^{(2)}(a_m, b_1)}{\partial t} &= -\frac{R}{z} \alpha_{1,\mathbf{m}} \rho^{(2)}(a_m, b_1) + p_a \rho^{(2)}(0_{\mathbf{m}}, b_1) + \frac{D}{z} \\ &\times \sum_n \alpha_{n,\mathbf{m}} [\rho^{(3)}(0_{\mathbf{m}}, b_1, a_n) - \rho^{(3)}(a_m, b_1, 0_n)] + \frac{p_b}{z} \\ &\times \sum_n \alpha_{n,1} \rho^{(3)}(0_{\mathbf{m}}, 0_1, 0_n) - \frac{R}{z} \sum_n \alpha_{n,\mathbf{m}} \rho^{(3)}(a_m, b_1, b_n) \\ &- \frac{R}{z} \sum_n \alpha_{n,1} \rho^{(3)}(a_m, b_1, a_n). \end{aligned} \quad (23)$$

After the transformation of the diffusion terms by Eq. (17) and using the superposition approximation, this equation reads

$$\begin{aligned} \frac{\partial Y(\mathbf{m})}{\partial t} &= p_a \frac{c f_b(\mathbf{m})}{c_a} + p_b \frac{c^2 f_0(1)}{c_b} f_a(\mathbf{m}) \hat{f}_a(\mathbf{m}) + D \Delta Y(\mathbf{m}) \\ &- D c_b Y(1) X_b(\mathbf{m}) \hat{Y}(\mathbf{m}) - \left[\mu_a + \mu_b \right. \\ &+ \frac{R-D}{z} \alpha_{0,\mathbf{m}} + (R-D) c_b Y(1) \hat{X}_b(\mathbf{m}) \left. \right] Y(\mathbf{m}) \\ &+ [R c_a Y(1) \hat{X}_a(\mathbf{m})] Y(\mathbf{m}). \end{aligned} \quad (24)$$

We have used the superposition approximation to truncate the infinite chain of equations. Therefore we want to discuss the precision of this approximation. The reaction model considered originates from the bimolecular reaction $A+B \rightarrow 0$ under the condition that the particles A and B are created in the system. The precision of the superposition approximation for this model is studied in Refs. 12–19 by comparison of theoretical calculations with data of direct statistical modeling. In Refs. 12–16, it was shown that the group of models which does not consider the creation of the particles in the superposition approximation leads to results which are comparable with the results of the direct statistical modeling. Any restrictions on the range of applicability are absent. More problematic is the use of the approximation for the case of the creation of particles. This question was studied in a number of articles (Refs. 17–19) for the problem of accumulating Frenkel defects in crystals under the influence of radiation. It was shown that the source for the restriction of the applicability of the superposition approximation is the choice of the reaction partner. An adsorbed particle A (B) may have several particles B (A) as nearest neighbors. Within the simulation, the choice of an annihilation partner is trivial and can be decided by a random number. Within the analytical ap-

proach, we are restricted by using only pair distribution functions. Many particle configurations which are necessary for the choice of an annihilation partner (especially for high concentrations of adsorbed particles) are only partially taken into account. In Ref. 19, a modification of the superposition approximation is introduced which leads to better results, but this modification uses special conditions of the Frenkel defect problem and cannot be used here.

To obtain a better precision of the superposition approximation, we use a model with $R=D$ and call this the local model because reaction between particles takes place in one cell. This happens if an A particle jumps into a cell which is occupied by a B particle. In this model, the choice of an annihilation partner (which appears in the model introduced by Ziff *et al.*¹) does not arise at all. In the model of Ziff *et al.* in which reaction takes place between nearest neighbors with an infinite reaction rate, larger aggregates of particles must be studied to make a correct decision of a reaction partner. This problem cannot be solved with pair correlation functions. We want to call this model the distance model because the reaction takes place between nearest neighbors and not within a cell. Furthermore, in the special case of the local model, a number of terms in Eqs. (19) and (24) which are obtained using the superposition approximation vanish. It should be pointed out that the question about the precision of the superposition approximation in the local model cannot be regarded as solved. Therefore we will compare our results with computer simulations.

The site mean-field approximation (discussed in Ref. 3 for this system) follows from the system of equations derived above by neglecting nearest neighbor correlations $X_a(1)=X_b(1)=Y(1)=1$.

IV. THE METHOD OF SOLUTION

The main problem is connected with the solution of an infinite system of nonlinear differential equations (19), (22), and (24) for a chosen type of lattice. To solve this problem practically, the following approximation is used. A threshold value m_0 is introduced. For $m < m_0$, the lattice equations are solved for all nonequivalent points of the lattice (here we use $m_0=5$). This first area determines several coordination spheres in which the lattice aspect of the problem is important and in which the oscillations of the correlation functions are observed (see below). In the second area, all properties change quascontinuously with the distance $|m|$. Therefore we can use a continuum approximation by introduction of the coordinates $r=|m|$ and substituting the correlation function $F_{\sigma\sigma'}(m)$ by the radial one $F_{\sigma\sigma'}(r)$. By the substitution

$$\Delta X_a(\mathbf{m}) \Rightarrow \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) X_a(r), \quad (25)$$

the equations transform into nonlinear equations in partial derivatives. As the left boundary condition (circumference of the circle with radius m_0), the solution within the first area at $|m|=m_0$ is used. Because of the weakness of the correlation, we can use $F_{\sigma\sigma'}(\infty)=1$ as the right boundary

condition (for $r \rightarrow \infty$). To perform the space averaging according to Eq. (18), we make use of the fact that for a large diffusion coefficient, D , correlations spread through the lattice by the diffusion mechanism. Because the correlation function changes smoothly, the local approximation $\hat{F}_{\sigma\sigma'}(l) \Rightarrow F_{\sigma\sigma'}(r)$ is justified. For small D , the nonlocal approximation is better justified, which takes into account the nondiffusional mechanism of the spreading of correlations more exactly. When evaluating Eq. (18), some space point l is chosen. We assign to this point the average value of the function in the first coordination sphere (nearest neighbors of l). The continuum analog of this operation is

$$\hat{F}_{\sigma\sigma'} \Rightarrow \frac{1}{\pi} \int_{-1}^{+1} F_{\sigma\sigma'}(r') \frac{ds}{\sqrt{1-s^2}}, \quad r' = \sqrt{r^2 + 1 - 2rs}. \quad (26)$$

After these transformations, the model can be solved effectively by numerical methods. In this procedure, we use the nondimensional time $t \rightarrow tp_0$. In our model, the following independent parameters appear: y_A , $D \rightarrow D/p_0$, $R \rightarrow R/p_0$ (in the local model y_A , $D=R$). As the initial condition, we must choose the concentration of adsorbed particles and the pair correlation function. For example, for noncorrelated distributed pairs, we set $X_a(\mathbf{m}) = X_b(\mathbf{m}) = Y(\mathbf{m}) = 1$.

V. RESULTS

In this section, we present the results for the local model ($R=D$) for the square and for the triangle lattice. First we want to discuss the relation of the local model to the distance model. Within the local model, the relation $Y(1) < 1 - 1/z$ is always valid. This means that AB pairs always exist. In the distance model, $Y(1)$ is equal to zero. If the lattice is nearly fully occupied by B particles ($c_b \approx 1$) which happens in the vicinity of y_1 , the absence of free cells suppresses the diffusion. In the distance model, the value of y_1 varies only in the third digit as a function of the diffusion rate. In the local model, the hindering of diffusion does not appear because reactive jumps in which a particle A jumps into a cell which is already occupied by B are possible. Therefore one cannot predict that the behavior of these two models should coincide. In the other case of a nearly empty lattice ($c_a, c_b \approx 0$), which is the normal case near y_2 , the reaction rate is dominated mainly by the transport of particles. Therefore the reaction is (especially for large D) under diffusion control. In this case, the differences between the two models are not very important. It is immaterial whether a pair of nearest neighbors are cleared by the reaction ($R = \infty$) or the reaction event takes place in one cell. Therefore one can expect that the behavior of the models (and the value of the phase transition point y_2) should be close to each other.

A. The square lattice

In Fig. 1, the coverages of A and B are shown as a function of the mole fraction of A in the gas phase (y_A) for the case of an initially empty lattice. The dashed line (B coverage) and the solid line (A coverage) are obtained from the theory discussed above for $D=1000$. The open squares represent the coverage of B for $D=10$. The filled

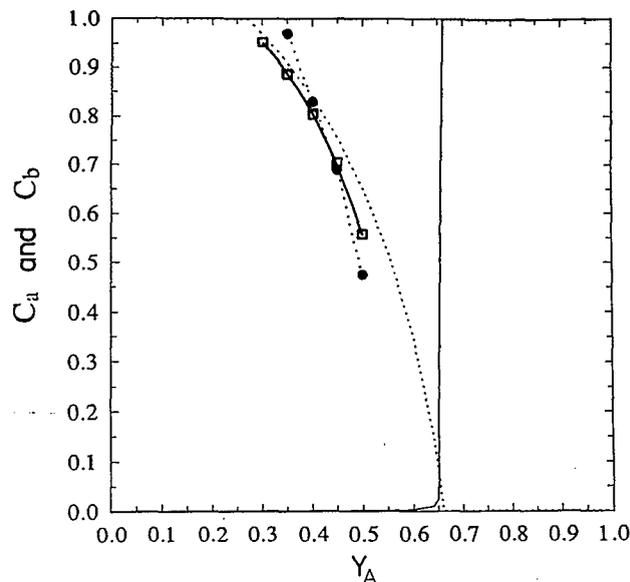


FIG. 1. Coverages of A and B as a function of the mole fraction y_A for an initially empty lattice. The dashed line represents the coverage of B for $D=1000$ and the open squares for $D=10$ (theory). The filled circles are the results of a simulation for $D=10$. The solid line shows the coverage of A for $D=1000$.

circles show the coverage of B which follows from a simulation (distance model) for $D=10$. One observes two phase transition points. For $y_A < y_1 = 0.27$, the lattice is completely covered by B particles. For $y_A > y_2 = 0.650$, the poisoning with A is obtained. The value of y_2 is exactly the same as was found for the distance model in the case of large diffusion rate.²³ The value of y_1 is (as expected) in not so good agreement with the value of the distance model for which we found $y_1 = 0.398$. The difference originates also from the superposition approximation which is not perfect in this parameter range because of the adsorbate structures (large clusters of B). In other models (Refs. 12–16), a difference of 10%–20% is also observed. In the distance model, we have found that the character of the phase transition at y_2 is of first order while it is of second order at y_1 . This behavior is essentially also obtained by the local model. It should be noted that the phase transition at y_2 is not exactly of first order which can be understood from the existence of AB pairs. If the diffusion rate is reduced ($D=10$), nearly the same value of y_1 is obtained which is in agreement with the result of the distance model.

In Fig. 2, the coverages are shown as in Fig. 1 ($D=1000$), but now we start with a lattice which is filled randomly with A particles ($c_a = 0.25$). The value of y_1 is not influenced by this change, but the value of y_2 is reduced to 0.598. This behavior is in excellent agreement with the results of the distance model, where we have obtained $y_2 = 0.596$ for the case of a large diffusion rate³ (the reason for this behavior is given in this reference).

The pair correlations are shown in Fig. 3 as a function of the distance r for $D=1000$. The solid line represents X_a , the dashed line X_b , and the dotted line Y . The group 1 of

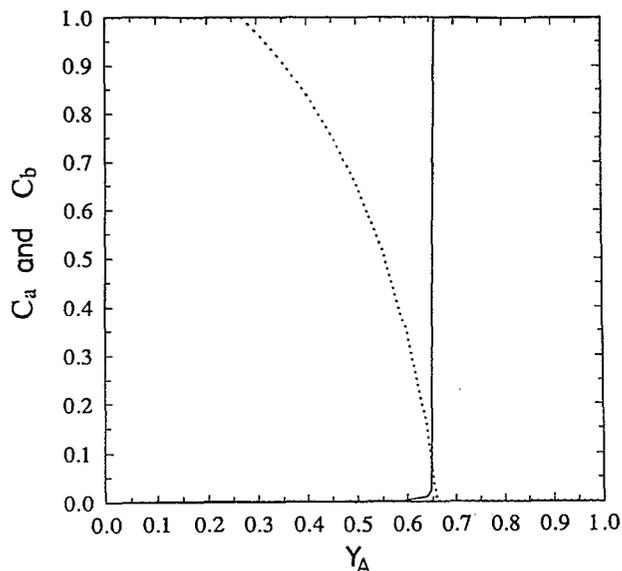


FIG. 2. Coverages of A (solid line) and B (dashed line) as a function of the mole fraction y_A for a lattice which is filled initially with 25% A particles (randomly distributed). The diffusion constant D is set to $D=1000$.

lines are obtained for $y_A=0.6$ and group 2 for $y_A=0.65$. In the first case, the correlations reach the asymptotic value very fast. At this mole fraction, only small correlations appear, which means that the correlations are given mainly by the nearest neighbor cells. In the second case (at the phase transition point y_2), very large correlations appear and the correlation length is in the range of 100 lattice units. This can be understood by the fact that at this value of y_A , the system is at a phase transition point where large fluctuations (which are of the size of the lattice) appear. The small maximum for X_b arises from the adsorption of B_2 , which takes place on nearest neighbor cells. For this mole fraction, adsorbed particles which are far away from one cell also influence its behavior.

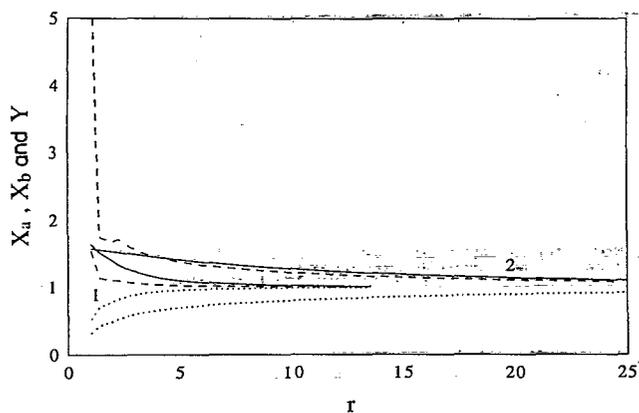


FIG. 3. Pair distribution functions X_a (solid line), X_b (dashed line), and Y (dotted line) as a function of the distance r for $D=1000$. Group one of the lines is obtained for $y_A=0.6$ and group two for $y_A=0.65$.

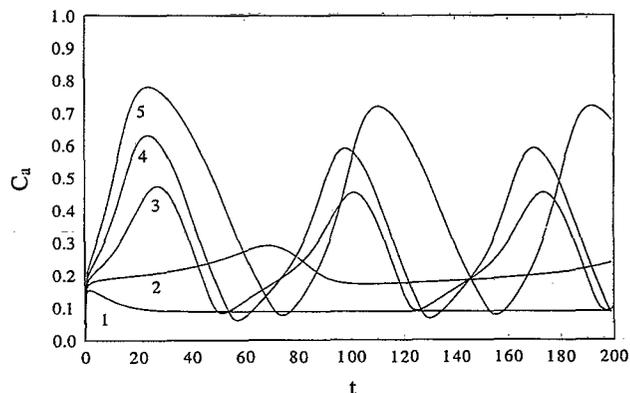


FIG. 4. Coverage of A particles as a function of the time t for $y_A=0.55$. The curves represent the result for different values of the diffusion constant $D=(1) 15$; (2) 12; (3) 10; (4) 8; and (5) 6.

In the distance model, we have not observed the appearance of oscillations.³ Within a mean-field approximation, we have shown (with the help of the negative criterion of Bendixon) that oscillations cannot appear, but in the local model, we observe oscillations of the coverages of A and B . The reason for the appearance of oscillations is in the present model the finite reaction rate. This leads to density fluctuations and the appearance of AB pairs. In the distance model, the reaction rate is infinite and AB pairs do not exist. This explains their absence in this model. The oscillations are shown in Figs. 4 and 5 as a function of the time t for different diffusion constants D and for $y_A=0.55$ which is well below the phase transition point y_2 . The diffusion constant D decreases from $D=15$ (line 1) to $D=6$ (line 5). For large diffusion rates, the coverages of A and B are small because of the large reaction probability. In this case, oscillations do not appear. Thus there should exist a critical diffusion constant D_c which is a function of the mole fraction y_A . For $D > D_c$, a stationary state is reached in which a mixture of A and B particles is adsorbed on the surface. For $D < D_c$, large clusters of A and B are formed in alternate order. In Fig. 6, the phase diagram for the oscillations is shown. One can see that the curves are

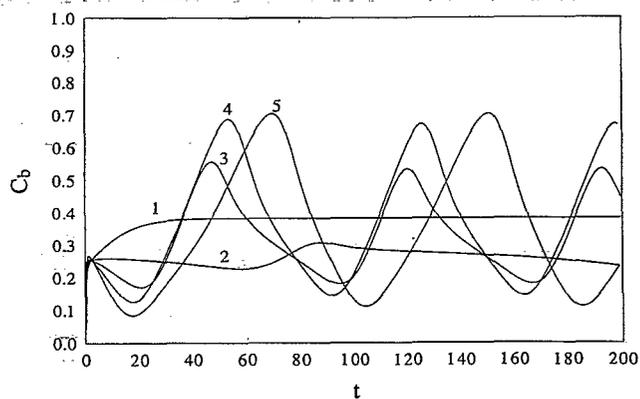


FIG. 5. Coverage of B particles as a function of the time t for $y_A=0.55$. The curves represent the result for different values of the diffusion constant $D=(1) 15$; (2) 12; (3) 10; (4) 8; and (5) 6.

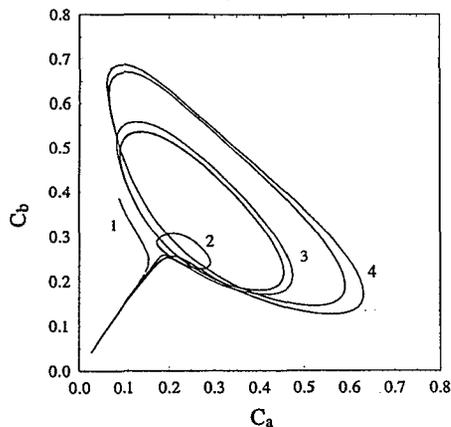


FIG. 6. Phase diagram for $y_A=0.55$. The curves represent the result for different values of the diffusion constant $D=(1) 15$; (2) 12; (3) 10; and (4) 8.

stable after two cycles (with the exception of line 5 which needs more cycles—that is why it is not shown in the figure).

Next we want to study the pair correlation functions for the minimum (Figs. 7 and 8) and for the maximum (Figs. 9 and 10) of the coverage of A particles for $y_A=0.55$ and $D=10$. For the case of the minimum, one can see from the small correlation length that only small clusters of A particles are present which are embedded in a matrix of B particles which are distributed nearly stochastically. For the case of a maximum value of C_a , the correlation length becomes much larger. Large A clusters are formed which are embedded in a porous cluster of B particles.

We have obtained that the value of the critical diffusion constant D_c depends on the mole fraction y_A [$D_c = D_c(y_A)$]. In Fig. 11, this dependence is shown. For small values of y_A , oscillations can only appear for very small values of D . Near y_2 oscillations are possible in a large range of D .

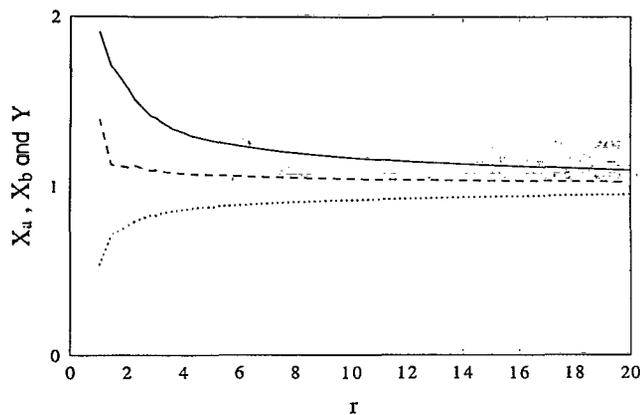


FIG. 7. Independent pair correlation functions X_a (solid line), X_b (dashed line), and Y (dotted line) as a function of the distance r for $D=10$ and for $y_A=0.55$. The data are obtained for the minimum of the coverage of A particles on the surface in the oscillation.

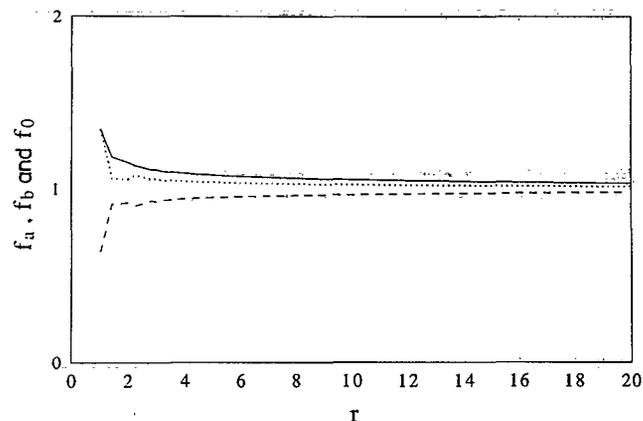


FIG. 8. Dependent pair correlation functions f_a (solid line), f_b (dashed line), and f_0 (dotted line) as a function of the distance r for $D=10$ and for $y_A=0.55$. The data are obtained for the minimum of the coverage of A particles on the surface in the oscillation.

B. The triangular lattice

To apply our theoretical ansatz to the triangular lattice, we must only take into account the different neighborhood and we must set the coordination number of the lattice to $z=6$. We obtain two phase transition points $y_1=0.19$ which is of second order and $y_2=0.650$ which is of first order. Comparing these values with the result of the square lattice, one can see that the value of y_1 is lowered, which means that the poisoning with B particles is more difficult to achieve. The first order phase transition remains fixed. The simulation of the distance model leads to $y_1=0.36$ and $y_2=0.641$. The values of y_2 are in good agreement with each other, but the values of y_1 are rather different. In the neighborhood of y_1 , the local model shows a different behavior as the distance model. The reason for this difference is given above. The value of y_2 is nearly not influenced by the type of the lattice and an agreement of the theoretical description of the local model and the simulation of the distance model is found. This can be under-

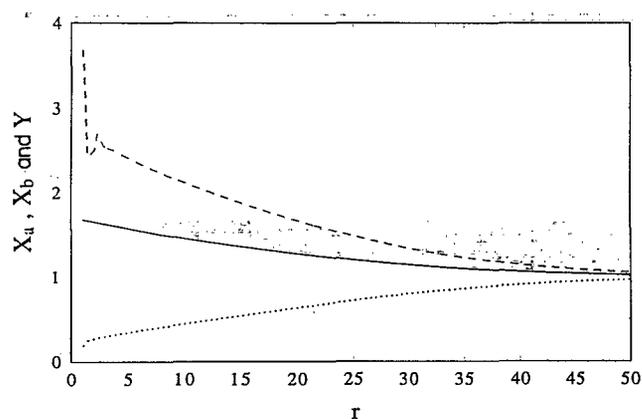


FIG. 9. Independent pair correlation functions X_a (solid line), X_b (dashed line), and Y (dotted line) as a function of the distance r for $D=10$ and for $y_A=0.55$. The data are obtained for the maximum of the coverage of A particles on the surface in the oscillation.

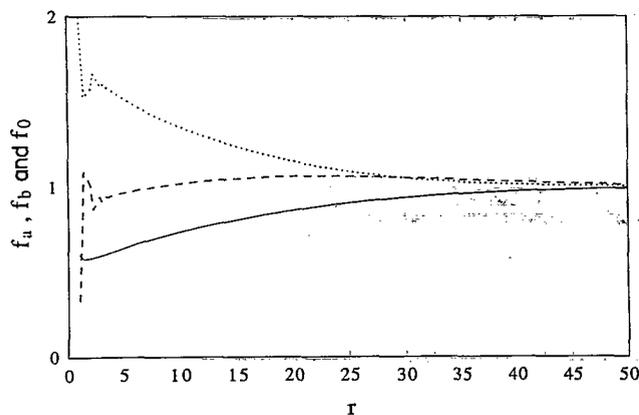


FIG. 10. Dependent pair correlation functions f_a (solid line), f_b (dashed line), and f_0 (dotted line) as a function of the distance r for $D=10$ and for $y_A=0.55$. The data are obtained for the maximum of the coverage of A particles on the surface in the oscillation.

stood from the fact that the behavior of the systems is dominated mainly by the diffusion which is of the same type in both models.

Similar to the square lattice, we also observe oscillations. A critical value of the diffusion coefficient D exists in this model. Because of the similarity of the behavior of the model on the different lattices, we do not repeat all the calculations which were performed for the square lattice.

VI. CONCLUSIONS

We have introduced a stochastic theory to describe a surface reaction model. To obtain a tractable model, we have changed the model with respect to the reaction rule. This leads to the local model in which reaction takes place if two reactive particles are residing in the same lattice cell. This model shows two phase transition points. The values

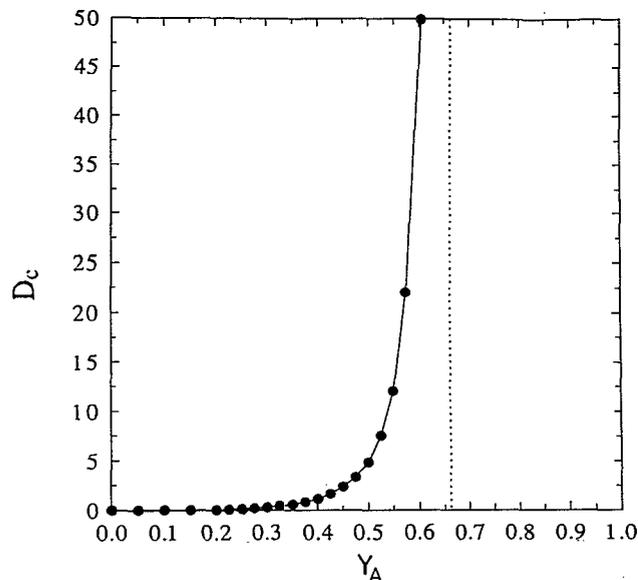


FIG. 11. Critical values of the diffusion constant D as a function of y_A .

of these points are in good agreement with the distance model (discussed earlier³) in the case of the square lattice. The character of the phase transitions remains unaltered under the different description of the reactive event. The dependence on an initial coverage of particles is the same in the theoretical approach as in the distance model. Therefore we may say that all properties of the distance model are shown correctly by this theoretical approach. In the vicinity of y_2 , the agreement is excellent, whereas near y_1 , the distinction between the two models plays a more important role and small differences in the value of y_1 arise.

Another interesting property which shows the differences between the local and the distance models is the appearance of oscillations of the particle coverages. Whereas in the distance model oscillations were not found, we find large oscillations in the local model in a large parameter range. This range depends on y_A and on a critical value of the diffusion constant D . For low values of y_A , oscillations can only appear for small values of D , whereas for larger values of y_A , the range of possible values of D is very large. In the local model, oscillations appear by density fluctuations of A and B . The reason for the difference between the local and the distance models is found in the reaction process. In the distance model, the reaction rate is infinite and therefore AB pairs cannot exist, but such pairs do exist in the local model in which the reaction rate is finite. The AB pairs are correlated on the surface and this leads to oscillations. In our model, we have looked at one point of the lattice and we find periodic fluctuations of the coverages. If we would study the surface on the whole, we may also find waves which are propagating over the surface. In the present model, the third parameter (which seems to be necessary for the appearance of oscillations in this model) is the existence of AB pairs which play the same role as the surface reconstructions in the model of Möller *et al.*⁹ and Eiswirth *et al.*¹⁰

Concluding we can say that the theoretical approach introduced here is well suited for the description of a large variety of so called surface reaction systems. The ansatz allows the study of correlation functions on different types of lattices and under different initial conditions. Moreover, this ansatz can be extended to more complicated situations where the structure of the surface itself plays an important role. An example for such a system is the model for the formation of NH_3 which will be studied in a further paper.

It should be noted that these simple systems show some aspects which are in agreement with real surface reaction systems² in the present case, the oxidation of CO . It is clear that only some aspects are included and only a restricted set of properties is consequently presented adequately, but with increasing complexity of the models by accounting of additional reaction aspects and other steps, these models may finally be able to describe a large variety of real systems.

ACKNOWLEDGMENTS

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