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# Catalytic surface reaction of the type $\frac{1}{2}A_2 + BA \rightarrow A_2B$

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Received 10 August 2000, in final form 2 January 2001

## Abstract

We consider a dimer–dimer catalytic surface reaction of the type  $\frac{1}{2}A_2 + BA \rightarrow A_2B$ . In our model, two nearest-neighbour sites are needed for the adsorption of both molecules. After deposition, BA molecules do not dissociate, while the  $A_2$  molecules dissociate into two free A atoms. The only possible reaction occurs when a free A atom is the nearest neighbour of a B atom of the dimer BA. After the reaction, three sites are left empty. We performed Monte Carlo simulations and pair approximation studies to obtain the phase diagram of the model. The relevant order parameter of the model is the number of nearest-neighbour pairs of empty sites. The pair approximation calculations predict a poor reactive window, while the Monte Carlo simulations give no reactive window for any value of the adsorption rate of dimers. By introducing diffusion of BA molecules we find an intense zero-width reaction window in the phase diagram of the model. On the other hand, desorption of BA molecules gives a reactive window for all values of the deposition rate of BA molecules above a critical value.

PACS numbers: 0570L, 0570F, 8220M, 8265J

## 1. Introduction

The study of catalytic surface reaction models continues to be a topic of great interest [1–4]. The systems that present these far-from-equilibrium reactions show complicated behaviours, such as irreversible phase transitions (IPTs) between active and absorbing (nonactive) states. Although many details concerning the nature of these IPTs have been elucidated, specially those related to the oxidation of CO, new simplified models have been proposed [5, 6]: monomer–monomer, dimer–dimer and monomer–dimer reactions are some examples. The reactions are in general expressed by letters unlike those used in the real reactions: this procedure has the aim to emphasize that the studied systems are only toy models compared with the real ones. The model proposed by Ziff, Gulari and Barshad [1], known as the ZGB model, is the simplest one used to explain the irreversible oxidation of CO molecules on a catalyst surface. In the ZGB surface reaction model, molecules of CO and  $O_2$  are adsorbed on a square lattice, that works as

the catalytic surface, according to their partial pressures in the gaseous phase. In this model, the CO molecules need only one vacant site to adsorb onto the catalytic surface; when a O<sub>2</sub> molecule arrives at the surface it dissociates completely. The reaction occurs instantaneously whenever a CO molecule sees a nearest-neighbour O atom. To describe the whole process we need only a single parameter, which is taken as the relative adsorption rate of CO molecules, denoted by  $y_{\text{CO}}$ . The Monte Carlo simulations performed by these authors show the appearance of active and inactive states in the phase diagram. For instance, for  $y_{\text{CO}} \leq y_1$ , an O poisoned state is observed, and for  $y_{\text{CO}} \geq y_2$  a completely poisoned CO state is found. On the other hand, for  $y_1 < y < y_2$ , a reactive steady state is established, with a nonzero number of vacant sites. Since two nearest-neighbour vacant sites are needed to adsorb a dimer, and the catalytic reaction occurs between a pair of nearest-neighbour monomers (conditions required by almost all proposed models of catalytic surface reactions), it is expected that the pair approximation procedure gives reasonable results: this is corroborated by the pair approximation calculation performed by Dickman [7], that predicts a reactive window for the ZGB kinetic model in qualitative agreement with the simulations.

In this paper we consider a dimer–dimer catalytic surface reaction model of the type  $\frac{1}{2}\text{A}_2 + \text{BA} \rightarrow \text{A}_2\text{B}$ , in which the adsorption of both molecules, A<sub>2</sub> and BA, requires two nearest-neighbour vacant sites of the lattice. Although the BA molecule occupies two sites, it does not dissociate in any case. On the other hand, when the A<sub>2</sub> molecule arrives at the catalytic surface, it dissociates completely. The reaction to produce A<sub>2</sub>B only occurs through nearest-neighbour pairs of B and free A atoms. The whole process follows the Langmuir–Hinshelwood mechanism and the following three steps must be considered:

- (1)  $\text{BA}(\text{g}) + 2\text{V} \rightarrow \text{BA}(\text{a})$ ,
- (2)  $\text{A}_2(\text{g}) + 2\text{V} \rightarrow 2\text{A}(\text{a})$ ,
- (3)  $\text{BA}(\text{a}) + \text{A}(\text{a}) \rightarrow \text{A}_2\text{B}(\text{g}) + 3\text{V}$ ,

where the labels a and g denote adsorbed and gaseous particles, respectively, and V is a vacant site. The steps (1) and (2) describe the adsorption of molecules BA and A<sub>2</sub>, respectively, and the third step represents the reaction between the adsorbed species to form the A<sub>2</sub>B molecule.

Albano [8] studied three models for the dimer–dimer surface reaction scheme of the type  $\frac{1}{2}\text{A}_2 + \text{B}_2 \rightarrow \text{B}_2\text{A}$  by means of Monte Carlo simulations. Both molecules, A<sub>2</sub> and B<sub>2</sub>, dissociate when they are adsorbed by the catalyst surface. The models involve the formation of intermediate species AB at a single site on the surface. Then, the molecule AB reacts with a nearest-neighbour atom B forming the B<sub>2</sub>A, leaving two new empty sites on the surface. For his first model, called M1, neither diffusion nor desorption of B is allowed, and he finds a zero-width window exactly at the critical point  $p_{\text{B}_2} = 2/3$ , where  $p_{\text{B}_2}$  means the deposition rate of B<sub>2</sub> molecules. The mean-field rate equations for this model were also considered by Maltz and Albano [9], and they found the same critical value  $p_{\text{B}_2} = 2/3$  of the simulations. For the second model, M2, diffusion of B atoms is allowed and the zero-width window at  $p_{\text{B}_2} = 2/3$  persists. The differences between M1 and M2 models are related to the coverages of species below and above the critical point. For instance, due to diffusion introduced in model M2, the small coverage of B observed for  $p_{\text{B}_2}$  less than 2/3 in the model M1 now disappears. In the third model, M3, diffusion of B atoms and recombination of nearest-neighbour adsorbed B atoms are considered. After recombination of B atoms, they form a B<sub>2</sub> molecule that desorbs from the surface, leaving two new vacant sites. B<sub>2</sub> desorption causes the occurrence of a reactive window in the range  $0.7014 < p_{\text{B}_2} < 1$ , where the production of B<sub>2</sub>A molecules remains stationary.

The model we consider in this paper is slightly different from those studied by Albano [8] and Maltz and Albano [9]. The molecule BA does not dissociate when it arrives at the surface.

It reacts with a free A atom only when this atom is a nearest neighbour of the B atom of the BA molecule. We also consider desorption of the BA molecules and diffusion of the A and BA species.

We think this model could represent the oxidation of carbon monoxide if two sites were needed to adsorb the CO molecule. Then, the model is a variant of the ZGB model. At first sight we would expect that this model could give a wider reactive window because three sites are freed during the reaction step. On the contrary, as we will see below, this model does not exhibit any reactive window, except when diffusion or desorption are taken into account. To investigate this particular surface reaction model we employed pair approximation calculations and Monte Carlo simulations. The order parameter to be associated with this model is not the usual density of empty sites but the density of nearest-neighbour pairs of vacant sites. Then, the site approximation cannot be used in this paper, and the simplest possible theory to understand the present model is the pair approximation. Neglecting diffusion and desorption, we show that at the level of the pair approximation the phase diagram exhibits a reactive window, although the density of nearest-neighbour pairs of vacant sites in the steady state, necessary to keep reactions running, is very small. However, Monte Carlo simulations show that this reactive window is an artefact of the pair approximation method: for all values of the deposition rate  $y_{BA}$ , there is no active steady state, and we obtain an infinite number of absorbing states. We arrived at these results by performing simulations on the square and triangular lattices. We show that introducing diffusion of A atoms and of BA molecules causes the appearance of a zero-width reactive window at the critical point  $y_{BA} = 2/3$ , where  $y_{BA}$  is the probability that a BA molecule arrives at the surface. This critical point is equivalent to that found by Albano [8] and by Maltz and Albano [9]. We also show that, allowing for desorption of BA molecules, a finite reactive window is opened in the phase diagram of the model. The remainder of this paper is organized as follows: in the next section, we present the model and the pair approximation procedure; in section 3, we describe the Monte Carlo simulation, and finally, in section 4, we present our results and conclusions.

## 2. Model and the pair approximation procedure

We recall the steps to be considered in our  $\frac{1}{2}A_2 + BA$  surface reaction model:

- (1)  $BA(g) + 2V \rightarrow BA(a)$ ,
- (2)  $A_2(g) + 2V \rightarrow 2A(a)$ ,
- (3)  $BA(a) + A(a) \rightarrow A_2B(g) + 3V$ .

The labels a and g denote adsorbed and gaseous species, respectively. In the first step, two nearest-neighbour adjacent sites are necessary for adsorption of BA molecule and, after adsorption, these molecules do not dissociate. In step (3) the reaction only occurs if the atom B of the BA dimer becomes the nearest neighbour of a free A atom. If the B atom is the nearest neighbour of an atom A which is bound to another B, the reaction cannot take place. We also assume that the whole process is controlled by the deposition rates of BA and  $A_2$  molecules, because the reactions occur instantaneously. In the pair approximation we need to consider all possible pairs of nearest-neighbour sites on the lattice: VV, VA, VB, BB, AA, BA and B'A, where V, A and B represent a vacant site, a site occupied by an A atom or one occupied by a B atom, respectively. The pair BA represents the proper BA dimer molecule, while the pair B'A denotes a nearest-neighbour pair of B and A atoms in the lattice not bound themselves.

In the pair approximation we introduce the pair probability  $P_{ij}$  that a random nearest-neighbour pair of sites is occupied by monomers of the type  $i$  and  $j$ , or that they are vacant. We study the time evolution of these pair probabilities by considering all the possible events

that increase or decrease the value of  $P_{ij}$ . That is, we write a master equation for all possible pair probabilities, considering that all transitions rates are of Markovian type. The details of this pair approximation procedure can be seen in [4] and [10]. In the following table we list the allowed transitions between nearest-neighbour pairs for our model. We assign numbers to the allowed transitions and leave blank space for the forbidden and redundant ones. For our particular model, we find 16 transition rates:

From:	VV	VA	VB	BB	AA	BA	B'A
To: VV		1	2	3		4	
VA	5				6		7
VB	8			9			10
BB			11				
AA	12	13					
BA	14						
B'A		15	16				

The next step in the method is to derive explicit expressions for the transition rates  $R_1 \dots R_{16}$ . In the horizontal lines of the table we have transitions that increase the corresponding pair probability, while in the vertical lines we display the ones that decrease the pair probability. For instance, for the  $P_{VV}$  pair probability, the corresponding master equation is

$$\frac{dP_{VV}}{dt} = 2(R_1 + R_2 + R_4 - R_5 - R_8 - R_{14}) + R_3 - R_{12} \quad (1)$$

where the overall factor of two arising in the above expression is due to the two possible ways of obtaining the same pair configuration (for example, VB and BV contribute equally to the formation of the pair VV). The expressions for these transition rates are, in general, very lengthy. For instance, a medium size transition rate is  $R_2$ , that we write below:

$$R_2 = 12 y_{A2} P_{VB}^2 P_{VV} \alpha_1 / (P_B P_V^3) + 9 y_{A2} P_{VB} P_{VV} \alpha_1 / P_V^3 + 4 y_{A2} P_{VB}^2 P_{VV} \alpha_2 / (P_A P_B P_V^2) + 2 y_{A2} P_{VB}^2 P_{VA} \alpha_1 / (P_A P_B P_V^2) \quad (2)$$

where

$$\alpha_1 = P_{VB}^2 / 3 + P_{VB} P_{BV} + P_{BV}^2 \quad (3)$$

and

$$\alpha_2 = P_{VB} P_{B'A} / 3 + (P_{VB} P_{B'A} + P_{BV} P_{B'A}) / 2 + P_{BV} P_{B'A}. \quad (4)$$

In the last expression, we write  $P_{BV}$  to indicate a pair probability where one site is vacant (V) and the other cannot be occupied by B.  $y_{A2}$  is the probability of arrival of an  $A_2$  molecule, and it is related to  $y_{BA}$  by  $4y_{BA} + 2y_{A2} = 1$ , because we have four possible orientations for a BA molecule impinging the surface and only two possible orientations for the  $A_2$  molecule. The normalization condition reads

$$P_{VV} + P_{AA} + P_{BB} + 2(P_{VA} + P_{VB} + P_{BA} + P_{B'A}) = 1 \quad (5)$$

and for the site probabilities we have

$$P_V = P_{VV} + P_{VA} + P_{VB} \quad (6)$$

$$P_A = P_{AA} + P_{VA} + P_{BA} + P_{B'A} \quad (7)$$

$$P_B = P_{BB} + P_{VB} + P_{BA} + P_{B'A}. \quad (8)$$

The set of equations obtained in the pair approximation is integrated numerically, using the fourth-order Runge–Kutta scheme [11], starting from an empty lattice. In [4] Dickman

and coworkers introduced the so-called PAS theory (pair approximation using sublattices) to explain the phase diagram for the NO + CO reaction model on the square lattice. Although the simple pair approximation gives a reactive window for the NO+CO surface reaction model, the PAS theory eliminated the reactive window, which is in agreement with simulations. We cannot apply this theory to the present model because the BA molecule occupies two neighbouring sites belonging to both sublattices of the square lattice. Then, the argument of Brosilow and Ziff [12], that the reaction NO + CO cannot ever occur on the square lattice, does not apply here. In section 4 we present the results and the phase diagram obtained using this approach.

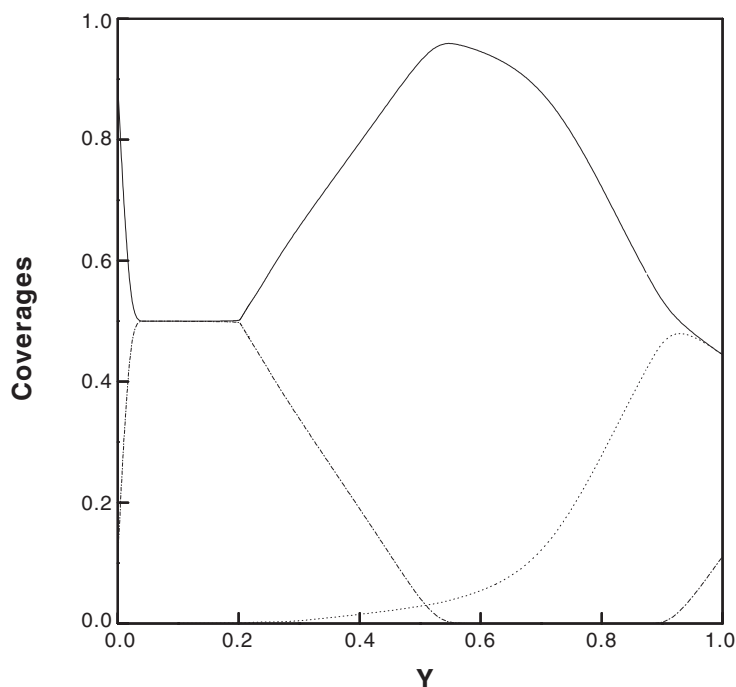
### 3. Monte Carlo simulation

We have performed simulations for this catalyst reaction model on a square lattice with linear dimensions  $L = 80$  and  $128$ . We started all simulations with an empty lattice and used periodic boundary conditions. For each value of the deposition rate  $y_{BA}$  of the BA dimer molecules, we generate a random number to determine what molecule will be deposited in the next step. If we choose BA, we generate another random number, to select a pair of nearest-neighbour vacant sites for its adsorption. If we find this pair, the adsorption occurs and we investigate the neighbourhood of B to search for free A atoms to react with BA. If we are successful the reaction occurs, producing  $A_2B$  and freeing three sites (in this model the BA dimer molecule does not dissociate, and it needs two nearest-neighbour sites for its adsorption). If more than one free A atom is found, we select, at random, which of them will leave the surface. If no free A atom is found the BA molecule remains adsorbed. If the chosen molecule is  $A_2$ , we again generate a random number to pick out a pair of nearest-neighbour vacant sites for its adsorption. Finding this pair, the molecule is completely dissociated, occupying the two adjacent sites of the pair. Then, we look for a B atom in the neighbourhood of both A atoms. If in the vicinity of a given A we find more than one B, we choose at random which of them will be liberated after reaction. In this step, if reaction occurs, three or six sites can be liberated. If no B atoms are found, the two A atoms remain adsorbed. In any case, the simulation is finished when a nearest-neighbour pair of vacant sites is not found for deposition of BA or  $A_2$ .

In this simulation a reactive state exists whenever pairs of nearest-neighbour vacant sites are found in the steady state. We have seen that for any value of the deposition rate  $y_{BA}$  the system always evolves to an absorbing state after a relatively small number of Monte Carlo steps (one Monte Carlo step is equal to  $L \times L$  trials of deposition). Therefore, although the number of vacant sites represents a reasonable fraction of total sites in the lattice, no more molecules can be deposited. The number of absorbing configurations for each value of  $y_{BA}$  is very large. The results of simulation from the two lattice sizes are almost the same. The only difference is related to the time to attain the absorbing state: the time required for the  $L = 80$  lattice is about 70% of that for the  $L = 128$  lattice.

We have also considered the effects of the diffusion of the species A and BA, as well as desorption of the BA molecules. In this case we need to introduce some details concerning these processes during the simulation. Considering only diffusional processes, first of all, we select the ratio  $r$  between the diffusion rate and the corresponding deposition rate of BA molecules. For instance, when we choose  $r = 10^{-3}$ , for each trial of diffusion we perform  $10^3$  trials of deposition of BA molecules.

In the event of a diffusion trial of an A atom, we select at random a site occupied by A. Then, a nearest neighbour of this site is randomly chosen and, if it is occupied, the trial ends. On the other hand, if it is empty, A is allowed to diffuse to this new site. After a successful diffusion event, we need to investigate the neighbourhood of this new occupied site, looking for possible reaction with BA molecules as described above.



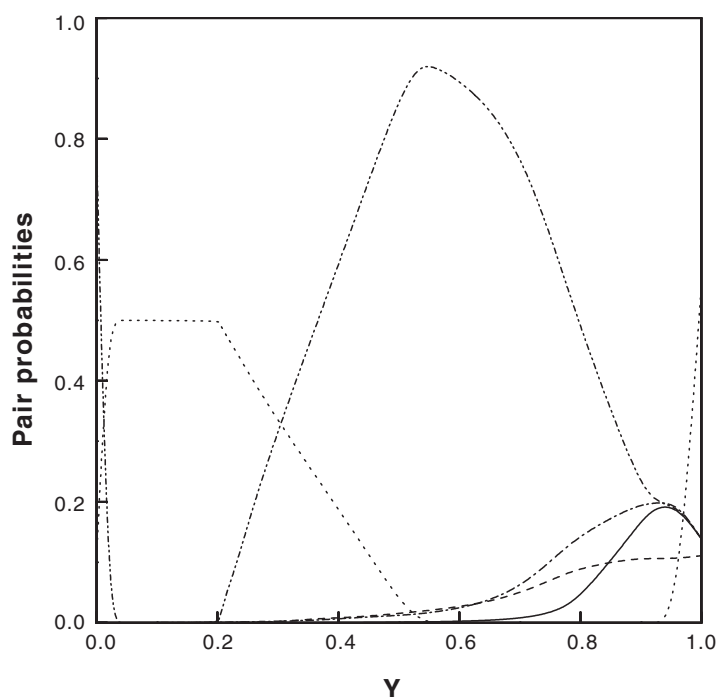
**Figure 1.** Pair approximation results for the coverages of the lattice as a function of  $Y$  ( $Y = 4y_{BA}$ , where  $y_{BA}$  is the deposition rate of BA molecules). The solid curve represents  $P_A$  (fraction of A atoms),  $P_V$  (fraction of vacant sites) is represented by the dashed-dotted curve and  $P_B$  (fraction of B atoms) is represented by the dotted curve.

If we are trying to diffuse a BA molecule, we consider two possible movements: translation perpendicular to its axis (two nearest-neighbour empty sites are needed) and simple displacement along the axis of the molecule (a single empty site is sufficient). In the case of a diffusion trial of BA we select, at random, what type of movement we will make. In the event of a simple displacement we select, also at random, a nearest-neighbour site along the rod of the molecule. If this site is occupied the trial ends, otherwise the BA molecule is rigidly displaced, moving one site along its axis. After a successful diffusion event, we investigate the new neighbourhood of this molecule, looking for free A atoms to proceed with the reaction step. On the other hand, in choosing a translation that is perpendicular to the axis of the BA molecule, we choose, at random, in what direction the diffusion trial will take place. Only when two neighbouring sites are vacant will the diffusion occur and, again, a new search for reacting free A atoms will be made.

In the case of desorption of BA molecules, we first select the ratio  $r$  between the desorption and deposition rates of BA molecules. If we are attempting to desorb a molecule, we randomly choose a BA molecule on the lattice, which is immediately desorbed, leaving an empty pair of adjacent sites on the lattice.

#### 4. Results and conclusions

Let us first consider the case where the diffusion and desorption processes are neglected. We show in figure 1 the plot of the coverages of V, A and B as a function of the deposition rate



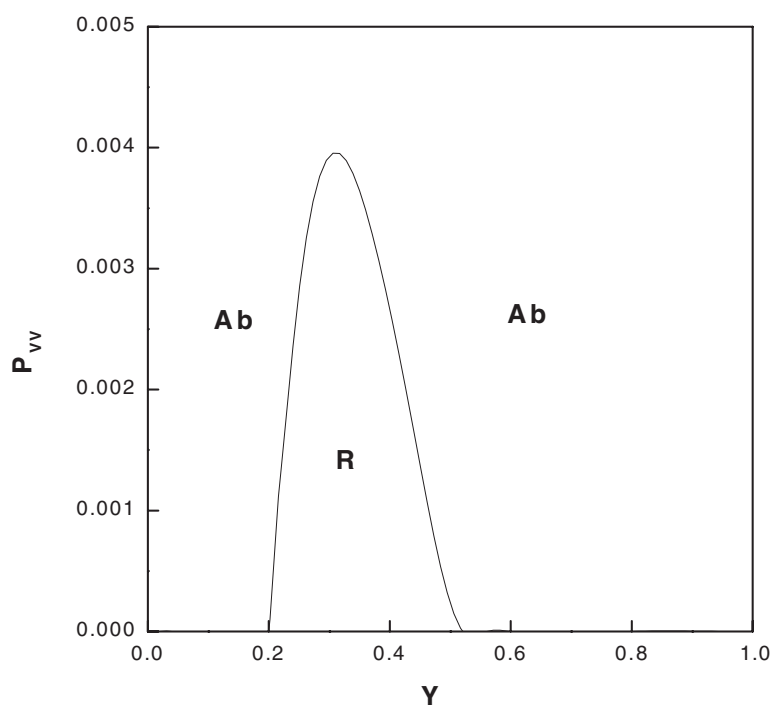
**Figure 2.** Pair probabilities as a function of  $Y$ . Dashed–dotted–dotted curve,  $P_{AA}$ ; dashed curve,  $P_{BA}$ ; dashed–dotted curve,  $P_{B'A}$ ; dotted curve,  $P_{VA}$ ; solid curve,  $P_{BB}$ .

of BA molecules. When  $Y = 0$ , that is, only  $A_2$  molecules arrive at the surface, the pair approximation predicts the value  $P_A = 0.8889$  for the coverage of A atoms. This value must be compared with the random dimer filling on a square lattice. The value we obtained for  $P_A$  corresponds to the first-order approximation in the expansion of the  $Q$  hierarchy, where  $Q_{j,\{n\}}$  is the conditional probability that site  $j$  is empty given that sites  $\{n\}$  are also empty [13]. The best value for this coverage,  $P_A = 0.9068$ , was obtained by Nord [14]. The result of our Monte Carlo simulation on the square lattice is in very close agreement with that of Nord. We have found, for the lattice of linear size  $L = 128$ , the value  $P_A = 0.9070$ . On the other hand, when  $Y = 1$ , which mimics only random deposition of BA molecules, we obtained the same lattice coverage as in the  $Y = 0$  case, in both pair approximation and Monte Carlo calculations, as expected.

In figure 1 we see that the coverage of B atoms is very low up to  $Y = 0.50$ . In the pair approximation, for values of  $Y < 0.50$ , the lattice is almost covered by vacant sites and A atoms. In particular, in the range  $0.02 < Y < 0.20$  the surface is covered by equal quantities of A and V (we will discuss this result in connection with figure 2). The coverage by A atoms attains its highest value at  $Y = 0.55$ . For values of  $Y$  in the range  $0.60 < Y < 0.88$ , the lattice becomes completely covered by BA molecules and free A atoms. In this range of values, the steady-state pair approximation solution predicts no vacant site on the lattice. Only for  $Y > 0.88$  do the vacant sites start to appear again in the lattice. In this small range of values of  $Y$  we observe the maximum in the distribution of B atoms.

In figure 2 we exhibit the pair probabilities as a function of  $Y$ . The maximum value of the pair probability  $P_{VV}$  is of the order of  $10^{-3}$ , and the pair probability  $P_{VB}$  is always less than  $10^{-7}$ . Therefore, these are too small to appear in this figure. For almost all values of  $Y$



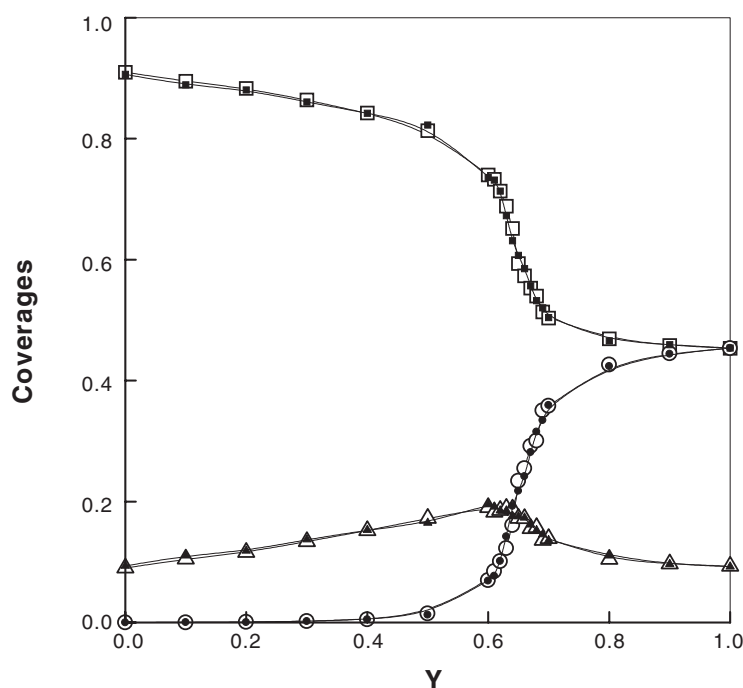


**Figure 3.** Pair probability for the nearest-neighbour vacant sites  $P_{VV}$  as a function of  $Y$ .  $Ab$  represents absorbing states and  $R$  the reactive ones.

the pair probability  $P_{AA}$  is the largest one, except in the region  $0.02 < Y < 0.20$ , where the probability  $P_{AA}$  is less than  $10^{-6}$ . Indeed, in this region, the only pair probability that survives is  $P_{VA}$ . This means that, within the accuracy of the pair approximation calculations, we have two interpenetrating sublattices: one formed by free A atoms, and the other formed by vacant sites. As expected, the maximum observed for  $P_A$  in figure 1 corresponds to the maximum value of the pair probability  $P_{AA}$ . Figure 3 shows the behaviour of the pair probability  $P_{VV}$  as a function of  $Y$ . We can see from this plot a steady-state reactive window, for  $Y$  ranging from 0.20 to 0.52. However, the production rate of  $A_2B$  molecules is very small because the maximum value of  $P_{VV}$  is of the order of  $10^{-3}$ .

We exhibit in figure 4 the results of our Monte Carlo simulations for the square lattice, for  $L = 80$  and 128. In this and the following figures for Monte Carlo simulations,  $Y$  is equal to  $y_{BA}$ . As we can see the results obtained for the coverages are essentially the same for both lattice sizes. This plot must be compared with the pair approximation results of figure 1. The coverage curves found in the Monte Carlo simulation are smoother than those obtained through the pair approximation:  $P_A$  does not exhibit any maximum, and  $P_V$  exhibits a slight maximum around  $Y = 0.60$ . The existence of vacant sites is in itself no guarantee of reactive steady states: in the present model we constrained the adsorption of both species of molecules to the existence of a pair of nearest-neighbour vacant sites. The pattern of two interpenetrating sublattices is not seen in the Monte Carlo approach. The concentration of B atoms in the lattice, similarly to figure 1, also begins to appear for values of  $Y$  around 0.50.

Although this model appears similar to model M1 of Albano [8] and to model (i) of Maltz and Albano [9], we have not seen a zero-width window at the special value of  $y_{BA} = 2/3$ .

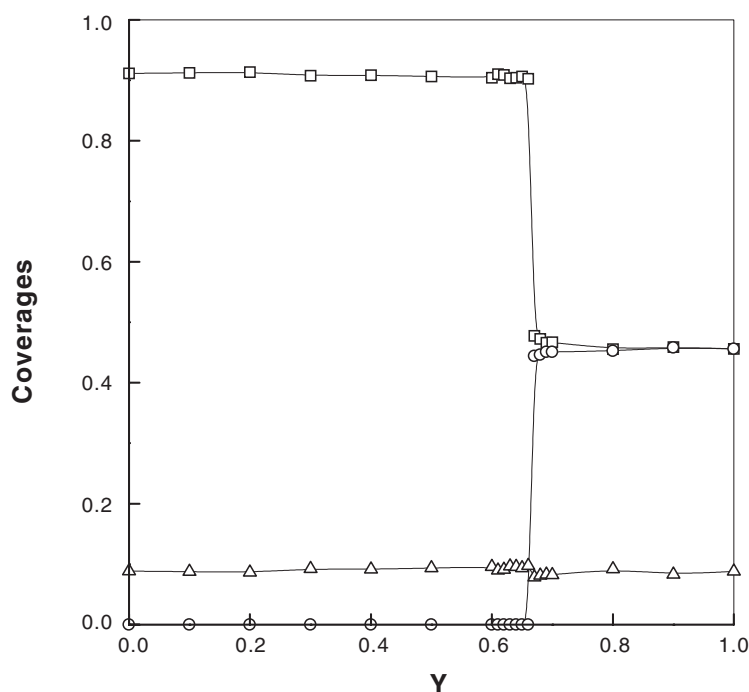


**Figure 4.** Monte Carlo simulations for the coverages of the square lattice as a function of  $Y$ . Squares,  $P_A$ ; triangles,  $P_V$ ; circles,  $P_B$ . Solid symbols represent simulations for  $L = 128$  and the open symbols for  $L = 80$ . The curves serve as guides to the eyes.

The appearance of the zero width window in their model is due to the coalescence of two different species at the same site, just before the step of reaction. In their model there can be up to four reaction channels, while in our simplified model only a maximum of three reaction channels can be opened. This happens because reactions involving the BA molecule, which occupies two nearest-neighbour sites, occur only when the B atom of this molecule finds a nearest-neighbour free A atom.

In order to increase the number of reaction channels in our model we decided to perform simulations on a triangular lattice, whose number of nearest neighbours is six. In figure 5, we exhibit the coverages obtained for this lattice with  $L = 80$ . We can observe that the fraction of vacant sites  $P_V$  is nearly constant, around 0.090 for any value of  $y_{BA}$ . On the other hand, the concentration of A atoms is nearly constant up to  $y_{BA} = 2/3$ , decreasing abruptly when we cross this point. For instance, we have  $P_A = 0.902$  when  $y_{BA} = 0.66$ , and  $P_A = 0.477$  when  $y_{BA} = 0.67$ . Also, when we go from  $y_{BA} = 0.66$  to 0.67, the concentration of B increases from  $P_B = 0$  to 0.444. The transition at the point  $y_{BA} = 2/3$  is of first-order type, although exactly at this point no zero-width window is observed as in the previous works of Albano [8] and Maltz and Albano [9].

We now turn our attention to the diffusion processes. Let us first consider the diffusion of the species A atom on the square lattice. In figure 6 we exhibit the phase diagram for  $r = 10^{-3}$ , where  $r$  is the ratio between the diffusion rate of the A species and the deposition rate of BA molecules. In this case of a very small value of  $r$ , we observe the appearance of a zero-width reaction window exactly at  $y_{BA} = 2/3$ . However, the density of nearest-neighbour pairs of vacant sites at this point is very small, that is,  $P_{VV} \approx 10^{-2}$ . Increasing the ratio  $r$ , this



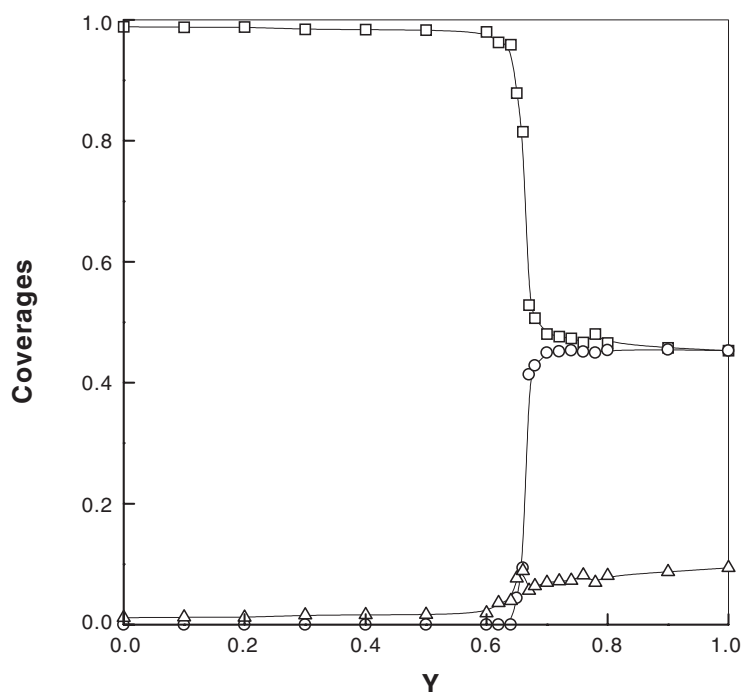
**Figure 5.** Monte Carlo simulations for the coverages of the triangular lattice ( $L = 80$ ) as a function of  $Y$ . Squares,  $P_A$ ; triangles,  $P_V$ ; circles,  $P_B$ . The curves serve as guides to the eyes.

zero-width window disappears, and the lattice becomes completely poisoned by A atoms for  $y_{BA} < 2/3$ . For values of  $y_{BA} > 2/3$  the coverage of free A atoms is zero, while the lattice becomes covered by BA molecules and by a fraction ( $P_V \approx 0.104$ ) of single vacant sites. Then, this model is similar to the M2 model of Albano [8] but with a very low reactivity at the special point  $y_{BA} = 2/3$ .

In the case of diffusion of BA molecules, for a small value of the rate  $r$ , the results obtained for the coverages of species are very similar to those already seen in figure 4. The only difference is the appearance of a zero-width reactive window at  $y_{BA} = 2/3$ , but of very low reactivity. For instance, when  $r = 10^{-3}$ , the density of nearest-neighbour pairs of vacant sites at this special point is  $\approx 10^{-2}$ . On the other hand, this picture changes dramatically when  $r$  becomes very large. We exhibit in figure 7 the phase diagram of the model for the special value  $r = 10^3$ . At the critical point  $y_{BA} = 2/3$ , the reactivity is very large, with a value of  $P_{VV} = 0.90$ . To study the steady state observed at this point, we performed averages over 100 samples with different initial conditions. We take averages in the time interval  $1.0 \times 10^4$  to  $1.5 \times 10^4$ , just after the steady state was reached for each sample. For values of  $y_{BA} > 2/3$  the lattice becomes completely poisoned by BA molecules, without the presence of any vacant site.

When we consider the simultaneous diffusion of A and BA species, and small values of  $r$  for both species, we observe again the zero-width reactive window at the point  $y_{BA} = 2/3$ , but with a very poor reactivity. A high reactivity is found at this special point only when we consider very large values of  $r$ , and also the diffusivity of BA is larger than the diffusivity of A by a factor as large as  $10^2$ .

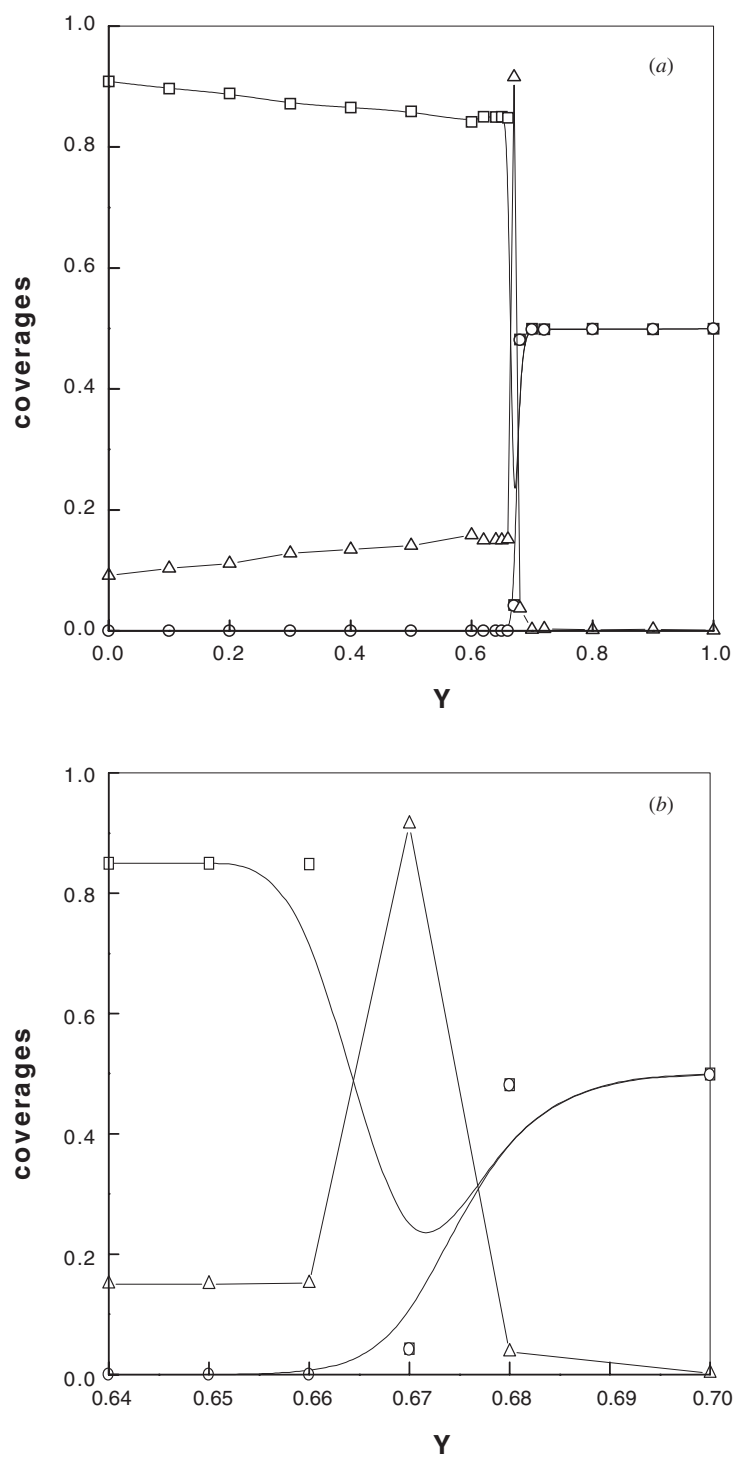
Finally, we present our results concerning the desorption of BA molecules. For very small values of the ratio  $r$  between the desorption and deposition rates of BA molecules, the



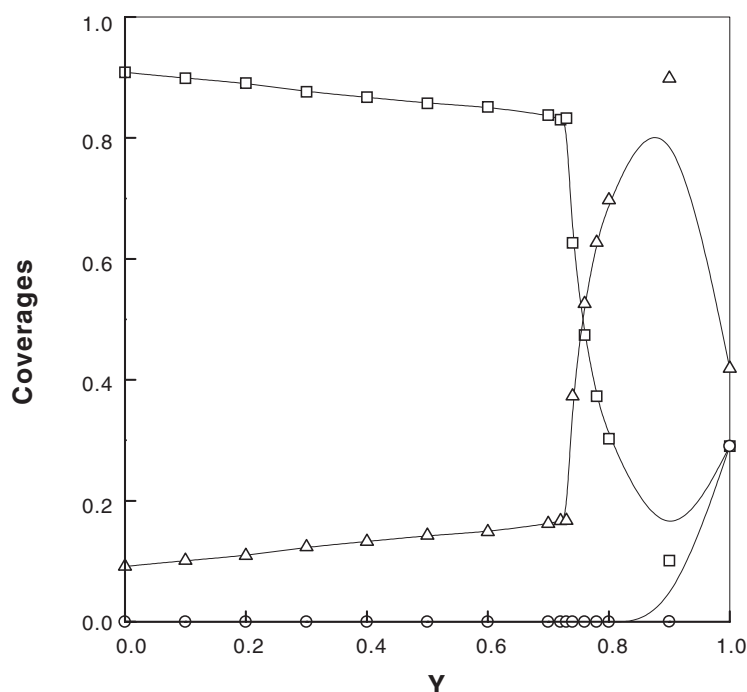
**Figure 6.** Monte Carlo simulations for the coverages of the square lattice ( $L = 80$ ) as a function of  $Y$ , considering diffusion of the A species, for  $r = 10^{-3}$ . Squares,  $P_A$ ; triangles,  $P_V$ ; circles,  $P_B$ . The curves serve as guides to the eyes.

phase diagram is similar to that of figure 4. However, increasing the rate  $r$ , a reactive window is opened for values of  $y_{BA}$  in the range  $0.73 \leq y_{BA} < 1$ . This behaviour can be seen in figure 8, where we take  $r = 1$ . This figure is very similar to figure 2(b) of the work of Maltz and Albano [9]. This is expected because during the desorption process a pair of nearest-neighbour particles leaves the lattice. In our work, the B and A atoms are already bound, while in the work of Maltz and Albano two nearest-neighbour identical particles react before leaving the surface.

In conclusion, we have considered a dimer–dimer catalytic surface reaction model where we require two nearest-neighbour vacant sites to adsorb the  $A_2$  and BA molecules. This model was studied within the pair approximation method and also employing Monte Carlo simulations. We calculated the concentration of different species as a function of the deposition rate of BA molecules. If we disregard diffusion and desorption mechanisms, the pair approximation for a square lattice gave a very poor reactive window, where the  $A_2B$  yield is very small. This window seems to be an artifact of the pair approximation, because it is not present in the Monte Carlo results for the same square lattice. We already seen this behaviour in the pair approximation employed by Dickman [7] in his study of the standard ZGB model. There, the approximation involved in the pair calculation augmented the width of the reactive window relative to that obtained from simulations. Even when we increased the coordination number of the lattice, we did not observe any reactive window for this model. This behaviour was corroborated for the simulations performed on the triangular lattice. However, the introduction of diffusion of species changes the phase diagram. We have seen that a zero-width reactive window, at the special deposition rate  $y_{BA} = 2/3$ , appears. The reactivity observed in this



**Figure 7.** Monte Carlo simulations for the coverages of the square lattice ( $L = 80$ ) as a function of  $Y$ , considering diffusion of BA molecules, for  $r = 10^3$ . Part (b) shows the coverages around the special point  $Y = 2/3$ . Squares,  $P_A$ ; triangles,  $P_V$ ; circles,  $P_B$ . The curves serve as guides to the eyes.



**Figure 8.** Monte Carlo simulations for the coverages of the square lattice ( $L = 80$ ) as a function of  $Y$ , considering desorption of BA molecules, for  $r = 1$ . Squares,  $P_A$ ; triangles,  $P_V$ ; circles,  $P_B$ . The curves serve as guides to the eyes.

window is intense only for large values of the diffusion rate of the BA molecules. On the other hand, a finite-width window can be opened in the phase diagram of the model taking into account the effects of desorption of BA molecules.

### Acknowledgments

This paper was supported by the Brazilian agencies CNPq and FINEP.

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