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Kinetic phase transitions in a surface-reaction model with diffusion: Computer simulations and mean-field theory

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A simple surface-reaction model based upon the oxidation of carbon monoxide on a catalytic surface, introduced by Ziff, Gulari, and Barshad (ZGB) [Phys. Rev. Lett. **56**, 2553 (1986)], has been extended in order to include diffusion of the adsorbed particles (both O and CO). The ZGB model is a nonequilibrium model exhibiting both a first- and a second-order phase transition. The effects of diffusion on the behavior of the model has been explored by means of computer simulations. The main effect of diffusion is to change the positions of the phase transitions and increase the rate of CO_2 formation. Fast diffusion causes the second-order transition to disappear from the system. Simple explanations of these changes are given. The extended version of the ZGB model has furthermore been studied by mean-field theory in the pair approximation. This approach gives qualitatively correct predictions about the effects of diffusion and yields quantitative predictions in good agreement with simulation results in the vicinity of the first-order transition.

I. INTRODUCTION

Recently, Ziff, Gulari, and Barshad[1] (ZGB) introduced a simple nonequilibrium surface-reaction model which exhibits interesting phase-transition-like behavior. The ZGB model is based upon some of the experimentally[2,3] well-known steps in the oxidation of carbon monoxide on a catalytic surface:

$$\mathrm{CO(gas)} \rightarrow \mathrm{CO(ads)}, \quad (1)$$

$$\mathrm{O_2(gas)} \rightarrow \mathrm{2O(ads)}, \quad (2)$$

$$\mathrm{O(ads)+CO(ads)} \rightarrow \mathrm{CO_2(gas)}. \quad (3)$$

Here (ads) indicates that the particle is adsorbed on the surface. In this model the catalytic surface is represented by a square lattice. Each site can be either empty or occupied by an oxygen (O) atom or a carbon monoxide (CO) molecule. CO is added to the surface with probability y_{CO} and is adsorbed if it strikes an empty site [process (1)]. O_2 is added with probability $y_O = 1 - y_{CO}$. If O_2 strikes a nearest-neighbor pair of empty sites, it dissociates into a pair of O atoms residing on separate (nearest-neighbor) sites [process (2)]. After each adsorption process the neighborhood of the newly adsorbed particle(s) is examined in order to determine whether any O-CO nearest-neighbor pairs were formed. If this is the case, an O-CO nearest-neighbor pair is randomly selected, O and CO reacts immediately, and the CO_2 molecules thus formed desorbs at once, leaving two empty sites on which new molecules can be adsorbed [process (3)]. The only parameter in the model is y_{CO}. Each time step in the ZGB model is defined as one attempted adsorption per lattice site. More specifically, the time variable is incremented by $1/N$ subsequent to each adsorption trial, where N is the number of lattice sites. A more detailed exposition of the simulation algorithm can be found in Ref. 1.

The system defined by the rules mentioned above is manifestly irreversible. Results from computer simulations[1,4] show that the system always reaches a steady state, characterized by the average concentrations of adsorbed O atoms and CO molecules. These results are summarized in Fig. 1. Depending on the value of the external control parameter y_{CO}, the system will end up in one of three phases: When y_{CO} is less than a critical value $y_1 = 0.390 \pm 0.001$, the lattice becomes completely covered with O atoms and all reactions cease (the O-poisoned phase). Above a second value, $y_2 = 0.526 \pm 0.001$, the system enters the CO-poisoned phase in which the lattice is completely covered with CO molecules. In the intermediate case, $y_1 < y_{CO} < y_2$, the system

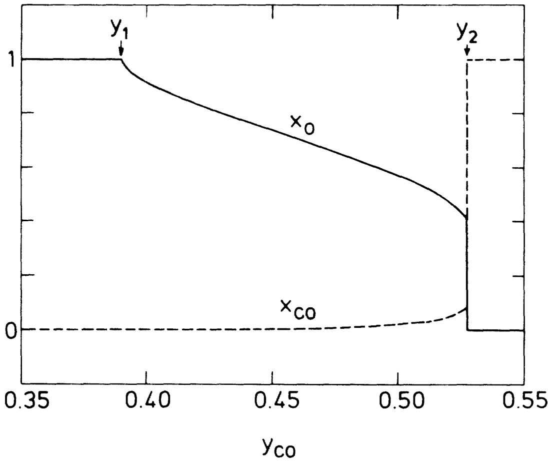

FIG. 1. Concentration of adsorbed O atoms (solid line) and CO molecules (dashed line) as a function of y_{CO}. The system exhibits a continuous transition, at y_1, from an O-poisoned state to an active state and a discontinuous transition, at y_2, into a CO-poisoned state.

reaches a reactive steady state in which the reactions between CO and O can proceed indefinitely. The steady-state concentrations of O atoms, x_{O}, and CO molecules, x_{CO}, on the lattice change continuously at y_1 and discontinuously at y_2. It is customary to characterize these transitions as second- and first-order kinetic phase transitions, respectively. The O-poisoning transition is similar to second-order kinetic phase transitions found in many other models, such as the contact process,[5] Schlögl's model,[6] directed percolation,[7] and Reggon field theory.[8] A common feature of these models is that they exhibit a continuous transition from an absorbing state (a configuration from which the system cannot escape) to an active state. Results from computer simulations[9] and series analysis[8,10,11] have revealed that these and other models[10–15] belong to the same universality class. Recently, computer simulations[16] showed that the O-poisoning transition of the ZGB model belongs to the same universality class as Reggeon field theory or directed percolation.[17]

It is evident that the ZGB model is much too simple to represent the complicated physical and chemical processes occurring in real catalytic systems. But it serves as an appropriate starting point for more complex models and may provide some understanding of the cooperative effects of some of the fundamental processes in real catalysts. Furthermore, it should be borne in mind that the ZGB model contains no parameters (such as binding energies, etc.) which relate it to any specific catalytic system. The ZGB model can therefore be regarded as a standard or minimal model for systems whose basic kinetic evolution rules can be described by the reaction schemes (1)–(3). We also want to point out that our main motivation for studying the ZGB model is that it provides an example of phase transitions in a nonequilibrium system.

In the present paper we extend the analysis of the ZGB model reported in Ref. 1. Constructing an extended version of the model, including diffusion of the adsorbed particles (both O and CO), we present computer-simulation results for the phase diagram. We furthermore construct a simple mean-field-theory description.

II. ZGB MODEL WITH DIFFUSION

Recently, results from computer simulations of extended versions of the ZGB model have been reported.[18,19] These extended versions include a variety of additional processes and features such as diffusion and desorption of carbon monoxide, finite reaction rates, and nearest-neighbor interactions between the adsorbed particles. The computer simulations show that the extended versions of the ZGB model give a good qualitative (and sometimes quantitative) understanding of the influence of processes such as adsorption, diffusion, and desorption of CO, etc., on the kinetics of the oxidation of carbon monoxide on single-crystal surfaces.

Although measurements on platinum-metal surfaces have shown that diffusion of oxygen is not important at typical reaction conditions,[2,3] we have nevertheless chosen to study the effects of O diffusion, first, because we mainly are interested in the ZGB model as an example of a system exhibiting kinetic phase transitions, and in this context diffusion of the adsorbed oxygen turns out to be very interesting. Second, our extended version of the ZGB model is still so general that it does not represent a specific system, and there might exist some catalytic systems in which diffusion of the species corresponding to oxygen in the ZGB model is important.

In order to include diffusion in the ZGB model, we introduced a new parameter p_D: The probability that in a single trial we attempt to move an adsorbed particle. Each trial in the simulation starts by selecting the process to be performed: Diffusion with probability p_D, CO adsorption with probability $(1-p_D)y_{\mathrm{CO}}$ and O_2 adsorption with probability $(1-p_D)(1-y_{\mathrm{CO}})$. A diffusion trial proceeds in the following manner: We choose a site randomly. If this site is empty, the trial ends because there is no particle to move. If the site is occupied, a nearest-neighbor site is randomly selected and the particle is moved to that site if it is empty. After a move the nearest neighbors are examined in order to determine whether any O-CO nearest-neighbor pairs were formed. If this is the case, an O-CO pair is chosen randomly, O and CO react, the CO_2 molecule thus formed desorbs at once, and the two sites are vacated. The adsorption of O_2 and CO proceeds according to the algorithm outlined earlier.

When the system is in the vicinity of the O-poisoned state, the number of empty sites is small. This means that with the algorithm outlined above, most adsorption and diffusion trials fail because the chosen site and its nearest neighbors are occupied. The efficiency of the algorithm can be improved substantially by employing a list of empty sites and only attempt adsorption on those sites. The procedure for updating time is changed accordingly so that time is incremented by $1/N_B$ for each adsorption trial, N_B being the number of empty sites. Note that this procedure ensures that one time step still, on the average, equals one attempted adsorption per lattice site. The algorithm for diffusion now reads as follows: We start by choosing an empty site from the list and subsequently randomly choose a nearest neighbor. If this site is occupied, we move the particle to the empty site and then check for O-CO nearest-neighbor pairs. Simple arguments based on counting the number of processes per time step show that the two algorithms are equivalent.

III. RESULTS

Before we present our results, we want to make a few general remarks about the simulations. In all simulations we used periodic boundary conditions. Most of the results presented below were obtained from an initially empty lattice, the only exceptions being that in order to get accurate results for the position of the second-order transition, we had to use lattices as large as 500×500. In order not to spend large amounts of computer time in reaching a state close to O poisoning, we used lattices initially covered with O, except for a few hundred randomly selected empty sites. Because of the great advantage of using a list of empty sites, we were able to make simulations with a duration of up to 10^5 time steps in the vicinity of y_1. The correlations are short ranged near the first-order transition, and so small lattices (50×50) suffices when it comes to determining y_2, and again it was possible to make simulations with a duration of 10^5 time steps. In the rest of the phase diagram, we mainly used lattices with 100×100 sites, and the duration of each run was normally 10^3 time steps for each value of y_{CO} and p_D.

Figure 2 shows the steady-state concentration of adsorbed O and CO as a function of y_{CO} for the extended ZGB model with $p_D=0.2$. Unless otherwise stated, we use the same probability of diffusion for both O and CO. The steady-state CO_2 production rate (defined as the average number of CO_2 molecules produced per collision or trial) is also plotted in Fig. 2. For comparison we have furthermore shown the results for the original model (no diffusion or $p_D=0$). From these results we first of all notice that the qualitative behavior of the model is not changed by the inclusion of diffusion. The system still exhibits a continuous transition from an O-poisoned state to an active steady state. But this transition takes place at a significantly lower value. We find that $y_1=0.305\pm0.001$ when $p_D=0.2$ as compared to 0.390 ± 0.001 in the absence of diffusion. Likewise, we still find a discontinuous transition from the active state to a CO-poisoned state. In this case we see a small increase in the value of y_2, namely, from 0.526 ± 0.001 without diffusion to 0.537 ± 0.001 when $p_D=0.2$. In addition to these changes in the position of the phase transitions, we notice an increase in the reactivity. Diffusion leads to a higher CO_2 production rate and to a lower average coverage fraction of CO and O.

These changes are common for all values of the diffusion parameter p_D. In Table I we have listed the values of the transition points y_1 and y_2 for different values of p_D. From this table it is clearly seen that the value of y_1 decreases dramatically as p_D is increased. In fact, it seems that fast diffusion causes the O-poisoned state to disappear. The change in y_2 is also systematic, although less dramatic, and we see that y_2 increases with increasing p_D. This is in full agreement with the results reported elsewhere.[18,19]

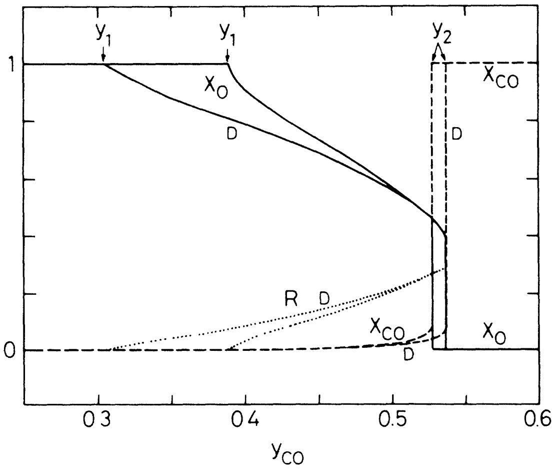

FIG. 2. Comparison of the results from simulations of the extended ZGB model with $p_D=0.2$ and the original model without diffusion. The curves show the concentration of adsorbed O atoms (solid lines) and CO molecules (dashed lines) and the CO_2 production rate (dotted lines). Curves labeled D represent the extended model.

TABLE I. Position of the second- and first-order transitions in the ZGB model with diffusion for different values of the diffusion parameter p_D.

p_D	y_1	y_2
0	0.390 ± 0.001	0.526 ± 0.001
0.1	0.350 ± 0.001	0.533 ± 0.001
0.2	0.305 ± 0.001	0.537 ± 0.001
0.3	0.244 ± 0.001	0.542 ± 0.001
0.4	0.180 ± 0.001	0.548 ± 0.001
0.5	0.112 ± 0.002	0.553 ± 0.002
0.7	≈0.02	0.566 ± 0.005
0.95	≈0	$0.59\ \pm0.01$

In order to study the effect of diffusion in more detail, we made some simulations in which only one of the two adsorbed species were allowed to diffuse at a time. In the absence of O diffusion, we detect no change in the value of y_1, and we conclude that oxygen diffusion is the sole cause to the change in the position of the second-order phase transition. This comes as no surprise since the concentration of adsorbed CO is very low when y_{CO} is only slightly greater than y_1, and therefore CO diffusion should have no effect on the transition between the O-poisoned state and the active state. We furthermore find that the change of y_2 is smaller when only one of the species is allowed to diffuse at a time. As an example, we mention that with $p_D=0.2$ the value of y_2 is 0.533 ± 0.001 when only CO diffuses and 0.534 ± 0.001 for O diffusion only as compared to the value 0.537 ± 0.001 when both O and CO diffuse with the same probability.

Diffusion of O is, as argued above, the sole cause for the change of the position of the second-order phase transition. The explanation of this change is rather straightforward. First of all, it must be stressed that adsorption of an O_2 molecule requires a nearest-neighbor pair of empty sites. Without diffusion of O, a nearest-neighbor pair of empty sites can change only through adsorption. O_2 adsorption leads, of course, to the destruction of such pairs and brings the system closer to O poisoning. When the system is close to the O-poisoned state, CO adsorption will most probably be followed by an immediate reaction with a neighboring O atom, and the main effect of CO adsorption will thus be to widen "holes" in the layer of adsorbed oxygen. When diffusion of O is allowed, a new effect comes into play, namely, the destruction of pairs of nearest-neighbor empty sites due to O diffusion. Diffusion of O can, of course, also lead to the creation of pairs of nearest-neighbor empty sites. For example, such a pair can be created in a single trial if two empty sites are next- or third-nearest neighbors (see Fig. 3). Simple considerations show, however, that the net effect of diffusion will be to reduce the average number of nearest-neighbor empty pairs. This makes the successful

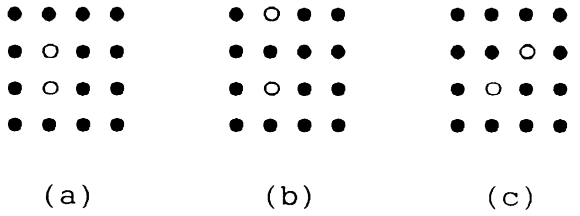

FIG. 3. (a) Typical configuration near y_1 and (b) and (c) the two additional types of configurations which can be the result of a single diffusion trial. Filled symbols denote O atoms and open symbols empty sites.

adsorption of an O_2 molecule less probable and thus O poisoning more difficult. In Fig. 3 we have shown a typical configuration (a) near the O-poisoned state, namely, a pair of empty sites surrounded by oxygen, and the two additional configurations (b) and (c) which can arise due to a single diffusion trial. Note that the probability of creating (or maintaining) a pair of empty sites from any of the configurations (a)–(c) via diffusion never exceeds $\frac{1}{2}$. This means that diffusion will tend to reduce the average number of pairs of nearest-neighbor empty sites. A more quantitative illustration of this effect can be seen in Fig. 4 where we have plotted the concentration of nearest-neighbor empty pairs versus the concentration of empty sites. From this figure we see that for a given concentration of empty sites, the concentration of nearest-neighbor empty pairs decreases when p_D is increased. But it is exactly the concentration of empty pairs which determines the rate of O_2 adsorption. We believe that these considerations are sufficient to explain the change in the value of y_1 due to diffusion of oxygen.

In order to explain the change in the position of the first-order transition, we have to look a little closer at the mechanism of CO poisoning. As argued by Ziff, Gulari, and Barshad,[1] CO poisoning takes place through the formation of large CO clusters, which once formed grow until the whole lattice is covered with CO. As can be seen from Fig. 2, diffusion causes the CO_2 production rate to increase and the concentration of adsorbed CO to decrease. The decrease in CO coverage can be seen more clearly in Fig. 5 where we have plotted the concentration of adsorbed CO as a function of y_{CO} in the vicinity of y_2 for three different values of p_D. We see that the concentration of adsorbed CO decreases significantly when p_D is increased. It is clear that a lower concentration of adsorbed CO makes it harder to form the large CO clusters, needed in order to poison with CO, and thus leads to an increase in the value of y_2.

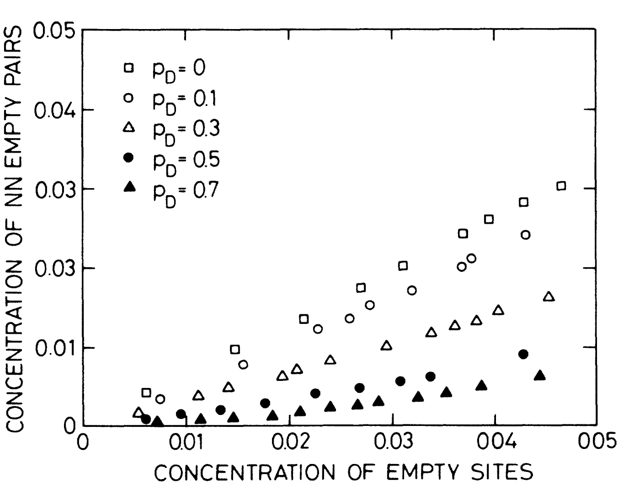

FIG. 4. Concentration of nearest-neighbor (NN) empty pairs as a function of the concentration of empty sites for five values of the diffusion parameter p_D.

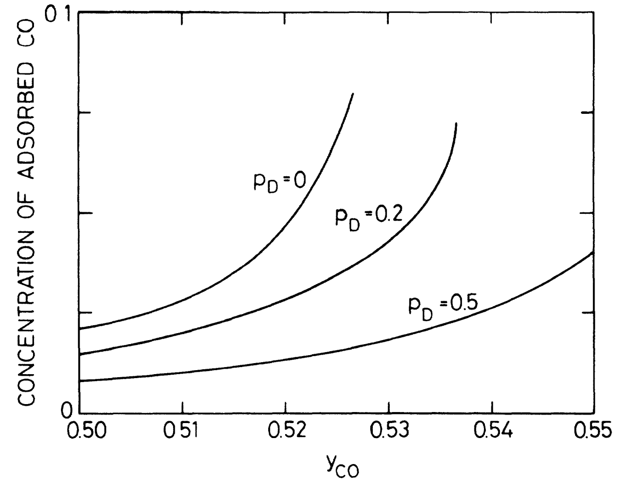

FIG. 5. Concentration of adsorbed CO as a function of y_{CO} in the vicinity of y_2 for three different values of p_D.

IV. MEAN-FIELD THEORY

A mean-field theory for the ZGB model has been constructed by Dickman[20] in the site and pair approximations. We have extended Dickman's analysis of the pair approximation in order to include diffusion. The basic idea of the pair approximation is to derive the equations of motion for the concentrations of allowed nearest-neighbor pairs or bonds. There are five different types of pairs in the ZGB model: *B*-*B*, *B*-O, *B*-CO, O-O, and CO-CO pairs, where *B* denotes a blank or empty site. Since the five concentrations add up to one, the time development of the system can be described by a set of four coupled differential equations for the concentrations x_{ij} ($i,j=B$, O, or CO) of nearest-neighbor pairs.

In order to analyze the kinetics of the ZGB model, one distinguishes between the following five processes:[20]

(a) $O_2\downarrow$,

(b) $O_2\downarrow, CO_2\uparrow$,

(c) $O_2\downarrow, 2CO_2\uparrow$,

(d) $CO\downarrow$,

(e) $CO\downarrow, CO_2\uparrow$.

In the first process an O_2 molecule adsorbs on a nearest-neighbor pair of empty sites. There are no CO molecules on the six nearest neighbors, and so no reactions take place and the two O atoms remain on the surface. In the second process an O_2 molecule is adsorbed, but now one of the O atoms has at least one CO as nearest neighbor. O and CO react, and the CO_2 molecule thus formed desorbs. The other processes proceed along similar lines.

To derive the equations of motion, one calculates the rates and changes in bond numbers for each process. This derivation is rather cumbersome as one has to distinguish both between different subprocesses leading to different changes in bond numbers and between the different configurations which might lead to a given process. The details and results of the calculations can be found in Ref. 20.

The equations of motion describing the development of the system are given by

$$\frac{dx_{ij}}{dt}=\sum_{k} R^{k}\Delta N_{ij}^{k} , \tag{4}$$

where R^k is the rate of process k and ΔN_{ij}^k is the corresponding change in the number of bonds of type i-j ($i,j=B$, O, or CO). Numerical integration of the equations of motion shows that the pair approximation predicts the qualitative features of the ZGB model correctly. The pair approximation predicts a continuous transition from an O-poisoned state to an active state at a value $y_1^P=0.2497$, which is substantially smaller than the value found in the simulations (0.390 ± 0.001). In addition, the pair approximation does not predict the critical behavior of the ZGB model correctly.[16] So the quantitative predictions are poor in this region of the phase diagram. The pair approximation also predicts a first-order transition from the active state to a CO-poisoned state. The predictions for the position of this transition depend on the initial conditions. From an initially empty lattice, $x_{B\text{-}B}=1$, and all other bond concentrations initially zero, one finds that the lattice poisons with CO when $y_{\mathrm{CO}}>y_s=0.5610$. If the initial state is a lattice half covered with a solid CO phase and half empty, represented by $x_{B\text{-}B}=x_{\mathrm{CO\text{-}CO}}=\frac{1}{2}$ (and all other bond concentrations initially zero), the lattice poisons with CO when $y_{\mathrm{CO}}>y_2^P=0.5241$, in good agreement with the simulations (0.526 ± 0.001). A comparison of the predictions from the pair approximation and simulation results is presented in Fig. 6. It is clearly seen that the pair approximation yields quite accurate predictions in the vicinity of the first-order transition.

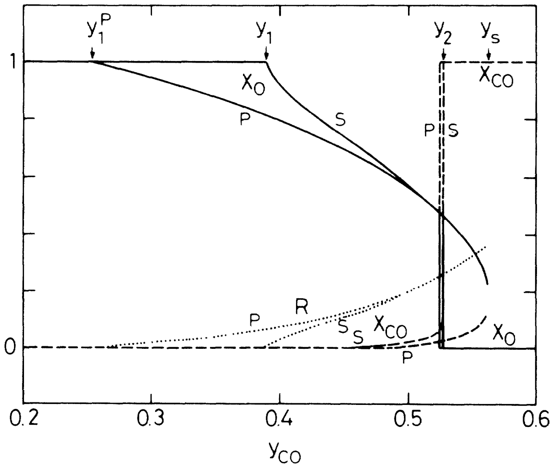

FIG. 6. Comparison of the predictions from the pair-approximation and simulation results. The curves show the concentration of adsorbed O atoms (solid lines) and CO molecules (dashed lines) and the CO_2 production rate (dotted lines) as a function of y_{CO}. Curves labeled P represent pair-approximation predictions; S denotes simulation results. The curves to the right of y_2 depict the reactive steady predicted by the pair approximation from an initially empty lattice.

V. PAIR APPROXIMATION WITH DIFFUSION

In order to include diffusion in the pair approximation, we must include the following four new processes:

(f) O→ ,

(g) O→,CO_2↑ ,

(h) CO→ ,

(i) CO→,CO_2↑ .

In process (f) an O atom moves to an empty site which has no CO nearest neighbors, and no reaction takes place. In process (g) the diffusing O atom meets a CO molecule, reacts with it, and CO_2 desorbs. Processes (h) and (i) are similar. In order to find the contributions to the equations of motions from processes (g) and (i), we have to distinguish between the two subprocesses shown in Fig. 7.

We are now in position to calculate the rates and changes in the number of bonds. This calculation is similar to the one made for the original ZGB model, and we will therefore not go through any details here. We just want to point out that the rate of O diffusion is calculated in the pair approximation in the following manner: The probability of diffusion is p_D, the probability of choosing an O atom is x_{O}, and the nearest neighbor chosen subsequently is empty with probability $P(i=B|j=\mathrm{O})=P(i=B,\, j=\mathrm{O})/P(j=\mathrm{O})=x_{B\text{-}\mathrm{O}}/2x_{\mathrm{O}}$. Multiplication of these probabilities gives as a result that the rate of O diffusion is $\frac{1}{2}p_D x_{B\text{-}\mathrm{O}}$. The rate of CO diffusion can be derived in a similar fashion. In order to derive the rate of a given process, we multiply the rate of diffusion with the probability of having a configuration leading to the pro-

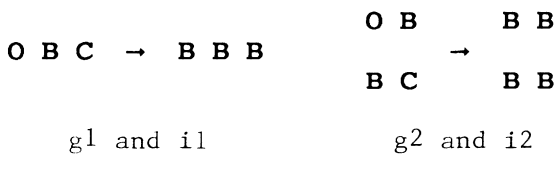

FIG. 7. Examples of processes (g1), (g2), (i1), and (i2), which are distinguished in the pair approximation.

cess under consideration. The results of the calculations of the rates and bond-number changes in the pair approximation due to diffusion are shown in Table II. Note that the calculation made by Dickman for the processes (a)–(e) can be taken over directly if we just multiply all the rates by a factor $1-p_D$. Alternatively, we can choose not to change the rates of these processes and instead divide Eq. (4) by $1-p_D$, make a rescaling of time $t \to t'=(1-p_D)t$, and change $p_D \to D = p_D/(1-p_D)$ in the rates of the processes (f)–(i).

A comparison of the results from simulations of the extended ZGB model with $p_D=0.2$ and the corresponding pair-approximation predictions is shown in Fig. 8. We still find a fair agreement near the first-order transition. Simulations give $y_2=0.537\pm0.001$, and the pair approximation predicts that $y_2^P=0.5283$ and $y_s=0.5722$. As before, y_2^P is obtained with the initial condition $x_{B\text{-}B}=x_{\text{CO-CO}}=\frac{1}{2}$ and y_s with the initial condition $x_{B\text{-}B}=1$. The pair approximation predicts a second-order transition at $y_1^P=0.0759$ as compared to the value from simulations $y_1=0.305\pm0.001$. So the quantitative prediction for the second-order transition is still poor. Note, however, that the qualitative predictions are rather good. The pair approximation correctly predicts that diffusion leads to a substantial decrease for y_1^P and a much smaller increase for y_2^P (and y_s).

In Table III we have listed the pair-approximation predictions for y_1^P and the results from simulations for different values of the diffusion parameter p_D. As anticipated, the quantitative predictions are poor; on the other hand, we obtain fair qualitative agreement.

Table IV shows the pair-approximation predictions for y_2^P and y_s for different values of p_D compared with the simulation results. We notice that the pair approximation yields the correct qualitative predictions about the change in y_2, but quantitatively the predictions get poorer as p_D increases. y_s is of course always larger than y_2, but we nevertheless find it noteworthy that the numerical change in y_s is almost equal to the change in y_2 we find

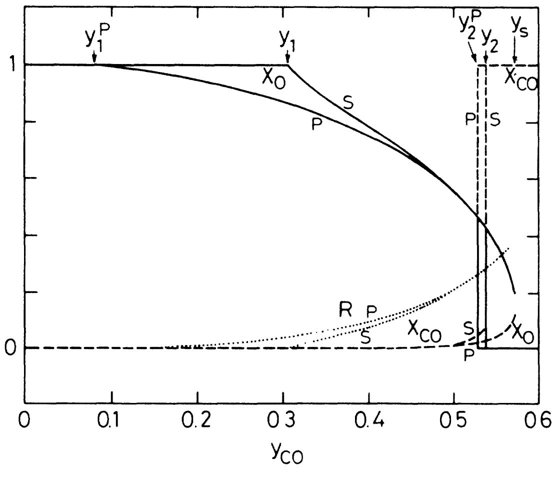

FIG. 8. Comparison of the predictions from the pair-approximation and simulation results with $p_D=0.2$. See the caption to Fig. 6 for further details.

TABLE II. Rates and bond number changes in the pair approximation due to diffusion.

Process	Rate	$\Delta N_{B\text{-}B}$	$\Delta N_{B\text{-O}}$	$\Delta N_{B\text{-CO}}$	$\Delta N_{\text{O-O}}$
(f)	$\frac{1}{2}p_D x_{B\text{-O}}(1-u)^3$	$\frac{3x_{B\text{-O}}}{2x_{\text{O}}}-6\alpha x_{B\text{-}B}$	$3\frac{2x_{\text{O-O}}-x_{B\text{-O}}}{2x_{\text{O}}}+3\alpha(2x_{B\text{-}B}-x_{B\text{-O}})$	0	$3\alpha x_{B\text{-O}}-3\frac{x_{\text{O-O}}}{x_{\text{O}}}$
(g1)	$\frac{1}{2}p_D x_{B\text{-O}}u(1-u+\frac{1}{3}u^2)$	$2+\frac{3x_{B\text{-CO}}}{2x_{\text{CO}}}+\frac{3x_{B\text{-O}}}{2x_{\text{O}}}$	$2\frac{x_{\text{O-O}}-x_{B\text{-O}}}{x_{\text{O}}}$	$2\frac{x_{\text{CO-CO}}-x_{B\text{-CO}}}{x_{\text{CO}}}$	$-3\frac{x_{\text{O-O}}}{x_{\text{O}}}$
(g2)	$2R^{g1}$	$4+\frac{x_{B\text{-CO}}}{x_{\text{CO}}}+\frac{x_{B\text{-O}}}{x_{\text{O}}}$	$-2\frac{x_{B\text{-O}}}{x_{\text{O}}}$	$-2\frac{x_{B\text{-CO}}}{x_{\text{CO}}}$	$-2\frac{x_{\text{O-O}}}{x_{\text{O}}}$
(h)	$\frac{1}{2}p_D x_{B\text{-CO}}(1-v)^3$	$\frac{3x_{B\text{-CO}}}{2x_{\text{CO}}}-6\beta x_{B\text{-}B}$	0	$3\frac{2x_{\text{CO-CO}}-x_{B\text{-CO}}}{2x_{\text{CO}}}+3\beta(2x_{B\text{-}B}-x_{B\text{-CO}})$	0
(i1)	$\frac{1}{2}p_D x_{B\text{-CO}}v(1-v+\frac{1}{3}v^2)$	$2+\frac{3x_{B\text{-CO}}}{2x_{\text{CO}}}+\frac{3x_{B\text{-O}}}{2x_{\text{O}}}$	$2\frac{x_{\text{O-O}}-x_{B\text{-O}}}{x_{\text{O}}}$	$2\frac{x_{\text{CO-CO}}-x_{B\text{-CO}}}{x_{\text{CO}}}$	$-3\frac{x_{\text{O-O}}}{x_{\text{O}}}$
(i2)	$2R^{i1}$	$4+\frac{x_{B\text{-CO}}}{x_{\text{CO}}}+\frac{x_{B\text{-O}}}{x_{\text{O}}}$	$-2\frac{x_{B\text{-O}}}{x_{\text{O}}}$	$-2\frac{x_{B\text{-CO}}}{x_{\text{CO}}}$	$-2\frac{x_{\text{O-O}}}{x_{\text{O}}}$

where $u=x_{B\text{-CO}}/x_B$; $v=x_{B\text{-O}}/x_B$; $\alpha=(2x_{B\text{-}B}+x_{B\text{-O}})^{-1}$; $\beta=(2x_{B\text{-}B}+x_{B\text{-CO}})^{-1}$

TABLE III. Position of the second-order transition for different values of p_D. y_1 are the results from simulations and y_1^P the predictions from the pair approximation.

p_D	y_1	y_1^P
0	0.390	0.2496
0.1	0.350	0.1716
0.2	0.305	0.0759
0.3	0.244	0.0028
0.4	0.180	<0.001
0.5	0.112	<0.001
0.7	≈ 0.02	<0.001

TABLE IV. Position of the first-order transition for different values of p_D. y_2, results from simulations; y_2^P, predictions from the pair approximation with the initial condition $x_{B\text{-}B}=x_{\text{CO-CO}}=\frac{1}{2}$; y_s, predictions from the pair approximation with the initial condition $x_{B\text{-}B}=1$.

p_D	y_2	y_2^P	y_s
0	0.526	0.5241	0.5610
0.1	0.533	0.5263	0.5666
0.2	0.537	0.5283	0.5722
0.3	0.542	0.5300	0.5773
0.4	0.548	0.5311	0.5831
0.5	0.553	0.5317	0.5897
0.7	0.566	0.5302	0.6044

from simulations. Finally, we want to point out that by choosing other initial conditions, we obtain better predictions for the position of the first-order transition, whereas the position of the second-order transition seems to be independent of initial conditions. It does not seem possible to find an initial condition which leads to good predictions for all values of p_D.

VI. CONCLUSIONS

We have extended the ZGB model in order to include diffusion of the adsorbed particles. The extended model has been studied by means of computer simulations and mean-field theory.

Diffusion causes a shift of y_1 to lower values and of y_2 to higher values as p_D is increased. The nature of the phase transitions is not altered by diffusion; O poisoning is still a second-order transition and CO poisoning a first-order transition. Fast diffusion seems to make the O-poisoned phase disappear from the system. We found that diffusion of O is the sole cause to the change of y_1. The reason for the change is that O diffusion leads to a lower average concentration of pairs of nearest-neighbor empty sites, which makes the successful adsorption of O_2 less probable and thus O poisoning more difficult. Diffusion (of both O and CO) leads to a higher CO_2 production rates and to a lower average CO coverage fraction. This makes the formation of large CO clusters harder and thus CO poisoning more difficult, causing an increase in the value of y_2.

The extended ZGB model has also been studied in the pair approximation. This approach gives qualitatively correct predictions about the nature of the phase transitions and the changes in y_1 and y_2 due to diffusion. The quantitative predictions are poor near the second-order transition. By "fine tuning" the initial conditions, we were able to obtain predictions in good agreement with simulation results in the vicinity of the first-order transition.

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