Kinetic oscillations in the catalytic CO oxidation on Pt single crystal surfaces: Theory and simulation

V. N. Kuzovkov
Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., LV-1063 Riga, Latvia and Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Straße 10, 38106 Braunschweig, Germany

O. Kortlüke[a)] and W. von Niessen
Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Straße 10, 38106 Braunschweig, Germany

A simple lattice gas model is studied for the description of the kinetic oscillations in the CO oxidation on the Pt(100) and Pt(110) surfaces. It takes CO diffusion and surface reconstruction into account and exhibits very interesting phenomena such as synchronized oscillations and mesoscopic pattern formation. The model uses only few parameters, the CO gas phase concentration y, the CO diffusion constant D, the surface phase propagation velocity V, and the ratio of the O_2 sticking coefficients on the two surface phases. This enables the study of the whole parameter regime and the theoretical stability analysis for the kinetic oscillations. It can be shown that it is only the ratio of the O_2 sticking coefficients on the reconstructed and non–reconstructed surfaces which determines the type of oscillations and the parameter range where these oscillations exist. © *1998 American Institute of Physics.* [S0021-9606(98)00413-9]

I. INTRODUCTION

The occurrence of kinetic oscillations during the catalytic oxidation of CO is well known and has been investigated extensively in the recent past,[1–3] mainly on the Pt(100) and Pt(110) single crystal surfaces.[4] A very comprehensive overview is given in the review article by Imbihl and Ertl.[5] Experimental results show that the kinetic oscillations are closely connected with the propagation of chemical waves, i.e. with the propagation of the borders between CO and O covered regions on the catalyst surface.[5,6] Also much theoretical work has been done on these oscillation phenomena, in most cases using mathematical modeling of coupled differential equations (DE) on the basis of the macroscopic mean field (MF) approximation.[7–11] Models based on simulations are in principal able to study systems on an atomic scale. Such models have been formulated including surface phase transition and phase nucleation.[12–14] For the initiation of the surface phase transitions a critical local CO coverage, determined by experimental results, on a mesoscopic length scale is used. A different approach uses a mechanism with a non–reactive coadsorbat which leads to oscillations because slow adsorption and desorption of this coadsorbat drives the system around a hysteresis loop.[15]

In a recent paper[16] we introduced a three parameter model which describes the kinetic oscillations in the CO $+\frac{1}{2}O_2$ reaction on a Pt(100) surface correctly in agreement with experimental results. This model is based completely on microscopic processes and does not use any experimental results. Formally the models we will present here for the CO oxidation on the Pt(100) and Pt(110) surfaces are identical.

The only difference lies in the ratio of the sticking coefficients for O_2 on the different surface phases. Let us call the reconstructed surface phase α [hex on Pt(100) and 1×2 on Pt(110)] and the non–reconstructed surface phase β (1×1 on both surfaces) with the O_2 sticking coefficients s_α and s_β, respectively. Experimental results give a ratio of $s_\alpha/s_\beta < 10^{-2}$ for Pt(100) and $s_\alpha/s_\beta \sim 1$ for Pt(110). We will show that it is only this small difference which leads to a decisive consequence for the system behavior: With s_α/s_β small we get a relatively broad interval where irregular oscillations occur, whereas with $s_\alpha/s_\beta \sim 1$ only a very narrow interval exists which exhibits regular oscillation phenomena. Furthermore the model leads to critical points for the ratio of the sticking coefficients where a transition from irregular to regular oscillations takes place.

The paper is organized as follows: In Sec. II we describe the model in detail. Section III contains the results of theoretical reflections upon the critical behavior of the model for both Pt(100) and Pt(110) surfaces. These are corroborated with simulation results. At the end of Sec. III simulation results are presented which show the conditions for regular and irregular oscillations, respectively. Conclusions are derived in Sec. IV.

II. THE MODEL

We examine the $A + \frac{1}{2}B_2 \rightarrow 0$ reaction with the $\alpha \rightleftharpoons \beta$ structural transformation on a square lattice with coordination number $z = 4$ and the lattice constant a. The occupation of the lattice is denoted by X with $X \in \{0, A, B\}$ which stands for an empty site, a site occupied by A or by B, respectively. For the surface coverages C_X the normalization condition

a)Electronic mail: O.Kortlueke@tu-bs.de

$$C_A + C_B + C_0 = 1, \tag{1}$$

holds. In addition the site itself belongs to the phase χ with $\chi \in \{\alpha, \beta\}$. For the surface phases we similarly get

$$\Theta_\alpha + \Theta_\beta = 1. \tag{2}$$

A. Adsorption and desorption

The present model uses the principal rules of the model by Ziff, Gulari, and Barshad[17] (ZGB model), i.e. A or B_2 particles are chosen randomly from the gas phase with probability $p_A = y$ or $p_B = 1 - y$, respectively, with $y \in [0,1]$. This normalization of the adsorption rate additionally introduces a time scale. An A particle needs an empty site to adsorb onto the surface, independent of the phase the site belongs to. A B_2 particle needs two vacant nearest neighbor sites (dissociative adsorption). From experiment it is known that the B_2 adsorption strongly depends on the surface structure.[5] Therefore we introduce a sticking coefficient s_χ for the B_2 adsorption into two vacant nearest neighbor sites belonging to the phase χ, i.e. on the α or the β phase the sticking coefficient is s_α or s_β, respectively. If B_2 adsorbs onto the phase border with one site belonging to the α phase and the other site belonging to the β phase we use $s_{\alpha\beta} = \sqrt{s_\alpha s_\beta}$ as the effective sticking coefficient. Desorption is only considered for the surface species A with the corresponding desorption rate k_A.
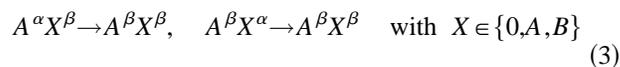
B. Diffusion and reaction

The most important difference between the model presented here and previous work by other groups[12,13,15] is the consideration of surface diffusion as an essential process in the catalytic CO oxidation. We take the high mobility of A particles into account by allowing them to diffuse via hopping from their sites to vacant nearest neighbor sites (independent of the phase of the sites involved). The diffusion rate is determined by the diffusion constant D, which is defined as a coefficient in the transition rate for bimolecular reaction steps.[18] It can be shown that the diffusion coefficient for A diffusion on an empty lattice is given by the equation $\hat{D}_A = (1/z)a^2 D$. Therefore the parameter D corresponds to the frequency factor for the diffusion (all transition rates in the stochastic theory are of dimension $[t]^{-1}$). The adsorbed B particles are considered to be immobile. Reaction occurs if an adsorbed A particle jumps onto a site which is occupied by B. Because of the large diffusion constant only small quantitative deviations to a model with an infinite reaction rate occur.[19] The reaction product AB desorbs instantly from the surface.

C. Structural phase transition

In the description of the structural phase transition $\alpha \rightleftharpoons \beta$ stimulated by the presence or absence of A particles one has to distinguish between two processes: (i) Spontaneous formation of a nucleus of the α phase in a matrix of the β phase or *vice versa* and (ii) propagation of the border between these two phases including the growth and decline of such nuclei. Experimental results[5] show that both the reconstructed and the non–reconstructed surfaces are homogeneous on a meso-

scopic length scale. Therefore one can suppose that the two processes (i) and (ii) show a significant difference in the kinetic parameters which can be explained via different activation energies. Here we make the assumption that process (ii) is much faster than process (i) and define the phase border propagation as follows:

$$A^\alpha X^\beta \rightarrow A^\beta X^\beta, \quad A^\beta X^\alpha \rightarrow A^\beta X^\beta \quad \text{with} \ X \in \{0,A,B\} \tag{3}$$

and

$$X^\alpha Y^\beta \rightarrow X^\alpha Y^\alpha \quad \text{with} \ X,Y \in \{0,B\}. \tag{4}$$

Equation (3) describes the propagation of the transition $\alpha \rightarrow \beta$ if a particle A exists on at least one of the lattice sites near the phase border. Equation (4) corresponds to the reverse process $\beta \rightarrow \alpha$ under the condition that no A is present. For simplification we assume that the transition rate is equal for both processes. The linear border between the α and the β phase moves in one distinct direction depending on the presence or absence of A, respectively, with velocity $\hat{V}_{\alpha\beta} = aV/z$, with V the phase propagation constant, which is defined analogous to the definition of D (see above). These transitions described by Eqs. (3) and (4) include all structural transformations (growth and decline of islands of one phase in a matrix of the other, fusion and division of such domains etc.) with only one exception: Breaking up the structure spontaneously is not considered, i.e. there is no nucleation inside a homogeneous structure.

This purely mathematical definition of the phase propagation leads to an important physical consequence: There exists a critical fractional coverage of A with $C_{A,\text{crit}} \approx 0.3$ for the dynamic stability of the heterogeneous state, which is in good agreement with experimental results.[5] Simulations and different analytical approximations which lead to this critical coverage will be presented in a separate paper.

The nucleation processes could in principal be neglected and do not contribute to the physical properties of the system but are necessary to overcome certain problems which arise from the finiteness of the simulation system. We use the spontaneous phase transformations

$$A^\alpha \rightarrow A^\beta \quad \text{and} \quad X^\beta \rightarrow X^\alpha \quad \text{with} \ X \in \{0,B\}. \tag{5}$$
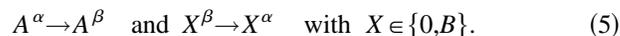
The spontaneous nucleation process is considered with a rate of $\gamma \in [10^{-4}, 10^{-5}]$ only in those simulation runs which are performed to investigate the critical properties. In those simulations where we neglect the spontaneous nucleation process (5) we used an empty lattice ($C_A = C_B = 0$) and randomly distributed surface phases with $\Theta_\alpha = \Theta_\beta = 0.5$ as the initial condition. If one considers process (5) even $\Theta_\beta = 0$ at $t = 0$ can be used.

As shown above we present a very simple model for the oscillating CO oxidation over the Pt(100) and Pt(110) single crystal surfaces which does not use any experimental results. Many simplifications have been made in comparison with the real reaction systems, such as neglecting the mass transport and the change of the coordination number in the surface reconstruction process. This can be done because the change of the coordination number only leads to a small quantitative change as it has been shown[20] for the original ZGB model. The consideration of the mass transport would

not lead to new reaction paths or large qualitative changes either. The basic physical property to consider is the growth and decline of the surface phases and the difference in the O_2 adsorption physics on these. Also all macroscopic rates for the different surface processes are neglected in order to get a simple and self–sufficient microscopic model which renders it possible to understand the basic mechanisms of the oscillating system. The model is simulated by means of Monte Carlo and cellular automata[19] techniques on square lattices with side lengths varying from $L=128$ up to $L=1024$.

III. RESULTS AND DISCUSSION

A. The case of homogeneous phases

Let us consider first the case of homogeneous surface phases, i.e. the homogeneous α phase with $\Theta_\alpha = 1$ or the homogeneous β phase with $\Theta_\beta = 1$, respectively. In this case the parameter V is removed and the model corresponds to the ZGB model except for the finite reaction rate which arises from the combination of diffusion and reaction. Let p_A and p_B be the adsorption rates for A and B, respectively, with $p_A = y$ and $p_B = s_\chi(1-y)$, where y is the mole fraction of A in the gas phase. For B_2 adsorption we assume different sticking coefficients $s_\chi, \chi \in \{\alpha, \beta\}$, on the α and β phase with $s_\beta = 1$ and $s_\alpha < 1$.

1. The β phase

For the homogeneous β phase the system corresponds to the ZGB model with the adsorption rates $p_A = y$ and $p_B = (1-y)$ and the normalization

$$p_A + p_B = 1. \tag{6}$$

The characteristic properties of this model are well known. For the case without desorption ($k_A = 0$) the system exhibits two critical points y_1 and y_2, where kinetic phase transitions occur. Because the model considered here is defined in a slightly different way we only reflect upon the case of large values of $D \gg 1$ for which the two models are practically equivalent.[19] Therefore we obtain the critical points $y_1 \approx 0.40$ and $y_2 \approx 0.65$ (fast diffusion). The second critical point y_2 is strongly dependent on the diffusion rate,[21] but for the values of D considered here ($D > 100$) one can suppose that both y_1 and y_2 have reached the asymptotic values. We have to emphasize that this model exhibits hysteresis properties, i.e. if the surface is initially not empty but partly covered with A, $C_A(0) = C_A^0 > 0$, the system shows a different reactive interval $y \in (y_1, \bar{y}_2)$[17,21] with $\bar{y}_2 < y_2$ ($\bar{y}_2 = \bar{y}_2(C_A^0)$). Therefore the upper region of the reactive interval (y_1, y_2) is metastable because large fluctuations in C_A are able to remove the reactive steady state and lead into an absorbing state.

2. The α phase

For the homogeneous α phase the normalization of the adsorption rates [Eq. (6)] does not hold but can be preserved by introduction of a new parameter which rescales the former variables:

$$t' = qt, \quad p_A' = p_A/q, \quad p_B' = p_B/q, \quad \text{and } D' = D/q, \tag{7}$$

with $q = p_A + p_B = y + s_\alpha(1-y)$. Using these new variables we obtain that the two reaction systems on the α and β phase are formally identical and have the same critical properties. The system on the α phase corresponds to a system on the β phase with a different mole fraction

$$y' = p_A' = \frac{y}{y + s_\alpha(1-y)}, \tag{8}$$

and with the diffusion parameter

$$D' = \frac{D}{y + s_\alpha(1-y)}, \tag{9}$$

which now depends on y. Because $D' \geq D$ holds for every y and we assume y_1, y_2 to be independent of D for large D the reaction system on the α phase leads to the same critical points as the system on the β phase. The reactive interval lies in the range $y_1 < y' < y_2$ or

$$\hat{y}_1 = \frac{s_\alpha y_1}{1 - y_1(1 - s_\alpha)} < y < \hat{y}_2 = \frac{s_\alpha y_2}{1 - y_2(1 - s_\alpha)}. \tag{10}$$

Note that on the y scale the critical values for the α phase are always smaller than the corresponding values for the β phase: $\hat{y}_1 < y_1$ and $\hat{y}_2 < y_2$.

3. The common reactive interval

Two or more macroscopic surface regions of the α and the β phase in common can lead to a reactive interval if

$$\hat{y}_2 > y_1, \tag{11}$$

holds. This condition leads to an upper critical value of the sticking coefficient

$$S_c' = \frac{y_1(1 - y_2)}{y_2(1 - y_1)}. \tag{12}$$

For $s_\alpha > S_c'$ the condition (11) holds. This case with a relatively large ratio of the sticking coefficients s_α / s_β can be defined as the case of the Pt(110) surface. For $s_\alpha < S_c'$ the condition cannot be fulfilled. This case (s_α / s_β small) can be assigned to the system on the Pt(100) surface. With $y_1 = 0.40$ and $y_2 = 0.65$ we get $S_c' \approx 0.36$.

B. The coexistence of two phases

1. The Pt(100) surface

For the case of the Pt(100) surface the order $\hat{y}_1 < \hat{y}_2 < y_1 < y_2$ holds. In the following we consider an almost homogeneous α surface phase, $\Theta_\alpha \approx 1$, with only very small islands of the β phase. These islands render the $\alpha \rightarrow \beta$ phase transition possible. The kinetic aspects of this transition (parameter V) are neglected in the following discussion in order to focus only on the main qualitative properties of the system as a function of the gas phase mole fraction of A.

(1) $y \leq \hat{y}_1$. The small β islands disappear because of the large adsorption rate of B_2 and therefore large surface coverage by B which results in a $\beta \rightarrow \alpha$ transition.

Therefore the surface is in a stable α phase and totally covered with B and neither reaction nor oscillations occur.

(2) $\hat{y}_1 < y \leqslant \hat{y}_2$. This range corresponds to the reactive interval on the pure α phase, but the surface concentration of A is too small to initiate the growth of the β islands. The local fluctuations of the A density can also be neglected because these values of y belong to the regime of B poisoning on the β phase. Therefore the β islands disappear leading to a homogeneous α phase.

(3) $\hat{y}_2 < y \leqslant y_1$. This is the domain of A poisoning on the α phase ($\hat{y}_2 < y$). Therefore the surface concentration of A increases and leads to the growth of the β islands. On the β phase the interval considered here belongs to the domain of B poisoning ($y \leqslant y_1$). Thus the B concentration increases and the A concentration decreases on the β islands which disturbs the growth and furthermore leads to the decline of the latter. When the β islands become small enough the A concentration starts to increase again. Therefore oscillations are possible in this parameter range, at least in principle. Whether oscillations occur at a certain value of y depends additionally on the kinetical parameters D and V. E.g. it is possible to reach a homogeneous β surface phase because the A surface concentration increases very fast thus removing the α phase. If we neglect spontaneous surface phase transitions the system slowly goes into the absorbing state poisoned with B. In our simulations for $s_\alpha = 0$ without phase nucleation ($\gamma = 0$) we observe oscillations in the range $0 < y < y_{max} < y_1$ with y_{max} as the upper boundary of y for oscillation phenomena. The value of y_{max} strongly depends on D and V (e.g. $y_{max} \approx 0.35$ for $D = 10^2$ and $y_{max} \approx 0.20$ for $D = 10^3$ with $V = 1$).[16]

(4) $y_1 < y \leqslant y_2$. There is a certain similarity to the previous case. The poisoning with B does not exist on the β phase but theoretically the coverage of B is large enough to disturb the growth of the β islands. Practically in the simulation with $\gamma = 0$ we always get a homogeneous β phase in a very short time and a reactive interval without oscillations which corresponds to the ZGB model.[17] If we consider spontaneous phase nucleation oscillations are possible in the range $0 < y < y_{max} < y_2$ even with $y_{max} > y_1$.

(5) $y > y_2$. Here no oscillations are possible because the system runs into an absorbing state with $\Theta_\beta = 1$ and $C_A = 1$.

Note that we use $s_\alpha = 0$ and $\gamma = 0$ in most of our simulations for the Pt(100) surface.[16] In this case the first two parameter regimes do not exist ($\hat{y}_1 = \hat{y}_2 = 0$) and the interval where oscillations can exist has its largest width $y \in (0, y_1)$. As stated above the largest value of $y = y_{max}$ where the system exhibits oscillations depends on the other parameter and is always smaller than y_1, $y_{max} < y_1$. For finite values $s_\alpha > 0$ the interval of oscillation phenomena narrows as the left border increases from $y_{min} \approx \hat{y}_2 = 0$ for $s_\alpha = 0$ to $y_{min} \rightarrow y_1$ for $s_\alpha \rightarrow S_c'$ [see Eq. (10)]. Because $y_{max} < y_1$ holds the oscillations disappear even for $s_\alpha < S_c'$. The system properties remain qualitatively the same if we consider phase nucleation.
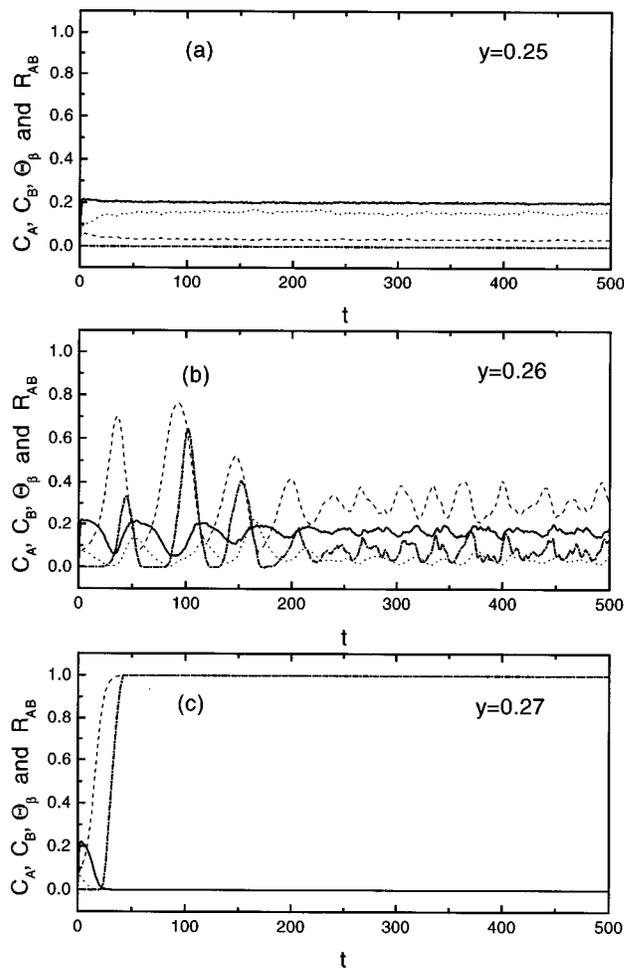

FIG. 1. The temporal evolution of the reaction rate R_{AB} (solid line), and the lattice coverages C_A (dashed line), C_B (dotted line), and Θ_β (dot-dashed line) for $y = 0.25$ (a), $y = 0.26$ (b) and $y = 0.27$ with $s_\alpha = 0.20$, $D = 100$ and $V = 10$ on a lattice with side length $L = 256$. The homogeneous α phase with a phase nucleation constant $\gamma = 10^{-5}$ is used as the initial surface state. This figure shows the different reactive domains and the existence of an upper critical ratio of the O_2 sticking coefficients for oscillations of the Pt(100) mechanism.

This is shown in Fig. 1. For $s_\alpha = 0.20$ one can see the transition from point 2 to 4 (see above) within a very small interval of $y \in (y_{min}, y_{max})$ where oscillations occur. Figure 1(a) with $y = 0.25$ correspond to the domain 2 described above where the system goes into a steady reactive state with $C_B > C_A$ and $\Theta_\alpha = 1$. For $y = 0.26$ [Fig. 1(b)] the system exhibits oscillations as described under 3. A slightly larger value of y [Fig. 1(c) with $y = 0.27 > y_{max}$] leads to an absorbing state with $C_A = 1$ and $\Theta_\beta = 1$. An estimate with Eq. (10) for $y_2 = 0.65$ and $s_\alpha = 0.2$ gives $\hat{y}_2 = 0.27$ which is in acceptable agreement with the simulation result. These results lead to the conclusion that the oscillation mechanism for the Pt(100) surface (small ratio s_α / s_β) leads to oscillations only for sticking coefficients $s_\alpha \in [0, s_{max}]$ with $s_{max} \approx S_c'$ (i.e. a ratio of $s_\alpha / s_\beta \leqslant S_c'$). Consideration of A desorption would introduce an additional parameter k_A influencing the kinetic aspects of the system and the positions of the above intervals because of different impingement rates of A for the same

value of y but has no influence on the basic physical properties of the system. The simulation of kinetic oscillation is possible even without A desorption.

2. The Pt(110) surface

For the Pt(110) surface we have the order $\hat{y}_1 < y_1 < \hat{y}_2 < y_2$. In this case new phenomena should occur because the two reactive intervals on the α and β phase overlap.

(1) $y < \hat{y}_1$. On both the α and the β phase the system reaches the absorbing state with $\Theta_\alpha = 1$ and $C_B = 1$.

(2) $\hat{y}_1 < y < \hat{y}_2$. On the α phase we get a reactive interval but the surface coverage of A is far too small to initiate the growth of the β islands. This holds even more for the β islands. Therefore we have a reactive interval with $\Theta_\alpha = 1$.

(3) $\hat{y}_2 < y < y_2$. For the α phase the value of y lies in the domain of A poisoning. The values of C_A and Θ_β increase. On the β phase the value of y lies in the reactive interval. In this parameter range the system reaches a homogeneous β phase ($\Theta_\beta = 1$). Whether reaction occurs depends on the hysteresis effects discussed above. For $y < \bar{y}_2 = \bar{y}_2(C_A^0)$ a steady state reaction exists. Otherwise the system runs into the absorbing state with $C_A = 1$.

(4) $y > y_2$. The absorbing state with $C_A = 1$ and $\Theta_\beta = 1$ is reached on both surface phases.

These theoretical investigations clearly show a bistable system with either $\Theta_\alpha = 1$ or $\Theta_\beta = 1$ without the possibility to show oscillations. For $y > \hat{y}_2$ the system properties strongly depend on the poisoning with A. If this poisoning could be suppressed the occurrence of oscillations should be possible. As in the ZGB model[17] the easiest way to prevent the surface from becoming fully covered with A is to consider A desorption with a desorption constant $k_A > 0$. The A desorption creates vacant sites on the lattice and renders further B_2 adsorption possible. Under certain conditions discussed below this leads to the growth of domains which are compactly covered with B.

The oscillations should be observable in the interval $\hat{y}_2 < y < y_2$ corresponding to A poisoning on the α phase and steady state reaction on the β phase. Because we now consider A desorption the complete A poisoning of the α phase is impossible. Nevertheless the coverage of A, C_A, increases and reaches a value C_A^0. Then the A coverage is sufficient to initiate the growth of the β islands. If $y > \hat{y}_2$ is sufficiently large to give the critical A coverage C_A^0 on the lattice then there exist three reaction domains depending on the value of k_A:

- Weak desorption. The A coverage increases very fast up to large values before the growth of the β islands can start. At this point the surface is already almost covered by A resulting in a very strong hindrance for B_2 adsorption. The α phase becomes kinetically unstable and we get $\Theta_\beta = 1$ without oscillations. This can lead to steady state reaction with $C_A \sim 1$ and $C_B \ll 1$.

- Medium desorption. In this case the β phase grows ($\alpha \to \beta$) to large values of Θ_β but is not able to remove the α islands completely (see below). However, the system forms a macroscopic β phase covering almost the whole lattice. Because $y < y_2$ holds steady state reaction should exist, but the system exhibits hysteresis properties as described above. For $y > \bar{y}_2$ the value of C_A increases too fast and the system reaches steady state reaction with $\Theta_\beta = 1$ and $C_A \sim 1$ and $C_B \ll 1$. For $y < \bar{y}_2$ the behavior is different. After the macroscopic β phase has been formed C_B increases and C_A becomes very small (normal steady state reaction conditions as in the original ZGB model[17]). Therefore the α islands start to grow ($\beta \to \alpha$). This leads to a very low A coverage and an almost homogeneous α phase with only small β islands inside. This state is very similar to the initial conditions and the whole process starts over again.

- Strong desorption. In this case the desorption rate is too large to reach the critical A coverage C_A^0. The β islands disappear and we get the homogeneous α phase with $\Theta_\beta = 0$.

The specific values of k_A for the above domains of desorption additionally depend on the other parameters (y, D, V). In our simulations we observe that $k_A = 0.05$ belongs to the domain of weak desorption, $k_A = 0.10$ leads to oscillations (medium desorption) and $k_A = 0.50$ results in $\Theta_\alpha = 1$ corresponding to strong desorption. The oscillations can be evoked and suppressed only by varying the desorption constant. The transition from weak to medium desorption at a certain critical value of $k_A = k_c$ for $y = 0.49$, $D = 100$ and $V = 1$ is shown in Fig. 2. For this set of parameters the value $k_A = 0.07$ belongs to the domain of weak desorption, whereas the value $k_A = 0.08$ shows oscillations and therefore corresponds to medium desorption. In addition one can see that the oscillation frequency strongly depends on the difference $(k_A - k_c)$.

These theoretical reflections for the Pt(110) surface model clearly show that oscillations are only possible in a certain parameter regime limited by the sticking coefficient s_α, the desorption constant k_A and the mole fraction y of A, of course. The range of oscillations lies in the interval $y \in (\hat{y}_2, \bar{y}_2)$. In order to estimate this range we assume that $\bar{y}_2 \approx y_2'$ holds, where $y_2' = 0.52$ is the critical point of the original ZGB model without diffusion.[17] This value is chosen because of the large A coverage on the initial α phase. Therefore surface diffusion is weakened and only plays a minor role. Of course the first order transition at y_2' in the ZGB model shows hysteresis effects and is affected by diffusion processes. A detailed analysis, however, is not the scope of our paper. With $s_\alpha = 0.5$ used in most of our simulation runs (see below) Eq. (10) gives $\hat{y}_2 \approx 0.48$, i.e. we get a very narrow interval $y \in [0.48, 0.52]$ where oscillations occur. This agrees well with our simulation results which give the interval $y \in [0.47, 0.52]$.

Another question that arises is, what happens if $\hat{y}_2 > \bar{y}_2$ holds instead of $\bar{y}_2 > \hat{y}_2$. The equation $\hat{y}_2 = \bar{y}_2$ gives a second
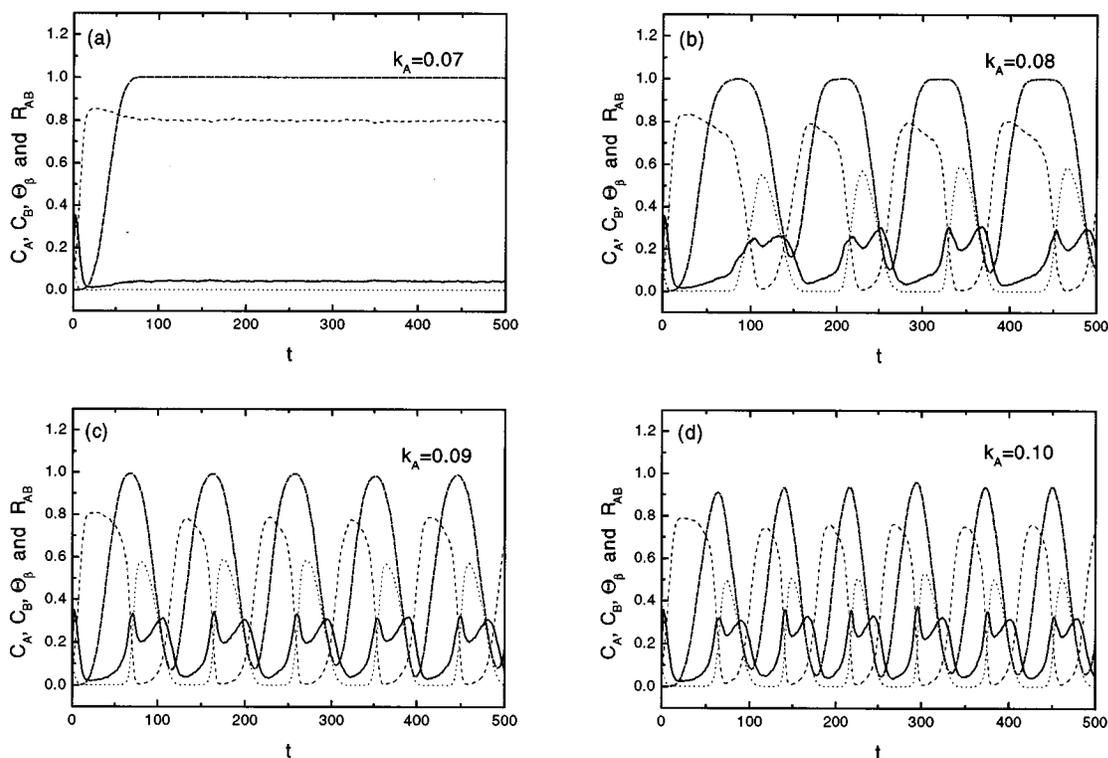
FIG. 2. The temporal evolution of the reaction rate R_{AB} (solid line), and the lattice coverages C_A (dashed line), C_B (dotted line), and Θ_β (dot-dashed line) for $k_A = 0.07$ (a), $k_A = 0.08$ (b), $k_A = 0.09$ (c), and $k_A = 0.10$ (d) with $y = 0.49$, $D = 100$, $V = 1$ and $s_\alpha = 0.5$ on a lattice with side length $L = 256$. The homogeneous α phase with a phase nucleation constant $\gamma = 10^{-4}$ is used as the initial surface state. As can be seen in this figure there occurs a transition from the domain of weak desorption (steady state reaction) to the domain of medium desorption (oscillations) at $k_A = 0.08$.

critical value for the sticking coefficient s_α as

$$S_c'' = \frac{\bar{y}_2(1-y_2)}{y_2(1-\bar{y}_2)}. \qquad (13)$$

The existence of such a second critical value is obvious. If the sticking coefficient of both the α and the β phase are almost equal no oscillations should occur because the difference of the sticking coefficients is the reason for different impingement rates and therefore for the growth and decline of the different surface phases. An estimate gives $S_c'' = 0.58$ leading to an interval $s_\alpha \in [0.36, 0.58]$ where oscillations in the Pt(110) surface model should be possible. Similar to the Pt(100) surface the interval of the oscillation phenomena has its maximum width for $s_\alpha \to S_c' = 0.36$ ($y \in [y_{\min}, y_{\max}]$ with $y_{\min} = y_1 = 0.40$ and $y_{\max} \approx 0.52$) and disappears for $s_\alpha \to S_c'' = 0.58$. The existence of the second critical point S_c'' is shown in Fig. 3. In the simulation this critical point S_c'' lies in the interval $(0.58, 0.59)$ which agrees with the theoretical predictions. For sticking coefficients $s_\alpha > S_c''$ (i.e. a ratio of $s_\alpha / s_\beta \geqslant 0.58$) the oscillation mechanism for the Pt(110) surface does not lead to oscillations because the two surface phases have very similar adsorption properties.

C. Synchronization

For all simulation runs for the Pt(110) surface we used $s_\alpha = 0.5$ and $k_A = 0.1$ except when stated differently. For these values kinetic oscillations are possible. As shown in

Figs. 4 and 5 the power spectra clearly show properties of a limit cycle with a basic frequency ω_0 and a frequency series $\omega_0, 2\omega_0, 3\omega_0 \ldots$, where the basic frequency strongly depends on the phase propagation constant V with $\omega_0 \propto \sqrt{V}$. The peak at $\omega = 0$ results from long time relaxation phenomena. This has been tested for values in the interval $V \in [0.1, 10]$. The other parameter y and D only show a very small influence on the basic frequency ω_0 (see Ref. 16).

Although the power spectra show properties of a limit cycle a real limit cycle is not reached. This can be seen from some irregularities in Fig. 4: For a time interval of magnitude $\Delta t \approx 2000$ the oscillations are very regular in shape. After that a strong disturbance much larger than stochastic fluctuations appears followed by another period of regular oscillations. Such a disturbance cannot be seen in Fig. 5. Such disturbances only occur in simulations in which a certain synchronization condition is not fulfilled (see below). Therefore the origin of this phenomenon should lie in synchronization problems.

In Fig. 6 the phase trajectories in the three dimensional C_A, C_B, Θ_β space are shown for simulations with $V = 1$ and different values of y. There exist strong synchronization disturbances in the oscillations giving a phase trajectory which almost covers a closed area in phase space. As shown in our previous work A diffusion is a synchronization mechanism[16] which occurs only in a domain of length l with $l = \sqrt{Dt}$ the so-called diffusion length.[22] In a simulation on a lattice with length L and oscillations with period T these oscillations can only be synchronized if the condition

J. Chem. Phys., Vol. 108, No. 13, 1 April 1998
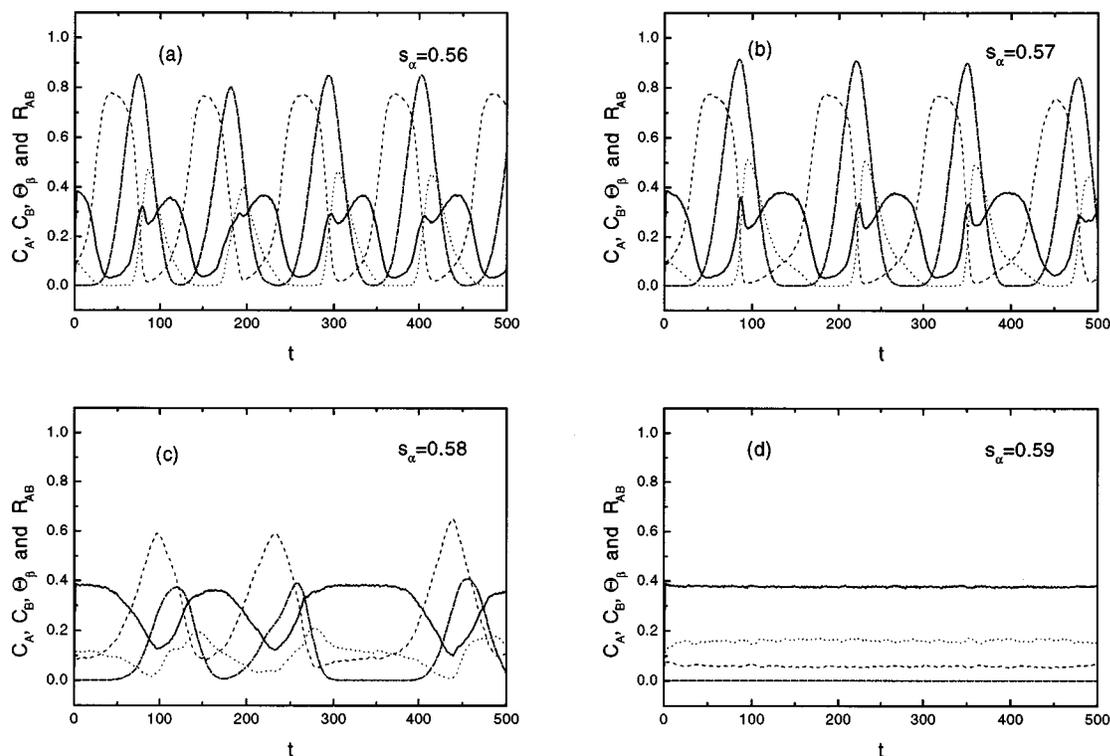
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FIG. 3. The temporal evolution of the reaction rate R_{AB} (solid line), and the lattice coverages C_A (dashed line), C_B (dotted line), and Θ_β (dot-dashed line) for $s_\alpha = 0.56$ (a), $s_\alpha = 0.57$ (b), $s_\alpha = 0.58$ (c), and $s_\alpha = 0.59$ (d) with $y = 0.49$, $D = 100$, $V = 1$ and $k_A = 0.1$ on a lattice with side length $L = 256$. The homogeneous α phase with a phase nucleation constant $\gamma = 10^{-4}$ is used as the initial surface state. This figure shows the existence of a critical ratio of the O_2 sticking coefficients. For values of s_α larger than $s_\alpha = 0.58$ oscillations cannot occur because the sticking coefficient on both surface phases are too similar.

$$\sqrt{DT} \gg L, \tag{14}$$

holds. For $V = 1$ (Fig. 4) the oscillations have a period of about $T = 80$. For these oscillation A diffusion with $D = 100$ gives synchronization in a domain of size $l \approx 90$ and there-
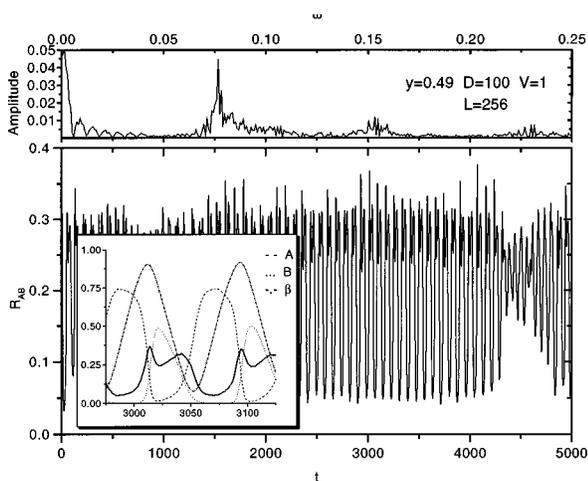

FIG. 4. Temporal evolution of all macroscopic variables for $y = 0.49$, $D = 100$ and $V = 1$. The lattice side length is $L = 256$. The upper part shows the power spectrum of the reaction rate R_{AB}, the lower part shows the oscillations in the reaction rate for the first 5000 time steps and the inset shows a section of oscillations in the lattice coverages. The peak at $\omega = 0$ results from long time relaxation phenomena. The oscillation disturbance at $t \approx 4500$ clearly shows that the synchronization condition is not fulfilled.

fore is not able to globally synchronize the oscillations on a lattice of size $L = 256$. The condition in Eq. (14) is not fulfilled.

Regarding Eq. (14) there exist different possibilities to increase the synchronization. The first one is to increase the oscillation period $T \propto V^{-1/2}$ via a smaller value V. In Fig. 7 it is clearly shown that for certain values of y the synchronization is almost global over the whole lattice [Figs. 7(b) and 7(c)], whereas for smaller or larger values of y the oscillations are only locally synchronized in smaller lattice regions [Figs. 7(a) and 7(d)].

Another possibility to increase the synchronization is the use of smaller lattices (Fig. 8) at constant synchronization length l. This leads to global synchronization with a limit cycle [Figs. 8(a) and 8(b)] but unfortunately also to larger noise because of larger stochastic fluctuations in the macroscopic variables. Another point is that small lattices cannot describe the phase propagation and other kinetic aspects correctly which can be seen in the very fast transition $\Theta_\beta \to 1$ in Fig. 8(d).

A third possibility to strengthen synchronization is fast diffusion.[16] In this case new problems arise because the oscillations now have such large amplitudes that the growth of a homogeneous lattice phase is very fast. This results in an even narrower interval $y \in [0.50, 0.51]$ where oscillations exist, but the corresponding figures (Figs. 9 and 10) are sufficient to explain the synchronization mechanism. However, in simulations with spontaneous phase nucleation this kinetic phenomenon should not occur. As shown in Fig. 9 the sys-
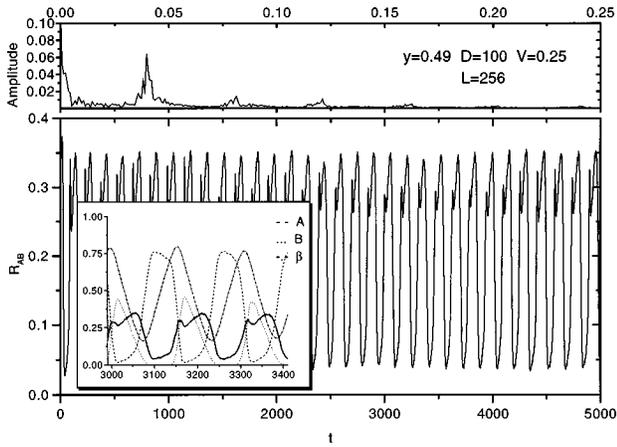
FIG. 5. Temporal evolution of all macroscopic variables for $y=0.49$, $D=100$ and $V=0.25$. The lattice side length is $L=256$. The upper part shows the power spectrum of the reaction rate R_{AB}, the lower part shows the oscillations in the reaction rate for the first 5000 time steps and the inset shows a section of oscillations in the lattice coverages. The peak at $\omega=0$ results from long time relaxation phenomena. In the case presented here the lattice is small enough to fulfill the synchronization condition. Therefore an oscillation disturbance is not observed.

FIG. 7. Phase trajectories in the three dimensional C_A, C_B, Θ_β space for (a) $y=0.46$, (b) $y=0.47$, (c) $y=0.49$, and (d) $y=0.51$ with $D=100$ and $V=0.25$ on a lattice with side length $L=256$. The slow phase propagation with $V=0.25$ allows global synchronization of the oscillations. In part (b) and (c) the properties of a limit cycle can clearly be seen.

tem reaches the limit cycle in a short time and exhibits very regular oscillations with only weak stochastic noise. In Fig. 10 the parameter y only is changed very slightly but this results in a strong disturbance of the synchronization. If one compares Figs. 9 and 10 and the other figures for $D=100$ one can see that large amplitudes in Θ_β coincide with synchronized oscillations. For the lattice phase coverages $\Theta_\alpha = 1 - \Theta_\beta$ and Θ_β there should exist two critical coverages where the α and the β phase, respectively, become macroscopic in size, i.e. one of the phases percolates over the lattice and the other only builds small islands. These two critical coverages Θ'_β and Θ''_β depend on the other parameter y, D, and V (also on s_α and k_A). For
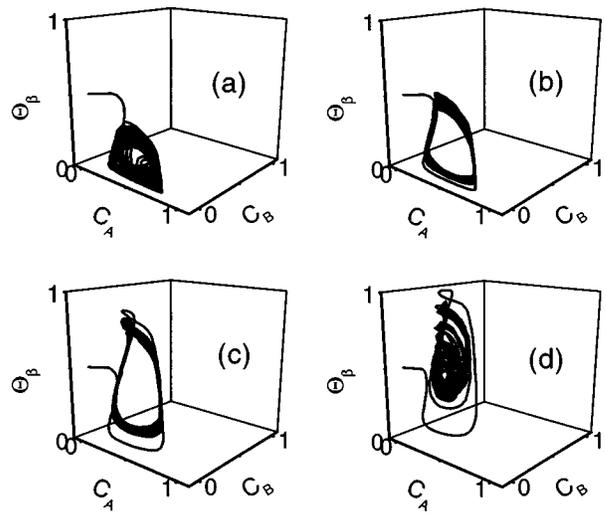
$$\Theta_\beta \geq \Theta''_\beta, \tag{15}$$

there exist a macroscopic β phase with finite α islands within. For

$$\Theta_\beta \leq \Theta'_\beta, \tag{16}$$

we have a macroscopic α phase with small β islands. If the phases would be distributed randomly Θ''_β should correspond to the site percolation density on the square lattice Θ_c with $\Theta''_\beta = \Theta_c \approx 0.6$ (Θ'_β should equal to $1 - \Theta_c$). Because the lattice phases are not distributed randomly (especially at large values of V we get mesoscopic homogeneous and dense islands) for the limiting phase coverages $\Theta''_\beta \geq \Theta_c$ and $\Theta'_\beta \leq (1 - \Theta_c)$ hold. If the β phase coverage exceeds the
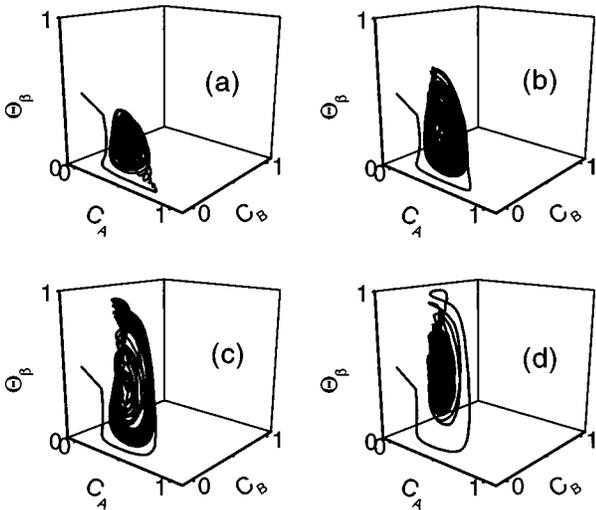

FIG. 6. Phase trajectories in the three dimensional C_A, C_B, Θ_β space for (a) $y=0.47$, (b) $y=0.48$, (c) $y=0.49$, and (d) $y=0.50$ with $D=100$ and $V=1$ on a lattice with side length $L=256$. The oscillations are not synchronized and far away from the limit cycle resulting in an trajectory covering almost a closed area in phase space.
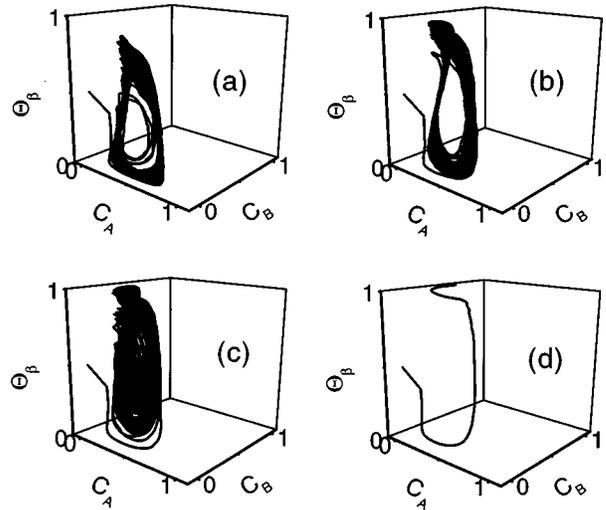

FIG. 8. Phase trajectories in the three dimensional C_A, C_B, Θ_β space for (a) $y=0.47$, (b) $y=0.48$, (c) $y=0.49$, and (d) $y=0.50$ with $D=100$ and $V=1$ on a lattice with side length $L=128$. Smaller lattices lead to globally synchronized oscillations but also to larger noise and partly to the incorrect description of kinetic aspects.
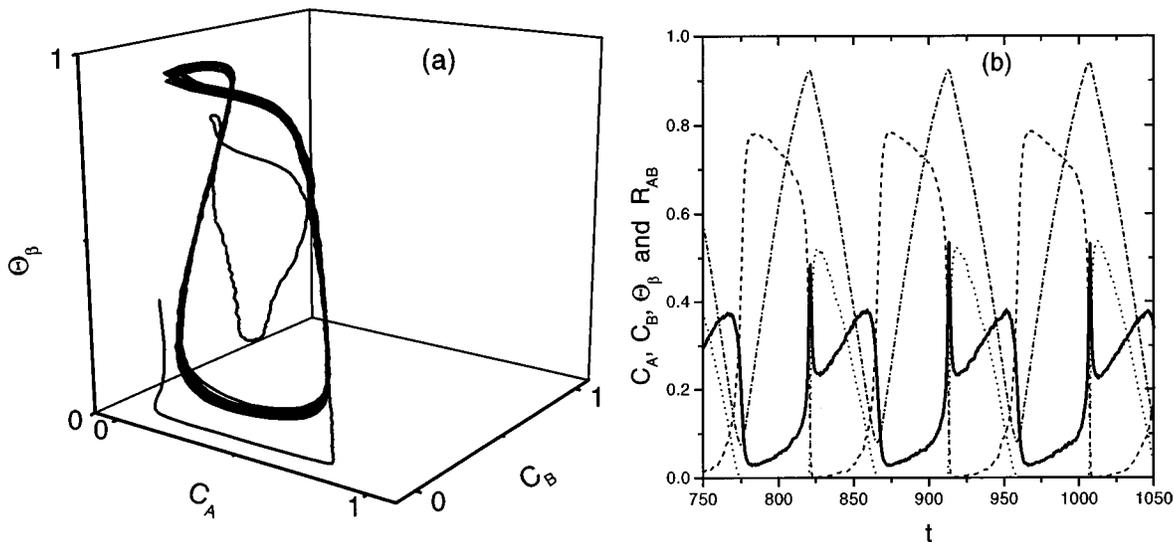
FIG. 9. Phase trajectories in the three dimensional C_A, C_B, Θ_β space (a) and (b) the temporal evolution of the reaction rate R_{AB} (solid line), and the lattice coverages C_A (dashed line), C_B (dotted line), and Θ_β (dot-dashed line) for $y = 0.50$ with $D = 1000$ and $V = 1$ on a lattice with side length $L = 256$. The system exhibits very regular oscillations as can be seen in the phase space trajectory which shows only very small stochastic noise.

critical coverage, Eq. (15), it becomes macroscopic in size and renders possible a macroscopic domain covered with B via enhanced B_2 adsorption. This is a condition for large values of C_B and small values of C_A. Similarly for Eq. (16) a macroscopic α phase exists which is almost completely covered with A in a short time because of A adsorption. This macroscopic α phase is a condition for large values of C_A and small values of C_B. The possibility to build macroscopic phase coverages (either the α or β phase) therefore is the condition for globally synchronized oscillations.

In the case of $\Theta_\beta < \Theta''_\beta$ only finite β islands exist on the lattice and therefore finite regions covered with B are formed and global synchronization of these regions is impossible. For $\Theta_\beta > \Theta'_\beta$ the regions of the α phase are only mesoscopic in size. Synchronization can only be reached via A

diffusion. In Fig. 9(b) the amplitude of the oscillation of Θ_β is sufficiently large (Θ_β varies between $\Theta_\beta = 0.1$ and $\Theta_\beta = 0.9$) to fulfill both conditions in Eqs. (15) and (16). In Fig. 10(b) the values of Θ_β are larger than 0.3, which presumably signifies a violation of condition (16). As a result the phase trajectory shows the irregularities in the range of small values of Θ_β. This also holds for a violation of condition (15), at least qualitatively. As can be seen from Fig. 7 there are strong synchronization disturbances if Θ_β never exceeds Θ''_β (a) or never falls below Θ'_β (d). There exists a certain parameter regime where both conditions can be fulfilled. This results in regular and macroscopic oscillations showing the properties of a limit cycle. At the border of this parameter regime one condition (15) or (16), respectively, cannot be fulfilled giving irregular oscillations.
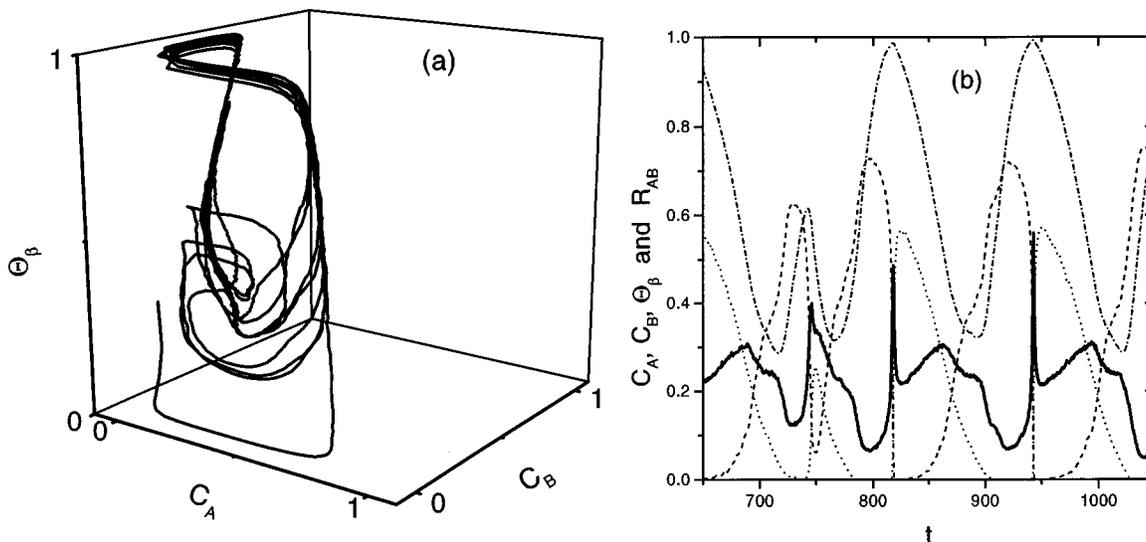

FIG. 10. Phase trajectories in the three dimensional C_A, C_B, Θ_β space (a) and (b) the temporal evolution of the reaction rate R_{AB} (solid line), and the lattice coverages C_A (dashed line), C_B (dotted line), and Θ_β (dot-dashed line) for $y = 0.51$ with $D = 1000$ and $V = 1$ on a lattice with side length $L = 256$. In the case presented here the synchronization is strongly disturbed for small values of the β–phase coverage Θ_β.

On Pt(100) we have the case of small β islands in a macroscopic α phase for every set of parameters. Therefore the oscillations of Θ_β are small and the system always shows irregular oscillations.

These results yield some novel informations as compared to previous work by other groups: (i) Because of the low number of parameters the whole parameter regime can be investigated. In addition all parameters have a clear physical meaning and have not been taken from experiment. In theoretical work based on MF theory at least a cubic term must be used to achieve oscillations or a term of second order if one takes surface reconstruction explicitly into account. The latter is often done via the consideration of a mezoscopic critical CO coverage.[9,10] Such a critical coverage is not an input for our theory it is a consequence of our model and turns out to be in good agreement with experimental results. This will be presented in a separate paper in detail. (ii) Surface diffusion is able to locally synchronize oscillations. This has been neglected in the literature[12] or did not alter the qualitative picture because there were regular oscillations even without surface diffusion.[7] (iii) Global coupling over the whole surface is possible if certain internal conditions are fulfilled without any external force. The existence of global oscillations has always been connected with coupling to the gas phase in previous work,[9] which, of course, is also a mechanism for global coupling.

IV. CONCLUSION

We have studied kinetic oscillations in the catalytic CO oxidation on Pt(100) (4 parameter model) and Pt(110) (5 parameter model). The only difference in our model between the Pt(100) and the Pt(110) surfaces is the ratio of the sticking coefficients on the reconstructed (α) and the non−reconstructed (β) surface phase. This ratio is the basic reason for the existence of kinetic oscillations and further determines the character of these oscillations.

With a small ratio (s_α very small) as observed for Pt(100) in experiments[5] the system shows a broad interval $y \in (y_{min}, y_{max})$ where irregular kinetic oscillations occur. The value of y_{min} depends mainly on the ratio s_α/s_β, whereas the value of y_{max} is dependent on the other parameters D and V. These oscillations can be observed even without desorption of A particles.

With a large ratio (s_α is of the same order of magnitude as s_β – as measured in experiments on the Pt(110) surface – oscillations are only possible if A desorption is allowed. Even then only a very narrow interval exists where regular oscillations can be observed. These results show very good agreement with experimental results where the $CO + \frac{1}{2}O_2$ reaction on Pt(100) and Pt(110) show irregular and regular oscillations, respectively. Also the widths of the parameter intervals giving oscillations can be reproduced at least qualitatively.

Additionally we have shown the existence of critical values for the sticking coefficient s_α (if we set $s_\beta = 1$) and the A desorption constant k_A. For $s_\alpha < S'_c \approx 0.36$ the systems shows the properties of the Pt(100) surface (irregular oscillations). For $S'_c < s_\alpha < S''_c \approx 0.58$ the system exhibits regular oscillations and therefore the properties of the Pt(110) surface. For $s_\alpha > S''_c$ the sticking coefficients for both surface phases are very similar and oscillations cannot exist. Similar to the sticking coefficient there exists a certain finite interval of the value of the desorption constant k_A, which we have called medium desorption. Only for values inside this interval the reaction system modeling the Pt(110) surface shows oscillations whereas outside this interval it reaches a steady state reaction or an absorbing state, respectively.

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