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Monte Carlo simulations of the periodically forced autocatalytic $A+B \rightarrow 2B$ reaction

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The one-parameter autocatalytic Lotka-like model, which exhibits self-organized oscillations, is considered on a two-dimensional lattice, using Monte Carlo computer simulations. Despite the simplicity of the model, periodic modulation of the only control parameter drives the system through a sequence of frequency locking, quasiperiodic, and resonance behavior.

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I. INTRODUCTION

Heterogeneous catalysis belongs to a class of very complicated self-organizing phenomena, which is characterized by the formation of spatiotemporal structures in the reacting system [1,2]. The recent attention to surface catalytic reactions was caused not only by the practical interest but also by a number of new experiments and methods [3], which resulted in a better understanding of the underlying microscopic processes. The most studied reaction is CO_2 catalysis on Pt(100) and Pt(110) monocrystal surfaces. It is found experimentally that the effective oxidation of CO on a Pt surface is accompanied by the formation of spatiotemporal structures such as periodical oscillations of the macroscopic CO_2 production rate and formation of waves of the reacting particles (for details, see [1] and references therein).

An important method for treating self-oscillating systems, in particular autocatalytic reactions, is the periodical variation of an external parameter and analysis of the system's response. This has been done experimentally in Ref. [4] for the autocatalytic $CO+\frac{1}{2}O_2$ reaction on a Pt(110) surface in the low-pressure limit. In this study the external parameter varied periodically in time was the partial pressure of O_2 gas above the Pt(110) sample. It was shown experimentaly that, depending on the modulation frequencies, the self-oscillations in the system exhibit sub- and superharmonic resonance, phase locking, and quasiperiodic behavior. In a more general case, the periodic modulation of external parameters can lead a system to chaos achieved via period doubling [5].

To understand the mechanisms of spatiotemporal structure formation, the standard procedure is to define a mathematical model based on the experimentally observed microscopic processes. Such a mathematical model can then be analyzed either analytically, in terms of the corresponding master equation, or via Monte Carlo computer simulations. The first successful mathematical model of CO_2 catalysis on Pt(100) and Pt(110) surfaces, which took into account adsorption, desorption, and reaction, was presented by Ziff, Gulari, and Barshad (hereafter the ZGB model) [6]. This model leads to reactant concentration oscillations only via introduction of blocked sites (see [7] and references therein). Later, in terms of the ZGB model, the spatiotemporal pattern formation and oscillatory behavior were analyzed incorporating particle diffusion and different (reconstructed and nonreconstructed) surface phases [8–11].

In this paper, we consider a simple Lotka-like model, which was first proposed by Mai *et al.* [12] for heterogeneous catalytic reactions on a surface. Using Monte Carlo computer modeling, it was shown there that this model demonstrates macroscopic concentration oscillations [12,13] within certain parameter variation ranges that are independent of the system's size. The solution of the corresponding master equations in the mean-field approximation led only to the stable solutions because this approximation does not take into account the long-range correlations [12]. Monte Carlo simulations of this model were extended for one and three dimensions by Hovi *et al.* [13] (see also the review articles [7,14]). For a more complicated Lotka-Volterra model the mean-field approximation predicts the oscillatory behavior which indeed has been observed in Monte Carlo computer simulations [15].

The standard Lotka-like model treats two species on a square lattice, referred to hereafter as A and B. Particles A (B) can be created (annihilated) with the probability ζ $(1-\zeta)$. The autocatalytic reaction step $A+B \rightarrow 2B$ takes place instantly if A and B are nearest neighbors. With an appropriate normalization, this model has only one control parameter and reveals spatiotemporal structures. We employ a Lotka-like model and introduce therein a small periodically oscillating contribution to the parameter ζ, in order to determine which phenomena of the forced systems can be reproduced within this simple autocatalytic model.

The paper is organized in the following way. The mathematical model with detailed microscopic rules and simulation algorithm is described in Sec. II. Analysis of the data is performed with Fourier transform and all poles methods which are introduced in Sec. III. In Sec IV the simulation results are discussed.

II. MATHEMATICAL MODEL AND SIMULATION ALGORITHM

The Lotka-like model treats reaction between two kinds of particles, labeled A and B and placed on a square discrete lattice. Particles A are adsorbed from a gas phase on empty lattice sites $(*)$ with the probability ζ,

$$A(gas)+* \overset{\zeta}{\rightarrow} A(ads), \qquad (1)$$

$$B(ads)\xrightarrow{1-\zeta}B(gas)+*, \tag{2}$$

$$A(ads)+B(ads)\rightarrow 2B(ads). \tag{3}$$

The autocatalytic reaction step occurs instantly if particles A appear to be the nearest neighbors to B, Eq. (3). With an appropriate time scaling, the desorption of the B particles from the surface, Eq. (2), is given by probability $1-\zeta$, thus leading to a single-parameter model. It is easy to introduce periodic modulations of this control parameter in the form

$$\zeta=\zeta_0+\Delta\zeta\sin(\omega_{mod}t), \tag{4}$$

where $\Delta\zeta\ll\zeta_0$ is the modulation amplitude, ω_{mod} the modulation frequency, and t the time.

In Monte Carlo computer simulations a discrete square lattice $L\times L$ with periodic boundary conditions is used. Let us denote the concentrations of A and B particles on the lattice as c_A and c_B, respectively. Then the initial conditions are $c_A(0)=0$ and $c_B(0)=0.5$, since B particles initially are distributed randomly on the lattice. The initial conditions in this model are not important; the only stipulation is that initially B particles should be present somehow on the lattice. The simulation loop consists of the following steps.

(1) The time is set to $t=0$.

(2) ζ is calculated from Eq. (4).

(3) A time step is determined as the time that is necessary for the quickest process, $dt=\min[1/\zeta,\ 1/(1-\zeta)]$.

(4) The time is updated $t=t+dt/L^2$.

(5) A site is chosen randomly.

(6) For this site the following cases are distinguished: (i) If the site is empty, A is created there with the probability ζdt. Then the four nearest-neighbor sites are checked for B particles. If one is found, the just created A transforms to B. The four nearest-neighbor sites of the newly created B are then checked for the presence of A particles; if any A is found, it transforms to B. This continues until no more A particles are connected to the B cluster. (ii) If the site is occupied by B, then B is annihilated with probability $(1-\zeta)dt$.

(7) The loop returns to the second step, if t is less than the given simulation time.

III. MATHEMATICAL METHODS

The concentrations of species obtained from computer simulations are recorded with sampling frequency f_{scan}. To analyze the oscillating quantities, one can calculate the power spectral density (PSD) [16]. In this paper two methods are used. The first one is straightforward and based on calculation of the discrete Fourier transform coefficients from a discrete set of N data c_j,

$$C_k=\sum_{j=0}^{N-1} c_j e^{2\pi ijk/N}, \quad k=0,\dots,N-1, \tag{5}$$

with the following calculation of PSD coefficients:

$$P^{FT}(\omega_k)=\frac{|C_k|^2}{N^2}, \quad k=0,N/2, \tag{6}$$

$$P^{FT}(\omega_k)=\frac{2|C_k|^2}{N^2}, \quad k=1,\dots,N/2-1 \tag{7}$$

at frequencies ω_k, where ω_k is defined as

$$\omega_k=2\pi\frac{k}{Nf_{scan}}, \quad k=0,\dots,N/2. \tag{8}$$

The PSD is normalized in such a way that the sum over all $N/2+1$ values of $P^{FT}(\omega_k)$ is equal to the mean-squared amplitude c_j. PSD values can be calculated only at discrete frequencies. But if one assumes that the system oscillates with some frequency between two such discrete quantities, one gets at least two nonzero PSD values at neighboring frequencies. The trick to get a clear spectrum function is based on variation of the length of the sampled data N in such a way that one value of ω_k coincides with the system's oscillation frequency. This allows us to determine the corresponding PSD value as well.

Another method is the all-poles (AP) technique [16] based on the Wiener-Khinchin theorem. The latter states that the Fourier transform of autocorrelation is equal to the PSD. The oscillation frequency range ω_k is extended to the complex ω plane and then this plane is transformed to the z plane by the transformation $z=e^{i\omega f_{scan}}$. The PSD is approximated with a Laurent series

$$P^{AP}(\omega)\approx\frac{a_0}{\left|1+\sum_{k=1}^{M}a_k z^k\right|^2}, \tag{9}$$

where M is the number of poles. To determine the coefficients of the Laurent series a_k, the Laurent series is mapped on the Fourier transform of the autocorrelation

$$\frac{a_0}{\left|1+\sum_{k=1}^{M}a_k z^k\right|^2}\approx\sum_{j=-M}^{M}\Phi_j z^j, \tag{10}$$

where the autocorrelation Φ at lag j is defined as

$$\Phi_j=\Phi_{-j}\approx\frac{1}{N+1-k}\sum_{k=0}^{N-k}c_k c_{k+j}, \quad k=0,1,\dots,N. \tag{11}$$

The coefficients a_k can then be found iteratively [16], e.g., at the first approximation $a_0^{(0)}=\Phi_0$, then at the next step $a_1^{(0)}=-\Phi_1/\Phi_0$ and $a_0^{(1)}=\Phi_0[1-(\Phi_1/\Phi_0)^2]$. This method can resolve very close oscillation frequencies, but its disadvantage is that it cannot be used for signals of a sinusoidal shape; in this case the AP method gives a singularity at the corresponding frequency.

IV. SIMULATION RESULTS

The Monte Carlo computer simulation was performed on a square lattice with the side length $L=1024$ (L is given in units of the lattice constant). For smaller system sizes oscillations are not clearly observable because of high noise level. Although at lattice size $L=1024$ the oscillation parameters

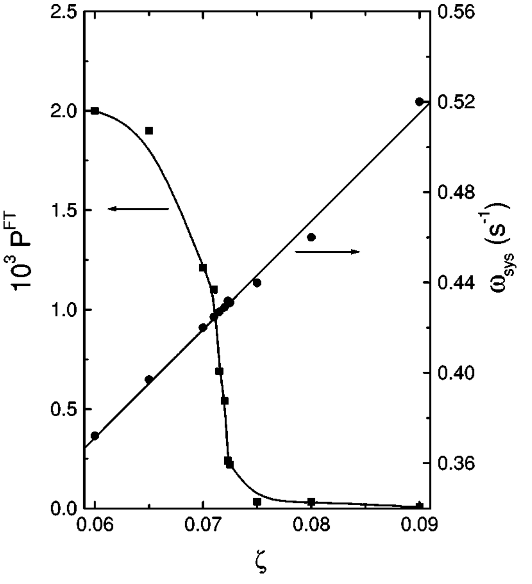

FIG. 1. The PSD (Fourier transform) at the system's self-oscillation frequency ω_{sys} vs A particle creation probability ζ (squares), and the self-oscillation frequency ω_{sys} vs A particle creation probability (circles).

still depend on the lattice size L, it is possible to reproduce all the qualitative properties of the system and it is a good compromise between system size and simulation time.

To describe the oscillations quantitatively, the PSD is used. It is directly connected to the amplitude of oscillations, e.g., it tends to zero if there are no oscillations.

The parameter's ζ variation can be approximately divided into two regions separated by the value of $\zeta_c \approx 0.07$. Particle concentration oscillations are observed for the A particle creation probability $\zeta < \zeta_c$ (see Fig. 1). The transition to the oscillatory regime occurs within a narrow interval of ζ around ζ_c. The system still exhibits oscillatory behavior for ζ slightly larger than ζ_c. In this region the height of the PSD peak at the system's self-oscillation frequency decreases for larger data interval in the PSD calculations, since this determines the higher-frequency resolution in the Fourier transform. As long as the system does not oscillate with one particular self-oscillation frequency, the PSD function peak at the system's self-oscillation frequency in the high-frequency resolution limits is distributed over a range of frequencies, which are close to the system's self-oscillation frequency. In the spectrum this is seen as the broadening and lowering of the peak at the self-oscillation frequency. For $\zeta < \zeta_c$ where the concentration oscillations are more stable, the lowering of the PSD peak at the self-oscillation frequency is not pronounced. To obtain stable PSD values, one has to find a compromise between the precision of determining the oscillation frequency and amplitude (e.g., the uncertainty in the frequency determination is 10% of the system's self-oscillation frequency). Both of them cannot be calculated simultaneously with an arbitrarily high precision (a kind of uncertainty relation holds here).

The frequency of the self-oscillation decreases nearly linearly with ζ, as seen in Fig. 1. This relation and the fact that the PSD values increase at small ζ is easy to illustrate with the following example. Let us imagine a region in the lattice where the A particle concentration is larger than average. Assume that there are a few B particles distributed randomly. As time goes on, A particles are created in empty sites and their probability of survival is larger if they form a cluster of A particles. Meantime, B particles generally are only annihilated. In this regime, the concentration of A continuously increases and that of B decreases. The A particles will create a percolating cluster, and as soon as it grows, eventually they touch a B particle that is still surviving. If this happens, the autocatalytic reaction $A+B \rightarrow 2B$ takes place immediately and a whole A cluster turns into a B cluster. This corresponds to the region where the A particle concentration decreases, but the B particle concentration correspondingly increases. At this stage the B particles are picked up very often and they are annihilated very quickly, leaving empty space for the creation of A particles, which will form a new cluster. Concentration oscillations arise in the system only if the creation of A particles and annihilation of B particles are in a range of parameters where A clusters can be formed and there are a few B left in the lattice. This explains the decrease of the oscillation frequency with decrease of ζ seen in Fig. 1. The period of oscillations increases, because A particles are created more slowly, which allows more B to be annihilated, and thus A particles have more space to create a larger percolating cluster. It takes a longer time for this cluster to meet some B particle. Simultaneously, the oscillation amplitude increases due to the fact that more A particles have accumulated in the lattice. This is reflected by an increase of PSD values for small ζ values.

Decrease of ζ to less than 0.055 leads to A poisoning. A particles are created so slowly that all B particles are annihilated before any catalytic reaction takes place. To treat this model for small ζ values one can use, for example, the method proposed in [13]. For our study this is irrelevant as long as our simulations are not performed for $\zeta < 0.055$.

Let us choose now the parameter $\zeta = 0.08$ in the region $\zeta > \zeta_c$, where oscillations are not pronounced. This allows us to clearly detect the influence of external modulation on the oscillatory behavior in the B particle concentration. For $\zeta < \zeta_c$, the effect of external modulation is weakly expressed. At $\zeta = 0.08$, the system's self-oscillation frequency is found to be $\omega_{sys} = 0.465\ \mathrm{s}^{-1}$.

Now we assume that a periodic external force Eq. (4) is applied to the system, where the external modulations are switched on after some time, with modulation frequency $\omega_{mod} \approx \omega_{sys}$. In this case the system is forced with a frequency close to its self-oscillation frequency and one can see that the oscillation frequency becomes locked to the external frequency and the PSD increases, indicating an increase in the oscillation amplitude.

Changing ω_{mod} and keeping $\Delta\zeta = 0.01$ constant, one can look for changes in the spectrum of oscillating species. It is found that in the PSD, in addition to the maximum at the system's self-oscillation frequency ω_{sys}, there now appears a maximum corresponding to the frequency ω_{mod} of an external modulation. The height of this maximum increases monotonically as ω_{mod} approaches the oscillation frequency ω_{sys}, or the doubled frequency $2\omega_{sys}$ (see Fig. 2). The external force is damped at small frequencies, but with an increase of the external modulation frequency the damping decreases. There is peculiarity in the region around frequency $\omega_{sys}/2$ where a small window exists in which the damping

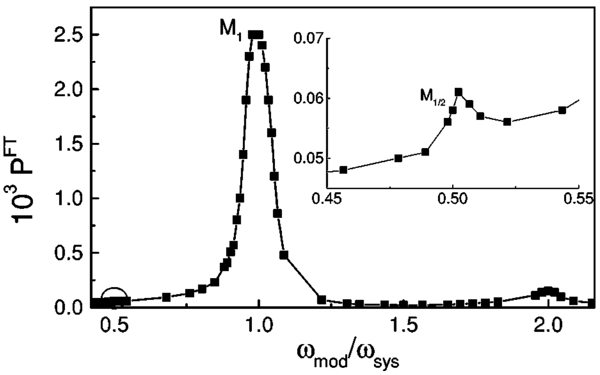

FIG. 2. The PSD (Fourier transform) at the modulation frequency ω_{mod} vs ratio $\omega_{mod}/\omega_{sys}$. Parameter $\zeta_0 = 0.08$ and modulation amplitude $\Delta\zeta = 0.01$.

decrease is more pronounced. This is more clearly shown in the inset of Fig. 2. Further damping again decreases monotonically, until the frequency of external modulation reaches the system's oscillation frequency, where damping starts to grow.

Let us compare the PSD changes at the system's oscillation frequency ω_{sys}, Fig. 3, with the PSD changes at the modulation frequency ω_{mod}, Fig. 2. It is easy to see that both PSDs have maxima at the same modulation frequencies, namely, at $\omega_{mod} = 1/2$, 1, and 2 times ω_{sys}. When ω_{mod} approaches one of these frequencies, ω_{sys} becomes locked to the modulation frequency ω_{mod}, i.e., the system oscillates with $2\omega_{mod}$, ω_{mod}, or $\omega_{mod}/2$, respectively. The ω_{sys} locking to the modulation frequency depends on the modulation amplitude $\Delta\zeta$. If $\Delta\zeta$ increases, ω_{sys} locks to the modulation frequency, even if ω_{mod} is far from the resonance ratios of 1/2, 1, or 2.

As an example of the PSD spectrum in the ω_{mod} resonance regions, one can consider Fig. 4. In Fig. 4(a), two maxima are observed for the modulation frequency: $\omega_{mod} = 0.23\ \mathrm{s}^{-1}$, i.e., close to $\omega_{sys}/2$, and the frequency ω_{sys}, which is locked now to the frequency $2\omega_{mod}$. To relate these observations to the previous figures, let us consider two points, one at the modulation frequency $M_{1/2}$ and the other at the system's oscillation frequency $S_{1/2}$, when the modulation frequency is half of the self-oscillation frequency. Now it is seen that the height of the PSD maximum at $\omega_{mod} = 0.23\ \mathrm{s}^{-1}$ (point $M_{1/2}$) corresponds to the point $M_{1/2}$ in Fig. 2, which is a local maximum. The PSD value (point $S_{1/2}$) at the frequency ω_{sys} corresponds to point $S_{1/2}$ in Fig. 3(a), which is also a local maximum. In Fig. 4(b) the modulation frequency $\omega_{mod} = 0.46\ \mathrm{s}^{-1}$ is chosen to be close to the system's oscillation frequency, which in its turn is captured by the external modulation frequency, leading to just one maximum $M_1 = S_1$ in the oscillation spectrum. This maximum corresponds to the points M_1 in Fig. 2 and S_1 in Fig. 3, which coincide in the locking region. This is the global maximum point, provided the system is forced with a modulation frequency close to its self-oscillation frequency.

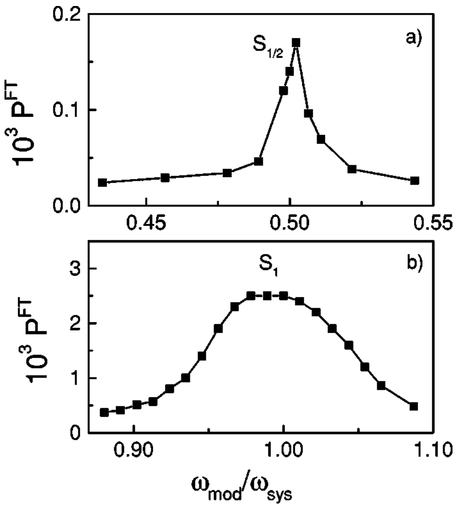

FIG. 3. The PSD (Fourier transform) at the system's self-oscillation frequency ω_{sys} vs ratio $\omega_{mod}/\omega_{sys}$. Parameter $\zeta_0 = 0.08$ and modulation amplitude $\Delta\zeta = 0.01$.

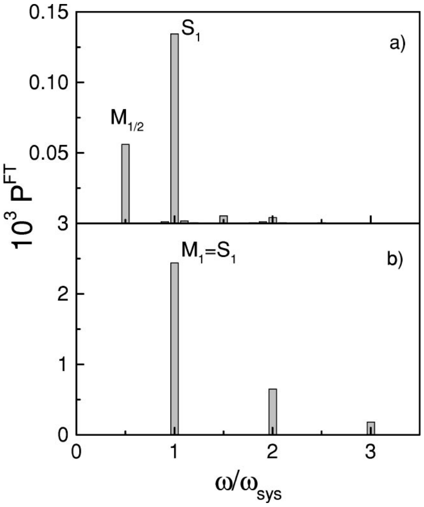

FIG. 4. The PSD (Fourier transform) for parameter $\zeta_0 = 0.08$, modulation amplitude $\Delta\zeta = 0.01$, and modulation frequencies $\omega_{mod} = 0.23\ \mathrm{s}^{-1}$ (a), $0.46\ \mathrm{s}^{-1}$ (b).

The AP method gives a clear picture of phase locking, occurring, for example, when ω_{mod} approaches the frequency $\omega_{sys}/2$, and starting at $\omega_{mod}/\omega_{sys} \approx 0.46$. Then in the PSD curves in Fig. 5 one can find a maximum corresponding to the self-oscillation frequency at ω/ω_{sys}

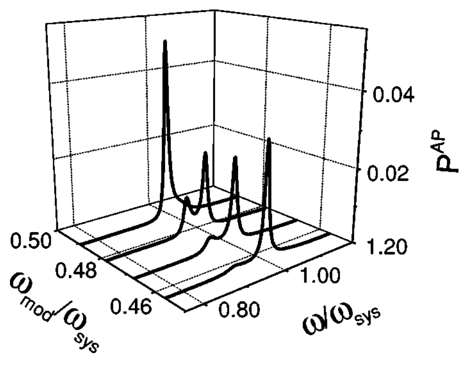

FIG. 5. The PSD (all-poles method) vs the modulation frequency ω_{mod}, approaching the resonance frequency 1/2 (scaled with respect to self-oscillation frequency ω_{sys}). Parameter $\zeta_0 = 0.08$ and modulation amplitude $\Delta\zeta = 0.01$.

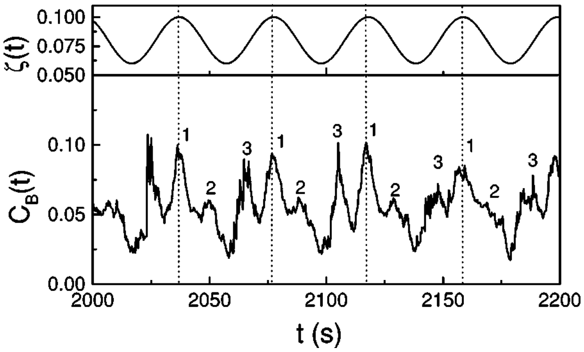

FIG. 6. Temporary oscillations in the B particle concentration. Parameter $\zeta_0=0.08$, modulation amplitude $\Delta\zeta=0.02$, and modulation frequency $\omega_{mod}/\omega_{sys}=1/3$. The top figure represents the periodic modulation $\zeta(t)$ of the A particle creation probability ζ_0.

$=1$ and a small maximum corresponding to the frequency $2\omega_{mod}$ at $\omega/\omega_{sys}\approx 0.9$. As ω_{mod} is increased, this small maximum approaches the ω_{sys} frequency and becomes more pronounced. At the ratio $\omega_{mod}/\omega_{sys}\approx 0.49$ the modulation frequency captures the self-oscillation frequency and forces the system to oscillate with $\omega_{sys}=2\omega_{mod}$ (but not with the self-oscillation frequency of the unmodulated system).

To determine the resonance behavior one can use a visual observation method as well. For example, forcing the system at frequencies close to the ratio $\omega_{mod}/\omega_{sys}=1/3$ with the forcing amplitude $\Delta\zeta=0.02$ shows resonance behavior (see Fig. 6). During one oscillation period of $\zeta(t)$, the B particle concentration reveals three oscillations, which implies resonance behavior at the frequency ratio $\omega_{mod}/\omega_{sys}=1/3$. In the case of $\Delta\zeta=0.01$, the maxima are not clearly distinguishable by visual observation of the concentration oscillations, but already as $\Delta\zeta=0.02$ the maxima are well pronounced. This method can be used as the first estimate of resonance behavior and as the only real method for more complicated cases when the system continuously exhibits transitions between two or more resonance regimes.

V. CONCLUSIONS

The periodically forced Lotka-like autocatalytic reaction model has been studied here by means of Monte Carlo computer simulations. Two mathematical methods were employed for analyzing the simulation results. The first one is based on a power spectral density calculation, using the Fourier transform. Using this method, the oscillations are analyzed in the unperturbed system and in the resonance regions of the modulated system. The second approach used to calculate the PSD is the all-poles method, which is employed for detecting frequency locking processes. One can use additionally a visual observation method to determine the resonance behavior.

The Lotka-like model considered is a remarkable simplification of theoretical models available for describing oscillatory systems. It differs strongly from real catalytic reactions (e.g., the CO catalytic transformation on the Pt surface) in the following respects: (i) concentration oscillations are not connected with surface reconstructions; (ii) diffusion of particles (a rapid and very important processin real systems) is not taken into account; (iii) our modelhas an original mechanism of oscillation synchronization (obviously different from that in real systems), which ensures macroscopic oscillations of particle concentrations independently of the lattice size without implicating any additional mechanisms of synchronization, like diffusion.

We have clearly detected the existence of resonance behavior when the frequency ratio (the external modulation frequency vs the system's self-oscillation frequency) is one of the three 1:2, 1:1, or 2:1 at forcing amplitude $\Delta\zeta\geqslant 0.01$. Resonance behavior is observed at the ratio 1:3 with forcing amplitude $\Delta\zeta\geqslant 0.02$, but its full demonstration is limited in Monte Carlo simulations due to a large noise level. Frequency locking is observed at the resonance frequencies and in their neighborhood. The region of observed frequency locking depends on the amplitude of the modulation force $\Delta\zeta$: the higher the amplitude of the modulation force, the larger the region of frequency locking.

The resonance behavior at frequency ratios 1:3, 1:2, 1:1, and 2:1 is similar to the experimentally obtained results for forced CO catalysis on a Pt surface [4]. Between the resonance frequencies, our simulations show a quasiperiodic behavior, similar to the real system. However, in contrast to this experiment, Monte Carlo computer simulations do not show resonance behavior for some frequency ratios, e.g., 1:4, 3:5, or 2:3. An increase of the modulation amplitude in the resonance regions does not lead to a quasiperiodic behavior, as is observed in the experiments for frequency ratios 3:5 or 2:3. The transition to chaos has not been detected. One should note that these discrepancies could arise from two causes: (i) The Lotka-like model suggests a quite simplified treatment of real autocatalytic reactions. Refining the model will lead to better agreement with the experimental data, and more effects will be reproduced. But this step unavoidably increases the number of parameters in the model and thus the origin of the resonance behavior will be harder to trace. (ii) A specific feature of the Monte Carlo method is a large noise level thus complicating detection of resonance phenomena. Most probably because of this particular fact we were not able to detect resonance behavior at other ratios (e.g., 1:4, 3:5, or 2:3).

A comparison of experimental data with our simulation results shows that resonance phenomena (like frequency locking, quasiperiodic, and resonance behavior) are not connected to a *specific* surface reaction, e.g., CO catalytic oxidation, but they reflect general aspects of oscillatory processes. The simplicity of the formulated Lotka-like model and the large number of observed oscillatory and resonance phenomena might suggest that the Lotka-like model could serve as the kinetic analog of the well known Ising model.

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