Internal Spatiotemporal Stochastic Resonance in a Microscopic Surface Reaction Model

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We show the existence of internal stochastic resonance in a microscopic stochastic model for the oscillating CO oxidation on single crystal surfaces. This stochastic resonance arises directly from the elementary reaction steps of the system without any external input. The lattice gas model is investigated by means of Monte Carlo simulations. It shows oscillation phenomena and mesoscopic pattern formation. Stochastic resonance arises once homogeneous nucleation in the individual surface phases (reconstructed and non-reconstructed) is added. This nucleation is modelled as a noise process. As a result, synchronization of the kinetic oscillations is obtained. Internal stochastic resonance may thus be an internal regulation mechanism of extreme adaptability.

The term stochastic resonance (SR) is given to the somewhat counter-intuitive phenomenon that in a non-linear system a weak signal can be amplified by the assistance of noise. It has been introduced in 1981 by Benzi et al. in the context of a study about the periodically recurrent ice ages. Over the last two decades it has continuously attracted increasing attention and was shown to occur in many systems, in biology [3–5], chemistry [16,17], and physics [12–14]. Generally systems showing SR are described in a formal mathematical way using phenomenological macroscopic equations of the mean field type including (i) a bistable system with an activation barrier or some sort of threshold, (ii) a weak coherent input, and (iii) a strong external noise which helps to overcome the activation barrier. These macroscopic equations in a sense are able to describe many different systems (because stochastic resonance is a general phenomenon which occurs in many natural systems) and have been used in the description of stochastic resonance phenomena in Nd-YAG lasers [15] homogeneous [16] as well as heterogeneous [17,18] chemical reactions, bistable quantum systems [19] or the Lotka-Volterra model [20]. More complex systems (e.g. a summing network of excitable units [21], sheep populations [22], two-dimensional excitable media showing spatio-temporal pattern formation [23], sensory systems in crayfish [24] or in the visual cortex [25], or neuron-like systems [26]) are generally modeled via Langevin equations or the Fitzhugh-Nagumo model.

In addition a few special systems have been investigated in a more general manner via a macroscopic mathematical description, e.g. an autonomous oscillating system [27], a system in the limit of weak noise [28], a system showing stochastic multiresonance [29], and non-dynamical systems with both internal and external noise [30]. Note that in the latter case the internal noise is modeled in the same way as an external noise and that it is only regarded as a general internal noise without specifying the physical background. Computer simulations performed to date consider coupled neurons or general threshold devices, which are mesoscopic models, i.e. the microscopic physical picture is again neglected.

Our present model system is very unusual in the research on SR. It gives for the first time a microscopic description of the phenomenon of internal stochastic resonance and demonstrates its physical reasons on the microscopic (atomic) length scale. It is based on stochastic transitions, each with a clear physical meaning. Without noise, the system exhibits a spatially extended heterogeneous stable state with inherent local oscillations. More important, the noise is not an external input but corresponds to a physically realistic internal nucleation process. Because of the clear physical picture on the microscopic (atomic) level our model is of course specialized and cannot describe a large variety of different systems. But on the other hand the results of this model and the conclusions which can be drawn are very general ones and suggest that internal SR may be the reason for inherent synchronization and cooperative phenomena in many physical, chemical and biological systems.

We consider a slightly modified version of a previously presented model for the catalytic CO+1/2 O_2 reaction on Pt single crystal surfaces [31,32], which shows different types of kinetic oscillations in agreement with experimental results. The model involves CO adsorption, desorption and diffusion, dissociative O_2 adsorption and two surface phases (reconstructed and non-reconstructed) which form and propagate governed by the coverage with CO. The details are given below. An extended version of the model for the CO+NO reaction on Pt(100) is able to describe the experimentally observed transition into chaotic behavior via the Feigenbaum route [33]. Our model follows the well known model by Ziff, Gulari and Barshad [34] (ZGB model) and is investigated by means of Monte Carlo (MC) simulations. The Pt(110) surface of the catalyst is represented by a square lattice of side length L and lattice constant $a = 1$. From experiment [35] it is well known that kinetic
oscillations are closely connected with the $\alpha \rightleftharpoons \beta$ reconstruction of the Pt(110) surface, where $\alpha$ and $\beta$ denote the 1 × 2 and the 1 × 1 surface phase, respectively. In our model CO is able to adsorb onto a free surface site with rate $y_{\text{CO}} = y$ and to desorb from the surface with rate $k$, independent of the surface phase the site belongs to. $O_2$ adsorbs dissociatively onto two nearest neighbor (NN) sites with different sticking coefficients $s$ onto the two phases ($s_\alpha = 0.5$, $s_\beta = 1$). Therefore we get the oxygen adsorption rates $y_\alpha^2 = 1 - y$ and $y_\beta^2 = 2(1 - y)$ for the $\alpha$ and $\beta$ phase, respectively. For $O_2$ adsorption directly at the phase border where one site belongs to the $\alpha$ and the other one to the $\beta$ phase the geometric mean of these adsorption rates is used. In addition, CO is able to diffuse with rate $D$ via hopping onto a vacant NN site. The CO+O reaction occurs, if CO hops to a site which is covered by O and the reaction product CO$_2$ desorbs immediately from the surface. All these processes are associated with the above kinetic transition rates of the stochastic model which therefore determine the relative speed of the individual reaction processes. In the present study we use $y = 0.51$, $D = 100$, and $k = 0.1$ as standard values because CO diffusion is by far the fastest process. For details see refs. [30][2][7].

The $\alpha \rightleftharpoons \beta$ phase transition is modeled as a linear phase border propagation. Consider two NN surface sites in the state $\alpha\beta$. The transition $\alpha\beta \rightarrow \alpha\alpha$ ($\alpha\beta \rightarrow \beta\beta$) occurs if none (at least one of these two sites is occupied by CO. This phase border propagation mechanism mimicks the growth of the $\beta$ phase because of the larger adsorption energy of CO on the 1 × 1 phase than on the 1 × 2 phase [34]. The individual phases are stable or metastable. The direct transition from a globally homogeneous $\alpha$ phase into a homogeneous $\beta$ phase (or vice versa) is impossible; the activation barrier is infinite. The stability of the individual phases depends on the chemical coverage $\Theta_i$ of species $i$ on the surface of the catalyst. For $\Theta_{\text{CO}} < 0.3$ the $\alpha$ phase, for larger values the $\beta$ phase is stable [31]. The coverages of CO and O vary in the course of the reaction because of the different sticking coefficients of O$_2$ on the two surface phases. Starting with a heterogeneous distribution of the $\alpha$ and $\beta$ phase the activation barrier for the surface phase transition is finite, but the transition into a globally homogeneous phase does not occur because of the finite surface phase propagation velocity, i.e. the $\alpha$ or $\beta$ phases cannot grow to macroscopic islands. Therefore the oscillations remain local, interfere and cancel each other on sufficiently large surfaces [34][35]. The system exists in a heterogeneous, dynamically stable state with oscillations, which are locally synchronized by CO diffusion but disappear on the macroscopic length scale for large lattices. The $\alpha$ and $\beta$ phase, however, build almost homogeneous islands on a mesoscopic length scale.

The nucleation is modeled as a spontaneous $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ transition of a single site, completely independent of its neighbors or the particle adsorbed onto this site. Therefore this nucleation is a homogeneous process which corresponds to a weak noise which generates dynamic defects on the surface. The term weak noise is used because the nucleation rate $\gamma \in [10^{-6}, 10^{-2}]$ is for the relevant values several orders of magnitude smaller than the other transition rates which are of the order of $10^{-1}$ to $10^3$. The defects grow or vanish via the $\alpha \rightleftharpoons \beta$ reconstruction depending on their chemical neighborhood, i.e. the presence or absence of CO. It has to be emphasized that all phenomena such as local oscillations, growth and decline of the heterogeneously distributed surface phase islands, quasiperiodical and chaotical behavior exist even without the consideration of the nucleation process [30][22]. Because of the very small nucleation rate, which introduces only very few defects into the existing heterogeneous surface state, one might suppose that the defects could have no influence on the oscillating system, but we shall demonstrate that the nucleation process may have a profound influence on the system behavior leading to cooperative phenomena and the synchronization of the local oscillations.

In comparison with the standard problem of SR there exist several major differences. (i) We have a two-phase system with an additional chemical coverage instead of a bi-stable system. In addition none of the two phases becomes homogeneous. Both coexist in a dynamically stable heterogeneous state. (ii) No external coherent input is considered in our model. The local oscillations originate from the kinetic definition of the model itself and are very small on a macroscopic, global length scale. These internal oscillations can be seen as a substitute of the commonly used coherent input. The macroscopic synchronization of the local oscillations then corresponds to a large output signal. (iii) The source of noise is an internal physical process of the system, the homogeneous nucleation, which breaks the mesoscopic homogeneity of the surface phase islands. The noise process is therefore not an addition to a periodic input but is independent of the oscillations. In most previous studies a weak coherent input is coupled with a strong external noise. (iv) The model is investigated via MC simulations which correspond most closely to a hierarchy of master equations with all correlations included and then mapped onto a finite lattice. The simulation procedure contains additional noise by its very nature but such a noise does not lead to SR. We may characterize the structure of our model by saying that practically all processes which give rise to SR (except for the particle flux to the surface) are internal to the system.

As can be seen in fig. [1] the nucleation (noise) has a strong influence on the system behavior. Without or with small nucleation rates $\gamma < 5 \cdot 10^{-5}$ only local oscillations exist. The amplitude of the global oscillations vanishes for simulations on large lattices [30][31]. With increasing nucleation rate (strength of the noise) the lo-
cal oscillations are synchronized on a macroscopic scale and almost reach the theoretical maximum of $S(\omega)=0.5$ ($\Theta_\beta$ varies between 0 and 1). This holds also for larger lattices up to $L=4906$ which is the current limit for our simulations. Further increase of the noise decreases this synchronization until at a nucleation rate of $\gamma = 10^{-1}$ the system is completely governed by strong noise. This behavior is the fingerprint of SR [3].

In addition the noise has an influence on the frequency of the oscillations (see fig. 3). The normal frequency of the system is $\omega_0$, which can only be observed in simulations on small lattices. For nucleation rates $\gamma > 5 \cdot 10^{-5}$ the phenomenon of SR occurs. The nucleation forces the system to oscillate with a different frequency $\omega$ starting at $\omega \approx 2/3 \omega_0$ for $\gamma = 5 \cdot 10^{-5}$. With increasing nucleation rate the frequency increases as well up to a value of about $\omega \approx 2 \omega_0$ at $\gamma = 5 \cdot 10^{-2}$. This increase in the frequency is based on the increasing number of dynamic phase defects which grow very fast and accelerate the corresponding phase transition. If the number or density of defects becomes too large the oscillating behavior breaks down. The shape of the curve in fig. 3 in the interval $\gamma \in [10^{-5}, 10^{-1}]$ is in very good agreement with the one obtained in the study of a general autonomous system by Haken et al. [26].

The underlying mechanism of this internal stochastic resonance effect is unexpectedly simple. During the growth and decline of the individual surface phases only a few very small residual phase islands remain in domains where the local synchronization leads to large amplitudes in the phase oscillations. These residual islands are spatially separated at a mean distance $R_r$. Adsorbate diffusion is well known to synchronize individual surface domains within the so-called synchronization length $\xi \propto \sqrt{DT}$ [30,31], where $D$ is the diffusion rate and $T$ is the time for one oscillation period. Without nucleation $\xi < R_r$ holds and only locally synchronized oscillations exist. In addition, the residual islands can only combine into a homogeneous phase if the second condition $R_c \sim VT$ for the phase border propagation is fulfilled. But this condition is also violated because $R_c > VT$ holds. Nucleation and subsequent growth now leads to new small phase islands (see fig. 3). The mean distance between the individual phase islands decreases to $R_a$, for which $R_a < \xi < R_c$ and $R_a \sim VT$ holds for proper nucleation rates. Therefore the separated phase islands can now be connected via island growth and synchronized via CO diffusion. This results in macroscopic synchronized oscillations.

The existence of the surface phase nucleation is well known but has not been investigated experimentally yet, in contrast to the initial growth of small surface phase domains [80]. The nucleation rate should depend on the temperature $\gamma = \gamma(T)$, but it is almost impossible to achieve an isolated variation of the nucleation rate under experimental conditions because all other parameter such as CO desorption and CO diffusion also strongly depend on the temperature. It might thus be very difficult to experimentally verify the mechanism behind the SR phenomenon in our model but there should be other systems where it is feasible.

The nucleation of dynamic surface defects as an internal process generates globally synchronized oscillations in our CO+O2/Pt(110) model reaction system via SR. Moreover, because noise is always present in real systems, this type of internal SR should be a very general phenomenon and it may be the reason for cooperative phenomena and internal synchronization via noise processes in many physical, chemical, and biological systems where it has not been investigated experimentally or even suspected to be present to date. This especially holds for systems which exhibit inherent oscillations which are synchronized on macroscopic length scales. In this case often noise effects are supposed to be negligible, but as shown above they can also be the origin of those cooperative phenomena. We believe that SR may thus be an internal regulation mechanism of extreme adaptability. This conclusion is drawn to search for internal SR in a variety of experiments, because to date experiments designed to study the role of internal noise have been inconclusive [37].

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FIG. 1. Global amplitude $S(\omega)$ of the $\beta$ phase coverage as a function of the nucleation rate $\gamma$ which gives the noise strength. A stochastic resonance maximum can be seen. The scatter of the points around the maximum are a result of the finite frequency interval due to FFT analysis. The values of the amplitude are averaged over 20 simulation results. All other parameters are kept constant at $y = 0.51$ (CO adsorption), $k = 0.1$ (CO desorption), $D = 100$ (CO diffusion), $V = 1$ (surface phase propagation), and $L = 256$.

FIG. 2. Ratio of the frequencies $\omega/\omega_0$ as a function of the nucleation rate $\gamma$ which gives the noise strength. Each value is averaged over 20 independent MC simulations. The errors are smaller than the symbol size. All other parameters are kept constant at $y = 0.51$ (CO adsorption), $k = 0.1$ (CO desorption), $D = 100$ (CO diffusion), $V = 1$ (surface phase propagation), and $L = 256$. 

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FIG. 3. New phase nuclei lead to a decreased mean distance $R_n$ between the individual phase islands. This then leads to global synchronization over the whole lattice. See text for details.