THEORETICAL AND NUMERICAL ANALYSIS OF THE NOISE INDUCED KINETICS

Željko Čupić, Srđan Petrović, Ljiljana Rožić, *Institut za hemiju, tehnologiju i metalurgiju - Centar za katalizu i hemijsko inženjerstvo, Njegoševa 12, 11000 Beograd, E-mail: zcupic@nanosys.ihtm.bg.ac.yu*

Sadržaj – *Razmatranje uticaja veličine fluktuacija na vremensku dinamiku procesa na površini materijala ima poseban značaj za nanostruktuirane katalizatore i procese koji se na njima odigravaju tokom sinteze i primene. U ovom radu je analiziran uticaj šuma na kinetiku procesa koji se odigravaju na površini katalizatora. Uvođenje graničnih uslova u odnosu na veličinu fluktuacija odražava se na prvo izlazno vreme dinamičkog sistema. Postavljena je metodologija za poredjenje teorijskih predviđanja i numeričke simulacije.*

1. INTRODUCTION

The study of the macroscopic fluctuations in extended systems is a challenging task since many important topics are still unraveled. Among them is the issue about the relation between the amplitude of the fluctuations and the long-term stability of the system. The latter calls for a boundedness of the fluctuations so that their amplitude does not exceed the thresholds of stability of the system. On the other hand, the exerting of the macroscopic fluctuations in extended systems implies certain spatial coherence of the local fluctuations. Otherwise, the lack of correlations would yield a permanent lack of macroscopic fluctuations for any signal that comes from the entire system. This is because the averaging of non-correlated local fluctuations would yield permanently zero. However, it is not clear what is the physical mechanism that brings the spatial coherence and limits the development of the fluctuations.

Recently, a mechanism that brings about a spatial coherence of the local fluctuations has been proposed by Koleva [1]. The mechanism proposed, constitute of the non-perturbative interactions on the surface, inducing the separation of the adsorption Hamiltonian into rigid and flexible parts and further non-radiative relaxation through the acoustic phonones. It is explicitly related to the boundedness of the macroscopic fluctuations [2]. One of its major consequences is that it generates new properties of the kinetics of surface reactions. It turns out that the spatial coherence of the fluctuations leads to chaotic properties of the state space and corresponding kinetics is characterized as the "chaotic" one.

The first task of the present paper is to evaluate explicitly the first exit time for the "chaotic" kinetics induced by the bounded fluctuations mechanism of Koleva [1]. The first exit time is the expected time when the system reaches for the first time an a priori given state. It is the one of the major properties of the stochastic dynamic systems. In the most interesting case it is the time needed for a fluctuation of a given size to appear for the first time. The estimation of the first exit time is important in the study of qualitative changes that happens in a system under the development of fluctuations of appropriate size. The qualitative changes can be: triggering of phase transitions, nucleation, change of the type of the dynamical regime etc. It should be stressed that such changes appears always, including exposure of a system to steady external constraints.

The second task is to define the appropriate modeling procedure for the stochastic dynamic processes on the nanostructured surfaces, which can be compared with the theory.

The foundations of the kinetics induced by the bounded fluctuations are briefly presented in the section 2. The evaluation of the first exit time is worked out in the section 3. Stochastic Monte Carlo simulation of the CO oxidation on Pt surface is described in section 4.

2. KINETICS INDUCED BY THE BOUNDED FLUCTUATIONS

So far the major tools for the description of the fluctuations in extended systems are the mean-field approach and the master equation one. They are associated with the account for the fluctuations on different levels, namely the master equation is related to mesoscopic level and the mean-field approach - with the evolution on macrolevel [3,4].

However, in the case of the surface reactions it was demonstrated that the non-correlated mobility of the adspecies should yields a permanent instability of the adlayer [5]. Moreover, it seems that the non-correlated mobility of the species should makes the rates of all the elementary processes divergent [6]. Both mentioned consequences are contradictory to experimental observations. Therefore, in order to eliminate the source of the adlayer instability two new viewpoints to the coupling adlayer-surface has been introduced by the mechanism of Koleva [1]. First is the separation of the adsorption Hamiltonian into rigid and flexible parts, and seccond is the nonradiative relaxation through the acoustic phonones. They ensure the suppressing of the adlayer instability and provide the boundedness of the rates of all the elementary processes. However, this happens at the expense of a coupling of the local fluctuations that makes the conjecture of the independence of the fluctuations inappropriate.

Yet, the spatial coherence of the fluctuations is necessary not only for providing the boundedness of the rates but to sustain a long-term stability of a system as well. Indeed, if the fluctuations are unbounded in size and space and develop independently one from another they would certainly produce local defects, such as local sintering, overheating, local reconstruction of the surface etc. Since the spatio-temporal configurations of the fluctuations vary in an uncontrolled way, due time course this process could produce either reaction termination or system breakdown.

Thus, the long-range coupling of the fluctuations and its relation to the long-term stability of the system calls for a new approach to the evolution. It has been recently introduced [2] and was founded on the mechanism of Koleva. The new approach relays on the assumption that the distance between the successive states through which the system evolves is limited so that the system stays permanently within its thresholds of stability. This is an aspect of the general idea introduced in [7] that a system stays stable if and only if the fluctuations that it exerts are bounded so that the system stays permanently within its thresholds of stability. This general condition imposes the requirement that the kinetics should be such that the

increments of the state variables are always bounded. In the case of the surface reactions this requirement is met by the boundedness of the rates of all the elementary processes [2] achieved by the coupling of the local fluctuations.

The major property of the introduced new assumptions about the adlayer-surface coupling is that as a result of the coupling all the species share the same rate, called global one. However, the global rate exhibits permanent variations in the course of the time. Therefore, the kinetic equations that couple the concentrations of the reactant and intermediates and their rates are modified by Koleva with a stochastic part that is responsible for the enduring variations of the global rate. This gives rise to a permanent motion in the state space. It was stated before that the boundedness of the state variable increments in the mechanism of Koleva, leads to strong chaotic properties of the state space [2]. It should be stressed that described chaotic kinetics deals with the global rates without involving any averaging protocol.

The major outcome of the above considerations is that any extended natural system permanently exerts macroscopic fluctuations. However, they can cause qualitative changes such as triggering of nucleation, surface reconstruction, change of the reaction route, it can induce bifurcation etc. Moreover, it can happen at any value of the external parameters such as partial pressure of the reactants and the temperature. The necessary condition is the development of a fluctuation whose amplitude is equal to the "distance" to the critical value.

Moreover, it has been proven [2,8,9] that the boundedness makes the successive fluctuations to be separated by a "silent" time interval. It prevents any possible exceed of the limits imposed on the amplitude of the fluctuations. Thus, though each fluctuation is characterized by three parameters: amplitude, duration and "embedding" time interval, only one of them is independent. Hereafter, it is considered that it is the size of the fluctuation.

3. FIRST EXIT TIME

A very important task is the evaluation of the first exit time, i.e. the expected time when the system reaches for the first time an a priori given state. Since the global rates exhibit everlasting fluctuations, it is to be expected the development of fluctuations of any admissible size in any system at any value of the external parameters. The task is complicated since the variations of the rates are set on the quantum level and their distribution cannot be specified a priori. Yet, the boundedness makes possible to work out certain generalization.

The first exit time has been studied for dynamical systems that exert small Gaussian fluctuations [10]. It has been found out that in general they follow the dependence:

$$T_{W-F} \propto \int_{A_{\min}}^{A_{cr}} \left(\exp\left(-\frac{A^2}{\sigma^2} \right) \right)^{-1} \qquad (1)$$

where A is the size of the fluctuations, i.e. the distance to the critical value, A_{cr} is the a priori given critical value and σ is the variance of the fluctuations.

However, evidently, the frequency $f(A)$ for occurrence of a fluctuation of large size A, is proportional to the probability for occurrence, and to the duration of a fluctuation of size A.

We are used to associate the frequency for an event with the probability for its emerging in a given time interval. Further, it is supposed that the probability uniformly converges to a well-defined limit on making the time interval infinitesimally small. So, in order to proceed accordingly, we decompose each fluctuation of a finite duration into a sequence of correlated infinitesimally thin "flash" fluctuations that emerges one after the other so that their envelop recover the original fluctuation. The probability for occurrence of a fluctuation of size A comprises the term $\exp\left(-\frac{A^2}{\sigma^2} \right)$ that seems to be associated with the normal distribution. The subject of our consideration are fluctuations whose short-range statistics is supposed to be arbitrary. However, the fundamental property of the considered in the present study fluctuations is their permanent boundedness. An immediate outcome of the Lindeberg theorem [11] states that every bounded irregular sequence (BIS) of infinite length has finite expectation value and finite variance. As a result, its distribution approaches the normal one. It should be stressed that the use of the normal distribution is relevant for the large coarse-grained fluctuations only. However, the short-range statistics has finite persistence a so that $a << A_{thres}$, where A_{thres} is the threshold of stability. Thus, any coarse-graining over the persistence length smooths out the particularities of the BIS and the large coarse-grained fluctuations emerge according to the normal distribution.

Further, the association of the duration of a fluctuation with the frequency is grounded on the following considerations. The shape is explicitly related to the fundamental conjecture called incremental boundedness introduced in [2]. It implies that not only the energy involved in each fluctuation is bounded, but the rate of its exchange is bounded as well. This idea is easily decoded if we associate any deviation from the expectation value with the energy involved. Then each fluctuation is composed by a sequence of elementary steps, so that the rate of exchanging energy is bounded in any time interval. Since the energy exchange may be either involved in or removed from the system, every fluctuation can be considered as a fractal Brownian walk where the "walker" is the energy involved in the system. The fractal Brownian walk sets a general relation between the size of a fluctuation and the time for its execution Δ - $A \propto \Delta^{\mu(\Delta)}$, where $\mu(\Delta) \in (0,1)$. The value of $\mu(\Delta)$ is strongly related to the short-range statistics. To elucidate this let us come back to the idea about the blobs. Evidently, they are also fractal Brownian walks whose properties are set entirely on the short-range statistics. So, $a \propto m^{\beta}$ where m is the number of steps involved in a blob and β is set on the short-range statistics $\beta \in (0,1)$. The limit points $\beta = 0$ and $\beta = 1$ are excluded because the first one corresponds to the lack of any persistence while the second one corresponds to a deterministic behavior. Further, a large fluctuation can be considered as a symmetric random walk of blobs. This presentation of a fluctuation is reflected in the complicated exponent $\mu(\Delta)$. Therefore, the relation between the duration and the size of every fluctuation is in the power form $A^{1/\mu(A)}$

Following [2,8] we found out the expected frequency for occurrence of a fluctuation of large size A :

$$f(A) \propto A^{1/\mu(A)} \exp\left(-\frac{A^2}{\sigma^2}\right) \quad (2)$$

where μ is a parameter specific to the system, that it is always confined in the range $\mu \in (0,1) \ \forall A$.

Intuitively, it seems that the time necessary for the emerging of a fluctuation of size A reads:

$$\tau(A) = \frac{1}{f(A)} \quad (3)$$

However, this is the case only with the Poissonian process whose parameter is apriori set. Yet, here we encounter a complicate process that comprises "different" events each of which has its own probability $f(A)$. Therefore, the time necessary for emerging a less probable event is the sum over the times neccesary for emerging of all more probable than that events. Therefore, the first exit time for a fluctuation of size A_{cr} reads:

$$T \propto \int_{A_{\min}}^{A_{cr}} \left(A^{1/\mu(A)} \exp\left(-\frac{A^2}{\sigma^2}\right)\right)^{-1} dA \quad (4)$$

where A_{cr} is the a priori given critical value.

Comparing equations (1) and (4) we obtaine that T deviates more and more from T_{w-F} when A approaches σ from below. However, this is the range of the most probable fluctuations. The presence of the term $A^{1/\mu}$ in (4) makes T much smaler than T_{w-F}. As a result, the occurrence of large fluctuations happens more frequently than it has been expected so far.

4. STOCHASTIC SIMULATION

For the numerical modeling the example was chosen of the catalytic CO oxidation over Pt-group metals, and the generic Turner, Sales and Maple (TSM) scheme [12] was used. It involves the Langmuir-Hinshelwood type reaction and the oxide formation and removal. The CO adsorption, dissociative O_2 adsorption and oxide formation are assumed to occur on the same vacant sites. Interactions between reacting adspecies are neglected. The evolution of the stochastic system is described by a master equation:

$$\frac{dP_\alpha}{dt} = \sum_\beta \left(P_\beta W_{\beta\alpha} - P_\alpha W_{\alpha\beta} \right) \quad (5)$$

for the probabilities P_α of all possible configurations of the adsorbates on the lattice. $W_{\alpha\beta}$ and $W_{\beta\alpha}$ are the intensities of the adsorbed layer transformations from configuration α into configuration β and vice versa, per unit time. For the simulation, probabilities of random events are defined, according to the TSM model, by the rate laws:

$$r_1 = k_1 P_{CO} \left(1 - \theta_{CO} - \theta_O - \theta_{O^*}\right) - k_{-1}\theta_{CO} \quad (6)$$

$$r_2 = k_2 P_{O_2} \left(1 - \theta_{CO} - \theta_O - \theta_{O^*}\right)^2 \quad (7)$$

$$r_3 = k_3 \theta_{CO} \theta_O \quad (8)$$

$$r_4 = k_4 \theta_O \quad (9)$$

$$r_5 = k_5 \theta_{CO} \theta_{O^*} \quad (10)$$

with initial values:

$$\theta_{CO}(0) = 0; \theta_O(0) = 0; \theta_{O^*}(0) = 0$$

The CKS program [13] was used for the simulation with the size of the system equal to 400 particles, which corresponds to 20x20 lattice.

In Fig. 1 the results of the simulations are presented for the case of rate constants corresponding to the one stable, but excitable, steady state in phase space. In this case, the simulation succesfully reproduced the results of Kurkina *et al*. [12] The fluctuations near the excitable steady state sometimes lead to the phenomena of induced oscillations [12, 14]. Our results demonstrated that induced oscillations in this case are not connected with diffusion and spatial relations. Observed oscillations are sensitive to the size of the system, e.g. relative size of the fluctuations.

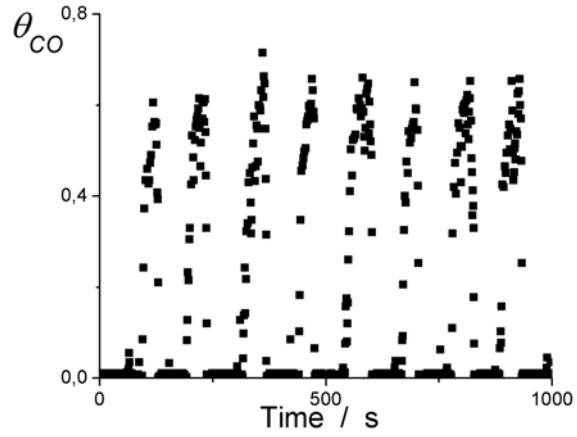

Fig.1. *Results of the MC simulation for $k_1 = 10^7\ s^{-1}\ Torr^{-1}$, $P_{CO} = 10^{-7}$ Torr, $k_{-1} = 0.2\ s^{-1}$, $k_2P_{O2} = 0.5\ s^{-1}$, $k_3 = 10^5\ s^{-1}$, $k_4 = 0.03\ s^{-1}$, $k_5 = 0.02\ s^{-1}$.*

The frequency of the induced oscillations corresponds to the frequency of the development of a fluctuation whose amplitude is equal to the "distance" to the critical value, threshold of stability of the system. The average period of the noise induced oscillations corresponds to the first exit time, calculated in the section 3. For the complete comparison between the simulation and theoretical analysis, detailed stability analysis of the TSM scheme seems to be necessary.

5. CONCLUSIONS

Our task is the evaluation of the first exit time for the reaction kinetics induced by the bounded fluctuations. The latter originates from the new properties of the state space imposed by the relation between the long-term stability of a system and the properties of the local fluctuations in the extended systems. It turns out that a necessary condition for the long-term stability is the spatial coherence of the fluctuations and the boundedness of their amplitude. In turn, the spatial coherence gives rise to everlasting fluctuations of the global rates that renders the importance of the problem for the first exit time.

Our evaluation shows that the occurrence of large fluctuations happens more frequently than it has been expected so far.

The fluctuations are particularly important if small nanoparticles are active phase of the catalyst surface, as it was studied by the Koleva et al. Here, it was demonstrated that some fascinating phenomena, as the time oscillations in catalyst coverage, can occur under the influence of large enough fluctuations.

REFERENCES

[1] M.K. Koleva, "Size-Independent Non-Equilibrium Fluctuations", http://arXiv.org/cond-mat/0212357.

[2] M.K. Koleva and L.A. Petrov, "Chaotic kinetics, macroscopic fluctuations and long-term stability", in: *Progress in Chemical Physical Research*, Nova Science Publisher, Inc, New York, *in press*.

[3] C.W. Gardiner, in "Handbook of Stochastic Methods for Physics, Chemistry and Natural Sciences", Springer-Verlag, Berlin-Heidelberg-NewYork-Tokyo (1985).

[4] N.G. van Kampen, in: "Stochastic Processes in Physiscs and Chemistry", North-Holland Publishing Company, Amsterdam-New York-Oxford, (1981).

[5] M.K. Koleva, "Non-perturbative interactions:a source of a new type noise in open catalytic systems", *Bulg. Chem. Ind.* 69 (1998) 119-128.

[6] M.K. Koleva, "The Failure of the Master equation for the Reactive Systems", http://arXiv.org/cond-mat/0412395.

[7] M.K. Koleva and V.Covachev, "Common and Different Features Between the Behavior of the Chaotic Dynamical Systems and the $1/f^{\alpha}$ - type Noise", *Fluct. Noise Lett.* 1 (2001) R131-R149.

[8] M.K. Koleva, "Coarse-Grained Structure of a Physical (Strange) Attractor. Analytical Solution", in: *Proceedings of 5-th Int. Conference "Symmetry in Non-Linear Mathematical Physics"*, Kyiv, 23-29 June (2003), pp.1375-1381.

[9] M.K. Koleva and L.A. Petrov, "$1/f$ Noise: a Criterion for a Long-Term Stable Evolution of the Open Catalytic Systems", in *Proceedings of the Conference "Self-Organization in Non-Equilibrium Systems"*, Belgrade, September, 2004, pp.41-49.

[10] A.D Wentzell and M.I. Freidlin, in: "Random Perturbations in Dynamical Systems", New York: Springer (1984)

[11] W. Feller, in: "An Introduction to the Theory of Probabilities", J. Willey&Sons: New York; (1970)

[12] E.S. Kurkina and N.L. Semendyaeva, "Fluctuation-induced transitions and oscillations in catalytic CO Oxidation: Monte Carlo simulations", *Surface Science* 558, (2004) 122-134.

[13] IBM Chemical Kinetics Simulator (CKS) program https://www.almaden.ibm.com/st/computational science/ck/msim/?cks.

[14] B. Nowakowski and A. Kawczynski, "Master Equation Simulations of Bistable and Excitable Dynamics in a Model of a Thermochemical System", *J. Phys. Chem.* 109 (2005) 3134-3138.

Abstract – The consideration of the influence of fluctuation size on the time dynamics is particularly interesting from the aspect of the nanostructured catalysts and processes on their surfaces during the synthesis and application. In present paper the influence of the noise on the kinetics of the processes on the catalyst surface is analized. Our evaluation shows that the occurrence of large fluctuations happens more frequently than it has been expected so far. The methodology is introduced to compare theoretical prediction with numerical simulation.

TEORIJSKA I NUMERIČKA ANALIZA KINETIKE INDUKOVANE ŠUMOM

Željko Čupić, Srđan Petrović, Ljiljana Rožić