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Master Equation Simulations of Bistable and Excitable Dynamics in a Model of a Thermochemical System

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The effect of fluctuations on the dynamics of a model of a bistable thermochemical system is studied by means of the master equation. The system has three stationary states and exhibits two types of bistability: the coexistence of two stable focuses and the coexistence of a stable focus with a stable limit cycle separated by a saddle point. Stochastic effects are important when the system is close to the bifurcation, in which the stable limit cycle disappears through a homoclinic orbit. In this case the distribution of the first passage time from the stable limit cycle to the stable focus has a multipeak form. The dependence of this distribution on the number of particles is presented. Near the homoclinic orbit bifurcation, the system also exhibits excitability due to a particular shape of the basin of attraction of the stable focus.

Introduction

Fluctuations play a negligible role in macroscopic, equilibrium systems, provided they are far from critical points. Close to critical points, fluctuations induce the so-called critical phenomena like opalescence. In far-from-equilibrium, nonlinear systems, the situation is in some sense similar. Far from bifurcations, at which qualitative changes in the dynamic behavior of a system develop, the influence of fluctuations on the dynamics is negligible. However, close to bifurcations fluctuations can qualitatively change the dynamics of nonlinear systems. The stochastic effects in the dynamics of nonlinear chemical systems have been for a long time studied theoretically for some simple models.[1−6] Recently, the influence of fluctuations has been observed in experiments for chemical systems close to bifurcations.[7−11]

Models of chemical systems, especially those consisting only of elementary reactions (mono- or bimolecular reactions without autocatalysis), are more complex to analyze than models of thermochemical systems. We have elaborated the simple model of the thermochemical system, which consists of two elementary reactions.[12−14] One of them is an exothermic, catalytic bimolecular reaction, and the other one is a monomolecular reaction. The dynamics of the system can be described by two variables, namely, the concentration of reactant and the temperature. The main nonlinearity in our model follows from the exponential dependence of the rate constant on the temperature. In the present paper we study the effect of fluctuations in our model for parameters at which the system has three stationary states coexisting with limit cycles. Although stable limit cycles are attractors of dynamics of nonlinear chemical systems, there is no relaxation mechanism for a phase of oscillations. Fluctuations in such oscillating systems cause the specific effect of unbounded phase diffusion.[15,16] In our model the unstable or stable limit cycles surround the steady states; two of them may be stable or unstable nodes or focuses, and the third one is a saddle point. Variation of a bifurcation parameter causes the following sequence of bifurcations. At small values of the bifurcation parameter, two stable focuses are separated by the saddle point. When this parameter is increased, one of the stable focuses becomes unstable and a stable limit cycle with “radius” growing from zero appears due to the supercritical Hopf bifurcation. In some interval of the bifurcation parameter, the system has two attractors: the stable limit cycle and the stable fixed point. With increase of the bifurcation parameter, the radius of the stable cycle grows and at some critical value a homoclinic trajectory appears. The stable limit cycle disappears, and the other stationary state remains the only attractor.

The model and the bifurcation analysis are described in the next two sections. The master equation approach to description of the stochastic dynamics is next presented. Since the solution to the master equation is unknown, we use numerical simulations of the master equation. Results of the simulations are described in the subsequent section. In the last section we discuss the obtained results.

Model

A well-mixed system which exchanges energy with its surroundings is considered. The system is composed of the reactant A, the product B, and the catalyst C. The following reactions occur in the system:

$$A + C \xrightarrow{k_1} B + C + Q \tag{1}$$

$$B \xrightarrow{k_2} A \tag{2}$$

The first reaction is exothermic with the reaction heat Q. We assume that the second reaction occurs on the walls of the system. This reaction imitates an unspecified mechanism allowing for the supply of the reactant A and the removal of the product B. It is easy to see that the composition of the system is uniquely determined by the concentration of A. The balance of energy is positive, but because the system is open this does not violate the law of energy conservation. We assume that the system exchanges energy with the surroundings by the Newtonian heat flow through the boundaries, which are kept at constant temperature T_b. For simplicity we consider the diluted gas system, for which the dependence of the internal energy U on the temperature T is given by the simple relation $U = (3/2)Nk_BT$, where N is the number of particles and k_B is the Boltzmann constant. The state of the system is completely characterized by the number density of A and the temperature. The rate equations for these variables are given by

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$$V\frac{dn_A}{dt} = -k_1 n_A n_C V + k_2 n_B S \qquad (3)$$

$$\frac{3}{2}Nk_B\frac{dT}{dt} = k_1 n_A n_C VQ - \kappa n S k_B(T - T_b) \qquad (4)$$

where V is the volume of the system; S is the surface of the system; n is the total number density; n_A, n_B, and n_C are the number densities of A, B, and C, respectively; and κ is the coefficient of heat exchange. Taking into account that $n = (n_A + n_B + n_C)$, the density of B can be eliminated from eq 3.

The rate constants and the coefficient of heat exchange for diluted gases can be presented in the following form:

$$k_1 = k_1^0\left(\frac{T}{T_b}\right)^{1/2}\exp\left(-\frac{E_A}{k_B T}\right) \qquad (5)$$

$$k_2 = \kappa p_B \qquad (6)$$

$$\kappa = \kappa^0\left(\frac{T}{T_b}\right)^{1/2} \qquad (7)$$

where p_B is the coefficient determining the probability of reaction 2 on the walls.

It will be useful to introduce the following dimensionless variables: the molar fractions $\alpha = n_A/n$ and $\eta = n_C/n$ of reagents A and C, respectively, the dimensionless temperature $\theta = T/T_b$, and dimensionless time $t' = nk_1^0 t$. Equations 3 and 4 have then the form

$$\frac{d\alpha}{dt'} = \sqrt{\theta}[-\alpha\eta\exp(-\epsilon/\theta) + c_2(1 - \alpha - \eta)] \qquad (8)$$

$$\frac{d\theta}{dt'} = \frac{2}{3}\sqrt{\theta}q[\alpha\eta\exp(-\epsilon/\theta) - c_1(\theta - 1)] \qquad (9)$$

where $\epsilon = E_A/k_BT_b$, $q = Q/k_BT_b$, $c_1 = \kappa^0 S/qk_1^0N$, and $c_2 = p_B\kappa^0 S/k_1^0 N$ are dimensionless parameters.

q does not change the position of the nullcline α_A for α and α_T for θ on the phase plane (θ,α). Therefore, q is convenient as the bifurcation parameter. The nullclines are given by

$$\alpha_A = \frac{c_2(1 - \eta)}{\eta e^{-\epsilon/\theta} + c_2} \qquad (10)$$

$$\alpha_T = \frac{c_1 e^{\epsilon/\theta}}{\eta}(\theta - 1) \qquad (11)$$

It is easy to check that α_A is the monotonic function of θ and that the necessary and sufficient condition for the existence of two extremes (the N-shape) on α_T is $\epsilon > 4$. Moreover, the intersection points of the nullclines can be determined by the intersections of α_T with straight line α_{A+T} given by

$$\alpha_{A+T} = (1 - \eta) + \frac{c_1}{c_2} - \frac{c_1}{c_2}\theta \qquad (12)$$

Relation 12 follows from the linear combination of the right-hand sides of eqs 8 and 9.

In the present paper we consider the case when the nullclines have three intersection points, all of them positioned on the repelling branch of the nullcline α_T. This corresponds to three stationary states. The middle one of them is a saddle point, and the extreme ones are nodes or focuses (stable or unstable). Assuming that values of η and ϵ are known and that $\alpha_T(\theta)$ and $\alpha_{A+T}(\theta)$ intersect themselves at two given values of the temperature equal to θ_2 and θ_3, one can determine values of c_1 and c_2 from the following relations:

$$c_1 = \frac{1 - \eta}{\frac{1}{\eta}e^{\epsilon/\theta_2}(\theta_2 - 1) + \frac{\theta_2 - 1}{c_2}} \qquad (13)$$

$$c_2 = \frac{(\theta_3 - \theta_2)\eta}{e^{\epsilon/\theta_2}(\theta_2 - 1) - e^{\epsilon/\theta_3}(\theta_3 - 1)} \qquad (14)$$

In the sequel we identify θ_2 with the saddle point and assume that it is placed at the inflection point of α_T. It is easy to check that $\theta_2 = \theta_{ip} = \epsilon/(\epsilon - 2)$. If $\theta_3 = \epsilon/(\epsilon - 2) + \Delta$, where Δ is sufficiently small, then all three stationary states are located on the repelling branch of α_T.

Bifurcation Analysis

We assume that $\epsilon = 8$, $\eta = 0.1$, and $\Delta = 0.3$; then from eqs 13 and 14 it follows that $c_1 = 4.747166 \times 10^{-4}$ and $c_2 = 6.048452 \times 10^{-4}$. For these values of the parameters, the two stationary states with coordinates SS_1 ($\theta_1 = 1.19273$, $\alpha_1 = 0.748734$) and SS_3 ($\theta_3 = 1.63333$, $\alpha_3 = 0.402924$) are nodes or focuses. These states are separated by the saddle point SP ($\theta_{ip} = 1.33333$, $\alpha_{ip} = 0.638381$).

From the linear stability theory, it follows that for $q = q_1 \cong 4.75$ the state SS_3 becomes unstable focus and the stable limit cycle (*SLC*) with radius equal to zero appears due to the supercritical Hopf bifurcation. In this range of q, the state SS_1 is the stable focus. With increasing q the radius of *SLC* increases, and at $q = q_2 \cong 5.0$ the stable limit cycle touches the separatrix S_2 of SP. In consequence the homoclinic orbit coming out and into the saddle point appears and the stable limit cycle disappears.[17−19] For $q_1 < q < q_2$ the system is bistable and two attractors are the stable focus SS_1 and the stable limit cycle *SLC*. Figure 1 shows the attractors, the nullclines, and the separatrices of the saddle point at $q = 4.76$ that is close to the disappearance of *SLC* through the homoclinic orbit bifurcation. The separatrices

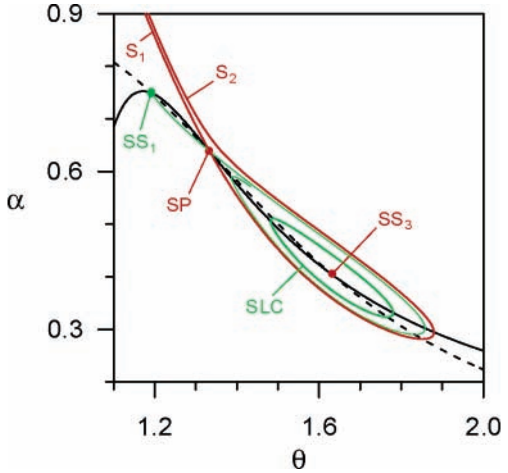

Figure 1. Nullclines for α (the dashed black line) and θ (the solid black line) for the following values of the parameters: $\epsilon = 8$, $\eta = 0.1$, $c_1 = 4.747166 \times 10^{-4}$, and $c_2 = 6.048452 \times 10^{-4}$. The plot shows the stationary states SS_1 (stable focus, green point), SP (saddle point, red point), and SS_3 (unstable focus, red point), the stable limit cycle *SLC* (green closed curve), and four separatrices of the saddle point for the bifurcation parameter $q = 4.76$. Two separatrices outgoing from SP and approaching SS_1 and *SLC* are marked in green, whereas separatrices S_1 and S_2, which separate the basins of attraction of SS_1 and *SLC*, are marked in red.

S_1 and S_2 determine the partition of the phase plane into the basins of attraction of SS_1 ($BASS_1$) and SLC ($BASLC$). As shown in Figure 1, the separatrix S_2 begins at the upper boundary of the phase plane determined by $\alpha = 0.9$ at $\theta \cong 1.2$, next winds round SLC, and ends at SP. The separatrix S_1 starts at the upper boundary at a little smaller value of θ and next approaches monotonically SP. These separatrices determine the shapes of $BASLC$ and $BASS_1$. The basin $BASLC$ is confined between S_1 and S_2 and is surrounded by $BASS_1$ on all sides excluding a small interval at the upper boundary of the phase plane. In consequence $BASLC$ has the shape of a feather. For $q > q_2$ the system has only one attractor SS_1 and is excitable.

Master Equation

In the stochastic description, the state of the system is given by the distribution function $P(\theta,N_A,t')$ of the temperature θ and the population N_A of species A. It is more convenient to use population N_A instead of α, because N_A is changed in the reactions by $\Delta N_A = \pm 1$. The dynamics of P is determined by the following master equation:[14]

$$\frac{\partial}{\partial t'}P(\theta,N_A,t') = \sum_{r=0,1,2}\int_{\Delta\theta<\theta} \mathrm{d}(\Delta\theta)P(\theta - \Delta\theta,N_A - \Delta N_{Ar},t') \times w_r(\theta - \Delta\theta,N_A - \Delta N_{Ar} \rightarrow \theta,N_A) - \sum_{r=0,1,2} P(\theta,N_A,t')\int_{\Delta\theta>-\theta} \mathrm{d}(\Delta\theta) \times w_r(\theta,N_A \rightarrow \theta + \Delta\theta,N_A + \Delta N_{Ar}) \quad (15)$$

Functions w_r describe the probability of transitions of the system from a state (θ,N_A) to $(\theta + \Delta\theta,N_A + \Delta N_{Ar})$ due to three different processes ($r = 0,1,2$) in the system. Term w_0 is related to pure energy exchange without reaction in nonelastic collisions of particles with the boundaries of the system. For this process $\Delta N_{A0} = 0$, and the following form of w_0 has been derived[14] under the assumption of Maxwellian distribution of molecules:

$$w_0(\theta,N_A \rightarrow \theta + \Delta\theta,N_A) = \frac{1}{2}Nqc_1[1 - p_B(1 - \alpha - \eta)]\sqrt{\theta}\omega(\theta,\Delta\theta) \quad (16)$$

where[14]

$$\omega(\theta,\Delta\theta) = \frac{\theta}{(\theta+1)^3}\left(2 + \frac{(\theta+1)\left(\frac{3}{2}N\right)|\Delta\theta|}{\theta}\right) \times \frac{3}{2}N \begin{cases} \exp\left(-\frac{3}{2}N\frac{|\Delta\theta|}{\theta}\right) & \text{for } \Delta\theta < 0 \\ \exp\left(-\frac{3}{2}N\Delta\theta\right) & \text{for } \Delta\theta > 0 \end{cases} \quad (17)$$

The component w_1 describes transitions of the system after a collision connected with reaction 1. In this process $\Delta N_{A1} = -1$ and θ increases by the fixed value $\Delta\theta_1 = q/(3/2)N$ due to release of the reaction heat q. The transition probability w_1 follows from the frequency of collisions.[1] For reaction 1, w_1 is given by

$$w_1(\theta,N_A \rightarrow \theta + \Delta\theta_1,N_A - 1) = N\alpha\eta\sqrt{\theta}\exp(-\epsilon/\theta)\delta(\Delta\theta - \Delta\theta_1) \quad (18)$$

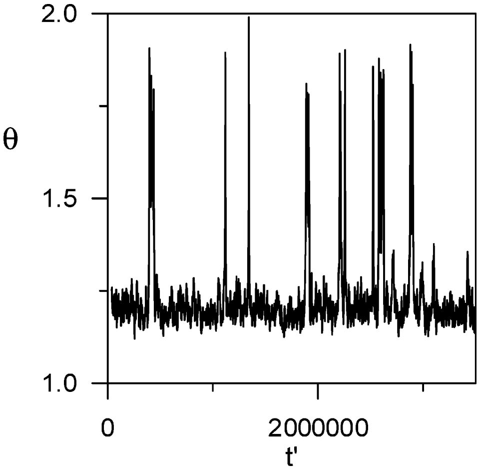

Figure 2. Changes of θ in time for the same values of the parameters as in Figure 1.

In contrast to w_1, the transition functions related to reaction 2 and the Newtonian heat exchange involve the continuous spectrum of $\Delta\theta$, because the amount of energy transferred at collision with the wall of the thermostat is not fixed. Inelastic particle−surface collisions of B particles can lead to reaction 2 for which the particle population increment is $\Delta N_{A2} = 1$. The transition function is then given by

$$w_2(\theta,N_A \rightarrow \theta + \Delta\theta,N_A + 1) = \frac{1}{2}Nc_2(1 - \alpha - \eta)\sqrt{\theta}\omega(\theta,\Delta\theta) \quad (19)$$

The analytical treatment of the master equation is really limited,[1−4] even if it has a discrete form. It is certainly much more difficult if this equation has the integro-differential form of eq 15. For this reason, we apply the Monte Carlo simulations of the dynamics described by this equation to study stochastic effects in our system. The Monte Carlo approach to the master equation for discrete variables is well-known,[22,23] and its appropriate modification for the continuous form of eq 15 has been presented in a recent paper.[20]

Results

The two-variable thermochemical system considered here can have various types of coexisting attractors. We study in detail the case of the coexistence of the stable focus and the stable limit cycle separated by the separatrices of the saddle point (see Figure 1). Figure 2 shows the time dependence of the temperature on time for $q = 4.76$. In this case the stable focus SS_1 coexists with the stable limit cycle SLC surrounding the unstable focus SS_3. The stochastic trajectory goes away from SS_1 and makes a few circulations along SLC but next comes back close to SS_1. These escapes and returns repeat, but the number of loops around the stable limit cycle and around the stable focus changes randomly. At the chosen value of q the system is close to the bifurcation through homoclinic orbit. The limit cycle is close to the separatrix S_2 entering SP, and therefore, it is relatively weak. In consequence the residence times around SS_1 are much longer than on SLC.

Near the homoclinic bifurcation, the distance between S_1 and S_2 in the neighborhood of SS_1 is small (see Figure 1). During the evolution around SS_1 fluctuations can push the system close to the separatrix S_2. Then the trajectory moves close to this curve, which winds around SLC. Even if the trajectory during its evolution along S_2 visits $BASLC$, there is a high probability that it escapes from $BASLC$ and returns to the vicinity of SS_1 after making only a single round. Thus, the large single impulses seen in Figure 2 strongly resemble excitability of the stable focus SS_1. Examples of trajectories which exhibit this property are

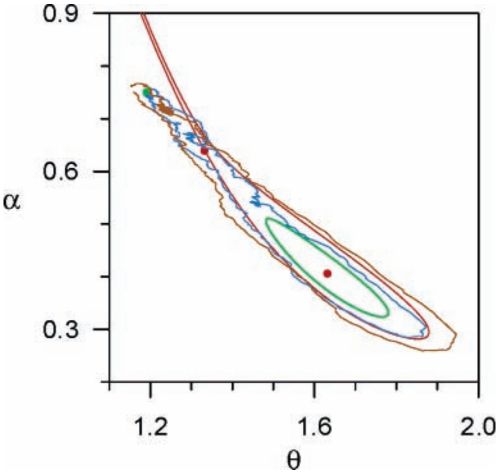

Figure 3. Two trajectories (blue and brown) on the phase plane (θ,α) illustrating excitability in the bistable regime of the system for the same values of the parameters as in Figure 1. Note that the brown trajectory does not enter *BASLC*. The stationary states and the separatrices are marked in the same colors as in Figure 1.

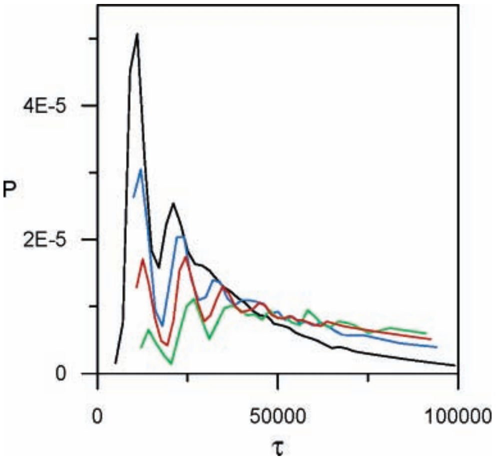

Figure 4. Distributions of first escape times from the basin of attraction of *SLC* to the close vicinity of SS_1 for different numbers of molecules $N = 20\,000$, black; 50 000, blue; 100 000, red; 200 000, green. The values of the parameters are the same as in Figure 1.

shown in Figure 3. Such specific excitability appears here even though the system is bistable.

The shapes of the basins of the attractions shown in Figure 1 have an important effect on the stochastic trajectories which circulate in *BASLC*. If a stochastic trajectory goes along the upper right-hand part of S_2 below *SP*, then fluctuations do not influence qualitatively its further evolution along this part of S_2. The situation changes qualitatively, if the trajectory attains the left part of S_2. When the trajectory approaches the vicinity of *SP*, fluctuations may force it either to make a next round along *SLC* or evolve toward SS_1. This possibility repeats at each round of the trajectory along *SLC*. The system has a chance to leave *BASLC* and evolve toward SS_1 or to remain in *BASLC*. To exclude the stochastic trajectories, which escape from *BASLC* and immediately return back to it, we apply the condition that the trajectory will stay a longer period of time in $BASS_1$, if it crosses the line $\theta = 1.3$. We have verified in thousands of simulations that after crossing this line all trajectories evolve toward SS_1 and stay close to it for some period of time. However, if during a circulation a stochastic trajectory remains in *BASLC* when passing near *SP*, then it turns round and has to make the next circulation before it can reach the vicinity of SS_1. Therefore, the maximum probability of escape time returns periodically, and the probability distribution of first passage time τ should exhibit several peaks separated by intervals of time approximately equal to the period of *SLC*. Such form of the distribution function reflects the circulations of the system along *SLC*. To confirm these predictions, we have performed numerical simulations of stochastic trajectories initialized at the point ($\theta = 1.49$, $\alpha = 0.51$) positioned on *SLC*.

From the ensemble of the stochastic trajectories (several thousands runs), we obtain the probability distribution function $P(\tau)$ of the first passage times τ from *BASLC* to $BASS_1$. Figure 4 shows $P(\tau)$ for the systems with different number of molecules N: 20 000, 50 000, 100 000, and 200 000 for $q = 4.76$. Each of these distributions has four or five peaks. The width of the peaks follows from dephasing of the stochastic trajectory on the limit cycle. The peaks are broader for small systems, because then fluctuations more easily wipe out the phase of the circulation. For larger systems the highest peak appears for longer time τ, because fluctuations become relatively weaker when N increases. The trajectory needs more time to escape from *BASLC* and evolve close to SS_1.

Discussion

Fluctuations in a bistable system can induce jumps of the system between two basins of attraction. In one-variable systems, attractors are stable stationary states and their basins of attraction are separated by a saddle point. Escapes of a stochastic trajectory can be described as transitions through a one-dimensional barrier located at the saddle point. The mean passage times between the attractors can be approximately calculated from the Fokker–Planck equation,[21,24] which is derived from the expansion of the master equation for large systems. No such theoretical treatment is known in the case of bistable multivariable systems.

In our two-variable system in which *SLC* coexists with SS_1, one can try to describe escapes from *BASLC* to $BASS_1$ as transitions through a two-dimensional barrier. The problem can be simplified by the assumption that a phase variable describing circulations along the limit cycle is fast as compared to a radial variable describing the distance of a stochastic trajectory from the limit cycle. In this case one can consider the escapes as transitions through a one-dimensional barrier which periodically changes in time with a period approximately equal to the period of the limit cycle oscillations. A similar approach has been used for the transition through an unstable limit cycle.[25]

The coexistence of a stable limit cycle and a stable stationary state has been observed experimentally in many chemical systems.[26−33] Models of these systems are quite complex and contain many variables. The model presented in this paper contains two variables only, and it describes a very simple chemical system. Its dynamics may be rich due to the nonlinear dependence of the rate constant on the temperature. In particular, in a previous paper[14] we studied the subcritical Hopf bifurcation in this model, while in the present paper we investigate the coexistence of the stable limit cycle and the stable focus separated by separatrices of the saddle point. Despite its simplicity, the model shows many phenomena which are characteristic for multivariable chemical systems as well as for simple systems with strong exothermic reactions. Therefore, the results presented in this paper give indications to look for similar effects in real chemical systems which have the same types of attractors.

Close to the homoclinic orbit bifurcation, the stochastic trajectory jumps between the regions close to SS_1 and *SLC* as shown in Figure 2. The system spends a much longer time around SS_1 than during oscillations on *SLC*, because the steady state is a relatively stronger attractor than *SLC*. The long time intervals in which the trajectory remains close to SS_1 are occasionally interrupted by a few rounds along *SLC*. Every time the number of the oscillations is random, and therefore, the time series of θ resemble the intermittency observed in deterministic chaotic systems. We previously obtained a similar type of oscillations in the same model close to the subcritical Hopf bifurcation,[14] where the two attractors are the stationary state and the limit cycle. It has also been found in a model with period-2 oscillations that fluctuations can induce transition to quasi chaotic dynamics due to merging of bands of two cycles broadened in stochastic systems.[34,35]

Escapes from *BASLC* to the close vicinity of SS_1 may be characterized by the mean first escape time, but such characteristic is only a rough one. More detailed information is contained in the distribution of the first passage time. The results presented in Figure 4 show that this distribution has a few peaks. The distance between them is approximately equal to the period of oscillations on the deterministic limit cycle. Such periodical enhancement of the influence of fluctuations is caused by the particular shape of the separatrix S_2. Fluctuations cause the Brownian dispersion of phase of the circulation around *SLC*, which leads to broadening of peaks of the escape time distribution. The oscillations around *SLC* are not uniform but have a relaxational character; the deterministic dynamics is the weakest in the vicinity of the saddle point, and the evolution is there significantly slowed. The fluctuations then become relatively more important, and trajectories most likely pass through this region in transitions to the basin of attraction of SS_1. This part of evolution gives the largest contribution to the dispersion of the oscillation phase which destroys the structure of the distribution function $P(\tau)$. The peaks are narrower for larger systems because the influence of fluctuations decreases with the total number of particles in a system. To our best knowledge, the distribution of the first passage time presented in this paper is the first example of the multipeak distribution reported in the literature.

The presented results have been obtained by direct Monte Carlo simulation of the master equation,[22,23] which is well recognized as the most accurate simulation method applied at the mesoscopic level of description of stochastic systems.[36,37] On the other hand, this approach requires relatively stronger computing power, and for this reason the distribution function for first passage times shown in Figure 4 still exhibits a considerable amount of noise. The convergence of the calculations is very slow, since the noise level decreases like the inverse of the square root of the volume of the statistical sample. The presented results are the compromise we have decided to choose between the desired accuracy and the demand for computation time. The observed oscillations are a prominent and qualitative property of the distribution function, and the obtained results, even though not very accurate, provide a sufficient confirmation of this effect. For large systems, the expansion of the master equation yields the Fokker−Planck equation which in turn is equivalent to Langevin equations that complement the deterministic dynamics by noise terms. Although it can be expected that calculations based on Langevin equations are relatively more efficient than the simulations of the master equations, the former are restricted by the limits of validity of the Langevin equations and so are valid only for large systems. However, in this limit computation time of any numerical calculations becomes prohibitively long, because the mean first passage time increases exponentially with the number N of particles in the system.[21,24] Moreover, the fluctuation-induced dispersion of oscillation phase expands with time, so the level of noise contained in the distribution $P(\tau)$ always increases for longer escape times τ. Therefore, for any system the peaks in the structure of P become for some sufficiently large τ strongly perturbed and practically blurred by the noise.

Although the system is in the bistable regime, it also exhibits the excitability. Small perturbations around SS_1 decay in time. Sufficiently large perturbations around SS_1 may switch the system to *BASLC* or to $BASS_1$. Due to the particular shape of *BASLC*, appropriate perturbations are necessary to switch the system from SS_1 to *SLC*. Slightly larger perturbations can switch the system outside *BASLC* and they induce the large impulses of α and θ, which are characteristic for excitability.

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