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Master equation simulations of a model of a thermochemical system

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Master equation approach is used to study the influence of fluctuations on the dynamics of a model thermochemical system. For appropriate values of parameters, the deterministic description of the system gives the subcritical or supercritical Hopf bifurcations. For small systems (containing 100 000 particles) close to the supercritical Hopf bifurcation, the stochastic trajectories obtained from numerical simulations do not allow to distinguish between damped oscillations around a stable focus and sustained oscillations around a small stable limit cycle. This uncertainty disappears if the number of particles in the system is increased (up to 1 000 000). Close to subcritical Hopf bifurcation the stochastic trajectory of the system jumps from the basin of attraction of a stable focus to the basin of attraction of a stable limit cycle. In this case the time dependencies of temperature and concentration of reactant in the system are apparently similar to intermittent chaotic oscillations. The mean first passage time for the transitions from the stable focus to the stable limit cycle show the characteristic exponential dependence on the number of particles. This passage time depends very strongly on the bifurcation parameter (reaction heat), which determines the distance between the stable focus and an unstable limit cycle.

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I. INTRODUCTION

Nonlinear dynamical systems often exhibit enhanced sensitivity to fluctuations [1–4]. The stochastic deviations from deterministic dynamics can be particularly significant in systems close to bifurcations, where fluctuations may induce effects that reach the macroscopic level. Bifurcations are turning points at which qualitative changes of features of deterministic dynamics develop. Since a stochastic evolution is to some extent indeterministic, it can be expected that the vicinity of bifurcation has a particular effect on stochastic dynamics.

Very rich nonlinear behavior such as excitability, bistability, and limit cycle oscillations can be observed in thermochemical systems [5–7]. In this paper we study stochastic effects in a thermochemical system close to the supercritical and subcritical Hopf bifurcations, related to different scenarios of the emergence of limit cycles. Deterministic dynamics of this system is based on two simple reactions only but nevertheless, it exhibits all kinds of nonlinear behavior mentioned above. The chemical model we study consists of two elementary reactions: one catalytic (but not autocatalytic) bimolecular reaction and one monomolecular reaction. More variables are necessary to obtain such rich behavior in isothermal chemical systems consisting of mono and bimolecular reactions only [8–11]. The simplicity of the model makes feasible in future microscopic simulations for values of parameters close to the Hopf bifurcations, which could be compared with the mezoscopic approach we apply in the present paper. Small scale microscopic simulations of this system far from bifurcations have been performed previously [12–14].

In studies of stochastic properties, especially efficient is the master equation formalism [1,4,15]. Its advantage is that it enables the basic description of fluctuations without going into the complexity of underlying microscopic dynamics. The master equation is directly developed from the kinetic theory of gases and it is appropriate to describe internal fluctuations. The other method, the Langevin approach, is usually applied to study the influence of an external noise. The master equation method has been well developed and widely applied to reaction and diffusion processes in isothermal systems [4]. However, this mesoscopic approach was much less advanced for thermal processes, in which temperature is not a discrete but a continuous variable. Recently, the master equation has been derived for the Semenov thermochemical system, which includes energy exchange with a thermostat [16,17]. The results of this mesoscopic approach have been confirmed by microscopic simulations. Following this recently developed method, in the present paper we apply the master equation to study fluctuations in the catalytic thermochemical system in the vicinity of the Hopf bifurcations.

In the following section we present the model of the thermochemical system as well as its deterministic description. Section III contains necessary details of the bifurcation analysis of deterministic equations, which allow to distinguish between the supercritical Hopf bifurcation and the subcritical one. In Sec. IV the master equation corresponding to the studied system is presented. The following section contains the results of stochastic simulations and their comparisons with the deterministic description. In the last section we discuss and explain the obtained results.

II. MODEL

We consider a well-mixed, nonadiabatic thermochemical system which exchanges energy with its surroundings. Boundaries of the system are kept at constant temperature T_b. The system is composed of the reactant A, the product B, and the catalyst C. We assume that the following reactions occur in the system:

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$$A+C \xrightarrow{k_1} B+C+\text{energy},\tag{1}$$

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

The first reaction is the exothermic one with a reaction heat Q. The second reaction occurs on the walls of the system and imitates an unspecified mechanism allowing for the supply of the reactant A and the removal of the product B. We assume that no heat effect is associated with reaction (2). It is noteworthy that the energetic balance of the two reactions is positive. This is possible because the system is open. The system considered here is a modification of the model elaborated by Vol'ter and Sal'nikov [5]. It has also been used in the previous papers on thermochemical systems [12–14].

Let us notice that the sum of the concentrations of A and B does not change in time and the concentration of the catalyst C is constant. Therefore, the composition of the system is uniquely determined by the concentration of A. Exchange of energy between the system and an environment occurs due to a heat flow through the boundaries. We consider the diluted gas system for which the internal energy U is related to the temperature T by the equation $U=(3/2)Nk_BT$, where N is the number of particles and k_B is the Boltzmann constant. The environment temperature is assumed constant and the heat transfer may be described by the Newton's law. Phenomenological behavior of the system is described by the balance equations for the number density of A and the temperature:

$$V\frac{dn_A}{dt}=-k_1n_An_CV+k_2n_BS,\tag{3}$$

$$\frac{3}{2}Nk_B\frac{dT}{dt}=k_1n_An_CVQ-\kappa nSk_B(T-T_b),\tag{4}$$

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, κ is the coefficient of heat exchange, and T_b is the a temperature of the boundary of the system. Due to the relation $n=(n_A+n_B+n_C)$, the density of B can be eliminated from Eq. (3).

From the kinetic theory of gases it follows that the rate constants and the coefficient of heat exchange depend on the temperature of the system and can be presented in the following form:

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

$$k_2=\kappa p_B,\tag{6}$$

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

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

In further discussion it will be useful to introduce the dimensionless variables $\alpha=n_A/n$ and $\eta=n_C/n$, which are molar fractions of A and C, respectively, $\theta=T/T_b$ is the dimensionless temperature and $t'=nk_1^0t$ is the dimensionless time. The balance equations (3) and (4) have then the form

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

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

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

The nullclines of the system have the form

$$\alpha_A=\frac{c_2(1-\eta)}{\eta e^{-\varepsilon/\theta}+c_2},\tag{10}$$

$$\alpha_T=\frac{c_1e^{\varepsilon/\theta}}{\eta}(\theta-1),\tag{11}$$

where α_A and α_T are the solutions to $f(\theta,\alpha)=0$ and $g(\theta,\alpha)=0$, respectively. In further discussion it will be convenient to use the combination of both the nullclines given by

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

The nullcline for α is a monotonic function of θ and therefore, it is attracting for all initial conditions. Thus, the necessary condition for the appearance of oscillations in the system is that the nullcline for θ must be nonmonotonic and have a branch which is repelling. It is easy to check that the necessary and sufficient condition for the nonmonotonic dependence (the existence of two extremes) of the nullcline on θ is $\varepsilon>4$.

In general, the nullclines may have one or three intersection points (stationary states). In the present paper we discuss only the case with one stationary state positioned on the repelling branch of α_T, because we limit ourselves to study the supercritical and subcritical Hopf bifurcations. The maximal negative slope of the nullcline for θ at the repelling branch is given by

$$\left.\frac{d(\alpha_T)}{d\theta}\right|_{\theta_3}=-\frac{c_1}{\eta\varepsilon}e^{\varepsilon-2}(\varepsilon-4),\tag{13}$$

where θ_3 denotes a value of θ at which $d^2\alpha_T/d\theta^2$ is equal to zero. This slope must be greater than the slope of the straight line α_{A+T} given by

$$\frac{d(\alpha_{A+T})}{d\theta}=-\frac{c_1}{c_2}.\tag{14}$$

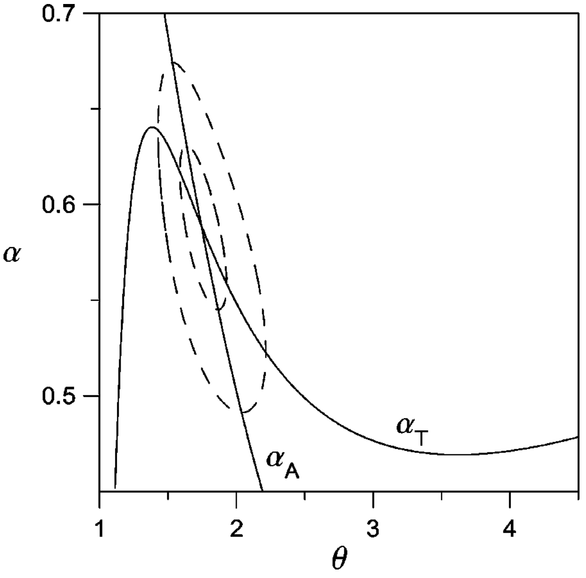

FIG. 1. The nullclines of the system for α and θ on the phase plane for the following values of the parameters: $\varepsilon = 5.0$, $\eta = 0.04$, $c_1 = 0.0018$, and $c_2 = 0.0036$. The supercritical Hopf bifurcation occurs at $q_{cr} = 21.968$. The dashed closed curves show the small stable limit cycle at $q = 22.5$ inside the big one at $q = 25.0$.

Therefore, to exclude the existence of three stationary states, it is necessary and sufficient that $c_2 \leq \varepsilon \eta/(\varepsilon - 4) e^{(\varepsilon - 2)}$. Figure 1 shows the nullclines for α and θ given by Eqs. (10) and (11).

Unfortunately, the coordinates of a stationary state α_∞ and θ_∞ cannot be found analytically. It is easy to check that all trajectories of the system starting from the boundary of the rectangle $(0,0),(0,1-\eta),(\theta_l,1-\eta),(\theta_l,0)$ flow into the rectangle, if θ_l is sufficiently large. Therefore, an attractor must exist inside the rectangle. If the stationary state is unstable, then the attractor must be a stable limit cycle.

Let us mention that for fixed values of the parameters ε, η, c_1, and c_2 the nullclines do not change their position on the phase plane. The stability of the stationary state depends then only on the reaction heat q, which we will use as the bifurcation parameter. In the sequel we choose two sets of values of c_1 and c_2, for which the supercritical and subcritical Hopf bifurcations occur, respectively.

III. BIFURCATION ANALYSIS

The stationary state of system (8) and (9) may be a stable or unstable node, or a stable or unstable focus. Its character is determined by the linear terms in the expansion of $f(\theta,\alpha)$ and $g(\theta,\alpha)$ in the Taylor series around α_∞ and θ_∞:

$$\frac{dx}{dt'} = ax + by + a_{20}x^2 + a_{11}xy + a_{02}y^2 + a_{30}x^3 + a_{21}x^2y + a_{12}xy^2 + a_{03}y^3 + \cdots \tag{15}$$

and

$$\frac{dy}{dt'} = cx + dy + b_{20}x^2 + b_{11}xy + b_{02}y^2 + b_{30}x^3 + b_{21}x^2y + b_{12}xy^2 + b_{03}y^3 + \cdots, \tag{16}$$

where $x = \alpha - \alpha_\infty$ and $y = \theta - \theta_\infty$.

If $(a+d)^2 - bc > 0$, then the stationary state is a node, otherwise it is a focus. The stationary state is stable provided $(a+d) < 0$ or unstable if $(a+d) > 0$. At $(a+d) = 0$ it changes its stability. The stable focus can lose its stability at a critical value of a bifurcation parameter by the supercritical Hopf bifurcation SF→UF+SLC. In this case the stable focus (SF) at the critical value of the parameter becomes the center and then the unstable focus (UF), from which the stable limit cycle (SLC) arises. The radius of SLC is growing from zero. The other possibility is that the unstable limit (ULC) cycle (surrounding SF) decreases its radius approaching zero at the critical value of the parameter. Then the complex focus is formed and next SF becomes UF. This bifurcation is possible, if before it the subcritical Hopf bifurcation SF→SF+ULC+SLC has appeared. In this case the stable focus remains stable, but a pair of SLC and ULC appears at some distance from the stable focus. Monotonic change of the bifurcation parameter causes an increase of the radius of SLC and a decrease of the radius of ULC. As the critical value of the parameter is approached, ULC and SF merge and form the complex focus, which then transforms to UF.

In order to distinguish between the subcritical and supercritical bifurcations, which occur at $(a+d) = 0$, we use the approach elaborated by Bautin and Andronov [18,19]. It is useful to transform the Taylor series for x and y to the canonical form

$$\frac{du}{dt'} = -\beta v + A_{20}u^2 + A_{11}uv + A_{02}v^2 + A_{30}u^3 + A_{21}u^2v + A_{12}uv^2 + A_{03}v^3 + \cdots \tag{17}$$

and

$$\frac{dv}{dt'} = \beta u + B_{20}u^2 + B_{11}uv + B_{02}v^2 + B_{30}u^3 + B_{21}u^2v + B_{12}uv^2 + B_{03}v^3 + \cdots, \tag{18}$$

where $u = x$, $v = -ax/\beta - by/\beta$, and $\beta = \sqrt{ad - bc}$. For further analysis it is convenient to change coordinates u,v to the polar coordinates $u = r\cos\Phi$, $v = r\sin\Phi$. This leads to

$$\frac{dr}{d\Phi} = r\frac{A_1(q)r + X_2\cos\Phi + Y_2\sin\Phi}{A_2(q)r + Y_2\cos\Phi - X_2\sin\Phi}, \tag{19}$$

where $A_1(q)$ and $A_2(q)$ are coefficients of the transformation from (u,v) to (r,ϕ) and $X_2 = X_2(r\cos\Phi, r\sin\Phi, q)$, $Y_2 = Y_2(r\cos\Phi, r\sin\Phi, q)$ are polynomials of at least second degree in $r\cos\Phi, r\sin\Phi$. Coefficients A_i depend on the dimensionless reaction heat q, which we use as the bifurcation parameter. For $r<1$ the right-hand side of Eq. (19) can be expanded into

$$\frac{dr}{d\Phi}=rR_1(\Phi,q)+r^2R_2(\Phi,q)+r^3R_3(\Phi,q)+\cdots. \tag{20}$$

Assuming that

$$r=r(\Phi,r_0,q) \tag{21}$$

is the solution to Eq. (20) for an initial value $r(\Phi_0)=r_0$ we can expand r with respect to r_0,

$$r=z_1(\Phi,q)r_0+z_2(\Phi,q)r_0^2+z_3(\Phi,q)r_0^3+\cdots. \tag{22}$$

Introducing Eq. (22) into Eq. (20) we obtain the system of recursive differential equations for the coefficients z_i for $i=1,2,3,\ldots,$

$$\frac{dz_1}{d\Phi}=z_1R_1(\Phi,q),$$

$$\frac{dz_2}{d\Phi}=z_2R_1(\Phi,q)+z_1^2R_2(\Phi,q). \tag{23}$$

The Poincaré transformation defined by

$$\psi(r_0,q)=r(2\pi,r_0,q)-r(0,r_0,q) \tag{24}$$

determines the stability of the solution. Introducing solution (22) into this function gives

$$\psi=a_1(q)r_0+a_2(q)r_0^2+a_3(q)r_0^3+\cdots, \tag{25}$$

where

$$a_1=\exp\frac{2A_1(q)}{A_2(q)}-1, \tag{26}$$

$$a_k=z_k(2\pi,q) \tag{27}$$

for $k=2,3,4,\ldots$. The condition for the existence of the limit cycle with the radius r_0 has the form

$$\psi(r_0,q)=a_1(q)+a_2(q)r_0+a_3(q)r_0^2+\cdots=0. \tag{28}$$

For $q=q_{cr}$ two initial coefficients of this expansion are equal to zero $[a_1(q_{cr})=a_2(q_{cr})=0]$. The first focus number a_3 in the notation used in Eqs. (17) and (18) has the form

$$a_3=\frac{\pi}{4\beta}[3(A_{30}+B_{03})+(A_{12}+B_{21})]-\frac{4\pi}{4\beta^2}[2(A_{20}q_{20}-A_{02}B_{02})-A_{11}(A_{02}+A_{20})+B_{11}(B_{02}+B_{20})]. \tag{29}$$

The stability of the solutions around $q=q_{cr}$ is determined by sign of the first focus number a_3 and by $a(q)+d(q)$, which gives the sum of eigenvalues of Eqs. (15) and (16). If $a_3<0$ in some interval of q around q_{cr} and $a(q)+d(q)$ changes its sign from negative to positive at $q=q_{cr}$, then SF becomes UF and SLC around UF appears. This means that at $q=q_{cr}$ the supercritical Hopf bifurcation occurs. However, if $a_3>0$ in some interval of q around q_{cr} and $a(q)+d(q)$ at $q=q_{cr}$ changes its sign from negative to positive, then at $q=q_{cr}$ ULC shrinks its radius to zero and SF becomes UF. This means that for $q<q_{cr}$ SF coexists with SLC. Therefore the subcritical Hopf bifurcation has to occur at some $q=q_{bf}<q_{cr}$, in which the pair of SLC and ULC is born.

IV. MASTER EQUATION

In the stochastic approach, a state of our system is described by the distribution function $P(\theta,N_A)$ for the temperature θ and the population N_A of species A. (It is more convenient to use N_A instead of α because N_A is changed in the reaction by $\Delta N_A=\pm 1$.) The dynamics of $P(\theta,N_A)$ is governed by the master equation, which can be written in the following form:

$$\begin{aligned}\frac{\partial}{\partial t'}P(\theta,N_A,t')=&\int_{\Delta\theta<\theta}d(\Delta\theta)P(\theta-\Delta\theta,N_A-\Delta N_A,t')\\&\times w(\theta-\Delta\theta,N_A-\Delta N_A\to\theta,N_A)\\&-P(\theta,N_A,t')\int_{\Delta\theta>-\theta}d(\Delta\theta)\\&\times w(\theta,N_A\to\theta+\Delta\theta,N_A+\Delta N_A).\end{aligned} \tag{30}$$

The transition probability w is composed of three terms corresponding to the separate processes which contribute to the dynamics of P. Two of them are connected to reactions (1) and (2), respectively, and the third one is related to the Newtonian exchange of energy without reaction:

$$\begin{aligned}w=&w_1(\theta,N_A\to\theta+\Delta\theta,N_A-1)+w_2(\theta,N_A\to\theta\\&+\Delta\theta,N_A+1)+w_e(\theta,N_A\to\theta+\Delta\theta,N_A).\end{aligned} \tag{31}$$

The transition probability w_e for exclusive energy exchange is a continuous function of $\Delta\theta$, and it does not involve any chemical changes. The explicit expression for w_e has been derived only recently [16,17], under the assumption that the velocity distribution of particles always remain Maxwellian. Using the dimensionless variables, w_e in our system can be cast in the following form:

$$\begin{aligned}&w_e(\theta,N_A\to\theta+\Delta\theta,N_A)\\&\quad=\tfrac{1}{2}Nqc_1[1-p_B(1-\alpha-\eta)]\sqrt{\theta}\,\omega(\theta),\end{aligned} \tag{32}$$

where

$$\omega(\theta)=\frac{\theta}{(\theta+1)^3}\left(2+\frac{(\theta+1)\left(\frac{3}{2}N\right)|\Delta\theta|}{\theta}\right)\times\frac{3}{2}N\begin{cases}\exp\left(-\frac{3}{2}N\frac{|\Delta\theta|}{\theta}\right) & \text{for } \Delta\theta<0\\ \exp\left(-\frac{3}{2}N\Delta\theta\right) & \text{for } \Delta\theta>0.\end{cases} \tag{33}$$

Expression (32) does not include these inelastic particle-surface collisions which are related not only to energy transfer but also to reaction (2). The transition probability w_2 corresponding to this latter process describes a change of the temperature by $\Delta\theta$, combined with an increment of population of A by $\Delta N_A=1$. With the use of Eq. (33), w_2 can be written as

$$w_2(\theta,N_A\rightarrow\theta+\Delta\theta,N_A+1)=\tfrac{1}{2}Nqc_1p_B(1-\alpha-\eta)\sqrt{\theta}\omega(\theta). \tag{34}$$

In contrast, the transition function related to reaction (1) involves only the discrete change of θ, because release of the reaction heat q always increases the temperature of the system by the fixed value $\Delta\theta_1=q/(\frac{3}{2}N)$. The decrement of N_A associated with reaction (1) is $\Delta N_A=-1$. The transition function w_1 has the well-known form [1] following from the frequency of collisions related to reaction (1):

$$w_1(\theta,N_A\rightarrow\theta+\Delta\theta_1,N_A-1)=N\alpha\eta\sqrt{\theta}\exp(-\varepsilon/\theta)\delta(\Delta\theta-\Delta\theta_1). \tag{35}$$

The problems related with analytical treatment of the discrete master equation are widely known [1–3]; they are certainly more serious, if the master equation has the integro-differential form of Eq. (30). Therefore, we study stochastic effects in our system by means of simulations of processes described by this equation. The method of the Monte Carlo simulations of the master equation for discrete variables is well founded [20] and its appropriate modification for the continuous form of Eq. (30) has been presented in the recent paper [16].

V. RESULTS

A. Supercritical Hopf bifurcation

In all our calculations we use the fixed values of the parameters $\varepsilon=5.0$ and $\eta=0.04$. For studies of the supercritical Hopf bifurcation we assume the following values of the remaining parameters $c_1=0.0018$ and $c_2=0.0036$. Equations (8) and (9) for the deterministic dynamics have only one stationary state with the coordinates $\alpha_\infty=0.589\,085\,937\,823\,495\,16$ and $\theta_\infty=1.741\,828\,124\,353\,618\,8$. This state is SF below $q=q_{cr}=21.968$ and UF above it. At these values of the parameters, the first focus number α_3 given by Eq. (30) is negative at q_{cr}. Thus, the supercritical Hopf bifurcation occurs at q_{cr}.

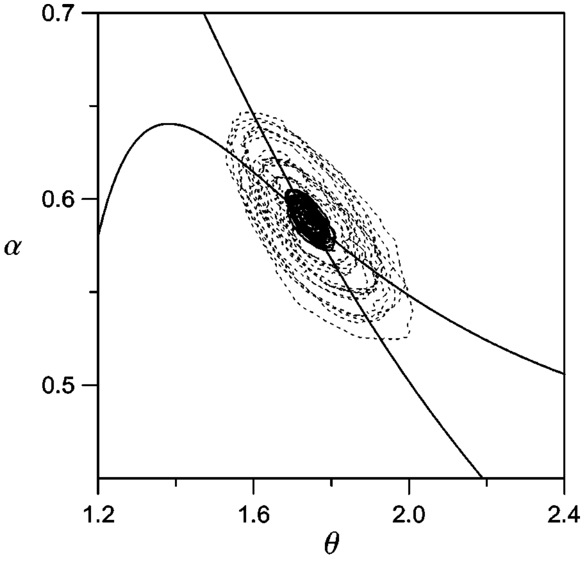

FIG. 2. Stochastic trajectories on the phase plane obtained from simulations of the master equation (31) for the following values of the parameters: $\varepsilon=5.0$, $\eta=0.04$, $c_1=0.0018$, $c_2=0.0036$, and $q=21.0$. At these values of the parameters the system is just below the supercritical Hopf bifurcation. Thin dashed line—$N=100\,000$ particles, the continuous line—$N=1\,000\,000$ particles. Thick continuous lines—the nullclines of the system.

Figure 2 shows the trajectories in the phase space obtained from simulations of the master equation for two systems containing 100 000 and 1 000 000 particles at $q=21.0$. These systems are very close to, but below the supercritical Hopf bifurcation. Similarly, Fig. 3 gives the results obtained for the corresponding systems at $q=22.5$. In this case the systems are above the bifurcation. The focus becomes unstable and SLC appears. For the smaller particle number, the stochastic trajectories below and above the bifurcation are very similar in Figs. 2 and 3, respectively. It is

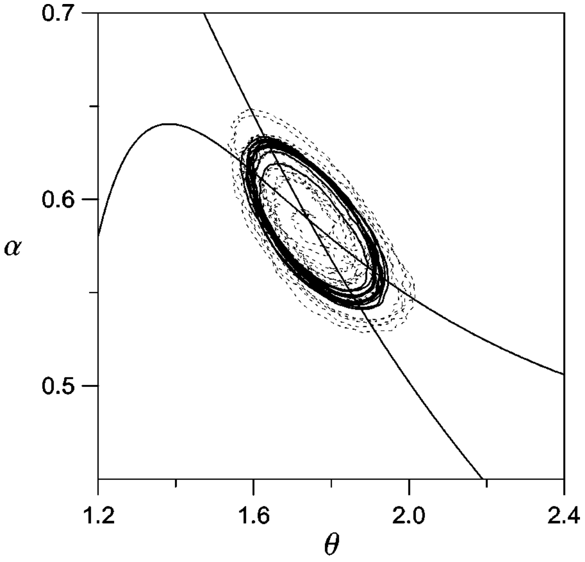

FIG. 3. Same as in Fig. 2 but $q=22.5$. The system is just above the supercritical Hopf bifurcation.

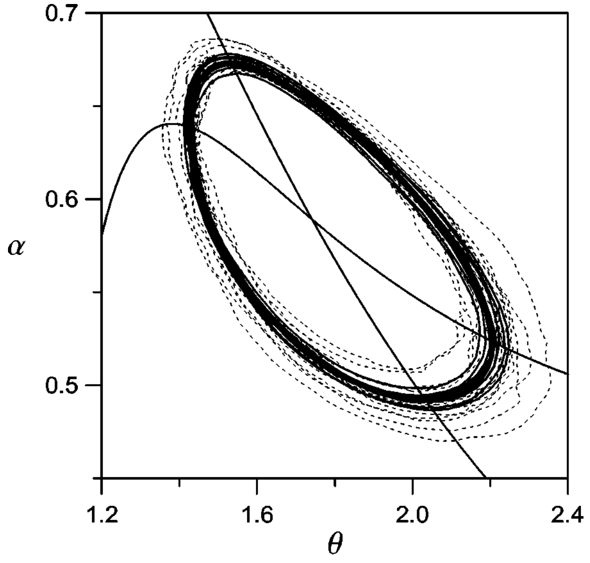

FIG. 4. Same as in Fig. 2 but $q=25.0$. The system is further from the supercritical Hopf bifurcation as compared with Fig. 3.

difficult to determine on the basis of the stochastic evolutions if the system is below or above the supercritical Hopf bifurcation. Close to this bifurcation, the dispersion of the stochastic trajectories around the deterministic attractors is large, because the Liapunov exponents then become small and the attraction towards the asymptotic solutions is weak. Rough estimations based on the Fokker-Planck equation show that the dispersion of stochastic trajectories around the deterministic solution is scaled by $1/|\mathrm{Re}(\lambda)|$, where λ is the eigenvalue of the linearized kinetic equations. Simultaneously, the size of SLC grows from zero and just above the supercritical Hopf bifurcation it is relatively small. Due to these two factors, for the systems with small particle number the magnitude of fluctuations is comparable to the size of the deterministic limit cycle. As the particle number in the system is increased, the fluctuations are diminished and the stochastic trajectories get closer to the deterministic attractors. Accordingly, Figs. 2 and 3 show that for $N=1\,000\,000$ the stochastic solutions are different below and above the bifurcation: they are either contained in a small region around SF or form a narrow ring around SLC. For values of q further from the bifurcation value q_{cr}, the attractors are stronger and the dispersion of the stochastic results is weaker. Figure 4 shows the trajectories in the phase space for $q=25.0$. In this case the system is above the Hopf bifurcation, but it is more distant from the bifurcation than the system presented in Fig. 3. For the same particle numbers as in Fig. 3, the stochastic solutions are stronger focused around the deterministic SLC, and already for $N=100\,000$ the stochastic trajectory forms a ring, corresponding to SLC as the asymptotic solution.

B. Subcritical Hopf bifurcation

Above the subcritical Hopf bifurcation the system has two deterministic attractors: SF and SLC which are separated by ULC. If the magnitude of fluctuations is sufficient, then in stochastic simulations one can observe transitions of the system between these two attractors which show very different dynamical behaviors. For studies of the subcritical Hopf bifurcation, we select the following values of the parameters: $c_1=0.0018$ and $c_2=0.0085$. At these values (and $\varepsilon=5.0$, $\eta=0.04$) the stationary state is located at $\alpha_\infty=0.470\,823\,867\,584\,482\,95$ and $\theta_\infty=3.309\,998\,403\,073\,369\,1$. The change of the stability from SF to UF occurs at $q_{cr}\simeq 266.5$. At this value of q the value of α_3 is positive, which means that for lower values of the bifurcation parameter, SF coexists with SLC, and ULC separates the basins of their attraction. Figure 5 shows the stochastic trajectory at $q=210.0$ for $N=50\,000$ particles. ULC and SLC are also shown. The value of the bifurcation parameter is not too far from its critical value. Figure 6 shows the time dependence of the concentration α obtained from the stochastic simulation of the system. This dependence is very similar to intermittent oscillations observed in deterministic chaotic dynamical systems [21]. In order to characterize them, we construct the Poincaré section of the stochastic trajectory on the phase plane at the straight line of fixed temperature $\theta=\theta_\infty$. The points of intersection, which the trajectory passes going from the left to the right, are only taken into account. The return map constructed from the Poincaré section is depicted in Fig. 7. The big squares show the values of α_∞ at SF and SLC, whereas the big cross indicates ULC. They are positioned on the diagonal and correspond to fixed points for a map of the deterministic system. The return map obtained from the stochastic trajectory shows the specific effect of fluctuations. In Fig. 7, most of the iterated points in the return map are concentrated around the fixed points corresponding to SF or SLC. However, the points far above (below) the diagonal are also seen. These

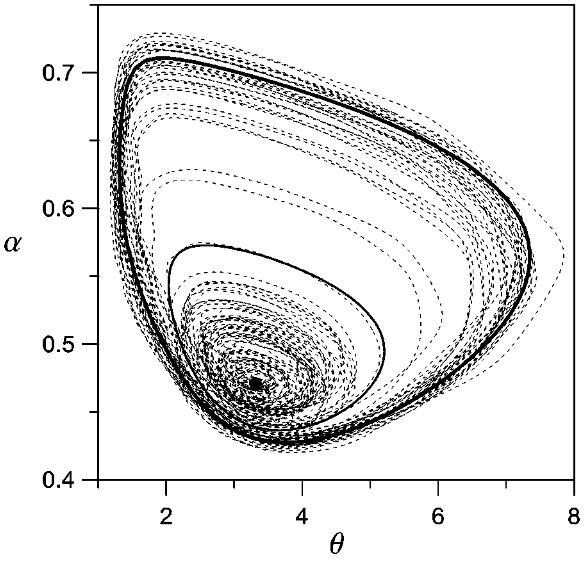

FIG. 5. Stochastic trajectory (the dashed line) on the phase plane obtained from simulations of the system ($N=50\,000$) for the following values of the parameters: $\varepsilon=5.0$, $\eta=0.04$, $c_1=0.0018$, $c_2=0.0085$, and $q=210.0$. At these values of the parameters the system is above the subcritical Hopf bifurcation. The deterministic stable limit cycle and focus are shown by the thick closed curve and the big point, respectively, and the unstable limit cycle is shown by the thin closed curve.

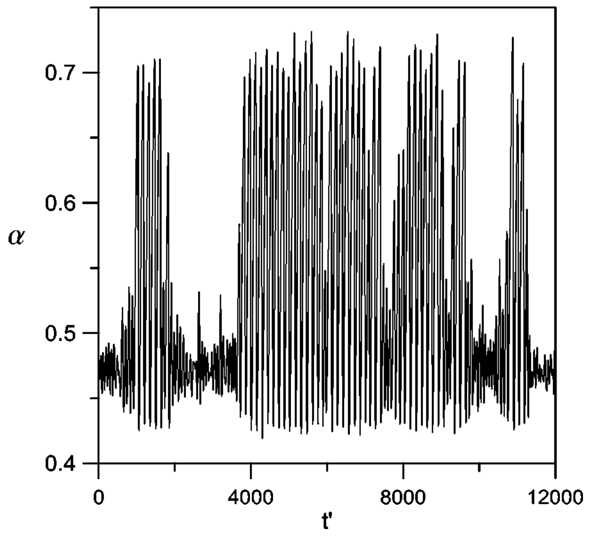

FIG. 6. Time dependence of the concentration α obtained from simulations of the system with the parameters same as in Fig. 5.

points correspond to transitions from the basin of attraction of SF (SLC) to the basin of attraction of SLC (SF).

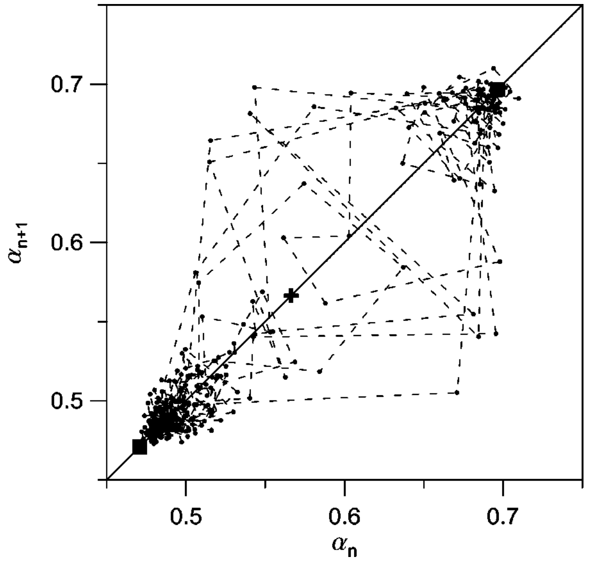

FIG. 7. Return map obtained from the Poincaré section of the stochastic trajectories depicted in Fig. 5. The sections were calculated for crossings with the line of fixed temperature $\theta_s = 3.309\,998\,403\,1$ when the trajectory intersects the line going from lower to higher temperatures. The big squares show the values of α corresponding to the stable focus and the stable limit cycle, whereas the big cross—the unstable limit cycle. The small points far and above (below) the diagonal correspond to transition from the basin of attraction of the stable focus (the stable limit cycle) to the basin of attraction of the stable limit cycle (the stable focus).

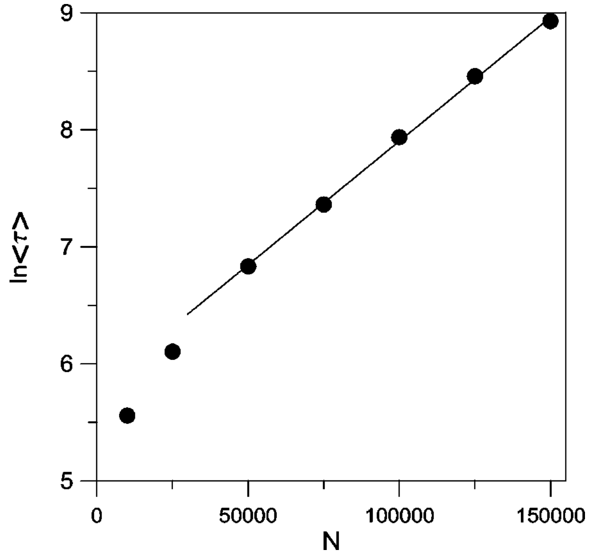

FIG. 8. The mean first passage time $\langle \tau \rangle$ from the basin of attraction of the stable focus to the basin of attraction of the stable limit cycle as a function of the total number of particles N. The straight line shows the linear fit to the results of the simulations for $N \geqslant 50\,000$.

The transitions between the basins of attraction are extremely sensitive to the magnitude of an effective barrier between the attractors. There are two main factors which determine this barrier. One of them is the ratio of deterministic dynamics to strength of fluctuations. This factor depends on the total number of particles N because the dispersion of fluctuations is inversely proportional to the size of the system. The probability of transitions may be characterized by the mean first passage time from one basin of attraction to the other one. In Fig. 8 we show the mean first passage time $\langle \tau \rangle$ from the basin of attraction of SF to the basin of attraction of SLC as a function of the number of particles N. In order to eliminate the possibility of "recrossing" of ULC during the transition, we have assumed that a trajectory had reached the basin of attraction of SLC only if it had crossed the vertical line $\theta = \theta_\infty$ above the point $\alpha = 0.62$, which is located outside of ULC. The mean first passage time has been calculated from several hundred independent runs for small N and about 100 runs for large N. Fig. 8 shows that $\langle \tau \rangle$ strongly depends on particle number N and for large N this dependence can be fitted by the exponential function.

The second factor determining the barrier is the distance in the phase space between an attractor (from which the system escapes) and an unstable state. When this distance increases, the mean first passage time rapidly grows. The distance separating SF and ULC in our system is a function of q. This distance is maximal at $q = q_{bf}$, at which the subcritical Hopf bifurcation occurs, and SLC and ULC appear. It decreases with increasing q and approaches zero at q_{cr}, when ULC collapses to SF. Figure 9 shows the influence of q on the mean first passage time $\langle \tau \rangle$ (calculated like in Fig. 8).

VI. DISCUSSION

The model presented in this paper should be treated as a simplification of real thermochemical systems. It could be useful as a tool in studies of the influence of fluctuations on the dynamics of complex chemical systems with exothermic reactions. Appropriate choice of the parameters allows us to obtain various dynamical regimes including coexistence of more than two attractors. The values of the parameters used

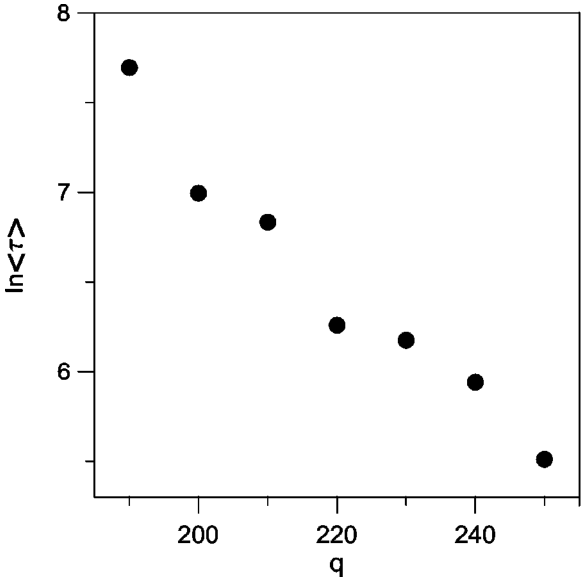

FIG. 9. The mean first passage time $\langle \tau \rangle$ from the basin of attraction of the stable focus to the basin of attraction of the stable limit cycle as a function of the bifurcation parameter q.

in the present paper are realistic [22,23]. The dimensionless activation energy ε must be greater than 4 in order to assure the N-shaped nullcline for temperature. Such values are often met in real systems. The value $\varepsilon = 5$ assumed in this paper is convenient, if one plans an extension of this work by applying microscopic simulations of the system. The values of dimensionless reaction heat are also typical for weak exothermic ($q \approx 20$) and strong exothermic ($q \approx 200$) reactions. The assumed concentration of the catalyst is an order lower than the concentrations of the reagents.

The strongest influence of fluctuations can be expected for systems which are close to a bifurcation. We study the specific effects appearing in these conditions using the master equation approach, which is the most direct way to study the influence of internal fluctuations. The other way is to use the Langevin approach, in which deterministic equations are supplemented by noise terms. The Langevin method is convenient to study the influence of external noise. For the description of the effect of internal fluctuations it may be used only if the magnitude of random forces is related to the level of internal fluctuations.

Our simulations show that close to the supercritical Hopf bifurcation it is very difficult (if possible at all) to decide whether the system is below or above the bifurcation. We illustrate this uncertainty for the system containing relatively small number of particles, but such a situation can appear in macroscopic systems as well, if they are sufficiently close to the Hopf bifurcation [24].

Close to the subcritical Hopf bifurcation, when two attractors (the stable focus and the stable limit cycle) coexist, fluctuations are able to switch the trajectory of the system from one basin of attraction to the other one. The typical behavior representing such transitions is shown in Fig. 6. The interlacement of small and large amplitude oscillations is the consequence of fluctuations and it should be distinguished from the intermittence observed in deterministic chaotic dynamical systems.

Rigorous analytical results for the mean first passage time are not available for systems described by many variables. It has been proven that $\langle \tau \rangle$ can be obtained from the stationary solution of the master equation [25], but this result does not allow us to obtain an analytical expression for $\langle \tau \rangle$ because of the integrodifferential form of Eq. (30). However, some theoretical predictions for multivariable systems can be based on the rigorous results for one-variable systems. The analytical expression for the mean first passage time for one-variable systems [2,26,27] can be derived from the Fokker-Planck equation, obtained from the expansion of the master equation for large systems [1,3]. This result shows the feature [2,26] that the mean first passage time depends exponentially on the magnitude of an effective activation barrier between the attractors. Similarly, as in physical systems with potential, this activation barrier may be calculated by integration of the "chemical force" along a path from an attractor to an unstable state. In chemical systems, the role of force plays the ratio of the reaction rate to the noise strength, which is one factor determining the barrier height. The second factor is the length of the integration interval in the phase space from the attractor (from which a system escapes) to the unstable state. Although such potential cannot be introduced rigorously in dissipative, multivariable systems, the asymptotic results for the weak-noise limit indicate that basic properties of transitions in one-variable systems can also be found in dissipative, multidimensional bistable systems in which two attractors are separated by the saddle point [28–32]. In such transitions stochastic trajectories pass through the region around the saddle point, which is related to a minimum of the activation barrier. This property cannot be directly extended to our system, in which no saddle point exists, and the trajectories must cross the unstable limit cycle.

However, the description of the stochastic transitions through the unstable limit cycle can be simplified in the following way. If the system circulates around the stable focus and inside the unstable limit cycle, its dynamics can be treated approximately as a deterministic drift along the cycle and a relatively slow diffusive motion in the direction perpendicular to the cycle. Following this approximation, one could then describe the transitions of trajectories across the unstable limit cycle as the one-dimensional stochastic dynamics through a potential barrier [33]. On the basis of the theoretical results for one-variable systems [28–33], one can expect that the transitions occur in the vicinity of the point of closest approach between the stable focus and the unstable limit cycle. Moreover, in this region the density of circulating trajectories is the highest, which shows that the vector field normal to the unstable limit cycle is the weakest and this property enhanced the weakening of the apparent potential barrier in this direction. Figure 5 indeed shows that the transitions occur effectively only if the stochastic trajectory remains in the region of the closest approach between the stable focus and the unstable limit cycles on the phase plane (θ, α). The minimal distance between these states is a function of the bifurcation parameter q, and Fig. 9 confirms that $\langle \tau \rangle$ depends strongly on q.

Due to circulation of the stochastic trajectory the height of the one-dimensional barrier changes periodically in time. The transitions are effective only in the region close to the minimal distance, where the barrier is smallest. Therefore, one can expect that the transition probability changes periodically in time [33].

The exponential factor including the effective barrier becomes many orders of magnitude smaller if the system is close to the bifurcations, which means that the unstable limit cycle and the attractor (the stable focus or the stable limit cycle) remain still relatively close. In these conditions the transitions from one basin of attraction to another one can appear not only in the small systems discussed above, but even in macroscopic systems.

In the present paper we limit ourselves to the case of one intersection point of the nullclines. The nullcline for θ can be approximated by a polynomial of the third degree. For planar vector fields described by polynomials of the third degree, for the codimension 12 problem, the number of possible limit cycles (attracting or repelling), which can appear after a bifurcation is limited from below and according to the recently proven theorem [34] is not less than 11.

[1] G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977).

[2] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1985).

[3] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1987).

[4] F. Baras and M. Malek Mansour, Adv. Chem. Phys. **100**, 393 (1997).

[5] B. V. Vol’ter and I. Ye. Salnikov, *Modeling and Optimization of Catalytic Processes* (Nauka, Moscow, 1965) (in Russian).

[6] D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics* (Plenum Press, New York, 1969).

[7] P. Gray, Ber. Bunsenges. Phys. Chem. **84**, 309 (1980).

[8] A. L. Kawczyński and B. Nowakowski, Pol. J. Chem. **70**, 1468 (1996).

[9] A. L. Kawczyński, J. Gorecki, and B. Nowakowski, J. Phys. Chem. A **102**, 7113 (1998).

[10] B. Nowakowski, J. Gorecki, and A. L. Kawczyński, J. Phys. Chem. A **102**, 7250 (1998).

[11] T. Wilhelm and R. Heinrich, J. Math. Chem. **17**, 1 (1995).

[12] A. L. Kawczyński and J. Gorecki, J. Phys. Chem. **96**, 1060 (1992).

[13] A. L. Kawczyński and J. Gorecki, J. Phys. Chem. **97**, 10 358 (1993).

[14] J. Gorecki and A. L. Kawczyński, J. Phys. Chem. **100**, 19 371 (1996).

[15] P. H. Richter, I. Procaccia, and J. Ross, Adv. Chem. Phys. **43**, 217 (1980).

[16] B. Nowakowski and A. Lemarchand, Phys. Rev. E **64**, 061108 (2001).

[17] B. Nowakowski and A. Lemarchand, Physica A **311**, 80 (2002).

[18] N. N. Bautin, *Behaviour of Dynamic Systems in the Neighborhood of Boundaries of Stability* (State Tekhnika, Moscow, 1949) (in Russian).

[19] A. A. Andronov, E. A. Leontovitch, I. I. Gordon, and A. G. Maier, *Bifurcation Theory of Dynamic System on the Plane* (Wiley, New York, 1972).

[20] D. T. Gillespie, J. Comput. Phys. **22**, 403 (1976).

[21] H. G. Schuster, *Deterministic Chaos* (Physik-Verlag, Weinheim, 1984).

[22] Ya. B. Zeldovitch, G. I. Barenblatt, V. B. Librovitch, and G. M. Makhviladze, *Mathematical Theory of Combustion and Explosion* (Nauka, Moscow, 1980) (in Russian).

[23] J. F. Griffiths, in *Oscillations and Traveling Waves in Chemical Systems*, edited by R. J. Field and M. Burger (Wiley, New York, 1985).

[24] H. M. Hastings, R. J. Field, and S. G. Sobel, J. Chem. Phys. **119**, 3291 (2003).

[25] P. Reimann, G. J. Schmid, and P. Hänggi, Phys. Rev. E **60**, R1 (1999).

[26] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).

[27] N. S. Goel and N. Richter-Dyn, *Stochastic Models in Biology* (Academic, New York, 1974).

[28] W. Ebeling, H. Herzel, and E. E. Sel’kov, Stud. Biophys. **98**, 147 (1983).

[29] R. S. Maier and D. L. Stein, Phys. Rev. E **48**, 931 (1993).

[30] R. S. Maier and D. L. Stein, SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. **57**, 752 (1997).

[31] Z. Schuss and A. Spivak, Chem. Phys. **235**, 227 (1998).

[32] Z. Schuss and A. Spivak, SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. **62**, 1698 (2002).

[33] R. S. Maier and D. L. Stein, Phys. Rev. Lett. **77**, 4860 (1996).

[34] H. Żołądek, Nonlinearity **8**, 843 (1995).