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Canards Oscillations, Noise-Induced Splitting of Cycles and Transition to Chaos in Thermochemical Kinetics

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Abstract: We study how noise generates complex oscillatory regimes in the nonlinear thermochemical kinetics. In this study, the basic mathematical Zeldovich–Semenov model is used as a deterministic skeleton. We investigate the stochastic version of this model that takes into account multiplicative random fluctuations of temperature. In our study, we use direct numerical simulation of stochastic solutions with the subsequent statistical analysis of probability densities and Lyapunov exponents. In the parametric zone of Canard cycles, qualitative effects caused by random noise are identified and investigated. Stochastic *P*-bifurcations corresponding to noise-induced splitting of Canard oscillations are parametrically described. It is shown that such *P*-bifurcations are associated with splitting of both amplitudes and frequencies. Studying stochastic *D*-bifurcations, we localized the rather narrow parameter zone where transitions from order to chaos occur.

Keywords: thermochemical oscillations; Canard cycles; stochastic bifurcations; stochastic splitting; chaos

MSC: 37H10; 37H20

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1. Introduction

Complex oscillatory regimes are observed in many dynamical systems, both natural and engineering [1–8]. Particular attention is paid to the investigation of oscillatory processes, the analysis of the mechanisms of their occurrence, and the study of their properties in thermochemical kinetics [9–14]. Mathematical models of thermochemistry are characterized by strong nonlinearity, which gives rise to a wide variety of oscillatory regimes. Significant progress has been made in the study of these regimes due to the application of mathematical methods of the bifurcations theory [1,15,16]. At present, in the study of nonlinear oscillations, along with the classical analytical apparatus, computer modeling and numerical methods are actively used.

In various nonlinear dynamical models, a phenomenon of Canard cycles was recently discovered and now actively studied (see, e.g., [17–23]). Canard cycles are a special kind of self-oscillations which are characterized by the sharp growth of the amplitude under the very small variation of parameters. The present paper aims to study the phenomenon of Canard explosion in thermochemical kinetics. We use the basic Zeldovich–Semenov dynamical model [12] that describes an interaction of the concentration of the reagent and temperature in the reactor. This slow–fast dynamical system models oscillatory regimes in thermochemical kinetics well. In Section 2, we provide a parametric description of the equilibrium and oscillatory regimes of this model. In the parameter zone of Canard cycles, abrupt changes of amplitude and frequency characteristics are discussed.

A key novel subject of this paper is the study of influence of inevitable random disturbances on thermochemical Canard-type oscillations. It should be noted that the constructive role of noise in systems with Canard cycles has attracted the attention of researchers from different fields of science [24–27]. The special sensitivity of the Canard cycles places high demands on the quality of mathematical modeling and numerical methods. In Section 3, we describe a stochastic version of the model, taking into account parametric random disturbances of the temperature. It is shown that even small random disturbances can result in qualitative changes of Canard oscillations. Here, P- and D-bifurcations are investigated. The novelty of this work lies in the study of the phenomenon of stochastic splitting of amplitudes and frequencies for Canard cycles as well as noise-induced transitions from order to chaos in the parameter zone of the Canard explosion.

2. Canard Cycles in the Deterministic System

We consider a conceptual mathematical model of the thermochemical process, which in the deterministic case is defined by the system of two differential equations:

$$\begin{aligned} \dot{x} &= \varphi(x,y) - \frac{x}{D} \\ \delta\dot{y} &= \varphi(x,y) - \tfrac{y}{S} \end{aligned} \tag{1}$$

with the strongly nonlinear interaction function $\varphi(x,y) = (1-x)\exp\left(\frac{y}{1+\beta y}\right)$. This slow–fast system describes dynamics of the slow variable x (concentration) and fast variable y (temperature). Kinetic parameters δ, β, D, and S are positive.

The dynamical model (1) exhibits both equilibrium and oscillatory regimes. Coordinates of equilibria of system (1) can be found from the following equations:

$$Sx = (D + \beta Sx)\ln\frac{x}{D(1-x)}, \qquad y = \frac{Sx}{D}.$$

In this paper, we consider D as a bifurcation parameter. The set of other parameters is given in Table 1, following [12].

Table 1. Set of parameters of the model (1).

$\delta = 0.02$	$\beta = 0.05$	$S = 0.7$

For this set of parameters, the bifurcation diagram of system (1) is shown in Figure 1 versus parameter D. As D passes the Andronov–Hopf bifurcation [28] point $D_* = 0.09256$, the equilibrium loses its stability, and the stable limit cycle is born. In Figure 1, extreme values of x- and y-coordinates of the corresponding cycles are plotted; the unstable equilibrium is shown with dashed lines.

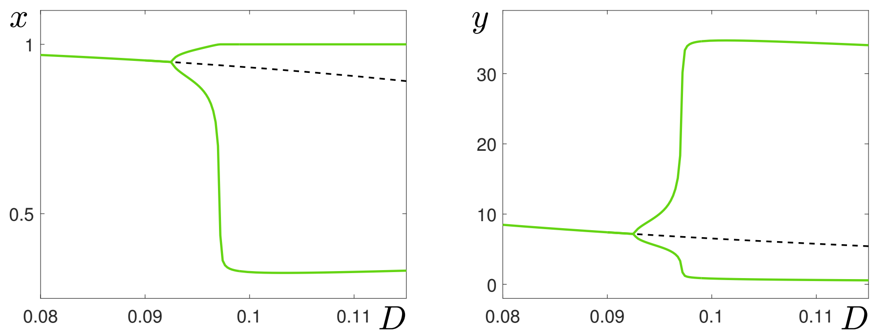

Figure 1. Bifurcation diagram of system (1): extreme values of x- and y-coordinates of the corresponding stable equilibria and cycles (green, solid) and unstable equilibria (black, dashed).

Here, one specific feature should be underlined. As the parameter D in the zone $D > D_*$ increases, the amplitude of self-oscillations, both x and y, grows. However, the growth rate is highly nonuniform: there exists a D-zone where the amplitude sharply jumps. This narrow D-zone is classified as the zone of the Canard explosion [27].

Peculiarities of oscillations in this zone are illustrated in Figure 2. In Figure 2a, three limit cycles are shown. Here, one can see how with small variation in D values from 0.094 to 0.1, the size of the limit cycle changes significantly. Along with geometrical transformations of cycles, the frequency of oscillations also changes. In Figure 2b, it is seen that in the D-zone of the Canard explosion, the period of cycles sharply increases. In Figure 2c–e, by time series, it is shown how the type of oscillations is transformed from quasi-harmonic to relaxation with sharp spikes.

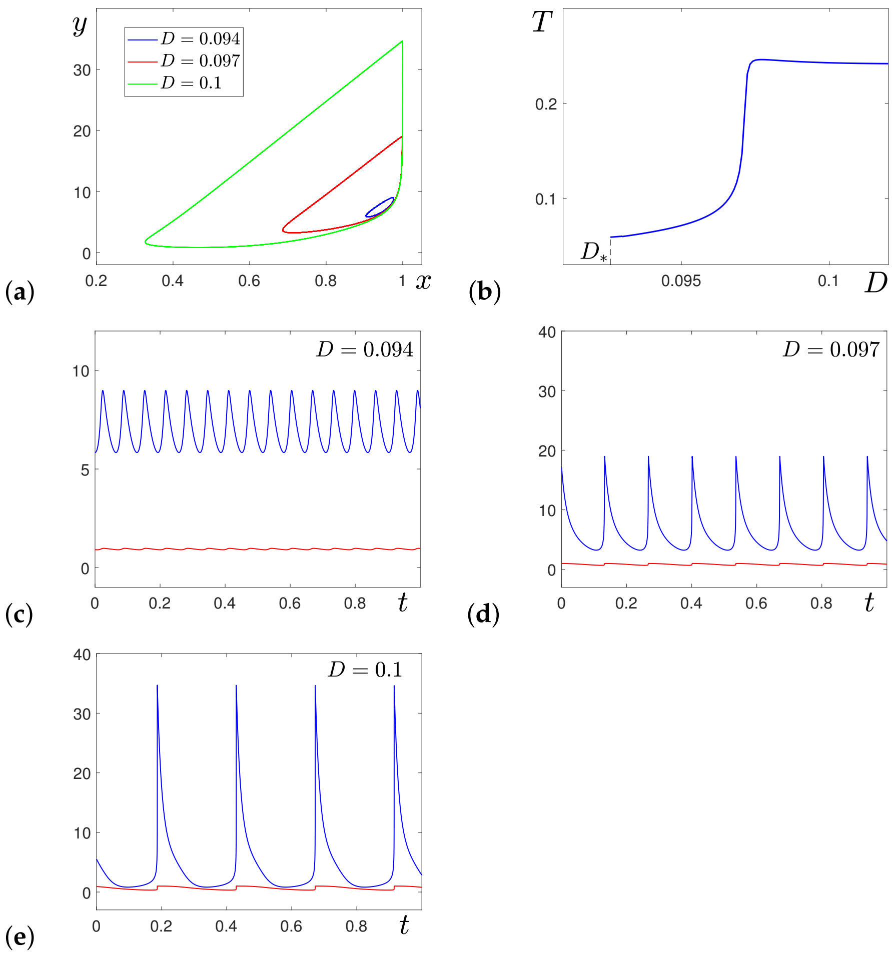

Figure 2. Self-oscillations in the parameter zone of the Canard explosion: (**a**) stable limit cycles; (**b**) period $T(D)$ of oscillations; (**c**–**e**) time series for different values of the parameter D. In time series, x-coordinates are shown in red and y-coordinates are plotted by blue.

In Section 3, we consider a stochastic version of model (1) and qualitative noise-induced transformations of the system dynamics.

3. Noise-Induced Phenomena in the Stochastic Model

Let us consider the impact of random disturbances in model (1). In this paper, we focus on the effects caused by multiplicative fluctuations $\varepsilon y\xi(t)$ in the temperature of the reactor:

$$\begin{aligned} \dot{x} &= \varphi(x,y) - \frac{x}{D} \\ \delta\dot{y} &= \varphi(x,y) - \frac{y}{S} + \varepsilon y\xi(t). \end{aligned} \tag{2}$$

In this stochastic model, $\xi(t)$ is the uncorrelated standard white Gaussian noise with parameters $\mathrm{E}\xi(t) = 0,\ \mathrm{E}\xi(t)\xi(\tau) = \delta(t-\tau)$, and ε is the noise intensity. In stochastic modeling of the solutions of system (2), we will use the standard Euler–Maruyama scheme [29] with the time step 10^{-6}.

Consider how stochastic disturbances impact the Canard cycle with $D = 0.097$. In Figure 3, the phase trajectories and time series of the solutions of system (2), starting at the deterministic limit cycle, are shown for three values of noise intensity.

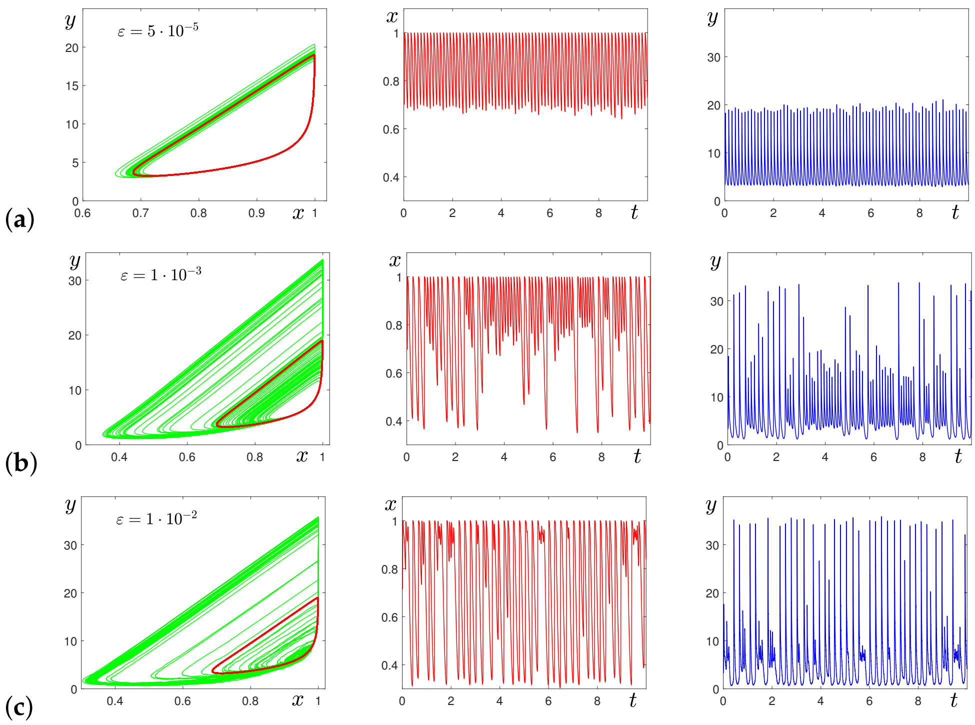

Figure 3. Phase trajectories and time series of system (2) with $D = 0.097$ for (**a**) $\varepsilon = 5 \times 10^{-5}$, (**b**) $\varepsilon = 1 \times 10^{-3}$, and (**c**) $\varepsilon = 1 \times 10^{-2}$.

For weak noise with $\varepsilon = 5 \times 10^{-5}$, random trajectories (green) slightly deviate from the orbit (red) of the deterministic cycle (see Figure 3a, left). It should be noted that the dispersion of random trajectories along the deterministic cycle is highly nonuniform: the dispersion in the "diagonal" part is significant compared with the other part, where the random trajectories practically coincide with the deterministic orbit.

With the increase in ε, the dispersion of random trajectories in the "diagonal" part significantly increases, and the stochastic splitting of the bundle occurs (see Figure 3b for $\varepsilon = 1 \times 10^{-3}$). In the corresponding time series, a mixed-mode oscillatory regime appears: small-amplitude oscillations alternate with the large-amplitude spikes. With a further increase in noise (see Figure 3c for $\varepsilon = 1 \times 10^{-2}$), the splitting becomes more evident, and in this bi-modal oscillatory regime, the portion of large-amplitude spikes grows.

These results of the numerical simulation of the stochastic solutions presented here have an important physical meaning. Indeed, it can be clearly seen how, for certain conditions, real physicochemical processes occurring in a reactor can suddenly, under the influence of even small random perturbations, significantly change the dynamic character, with unexpected temperature and concentration outbreaks.

Note that the parameter value $D = 0.097$ is located in the center of the D-zone of the Canard explosion, where the Canard cycle is extremely sensitive to noise. This is confirmed by Figure 4, where stochastic trajectories (green) and deterministic cycles (red) are shown for $\varepsilon = 1 \times 10^{-3}$ and two neighbor values of D: for $D = 0.094$ (Figure 4a) and $D = 0.1$ (Figure 4b). As can be seen, here, the noise with $\varepsilon = 1 \times 10^{-3}$ does not cause the stochastic splitting as for $D = 0.097$ (compare with Figure 3b).

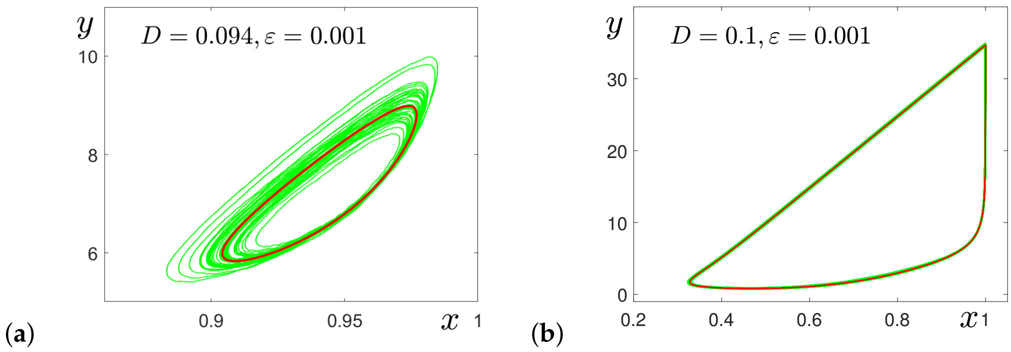

Figure 4. Deterministic limit cycles (red) and random trajectories (green) of stochastic system (2), with $\varepsilon = 0.001$ for (**a**) $D = 0.094$, (**b**) $D = 0.1$.

Let us consider the reasons for the above-described nonuniformity of the dispersion of random trajectories around the Canard cycle. Of course, the Canard cycle, as a whole, is stable. However, separate fragments of the Canard cycle orbits can be locally highly unstable. In Figure 5, we show the deterministic phase trajectories (black) near the lower part of the Canard cycle (red) of system (1) with $D = 0.097$. Here, the nullcline $\dot{x} = 0$ is shown in green, and the nullcline $\dot{y} = 0$ is plotted by blue. The unstable equilibrium (empty circle) is the intersection point of these nullclines.

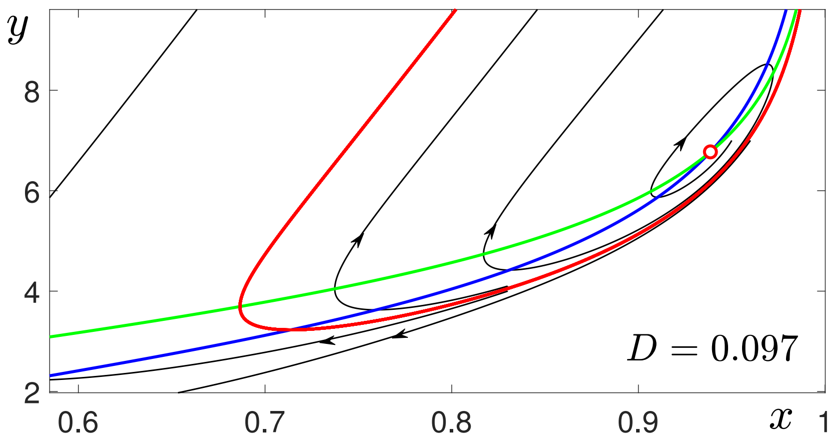

Figure 5. Local instability of the Canard cycle of system (1) with $D = 0.097$: deterministic phase trajectories (black) near the lower part of the Canard cycle (red), nullcline $\dot{x} = 0$ (green), nullcline $\dot{y} = 0$ (blue), and the unstable equilibrium (empty circle).

As can be seen, in the lower part, trajectories move away from the cycle, so this part of the Canard cycle is highly unstable. In the presence of noise, trajectories with even very small deviation from the deterministic cycle in this instability zone scatter in different directions. This results in a sharp increase of their dispersion and splitting of the stochastic bundle.

In more details, the phenomenon of the noise-induced splitting can be studied with the help of statistics. In Figure 6, for stochastic solutions of system (2) with $D = 0.097$, we show the probability density functions $\rho(x)$ of random distributions of x-coordinates of intersection points with the line $L: \; 0.7(x - \bar{x}) + 33(y - \bar{y}) = 0$ for $x < \bar{x}$. Here, $\bar{x} = 0.93858$, $\bar{y} = 6.77328$ are coordinates of the unstable equilibrium.

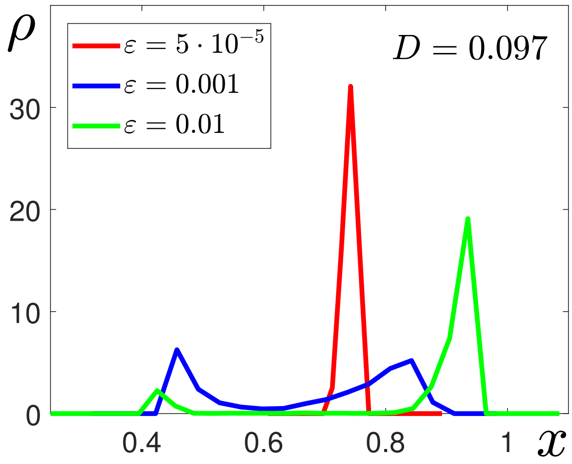

Figure 6. Stochastic splitting of the cycle in system (2) with $D = 0.097$: transformations of the probability density function $\rho(x)$.

For weak noise with $\varepsilon = 5 \times 10^{-5}$, the plot (red) of the function $\rho(x)$ has a narrow high peak corresponding to the unimodal probabilistic distribution in the "diagonal" part of the stochastic bundle. With an increase in noise, the function $\rho(x)$ becomes bimodal. For $\varepsilon = 1 \times 10^{-3}$, one can see two well-separated peaks (blue), justifying the splitting of stochastic oscillations. The left peak characterizes a distribution of large-amplitude oscillations, and the right peak corresponds to small-amplitude oscillations. Such a qualitative transformation of the probability density $\rho(x)$ form from one peak into two peaks can be interpreted as a so-called stochastic phenomenological bifurcation, i.e., a P-bifurcation [30]. With a further increase in the noise intensity, the distance between the peaks increases, and the right peak, corresponding to the low-amplitude oscillations, begins to dominate in the overall distribution (see the green curve in Figure 6 for $\varepsilon = 0.01$).

It is interesting to compare a response to the random forcing for the quasi-harmonic regime with $D = 0.094$ (see Figure 2c) and Canard relaxation cycle (see Figure 2d) with $D = 0.097$. As shown above, noise with intensity $\varepsilon = 0.001$ crucially changes the dynamics of the system with $D = 0.097$ (see Figure 3b), while the stochastically forced cycle for $D = 0.094$ preserves the unimodal form (see Figure 4a). In order to change the system dynamics for $D = 0.094$ qualitatively, it is necessary to apply stronger noise. Such noise-induced transformations are illustrated in Figure 7 by phase trajectories and probability density function $\rho(x)$. In Figure 7a, one can see how noise of intensity $\varepsilon = 0.01$ causes excitement of large-amplitude stochastic oscillations: green random trajectories are located far from the orbit of the unforced deterministic cycle (red).

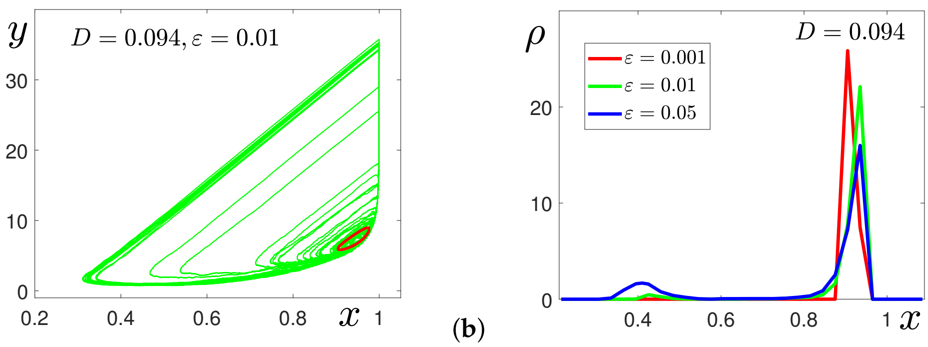

Figure 7. Noise-induced excitement in system (2) with $D = 0.094$: (**a**) phase trajectories of the deterministic (red) and stochastic (green) system; (**b**) probability density function $\rho(x)$ for different values of noise intensity.

Details of changes in the form of probabilistic distributions $\rho(x)$ of amplitudes of generated stochastic oscillations are presented in Figure 7b. For $\varepsilon = 0.001$, the function $\rho(x)$ (red) is unimodal, while for larger noise, a new additional local maximum appears (see green for $\varepsilon = 0.01$ and blue for $\varepsilon = 0.05$). This maximum reflects large-amplitude oscillations induced by noise. With increasing noise, the probability of such oscillations grows. Note that unlike in the case of $D = 0.097$, where noise moves the right peak of $\rho(x)$ (see Figure 6), for $D = 0.094$, this peak corresponding to small-amplitude oscillations does not change its location (see Figure 7b).

Along with the noise transformations of the amplitudes of the cycles, their frequency characteristics also change qualitatively. Let τ_i be the time intervals between successive intersections of random trajectories with the line L. In the absence of noise, $\tau_i \equiv T$, where T is a period of the deterministic cycle. In the presence of noise, τ_i are random variables which can be characterized by the probability density function $\rho(\tau)$. In Figure 8a, plots of $\rho(\tau)$ are shown for three values of the noise intensity. For weak noise $\varepsilon = 0.0001$, the function $\rho(\tau)$ has one peak localized near the period T of the unforced cycle. For larger noise, this unimodal form transforms into a bimodal one: the single peak above T splits into two peaks (see the green curve for $\varepsilon = 0.0003$). After a further increase of noise, distance between two peaks increases, and the weight of the right peak corresponding to large-amplitude oscillations grows (see the blue curve for $\varepsilon = 0.003$). An analogous stochastic P-bifurcation is also observed for $D = 0.094$, but for larger noises.

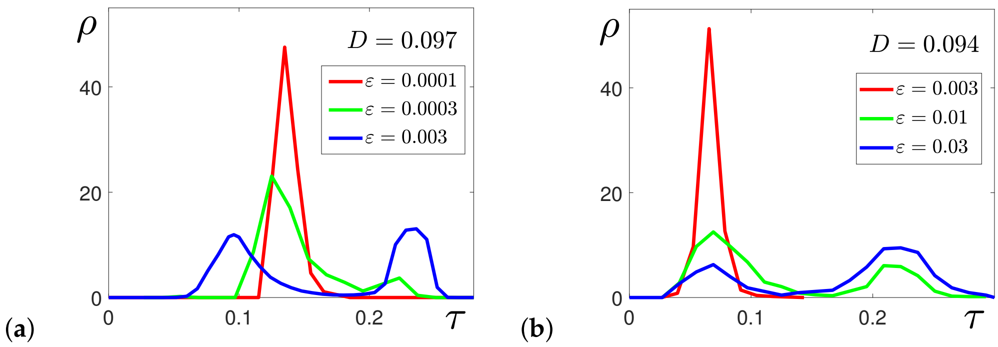

Figure 8. Noise-induced frequency splitting: transformations of the probability density function $\rho(\tau)$ for (**a**) $D = 0.097$ and (**b**) $D = 0.094$.

Let us consider now how noise changes internal dynamic characteristics of stochastic flows in system (2). For quantitative analysis of these changes, we will use the largest Lyapunov exponent Λ. If $\Lambda < 0$, trajectories in the flow converge, and the system dynamics are regular. If $\Lambda > 0$, the trajectories mostly diverge, and the system dynamics are characterized as chaotic.

In Figure 9, we present the results of our analysis of the largest Lyapunov exponents, independent of the parameter D and noise intensity ε. As can be seen in Figure 9a, for $D = 0.0965$ and $D = 0.097$ from the parameter zone of the Canard explosion, under increasing ε, the largest Lyapunov exponent becomes positive. Thus, there is a threshold value of the noise intensity at which the system dynamics become chaotic. Mathematically, such a qualitative transformation is interpreted as stochastic D-bifurcation [30]. In Figure 9a, one can see that the Canard cycle with $D = 0.097$ is much more sensitive to noise: the transition to chaos occurs for smaller value of ε.

More details of this effect of the noise-induced transition to chaos can be extracted from the parametric diagram in Figure 9b, where values of $\Lambda(D, \varepsilon)$ are shown by color. As can be seen, the rather narrow chaotic zone is located in the center of the Canard explosion.

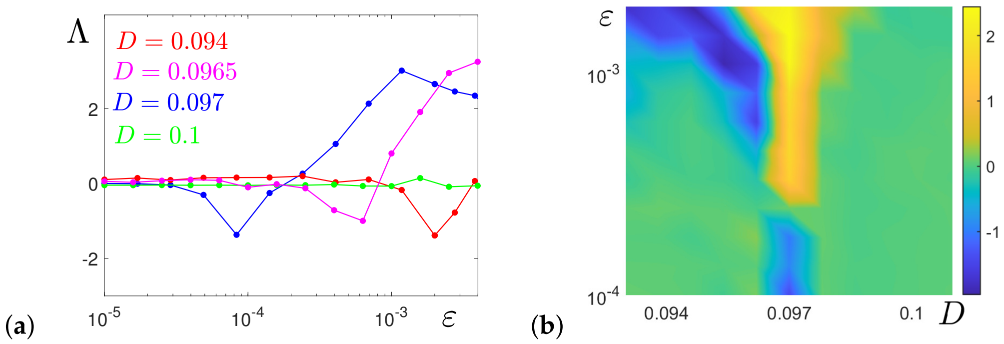

Figure 9. Largest Lyapunov exponent Λ for the stochastic system (2): (**a**) versus parameter ε for different D; (**b**) colored (D, ε)-diagram.

Thus, extremely sensitive Canard cycles in the presence of random perturbations give rise to new oscillatory regimes in thermochemical kinetics with qualitative effects of splitting and transitions to chaos.

4. Conclusions

This paper was devoted to the problem of analyzing the underlying mechanisms of the generation of complex oscillatory regimes in the nonlinear thermochemical kinetics. In our study, we used the conceptual mathematical Zeldovich–Semenov model, which describes the dynamics of the concentration and temperature in the reactor. A parameter zone of Canard cycles was identified and studied. It was shown that these cycles are highly sensitive to even small variations of parameters, both deterministic and stochastic. In this paper, we studied an impact of parametric stochastic disturbances in the temperature of the reactor. Stochastic P- and D-bifurcations of Canard cycles were found and investigated. For the model under consideration, P-bifurcations reflect the phenomenon of noise-induced splitting of unimodal oscillations into bimodal ones. It was shown that, as a result of such a P-bifurcation, both amplitudes and frequencies of stochastic oscillations split under increasing noise. The stochastic D-bifurcations, analyzed by the largest Lyapunov exponents, are connected with the transition from order to chaos in the rather narrow parameter zone of the Canard explosion.

Author Contributions: Conceptualization, I.B. and L.R.; methodology, I.B.; software, I.B., G.I. and D.M.; writing—I.B. and L.R. All authors have read and agreed to the published version of the manuscript.

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