CANARDS, BLACK SWANS AND CONTROL OF CHEMICAL REACTIONS

By

Vladimir Sobolev

and

Elena Shchepakina

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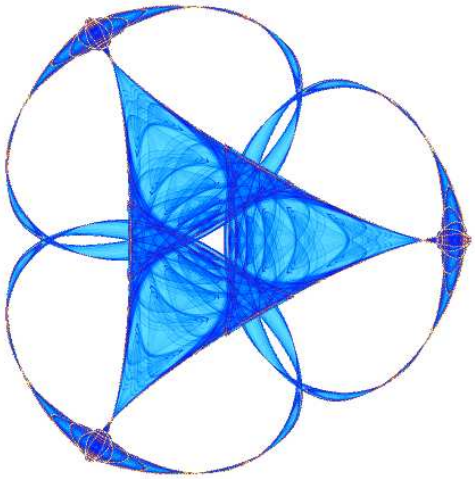


INSTITUTE FOR MATHEMATICS AND ITS APPLICATIONS

UNIVERSITY OF MINNESOTA

400 Lind Hall

207 Church Street S.E.

Minneapolis, Minnesota 55455–0436

Phone: 612-624-6066 Fax: 612-626-7370

URL: http://www.ima.umn.edu

Canards, Black Swans and Control of Chemical Reactions

V. Sobolev and E. Shchepakina
Department of Differential Equations and Control Theory
Samara State University, P.O.B. 10902
Samara (443099), Russia
e-mail: hsablem@yahoo.com

Abstract

The work is devoted to the investigation of critical phenomena using the geometric theory of singular perturbations, namely, the black swans and canards techniques. The interest to critical phenomena is occasioned by not only of safety reason, in many cases namely the critical regime is the most effective in technological processes. The sense of criticality here is as follows. The critical regime corresponds to chemical reaction separating the domains of self-accelerating reactions and domains of slow reactions. Recall that a canard (or French duck) is a trajectory of a singularly perturbed system of differential equations if it, at first, follows a stable slow integral manifold, and then an unstable one. In both cases the distances travelled are more than infinitesimally small. The slow integral manifold is defined as an invariant surface of slow motions. A canard trajectory may be considered as the result of gluing stable (attractive) and unstable (repulsive) slow integral manifolds at one point of the breakdown surface, due to the availability of an additional scalar parameter in the differential system. If we take an additional function of a vector variable parameterizing the breakdown surface, we can glue the stable and unstable slow integral manifolds at all points of the breakdown surface simultaneously. As a result we obtain the continuous stable/unstable integral surface or black swan. It is possible to consider the gluing function as a special kind of incomplete feedback control. This guarantees the safety of chemical regimes, even with perturbations, during a chemical process.

Keywords: canards, black swans, invariant manifolds, singular perturbations, thermal explosion, chemical kinetics.

MSC 2000: 34C45, 34D15, 37D10, 80A30

Contents

Chapter 1

Introduction

The problem of evaluation of critical regimes thought of as regimes separating the regions of explosive and nonexplosive ways of chemical reactions is the main mathematical problem of the thermal explosion theory. The interest to critical phenomena is occasioned by not only of safety reason, in many cases namely the critical regime is the most effective in technological processes. The sense of criticality here is as follows. The critical regime corresponds to chemical reaction separating the domains of self–accelerating reactions and domains of slow reactions.

Investigation of critical phenomena of the thermal explosion theory was hold by N. N. Semenov [31], Ya. B. Zeldovich [50], D. A. Frank-Kamenetsky [9], O. M. Todes and P. V. Melent'ev [44], A. G. Merzhanov and F. I. Dubovitsky [24, 25], B. Gray [16] *et al.* Because of considerable difference between velocities of thermal and concentrational changes, singularly perturbed systems [27] of differential equations serve as mathematical models of such problems. But in the above works the authors restrict their consideration to the study of zero order approximation. It does not let them explain the strong parametric sensitivity of this problem as well as to examine the transformation of solutions in the vicinity of the limit of self–ignition.

The important part of the paper is dedicated to modelling of critical regimes of combustion and critical values of control parameters using the new mathematical methods based on the theory of "canards" [5]. In a majority of the papers devoted to canards the term "canard" is associated with the periodic trajectories [6]. In our work *a canard* is a trajectory of a singularly perturbed system of differential equations if it follows at first a stable invariant manifold, and then an unstable one. In both cases the distances travelled are not infinitesimally small. It should be noted that a canard may be considered as a result of gluing stable (attractive) and unstable (repelling) slow invariant manifolds at one point of the breakdown surface due to the availability of an additional scalar parameter in the differential system. We shall use canards as *separating solutions* corresponding to the critical regimes of chemical reactions. This approach was proposed for the first time in [13, 14] and was then applied in [15, 35, 40, 41]. This approach permits to work out the algorithms of asymptotic representations of the critical values of the parameter of initial conditions and to describe the transfer regimes. A canard trajectory is considered as the result of gluing stable (attractive) and unstable (repulsive) slow integral manifolds at one point of the breakdown surface, due to the availability of an additional control parameter in the differential system. If we take an additional function of a vector variable parameterizing the

breakdown surface, we can glue the stable (attractive) and unstable (repulsive) slow integral manifolds at all points of the breakdown curve at the same time. As a result we obtain the continuous stable/unstable (attractive/repulsive) integral surface or *black swan* [33, 34]. Such surfaces are considered as a multidimensional analogue of the notion of a canard. It is possible to consider the gluing function as a special kind of partial feedback control. This guarantees the safety of chemical regimes, even with perturbations, during a chemical process.

1.1 Singular perturbations and canards

The main object of our consideration is the following singularly perturbed system

$$\frac{dx}{dt} = f(x, y, \varepsilon), \tag{1.1}$$

$$\varepsilon\frac{dy}{dt} = g(x, y, \alpha, \varepsilon), \tag{1.2}$$

where ε is a small positive parameter, α is a scalar parameter, y is a scalar variable, x is a vector of dimension n. The case of the vector variable y can be considered also.

Recall (see [26]) that the slow surface S (or S_α) of system (1.9), (1.10) is the surface described by the equation

$$g(x, y, \alpha, 0) = 0. \tag{1.3}$$

Let $y = \phi(x, \alpha)$ be an isolated solution of equation (1.10). We call the subset S^s_α (S^u_α) of S defined by

$$\frac{\partial g}{\partial y}(x, \phi(x, \alpha), \alpha, 0) < 0 \ \ (> 0)$$

the stable (unstable) subset of S_α.

The set of irregular points (critical points of the projection of the slow surface onto the base) defined by

$$\frac{\partial g}{\partial y}(x, \phi(x, \alpha), \alpha, 0) = 0$$

on S_α is called the breakdown surface. Its dimension is equal to $n - 1$. At all points of this surface the linearization of the fast subsystem (1.10) in a fiber has a zero eigenvalue [1].

In an ε–neighborhood of S^s_α (S^u_α) there exists a stable (unstable) slow invariant manifold $S^s_{\alpha,\varepsilon}$ ($S^u_{\alpha,\varepsilon}$). This means that the slow surface is an approximation of slow invariant manifold (for $\varepsilon = 0$) [39].

The availability of the additional scalar parameter α provides the possibility of gluing the stable and unstable invariant manifolds at one point of the breakdown surface. The canard trajectory passes through this point.

It should be noted that in the early papers devoted to canards in the case $\dim x = 1$, the existence of a unique canard corresponding to a unique value of the parameter $\alpha = \alpha^*$ was stated (more precisely, the "canard" value of parameter α^* exists on an interval of order $O(e^{-1/\varepsilon})$). But in the case $\dim x > 1$ another picture is beginning to emerge. It was shown that a one–parameter family of canards exists [40].

1.2 Examples

Example 1

Consider the planar system

$$\begin{aligned} \dot{x} &= 1 - y, \\ \varepsilon\dot{y} &= y - x, \end{aligned} \tag{1.4}$$

for some small positive parameter ε on $t \geq 0$.

Setting $\varepsilon = 0$, we obtain the *degenerate problem*:

$$\begin{aligned} \dot{x} &= y, \\ 0 &= y - x. \end{aligned} \tag{1.5}$$

The *slow curve* is described by the equation

$$0 = y - x.$$

The solution to (1.4) is

$$x(t) = x_{slow} + x_{fast}, \quad y(t) = y_{slow} + y_{fast},$$

where

$$\begin{aligned} x_{slow} = C_1 e^{-\lambda_1 t} + 1, \quad y_{slow} = C_1\lambda_1 e^{-\lambda_1 t} + 1, \\ x_{fast} = C_2 e^{\lambda_2 t}, \quad y_{fast} = C_2\lambda_2 e^{\lambda_2 t}, \end{aligned}$$

and λ_1, λ_2 are given by

$$\lambda_1 = \frac{-1 + \sqrt{1 + 4\varepsilon}}{2\varepsilon} = 1 - \varepsilon + O(\varepsilon^2), \quad \lambda_2 = \frac{1 + \sqrt{1 + 4\varepsilon}}{2\varepsilon} = \varepsilon^{-1}(1 + \varepsilon + O(\varepsilon^2)),$$

as $\varepsilon \to 0$, and C_1, C_2 are arbitrary constants.

An important role is played by the the straight line

$$y = \lambda_1 x + \mu, \quad \mu = \frac{\varepsilon\lambda_1}{1 + \varepsilon\lambda_1} = 1 - \lambda_1 = \varepsilon + O(\varepsilon^2).$$

This line is not a trajectory, it consists of three trajectories

$$y = \lambda_1 x + \mu, \ x < 1; \quad x = y = 1; \quad y = \lambda_1 x + \mu, \ x > 1.$$

Using the asymptotic representations $\lambda_1 = 1 - \varepsilon + O(\varepsilon^2)$, $\lambda_2 = \varepsilon^{-1}(1 + \varepsilon + O(\varepsilon^2))$ as $\varepsilon \to 0$, it is easy to see that the line $y = \lambda_1 x + \mu$ is *repulsive*.

It is possible to say that $y = \lambda_1 x + \mu$ is the *slow invariant manifold* and it plays the role of *a watershed line* in the system under consideration. Fig. 1.1 demonstrates the behaviour of trajectories.

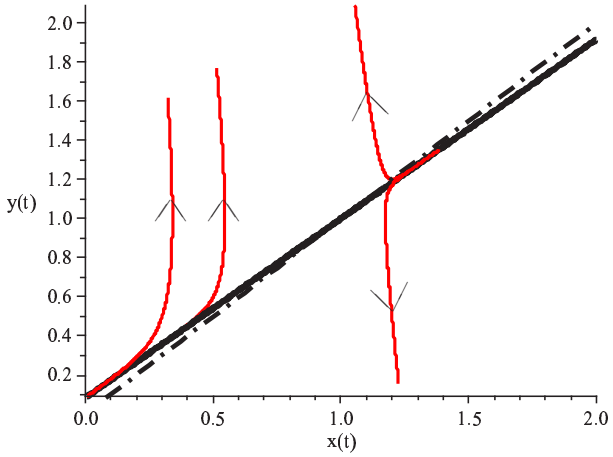


Figure 1.1: The slow curve (dash-dotted straight line), and trajectories (red lines) running away from the slow invariant manifold (black solid straight line)($\varepsilon = 0.1$).

Example 2

As the simplest system with a canard we propose

$$\dot{x} = 1, \;\; \varepsilon\dot{y} = 2xy + \alpha. \tag{1.6}$$

It is clear that for $\alpha = 0$, the trajectory $y = 0$ is a canard, and it plays the role of a watershed line.

Example 3

For example, in the system

$$\frac{dx}{dt} = 1, \qquad \varepsilon\frac{dy}{dt} = y^2 - x^2 + \alpha, \tag{1.7}$$

with $\alpha = \pm\varepsilon$, the lines $y = \pm x$ pass along the slow curve $y^2 - x^2 + \alpha = 0$ over an infinitely long distance, see Fig. 3.2. Note that the canard is only the $y = x$ trajectory. In this example [14], the point $x = 0$, $y = 0$ is the point of self–intersection of the slow curve at $\alpha = 0$. Such problems were examined in [1, 13, 14]. The same systems appear in thermal explosion models in the case of autocatalytic reactions. In this case the canards are the natural mathematical objects which allow us to model critical phenomena and discover critical parameter values as asymptotic expansions involving powers of the small parameter ε.

In this case the canard plays the role of a watershed line.

Example 4: Jump point

Consider the following piecewise linear differential system

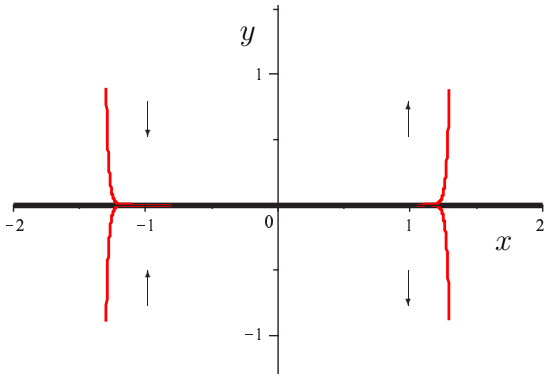


Figure 1.2: Canard (black) and the trajectories of the system (1.6) with different initial points (red) for $\varepsilon = 0.05$.

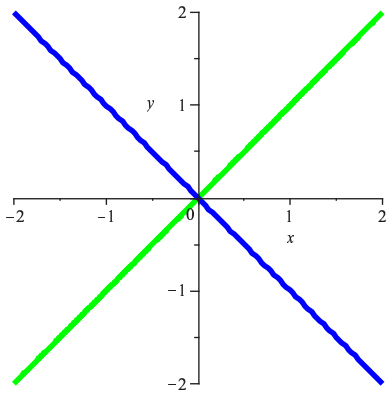


Figure 1.3: Canard (green) and false canard (blue) of the system (1.7). Canard corresponds to $\alpha = \varepsilon$, false canard corresponds to $\alpha = -\varepsilon$.

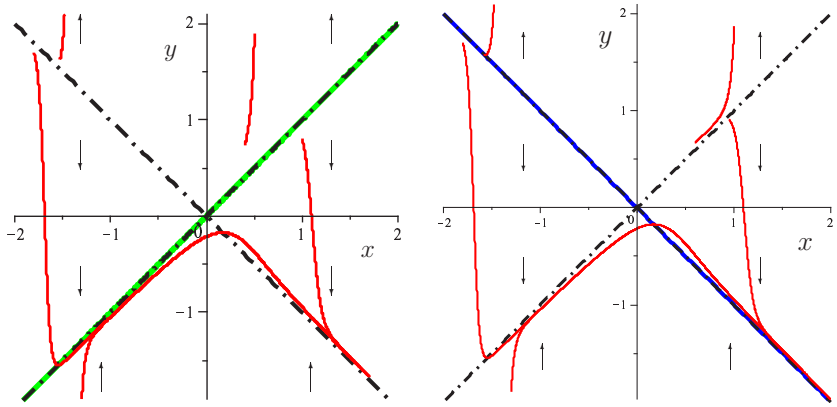


Figure 1.4: The slow curve (dash-dotted straight line), and trajectories (red lines) of the system (1.7) with different initial points for $\alpha = 0$ and (a) $\varepsilon = 0.05$, (b) $\varepsilon = 0.2$.

$$\begin{aligned} \dot{x} &= -1, \\ \varepsilon\dot{y} &= x - 1 - \alpha + |y - 1|, \end{aligned} \tag{1.8}$$

corresponding to the phase plane equation

$$\varepsilon\frac{dy}{dx} = x - 1 - \alpha + |y - 1|.$$

The slow curve is described by the equation

$$x - 1 - \alpha + |y - 1| = 0,$$

and consists of an attractive part ($y < 1$) and a repulsive one ($y > 1$), which are separated by the *jump point* $x = 1 + \alpha, \quad y = 1$.

As usual, an important role is played by the attractive slow invariant manifold

$$y = x + \varepsilon - \alpha, y < 1$$

and the repulsive slow invariant manifold

$$y = -x + 2 + \varepsilon + \alpha, y > 1,$$

hand in hand with their extensions

$$y = \begin{cases} -x + 2 + \varepsilon + \alpha, & x < 1 + \varepsilon + \alpha \\ -2\varepsilon e^{(x-1-\alpha-\varepsilon)/\varepsilon} + x - \alpha + \varepsilon, & x \geq 1 + \varepsilon + \alpha, \end{cases}$$

and

$$y = \begin{cases} x + \varepsilon - \alpha, & x < 1 - \varepsilon + \alpha, \\ -2\varepsilon e^{-(x-1+\varepsilon-\alpha)/\varepsilon} - x + 2 + \alpha + \varepsilon, & 1 - \varepsilon + \alpha \leq x < 1 - \varepsilon + \alpha + \varepsilon\nu, \\ -\varepsilon\nu e^{(x-1+\varepsilon-\alpha-\nu\varepsilon)/\varepsilon} + x - \alpha + \varepsilon, & 1 - \varepsilon + \alpha + \varepsilon\nu \leq x, \end{cases}$$

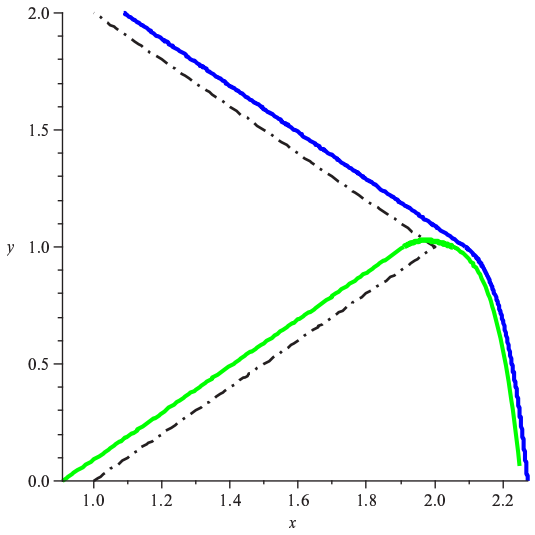


Figure 1.5: The slow curve (dash-dotted line), attractive (green) and repulsive (blue) slow invariant manifolds and their extensions.

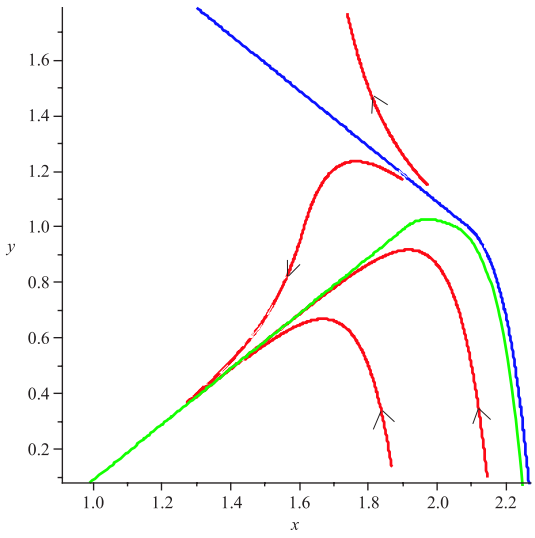


Figure 1.6: Slow invariant manifolds, their extensions and the trajectories of (1.8) with different initial points ($\varepsilon = 0.09$).

where ν is the root of $2e^{-\nu} + \nu - 2 = 0$ (see Fig. 1.5).

The phenomenon of a jump point is common in the theory of relaxation oscillations [26]. In this case the attractive slow invariant manifold together with its extension plays the role of a watershed line.

Consider now α as a control parameter. Let it is necessary to choose the value of α in such a way that the trajectory involving the repulsive slow invariant line $y = -x + 2 + \varepsilon + \alpha$, $y > 1$ is satisfies the fixed initial condition $y = 0$ as $x = 1$. This condition in the case under consideration takes the form

$$0 = -2\varepsilon e^{-(1-1-\alpha-\varepsilon)/\varepsilon} + 1 - \alpha + \varepsilon.$$

It is a straightforward exercise now to obtain the following asymptotic representation

$$\alpha = \varepsilon \ln \varepsilon + \varepsilon(\ln 2 - 1) + \varepsilon^2 \ln \varepsilon + O(\varepsilon^2)$$

from the last equality. It should be noted that problems of this sort appear in the combustion theory and we shall consider these problems later.

1.3 Black swans

In a majority of papers devoted to canards the term "canard" is associated with periodic trajectories. In our work a canard is a trajectory of a singularly perturbed system of differential equations if it, at first, follows a stable integral manifold, and then an unstable one. In both cases the distances travelled are more than infinitesimally small. A canard may be considered as the result of gluing stable (attractive) and unstable (repelling) slow integral manifolds at one point of the breakdown surface, due to the availability of an additional scalar parameter in the differential system. If we take an additional function of a vector variable parameterizing the breakdown surface, we can glue the stable (attractive) and unstable (repelling) slow integral manifolds at all points of the breakdown curve at the same time. As a result we obtain the continuous stable/unstable (attractive/repelling) integral surface or black swan. Such surfaces are considered as a multidimensional analogue of the notion of a canard. It is possible to consider the gluing function as a special kind of incomplete feedback control. This guarantees the safety of chemical regimes, even with perturbations, during a chemical process.

We shall use canards as *separating solutions* (watershed line) corresponding to the critical regimes of chemical reactions and this approach is extended to black swans.

The main object of our consideration is the following singularly perturbed system

$$\begin{aligned} \dot{x} &= f(x, y, z, \varepsilon), \\ \dot{y} &= g(x, y, z, \varepsilon), \\ \varepsilon\dot{z} &= p(x, y, z, \alpha, \varepsilon), \end{aligned} \tag{1.9}$$

where ε is a small positive parameter, α is a scalar parameter, x and z are scalar variables, y is a vector of dimension n, and the dot refers to differentiation with respect to time t. Note that we detach the variable x for the following reason: it will be used as a new independent

variable when the original variable t is excluded. For nonautonomous systems the variable t plays the role of the variable x and $f \equiv 1$ in this case. The case of a vector variable z will also be considered.

Recall that the slow surface S (or S_α) of the system (1.9) is the surface described by the equation

$$p(x, y, z, \alpha, 0) = 0. \tag{1.10}$$

Let $z = \phi(x, y, \alpha)$ be an isolated solution of equation (1.10). We call the subset S^s_α (S^u_α) of S, defined by

$$\frac{\partial p}{\partial z}(x, y, \phi(x, y), \alpha, 0) < 0, \ \ (> 0),$$

the stable (unstable) subset of S_α.

The subset of S_α defined by

$$\frac{\partial p}{\partial z}(x, y, \phi(x, y), \alpha, 0) = 0$$

is called the *breakdown surface*. Its dimension is equal to $\dim y$.

In an ε–neighborhood of S^s_α (S^u_α) there exists a stable (unstable) slow integral manifold. The slow integral manifold is defined as a invariant surface of slow motions.

The availability of the additional scalar parameter α provides the possibility of gluing the stable and unstable integral manifolds at one point of the breakdown surface. The canard trajectory passes through this point.

It should be noted that in the early papers devoted to canards in the case $\dim y = 0$, the existence of a unique canard corresponding to a unique value of the parameter $\alpha = \alpha^*$ was stated (more precisely, the "canard" value of the parameter α^* exists on an interval of order $O(e^{-1/\varepsilon})$). This property is known as the *short life of canards*. But, in the case $\dim y = 1$, another picture is beginning to emerge. It was shown that a one-parameter family of canards exists [40]. If we take the parameter α as a function of y we can glue the stable and unstable integral manifolds along all points of the breakdown curve at the same time.

Example 5.

Consider the system

$$\dot{x} = 1, \ \ \dot{y} = 0, \ \ \varepsilon \dot{z} = 2xz + \alpha - y.$$

If α is a parameter then the different canards are determined by

$$\dot{x} = 1, \ \ y = y_0, \ \ z = 0,$$

that is, they pass through the unique gluing point $x = 0$, $y = y_0$, $z = 0$ on the breakdown curve $x = 0$ of the slow surface $2xz + y_0 - y = 0$ for $\alpha = y_0$.

If α is a function of the variable y then for $\alpha = y$ the integral manifold $z = 0$ is attractive for $x < 0$ and repulsive for $x > 0$.

Example 6.

In the system

$$\dot{x} = x^2 + z^2, \quad \varepsilon\dot{z} = xz,$$

the straight line $z = 0$ plays the role of a black swan on a plane. It should be noted that this line represents an invariant manifold, but it is not a canard trajectory because it is not a trajectory; it consists of three trajectories: $x < 0, z = 0$; $x = z = 0$, and $x > 0, z = 0$.

It is important to note, that it is impossible without loss of generality to consider *the black swan* as a *canard surface* [21, 22, 45]. Additionally to the previous example, consider

Example 7.

$$\dot{x} = 0, \ \ \dot{y} = 0, \ \ \varepsilon\dot{z} = xz.$$

The plane $z = 0$ is a black swan with attractive part $x < 0, z = 0$ and repulsive part $x > 0, z = 0$, but there is no canards in the system under consideration.

Chapter 2

Critical Phenomena in Combustion Models

2.1 The classical combustion models

Thermal explosion occurs when chemical reactions produce heat too rapidly for a stable balance between heat production and loss. The exothermic oxidation reaction is usually modelled as a single step reaction obeying an Arrhenius temperature dependence. The first model for the self-ignition was constructed by Semenov in 1928 (see, for example [32]). The basic idea of the model was a competition between heat production in the reactant vessel (due to an exothermic reaction) and heat losses on the vessel's surface. Heat losses were assumed proportional to the temperature excess over the ambient temperature (Newtonian cooling). The main assumption was that there is no reactant conversion during the fast highly exothermic reaction. This assumption implies the absence of the energy conservation law in the model. This gave the possibility of constructing an extremely simple and attractive mathematical model. Spatial uniformity of the temperature was also assumed so that the governing equation was one first-order ordinary differential equation for the temperature changes:

$$c\rho V\frac{dT}{dt} = QV\left(-\frac{dC}{dt}\right) - \chi S(T - T_0),$$

$$-\frac{dC}{dt} = \Psi(C)A\exp\left(-\frac{E}{RT}\right),$$

where Ψ expresses the dependence of reaction rate on reactant concentration. Here Q is an exothermicity per mole reactant; C and C_0 are a reactant concentration and its initial value; A is constant which is known as a pre-exponential rate factor; c is specific heat capacity; ρ is reactant density; χ is the heat-transfer coefficient; E is the Arrhenius activation energy; R is the universal gas constant; V is the reactant vessel volume; S is the surface area of the reactant vessel; t is a time variable; T is absolute temperature; T_0 is ambient temperature. The initial temperature is assumed to be equal to the ambient temperature T_0.

Dimensionless variables τ, η, θ are introduced by

$$\tau = tC_0^{n-1}A\exp\left(-\frac{E}{RT_0}\right), \quad \eta = 1 - C/C_0, \quad \theta = \frac{E}{RT_0}(T - T_0),$$

(n is the order of the chemical reaction) and we obtain the classical model of thermal explosion with reactant consumption [16, 50]:

$$\varepsilon\frac{d\theta}{d\tau} = \Psi(\eta)\exp\left(\theta/\left(1+\beta\theta\right)\right) - \alpha\theta, \tag{2.1}$$

$$\frac{d\eta}{d\tau} = \Psi(\eta)\exp\left(\theta/\left(1+\beta\theta\right)\right), \tag{2.2}$$

$$\eta(0) = \eta_0/\left(1+\eta_0\right) = \bar{\eta}_0, \;\; \theta(0) = 0.$$

Here η_0 is the criterion for autocatalyticity, where the small dimensionless parameters

$$\beta = \frac{RT_0}{E} \text{ and } \varepsilon = \frac{c\rho}{QC_0}\frac{E}{RT_0^2}$$

characterize the physical properties of gas mixture, and

$$\alpha = \frac{\chi S}{VQC_0^n A}\frac{RT_0^2}{E}\exp\left(\frac{E}{RT_0}\right)$$

is the dimensionless heat loss parameter.

The following cases are examined:

$$\Psi(\eta) = \begin{cases} 1-\eta, & \text{first-order reaction}(\eta_0 = 0), \\ \eta(1-\eta), & \text{autocatalytic reaction.} \end{cases}$$

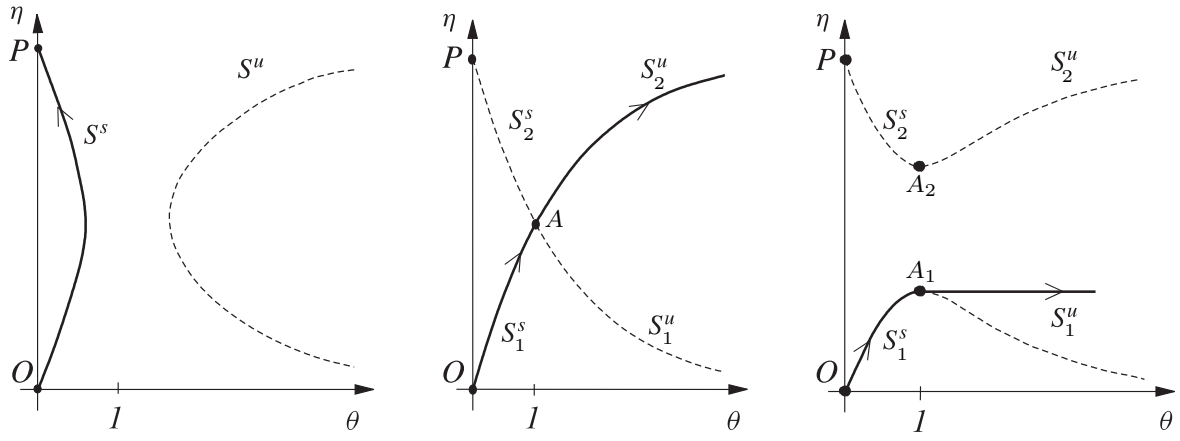
It should be noted that the system (2.1), (2.2) is singularly perturbed. According to the standard approach to such systems the limiting case $\varepsilon \to 0$ is examined, and discontinuous solutions of the reduced system are analyzed. This makes it possible to determine some critical values of initial conditions, which provide a jump transition from the slow regime to the explosive ones. The study of transitional regimes requires the application of higher approximations in the asymptotic analysis of the systems of the type given in equation (2.1), (2.2). The integral manifold technique [39, 42, 43] is applied below to the qualitative analysis of critical and transitional regimes for both types of chemical reaction.

2.1.1 Autocatalytic reaction

The system showing autocatalytic features of the reaction is [16] The system showing autocatalytic features of reaction is

$$\varepsilon\frac{d\theta}{d\tau} = \eta(1-\eta)\exp\left(\theta/\left(1+\beta\theta\right)\right) - \alpha\theta, \tag{2.3}$$

$$\frac{d\eta}{d\tau} = \eta(1-\eta)\exp\left(\theta/\left(1+\beta\theta\right)\right). \tag{2.4}$$



(a) $\alpha > e/4$ (b) $\alpha = e/4$ (c) $\alpha < e/4$

Figure 2.1: The slow curve of the system (2.3), (2.4) in the case $\beta = 0$.

To simplify the demonstration of the main qualitative effects we use a widespread assumption, $\beta = 0$, in thermal explosion theory (more detailed analysis shows that the differences between the results obtained for cases $\beta = 0$ and $\beta \neq 0$ are not essential). In the case $\beta = 0$ the slow curve S of the system (2.3), (2.4) is described by the equation

$$\eta(1-\eta)e^{\theta} - \alpha\theta = 0.$$

The curve S has a different form depending on whether $\alpha > e/4$ or $\alpha < e/4$ (see Figure 2.1). In the region $\theta < 1$ connected components of the curve S will be stable and in the region $\theta > 1$ it will be unstable. We shall denote a stable part S as S^s and an unstable part as S^u. There exist invariant manifolds S^s_ε and S^u_ε at a distance of $O(\varepsilon)$ from the curve S, corresponding to S^s and S^u.

We shall give a qualitative description of the behavior of the system (2.3), (2.4) with the changing parameter α. When $\alpha > e/4$ the trajectories of the system in the phase plane move along the stable branch S^s and the value of θ does not exceed 1. These trajectories correspond to the slow regimes.

With $\alpha < e/4$ the stable part S^s of the curve S consists of two separated branches and the system's trajectories, having reached the jump point at the tempo of the slow variable along S^s, jumps into the explosive regime.

Due to the continuous dependence the right–hand side of (2.3), (2.4) on the parameter α we can consider that there are some intermediate trajectories in the region between those shown above in the neighborhood of $\alpha = e/4$, and a critical one also. With $\alpha = e/4$ the slow curve S^s has a self–intersection point $(1, 1/2)$, and in this case it is possible to find the critical value of the parameter α in the form

$$\alpha = \alpha(\varepsilon) = \alpha_0 + \varepsilon\alpha_1 + \varepsilon^2\alpha_2 + \dots\,, \quad \alpha_0 = e/4. \tag{2.5}$$

There are two values of parameter $\alpha = \alpha^*$ and $\alpha = \alpha^{**}$ at which the trajectory of (2.3),

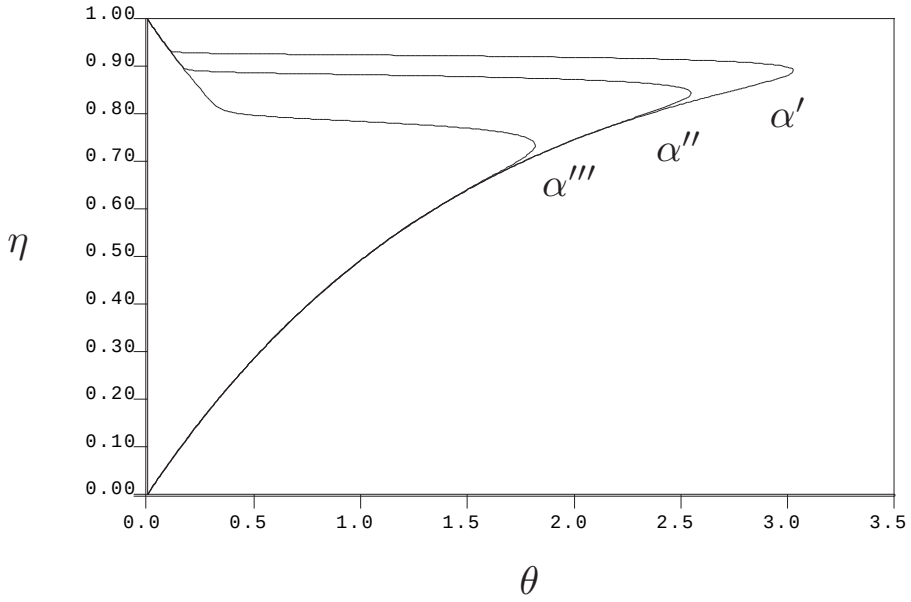


Figure 2.2: Canard trajectories of the system for $\varepsilon = 0.05$, $\alpha' = 0.659941603$, $\alpha'' = 0.659941646$, $\alpha''' = 0.659952218$.

(2.4) passes along the stable and the unstable parts of the slow curve for times that are not infinitesimally small.

The value $\alpha = \alpha^*$ corresponds to the canard, passing along the lower part of S^s and then along the upper part of S^u. The canard is taken as a mathematical object to model the critical trajectory, which corresponds to a chemical reaction separating the domain of self–acceleration reactions ($\alpha < \alpha^*$) and the domain of non–explosive reactions ($\alpha > \alpha^*$).

The value $\alpha = \alpha^{**}$ is also important in the qualitative analysis of the system (2.3), (2.4). With $\alpha = \alpha^{**}$ there exist the trajectory (so–called false canard), passing along the lower part of S^u and then along the upper part of S^s. At $\alpha > \alpha^{**}$ we get a region of slow regimes and the trajectories of system (2.3), (2.4) will pass along the stable part of slow curve.

Figure 2.2 shows numerical investigations of the canard trajectories of the system (2.3), (2.4) for α from the interval (α^*, α^{**}) $\quad(\alpha^* < \alpha' < \alpha'' < \alpha''' < \alpha^{**})$.

The coefficients of the asymptotic series for α^* and α^{**} can be found by the methods of [13]. To calculate the critical value of the parameter $\alpha = \alpha^*$ we substitute (2.5) and the expression for corresponding canard

$$\eta = H(\theta, \varepsilon) \equiv H_0(\theta) + \varepsilon H_1(\theta) + \dots$$

into (2.3), (2.4) and obtain

$$\Big(H(\theta,\varepsilon)\,(1 - H(\theta,\varepsilon))\,e^{\theta} - \alpha(\varepsilon)\theta\Big)\,H'(\theta,\varepsilon) = \varepsilon H(\theta,\varepsilon)\,(1 - H(\theta,\varepsilon))\,e^{\theta}$$

or, in more detailed form,

$$\Big(\big(H_0(\theta) + \varepsilon H_1(\theta) + \dots\big)\,\big(1 - H_0(\theta) - \varepsilon H_1(\theta) - \dots\big)\,e^{\theta}$$

$$-(\alpha_0 + \varepsilon\alpha_1 + \dots)\theta\Big)\,\Big[H_0'(\theta) + \varepsilon H_1'(\theta) + \dots\Big]$$

$$= \varepsilon \left(H_0(\theta) + \varepsilon H_1(\theta) + \dots\right) \left(1 - H_0(\theta) - \varepsilon H_1(\theta) - \dots\right) e^{\theta}.$$

Equating the coefficients of like powers of ε in the left and right members of last equation, we obtain

$$H_0(\theta) = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \alpha_0 \theta e^{-\theta}},$$

$$H_1(\theta) = \frac{\theta(\alpha_1 H_0' + \alpha_0)}{H_0'(1 - 2H_0)e^{\theta}},$$

$$H_2(\theta) = \frac{\theta\left(\alpha_1 H_1' + \alpha_2 H_0'\right) + H_0' H_1^2 e^{\theta} + H_1\left(1 - H_1'\right)\left(1 - 2H_0\right) e^{\theta}}{H_0'(1 - 2H_0)e^{\theta}}.$$

The coefficients in the expression (2.5) α_i $(i = 0, 1, 2, \dots)$ are found due to functions $H_i = H_i(\theta)$ continuity at $\theta = 1$. Thus, we have

$$\alpha^* = e/4(1 - 2\sqrt{2}\varepsilon - 49/9\varepsilon^2) + O(\varepsilon^3).$$

In the case $\beta \neq 0$ we obtain the following approximate formula

$$\alpha^* = (1 - \beta)e/4(1 - 2\sqrt{2}\varepsilon) + \dots \ .$$

The value $\alpha = \alpha^{**}$ and corresponding false canard can be found by the same way. For this case we obtain

$$\alpha^{**} = e/4(1 + 2\sqrt{2}\varepsilon - 49/9\varepsilon^2) + O(\varepsilon^3).$$

The transition trajectories between S_ε^s and S_ε^u correspond to the interval (α^*, α^{**}). The canard corresponding to α^* is given by the formulas, see [13, 14]

$$\eta = H(\theta, \varepsilon) \equiv H_0(\theta) + \varepsilon H_1(\theta) + \dots .$$

$$H_0(\theta) = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \alpha_0 \theta e^{-\theta}},$$

$$H_1(\theta) = \frac{\theta(\alpha_1 H_0' + \alpha_0)}{H_0'(1 - 2H_0)e^{\theta}},$$

$$H_2(\theta) = \frac{\theta\left(\alpha_1 H_1' + \alpha_2 H_0'\right) + H_0' H_1^2 e^{\theta} + H_1\left(1 - H_1'\right)\left(1 - 2H_0\right) e^{\theta}}{H_0'(1 - 2H_0)e^{\theta}}.$$

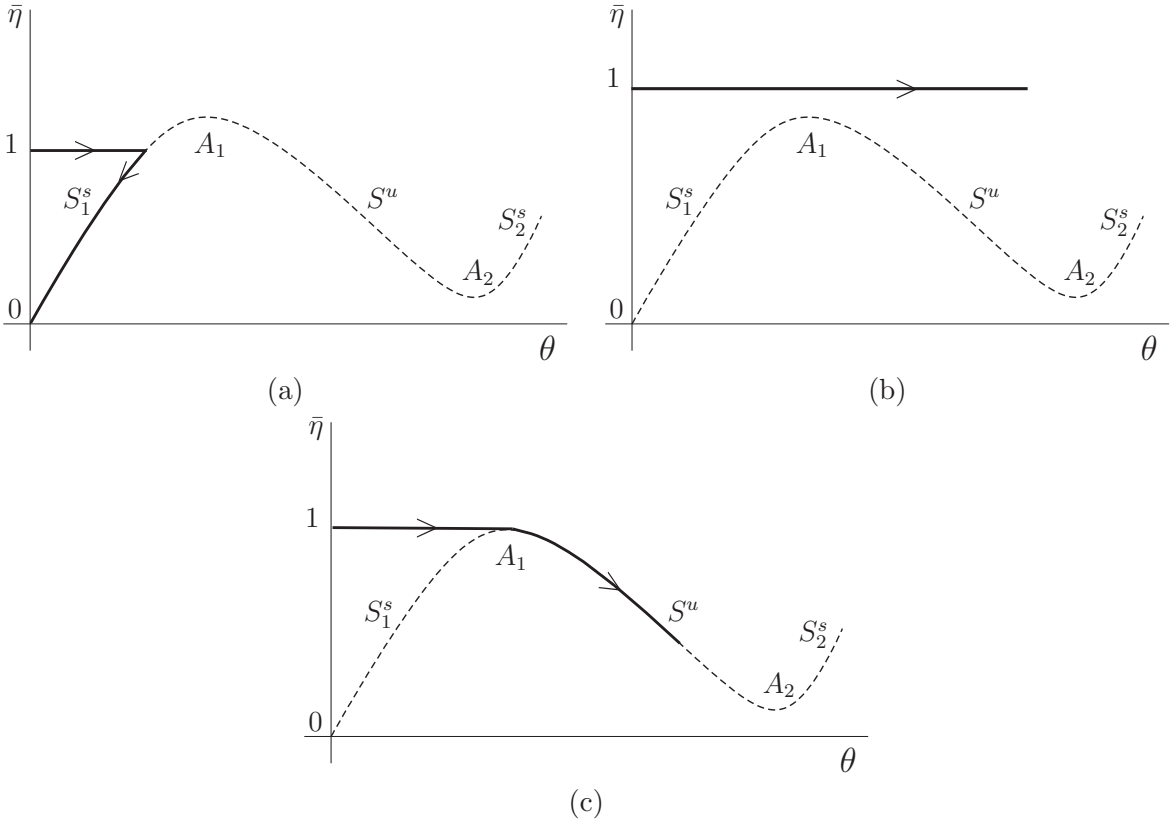


Figure 2.3: The slow curve (the dashed line) and trajectory of (2.3)–(2.4) (the solid line) in the limiting case: (a) slow combustion; (b) thermal explosion; (c) critical regime.

2.1.2 First-order reaction

Now we consider the system (2.1), (2.2) with the first–order reaction case, when $\Psi(\eta) = 1 - \eta$ and the dimensionless concentration $\bar{\eta} = 1 - \eta$ replaces η. The system (2.1), (2.2) in this case is

$$\varepsilon \frac{d\theta}{d\tau} = \bar{\eta} \exp\left(\theta / \left(1 + \beta\theta\right)\right) - \alpha\theta, \tag{2.6}$$

$$\frac{d\bar{\eta}}{d\tau} = -\bar{\eta} \exp\left(\theta / \left(1 + \beta\theta\right)\right). \tag{2.7}$$

The initial conditions are

$$\bar{\eta}(0) = 1, \;\; \theta(0) = 0. \tag{2.8}$$

The control parameter α characterizes the initial state of the chemical system. Depending on its value the chemical reaction either changes to a slow regime with decay of the reaction, or into a regime of self–acceleration which leads to an explosion. For some value of α (we call it critical) the reaction is maintained and gives rise to a rather sharp transition from slow motions to explosive ones. The transition region from slow regimes to explosive ones exists due to the continuous dependence of the system (2.6), (2.7) on the parameter α. To find the critical value of the parameter α, it is possible to use special asymptotic formulae [26]. That approach was used in [4, 20, 3, 14].

The equation

$$\bar{\eta} \exp\left(\theta / \left(1 + \beta\theta\right)\right) - \alpha\theta = 0$$

gives the slow curve S of the system (2.6), (2.7). The curve S has two jump points given by the equation

$$\frac{\partial}{\partial\theta}\left(\bar{\eta} \exp\left(\theta / \left(1 + \beta\theta\right)\right) - \alpha\theta\right) = 0.$$

The jump points divide the slow curve into three parts S_1^s, S_2^u, S_3^s (see Fig. 3.7) which are zeroth order approximations for the corresponding slow integral manifolds $S_{1,\varepsilon}^s$, $S_{2,\varepsilon}^u$ and $S_{3,\varepsilon}^s$. Manifolds $S_{1,\varepsilon}^s$ and $S_{3,\varepsilon}^s$ are stable and $S_{2,\varepsilon}^u$ is unstable. It is clear that each value of α has a corresponding slow curve but these curves merge in the domain of critical values. Each manifold $S_{1,\varepsilon}^s$, $S_{2,\varepsilon}^u$ and $S_{3,\varepsilon}^s$ is at the same time part of some trajectory of the system (2.6), (2.7).

With some values of α, trajectories of equations (2.6)–(2.8) move along the manifold $S_{2,\varepsilon}^u$, sooner or later either falling into an explosive regime, or rapidly passing into a slow regime (see Fig. 3.7). The value of α_2, at which the trajectory $\mathcal{T}_2$ of (2.6)–(2.8) contains manifold $S_{2,\varepsilon}^u$, is supposed to be critical. This regime is not slow, since $\theta > 1$, and is not explosive, as the temperature increases at the tempo of the slow variable. The value α_1, at which the trajectory $\mathcal{T}_1$ contains the manifold $S_{1,\varepsilon}^s$ (see Fig. 2.8), is called the slow critical value. The trajectory $\mathcal{T}_3$ contains the manifold $S_{3,\varepsilon}^s$ and does not determine any critical regime, since it does not intersect the axis $\bar{\eta}$. We point out that any trajectory of the system starting at the point $\bar{\eta} = 1$, $\theta = 0$ runs to the left from $\mathcal{T}_3$.

Thus the value of α_1 gives the critical trajectory. It separates the transition region from slow regimes which are characterized by a slowdown of the reaction with small degrees of conversion and heating up is limited from above by $\theta < 1$.

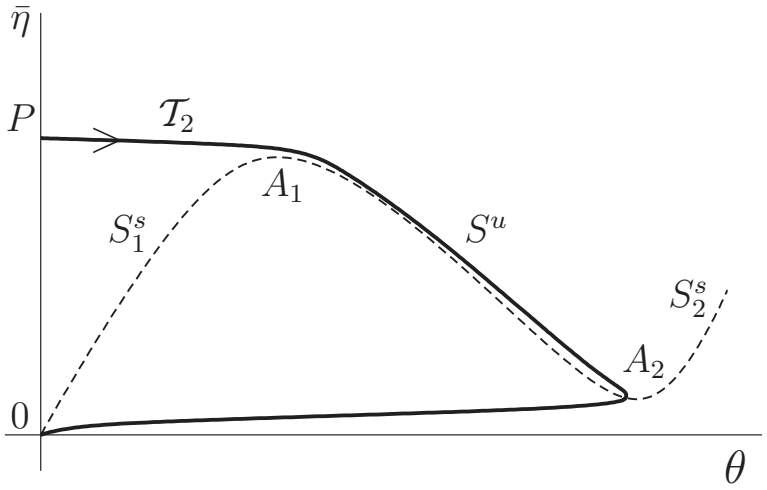


Figure 2.4: The slow curve (the dashed line) and the trajectory $\mathcal{T}_2$ (the solid line)

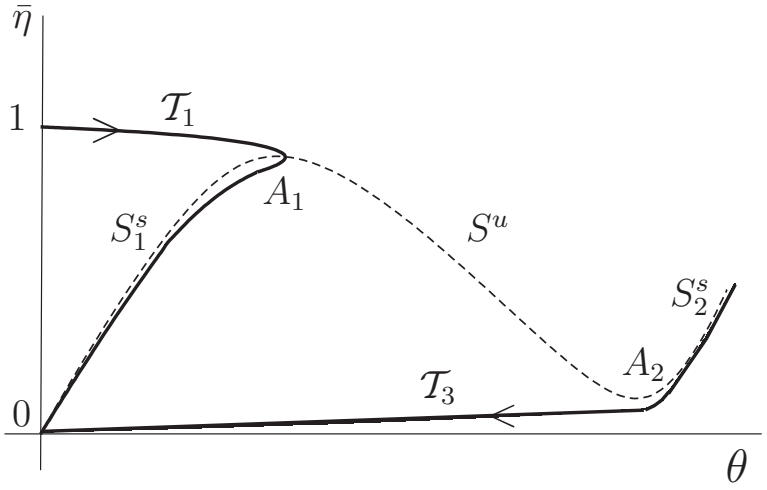


Figure 2.5: The slow curve (the dashed line) and the trajectories $\mathcal{T}_1$ and $\mathcal{T}_3$ (the solid line)

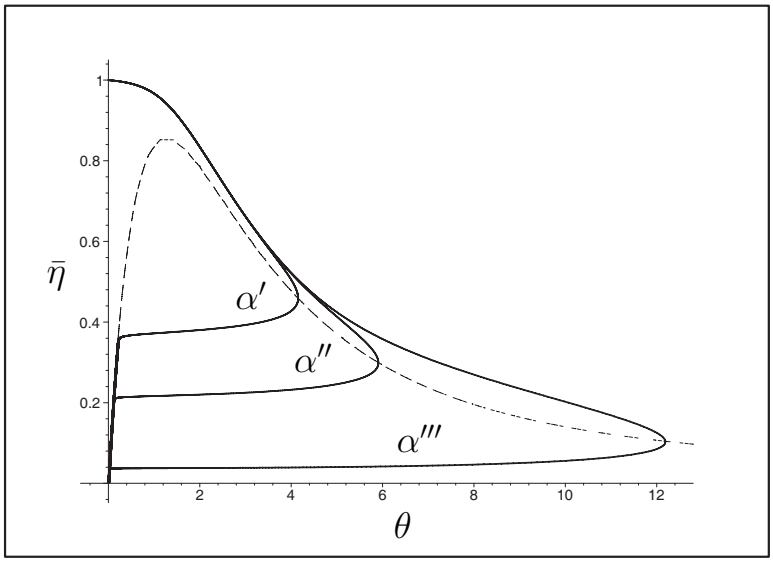


Figure 2.6: The slow curve and the trajectories of (2.6)–(2.8) for $\varepsilon = 0.01$, $\beta = 0.1$, $\alpha' = 2.08039$, $\alpha'' = 2.0803865$, $\alpha''' = 2.080386$

The region of slow transitional trajectories corresponds to the interval (α_2, α_1). They are characterized by a comparatively rapid (but not explosive) flow of the reaction till the essential degree of conversion takes place and then a jump slow-down and a transition to the slow flow of the reaction, Fig. 3.9.

The critical value α_2 was obtained by means of the asymptotic expansion technique given in [26]:

$$\alpha_2 = e(1-\beta)\left[1 - \Omega_0 \sqrt[3]{2}\left(1 + \frac{7}{3}\beta\right)\varepsilon^{2/3} + \frac{4}{9}(1+6\beta)\varepsilon \ln\frac{1}{\varepsilon}\right] + O(\varepsilon + \beta^2),$$

where $\Omega_0 = 2.338107$.

2.2 Gas combustion in a dust–laden medium

We now consider models of combustion of a rarefied gas mixture in an inert porous or in a dusty medium. We assume that the temperature distribution and phase–to–phase heat exchange are uniform. The chemical conversion kinetics are represented by a one–stage, irreversible reaction. The dimensionless model in this case has the form [4, 12]

$$\varepsilon\dot{\theta} = \Psi(\eta)\exp\left(\theta/\left(1+\beta\theta\right)\right) - \alpha(\theta - \theta_c) - \delta\theta,$$

$$\gamma_c\dot{\theta}_c = \alpha(\theta - \theta_c),$$

$$\dot{\eta} = \Psi(\eta)\exp\left(\theta/\left(1+\beta\theta\right)\right),$$

$$\eta(0) = \eta_0/\left(1+\eta_0\right) = \bar{\eta}_0,\ \ \theta(0) = \theta_c(0) = 0.$$

Here, θ and θ_c are the dimensionless temperatures of the reactant phase and of the inert one; η is the depth of conversion; η_0 is the criterion of autocatalyticity; the small parameters β and ε characterize the physical properties of a gas mixture. The terms $-\delta\theta$ and $-\alpha(\theta-\theta_c)$ reflect the external heat dissipation and phase-to-phase heat exchange. The parameter γ_c characterizes the physical features of the inert phase. Depending on the relation between values of the parameters, the chemical reaction either changes to a slow regime with decay of reaction, or into a regime of self–acceleration which leads to an explosion. So, if we change the value of one parameter with fixed values of the other parameters we can change the type of chemical reaction. Thus, it is possible to consider this problem as a special control problem. For example, if we take a heat loss from the gas phase as a control action, we consider δ as a control variable. If the control variable is γ_c it means a regulation of the dust level in the reactant vessel.

The following cases are considered:

$$\Psi(\eta) = \begin{cases} 1-\eta, & \text{first-order reaction}(\eta_0 = 0), \\ \eta(1-\eta), & \text{autocatalytic reaction.} \end{cases}$$

2.2.1 Autocatalytic reaction

Let us consider the combustion model for the case of autocatalytic reaction ($\Psi(\eta) = \eta(1-\eta)$).

In the absence of external heat dissipation ($\delta = 0$) the system of differential equations possesses a first integral

$$\eta - \varepsilon\theta - \gamma_c\theta_c = \bar{\eta}_0,$$

and therefore we obtain

$$\varepsilon\frac{d\theta}{d\tau} = \eta(1-\eta)\exp\left(\frac{\theta}{1+\beta\theta}\right) - \alpha\left(1+\frac{\varepsilon}{\gamma_c}\right)\theta + \frac{\alpha}{\gamma_c}(\eta-\bar{\eta}_0), \tag{2.9}$$

$$\frac{d\eta}{d\tau} = \eta(1-\eta)\exp\left(\frac{\theta}{1+\beta\theta}\right), \tag{2.10}$$

with initial conditions

$$\eta(0) = \bar{\eta}_0, \quad \theta(0) = 0.$$

The dependence of the slow curve S

$$F(\eta,\theta,\alpha) = \eta(1-\eta)\exp\left(\frac{\theta}{1+\beta\theta}\right) - \alpha\left(\theta - \frac{\eta-\bar{\eta}_0}{\gamma_c}\right) = 0$$

on the relation between parameter values gives different forms (see Figures 3.2).

We take α as control parameter with fixed γ_c. The point $\theta = \theta^*$, $\eta = \eta^*$ is the self–intersection point of the slow curve at $\alpha = \alpha_0$. Here, $\alpha = \alpha_0$, $\theta = \theta^*$, $\eta = \eta^*$ satisfy the system

$$F(\eta,\theta,\alpha) = F_\eta(\eta,\theta,\alpha) = F_\theta(\eta,\theta,\alpha) = 0.$$

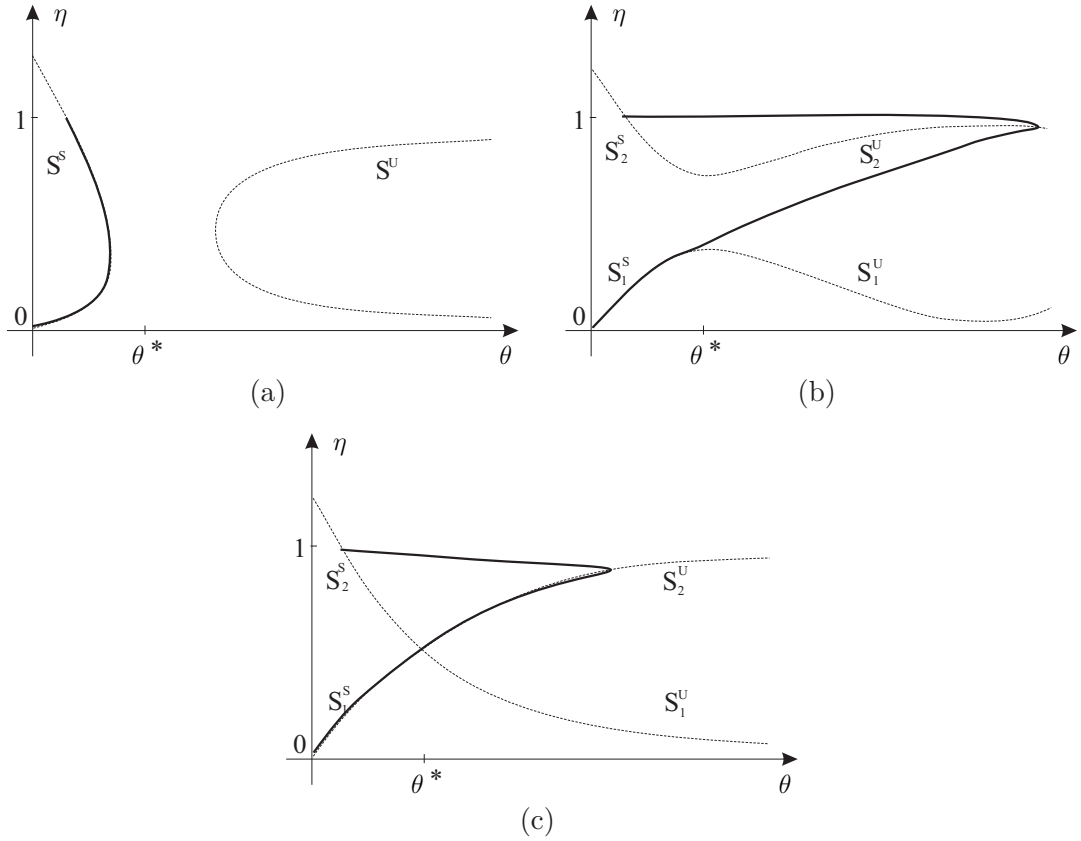


Figure 2.7: The trajectories (the solid line) of the system (2.9), (2.10) and the slow curve (the dashed line) in various cases.

In the case $\alpha > \alpha_0$ each set S^s and S^u of S consists of a single connected curve, see Figure 3.2 (a). Hence the system has an stable invariant manifold S^s_ε and a unstable invariant manifold S^u_ε near S^s and S^u, respectively.

Since the initial point $(0, \bar{\eta}_0)$ belongs to the basin of attraction of the set S^s_ε, after a short time the trajectory follows the stable slow invariant manifold S^s_ε and tends to the equilibrium $P\left((1-\bar{\eta}_0)/(\varepsilon+\gamma_c), 1\right)$ as t tends to ∞. This behavior corresponds to the slow combustion regime.

In the case $\alpha < \alpha_0$ each set S^s and S^u consists of two different components (Figure 3.2 (b)) and the system has an stable invariant manifold S^s_ε (unstable invariant manifold S^u_ε) near each component of S^s (S^u). For ε sufficiently small and after a short time, the solution will follow the component of S^s_ε to breakdown point. After this time, $\theta(t)$ will increase rapidly. This behavior characterizes the explosive regime.

The transition region from the slow regime to explosive one exists due to the continuous dependence of our system on the parameters α and γ_c ($\gamma_c > 0$). In this special case ($\alpha = \alpha_0$) the slow curve has an intersection point (θ^*, η^*), see Figure 3.2 (c). Here the system has an stable invariant manifold S^s_ε (unstable invariant manifold S^u_ε) near each component of the slow curve S^s (S^u).

We can observe the existence of canard solutions which describe the following regime: the temperature increases as high as is possible but without explosion, that may be the aim of technological process. We note that this regime is critical, and it corresponds to a chemical reaction separating the domain of self–accelerating reactions and the domain of slow reactions.

We can find the canard solution and corresponding value of α by following asymptotic expansions

$$\alpha^* = \alpha(\varepsilon) = \alpha_0 + \varepsilon\alpha_1 + \varepsilon^2\alpha_2 + ...,$$
$$\eta = H(\theta, \varepsilon) = H_0(\theta) + \varepsilon H_1(\theta) + \varepsilon^2 H_2(\theta) + ...$$

We substitute these expansions into (2.9), (2.10) and obtain

$$\left(H(\theta,\varepsilon)\left(1 - H(\theta,\varepsilon)\right)\exp\left(\frac{\theta}{1+\beta\theta}\right) - \alpha(\varepsilon)\left(1+\frac{\varepsilon}{\gamma_c}\right)\theta \right.$$
$$\left. + \frac{\alpha(\varepsilon)}{\gamma_c}(H(\theta,\varepsilon) - \bar{\eta}_0)\right) H'(\theta,\varepsilon) = \varepsilon H(\theta,\varepsilon)\left(1 - H(\theta,\varepsilon)\right)\exp\left(\frac{\theta}{1+\beta\theta}\right)$$

or, in more detailed form,

$$\left(\left(H_0(\theta) + \varepsilon H_1(\theta) + \dots\right)\left(1 - H_0(\theta) - \varepsilon H_1(\theta) - \dots\right)\exp\left(\frac{\theta}{1+\beta\theta}\right) \right.$$
$$-\left(\alpha_0 + \varepsilon\alpha_1 + \dots\right)\left(1+\frac{\varepsilon}{\gamma_c}\right)\theta$$
$$\left. + \frac{(\alpha_0 + \varepsilon\alpha_1 + \dots)}{\gamma_c}(H_0(\theta) + \varepsilon H_1(\theta) + \dots - \bar{\eta}_0)\right)\left[H_0'(\theta) + \varepsilon H_1'(\theta) + \dots\right]$$
$$= \varepsilon\left(H_0(\theta) + \varepsilon H_1(\theta) + \dots\right)\left(1 - H_0(\theta) - \varepsilon H_1(\theta) - \dots\right)\exp\left(\frac{\theta}{1+\beta\theta}\right).$$

Equating the coefficients of like powers of ε in the left and right members of last equation and using the continuity condition for functions $H_i = H_i(\theta)$ $(i = 0, 1, 2, \dots)$ at $\theta = \theta^*$, we obtain

$$\alpha_0 = \gamma_c(2\eta^* - 1)\exp\left(\frac{\theta^*}{1+\beta\theta^*}\right),$$

$$\alpha_1 = -\alpha_0\Bigg[\frac{\theta^*}{\gamma_c\theta^* - \eta^* + \bar\eta_0}$$

$$+\frac{-1+2\eta^*+\sqrt{(1-2\eta^*)^2+2\eta^*(1-\eta^*)\left(1-2\beta(1+\beta\theta^*)\right)}}{\eta^*(1-\eta^*)\left(1-2\beta(1+\beta\theta^*)\right)}$$

$$\times(1+\beta\theta^*)^2\Bigg].$$

Here, $\theta = \theta^*$ is a root of the equation

$$\gamma_c\,(1+\beta\theta)^4 = \gamma_c\theta^2 - \theta(1-2\bar\eta_0) + \gamma_c^{-1}(\bar\eta_0^2 - \bar\eta_0),$$

and $\eta^* = H_0(\theta^*)$, where the function $H_0 = H_0(\theta)$ is determined by

$$H_0(1-H_0)\exp\left(\frac{\theta}{1+\beta\theta}\right) - \alpha_0\theta + \alpha_0\frac{H_0-\bar\eta_0}{\gamma_c} = 0.$$

In the case $\beta = 0$ we have

$$\theta^*|_{\beta=0} = \theta_0^* = \frac{1}{2}\left(\gamma_c^{-1}(1-2\bar\eta_0) + \sqrt{4+\gamma_c^{-2}}\right),$$

$$\eta^*|_{\beta=0} = \frac{1}{2}\left(1+\sqrt{1+4\gamma_c^2}\right) - \gamma_c,$$

$$\alpha_0|_{\beta=0} = \frac{\exp\theta_0^*}{2+\sqrt{4+\gamma_c^{-2}}}.$$

For example, in the case $\bar\eta_0 = 0$, the asymptotic expansion of the canard value of parameter α is [40, 41] (we take the zero–approximation term with order $O(\beta)$ and the first–approximation term with order $O(\varepsilon)$)

$$\alpha^* = \frac{1-\beta\theta_0^{*2}}{2+\sqrt{4+\gamma_c^{-2}}}e^{\theta_0^*}\Bigg[1-\varepsilon\Bigg(\frac{1}{2}\gamma_c^{-2} + \frac{1}{2}\gamma_c^{-1}\left(2+\sqrt{4+\gamma_c^{-2}}\right)$$

$$+\sqrt[4]{4+\gamma_c^{-2}}\sqrt{2+\sqrt{4+\gamma_c^{-2}}}\Bigg)\Bigg],\ \ \theta_0^* = \frac{1}{2}\left(\gamma_c^{-1}+\sqrt{4+\gamma_c^{-2}}\right).$$

In the case $\delta \neq 0$ we obtain the problem of construction of critical trajectory in R^3. The breakdown curve separates the stable subset (S^s) of the slow surface S and the unstable one (S^u), see Figure 2.8. Here S is described by the equation

$$F(\eta,\theta,\theta_c,\alpha) = \eta(1-\eta)\exp\left(\frac{\theta}{1+\beta\theta}\right) - \alpha(\theta-\theta_c) - \delta\theta = 0,$$

$$S^s = \{(\eta, \theta, \theta_c): \quad F_\theta(\eta, \theta, \theta_c, \alpha) < 0\},$$
$$S^u = \{(\eta, \theta, \theta_c): \quad F_\theta(\eta, \theta, \theta_c, \alpha) > 0\}.$$

The different types of chemical regimes take place depending on the relation between values of the parameters, see Figures 3.9–3.11. We shall use a canard as *a separating solution* corresponding to the critical regime of chemical reaction. We can find the canard solution and corresponding value of α by following asymptotic expansions

$$\alpha^* = \alpha(\varepsilon) = \alpha_0 + \varepsilon\alpha_1 + \varepsilon^2 \dots ,$$
$$\theta = \theta(\eta, \varepsilon) = \phi_0(\eta) + \varepsilon\phi_1(\eta) + \varepsilon^2 \dots ,$$
$$\theta_c = \theta_c(\eta, \varepsilon) = \psi_0(\eta) + \varepsilon\psi_1(\eta) + \varepsilon^2 \dots .$$

From the differential system under consideration we have

$$\varepsilon\theta'(\eta, \varepsilon)\eta\,(1-\eta)\exp\left(\frac{\theta(\eta, \varepsilon)}{1+\beta\theta(\eta, \varepsilon)}\right)$$
$$= \eta\,(1-\eta)\exp\left(\frac{\theta(\eta, \varepsilon)}{1+\beta\theta(\eta, \varepsilon)}\right) - \alpha(\varepsilon)\,(\theta(\eta, \varepsilon) - \theta_c(\eta, \varepsilon)) - \delta\theta(\eta, \varepsilon),$$
$$\gamma_c\theta_c'(\eta, \varepsilon)\eta\,(1-\eta)\exp\left(\frac{\theta(\eta, \varepsilon)}{1+\beta\theta(\eta, \varepsilon)}\right) = \alpha(\varepsilon)\,(\theta(\eta, \varepsilon) - \theta_c(\eta, \varepsilon))\,.$$

Substituting the asymptotic expansions for $\alpha(\varepsilon)$, $\theta(\eta, \varepsilon)$, $\theta_c(\eta, \varepsilon)$ in last relationships and equating the coefficients of like powers of ε in the left and right members we obtain the equations for functions $\phi_i = \phi_i(\eta)$ and $\psi_i = \psi_i(\eta)$ $(i = 0, 1, 2, \dots)$. The coefficients α_i are found due to the continuity condition for these functions at $\eta = \eta^*$. The equations

$$\eta(1-\eta)\exp\left(\frac{\phi_0}{1+\beta\phi_0}\right) - \alpha_0\,(\phi_0 - \psi_0) - \delta\phi_0 = 0,$$
$$\gamma_c\psi_0'\eta(1-\eta)\exp\left(\frac{\phi_0}{1+\beta\phi_0}\right) = \alpha_0\,(\phi_0 - \psi_0)\,, \quad \psi_0(\bar\eta_0) = 0,$$
$$\eta^*(1-\eta^*)\exp\left(\frac{\phi_0(\eta^*)}{1+\beta\phi_0(\eta^*)}\right)\frac{1}{(1+\beta\phi_0(\eta^*))^2} - (\alpha_0 + \delta) = 0,$$
$$(1-2\eta^*)\exp\left(\frac{\phi_0(\eta^*)}{1+\beta\phi_0(\eta^*)}\right) + \alpha_0\psi_0'(\eta^*) = 0$$

define the value α_0 and the functions $\phi_0 = \phi_0(\eta)$ and $\psi_0 = \psi_0(\eta)$. For the calculations the value α_1 and the functions $\phi_1 = \phi_1(\eta)$ and $\psi_1 = \psi_1(\eta)$ we have

$$\phi_0'\eta(1-\eta)\exp\left(\frac{\phi_0}{1+\beta\phi_0}\right)$$
$$= \left[\eta(1-\eta)\exp\left(\frac{\phi_0}{1+\beta\phi_0}\right)\frac{1}{(1+\beta\phi_0)^2} - (\alpha_0 + \delta)\right]\phi_1$$

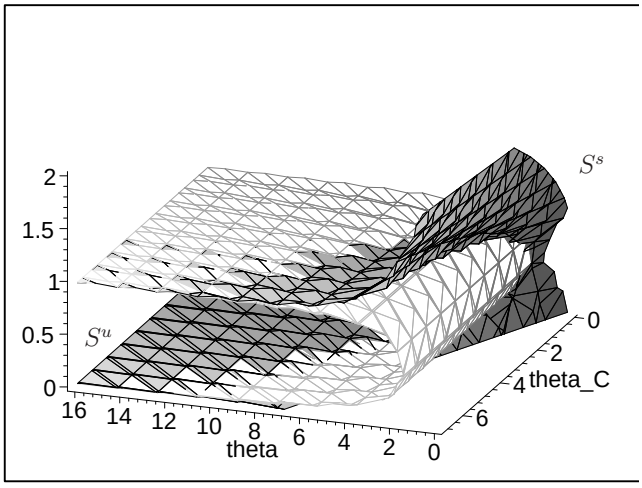


Figure 2.8: The slow surface (the dark area) and the surface of irregular points (the light area).

$$+\alpha_0\psi_1 - \alpha_1\left(\phi_0 - \psi_0\right),$$

$$\eta(1-\eta)\exp\left(\frac{\phi_0}{1+\beta\phi_0}\right)\left[\phi_0' + \gamma_c\psi_1' + \frac{\phi_1(\gamma_c\psi_0' - 1)}{(1+\beta\phi_0)^2}\right] = -\delta\phi_1, \quad \psi_1(\bar{\eta}_0) = 0,$$

$$\alpha_1 = \frac{1}{\phi_0(\eta^*) - \psi_0(\eta^*)}\left[\alpha_0\psi_1(\eta^*) - \phi_0'(\eta^*)\eta^*(1-\eta^*)\exp\left(\frac{\phi_0(\eta^*)}{1+\beta\phi_0(\eta^*)}\right)\right].$$

The effect of the external cooling may be observed: in the case $\delta \neq 0$ the critical value of the parameter $\alpha = \alpha^*$ decreases, see Figures 3.6, 3.10.

This approach was used in [12] in the case of the first order reaction.

2.2.2 First-order reaction

The case of the first-order reaction ($\Psi(\eta) = (1-\eta)$) is studied now. For simplicity we introduce the dimensionless concentration $\bar{\eta} = 1 - \eta$.

In the absence of external heat dissipation ($\delta = 0$) the system

$$\varepsilon\dot{\theta} = \bar{\eta}\exp\left(\theta/\left(1+\beta\theta\right)\right) - \alpha(\theta - \theta_c),$$

$$\gamma_c\dot{\theta}_c = \alpha(\theta - \theta_c),$$

$$\dot{\eta} = -\bar{\eta}\exp\left(\theta/\left(1+\beta\theta\right)\right),$$

with initial conditions

$$\bar{\eta}(0) = 1, \;\; \theta(0) = \theta_c(0) = 0,$$

possesses a first integral

$$\varepsilon\theta + \gamma_c\theta_c + \bar{\eta} = 1,$$

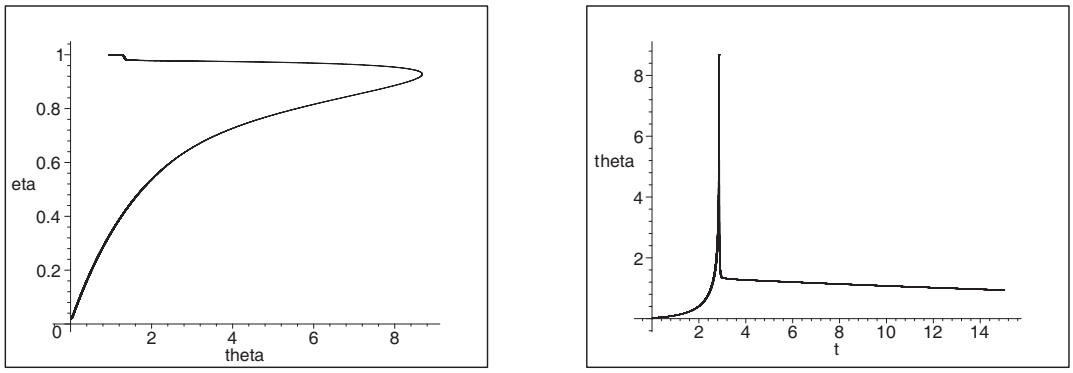


Figure 2.9: The trajectory and the temperature–time characteristics in the case of critical regime for $\alpha = \alpha^* = 0.9033$, $\beta = 0.1$, $\varepsilon = 0.01$, $\gamma_c = 0.7$, $\bar{\eta}_0 = 0.02$, $\delta = 0.02$.

and we obtain $\dim y = 0$ in (1.9).

The slow curve S is defined by the equation

$$\bar{\eta} \exp\left(\theta / \left(1 + \beta\theta\right)\right) - \alpha\big(\theta - \gamma_c^{-1}(1 - \bar{\eta})\big) = 0.$$

With different relations between values of the parameters α, δ and γ_c we can observe the following chemical regime types:

— the slow combustion regime;

— the classic thermal explosion;

— thermal explosion with delay [4, 12].

The last regime consists of three stages: fast initial, slow (delay) and explosive, see Fig. 3.15. This regime is characterized by a rather long induction period and a significant time for reactant conversion before a thermal explosion.

It should be noted that there are two types of slow regimes: the slow regime with essential initial heating (EIH, see Fig. 2.11) and the slow regime with nonessential initial heating (NIH, see Fig. 2.12).

Thus, in this case there are two critical regimes which separate fast explosive, explosive with delay and non-explosive regimes, see Fig. 2.13. The first critical regime takes place when, after a short time, the trajectory reaches the jump point and then follows the unstable slow integral manifold. This trajectory and the corresponding value of the control parameter can be found by Mishchenko–Rozov asymptotics [26], and if we take α as a control parameter we get

$$\alpha^* = (1 - \beta)e - \varepsilon^{2/3}\Omega_0 \sqrt[3]{2(1 - \gamma_c^{-1})^2}e \left[1 + \beta\left(1 + \frac{4\gamma_c^{-1}}{3(1 - \gamma_c^{-1})}\right)\right] +$$

$$+\frac{4}{9}\varepsilon \ln\frac{1}{\varepsilon}e\left(1 - \gamma_c^{-1}\right) + O\left(\beta + \varepsilon\ln\frac{1}{\varepsilon}\right).$$

The second critical regime is modelled by a canard, see Fig. 2.15. The asymptotic expansion of the canard value α^{**} is [12]

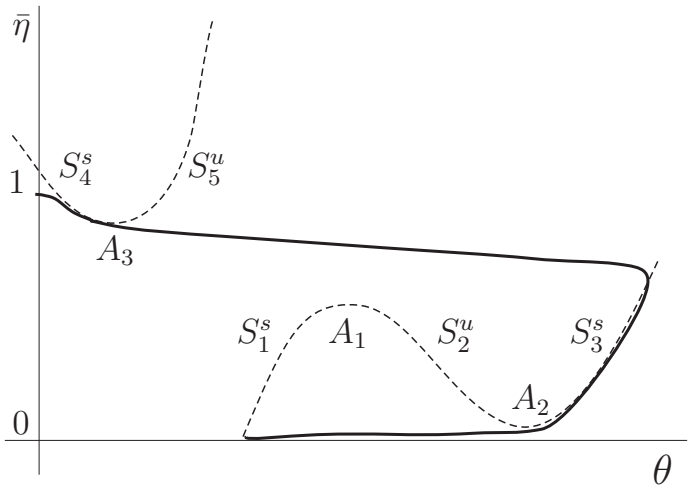


Figure 2.10: The slow curve (the dashed line) and the trajectory (the solid line) in the case of thermal explosion with delay

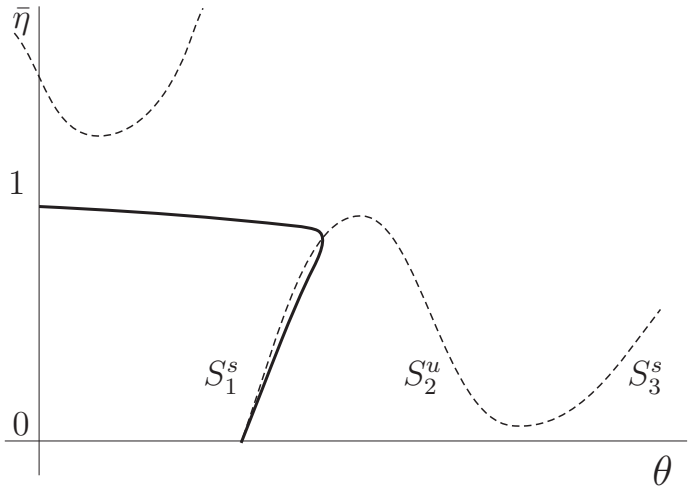


Figure 2.11: The slow curve (the dashed line) and the trajectory (the solid line) in the case of slow combustion regime with essential initial heating

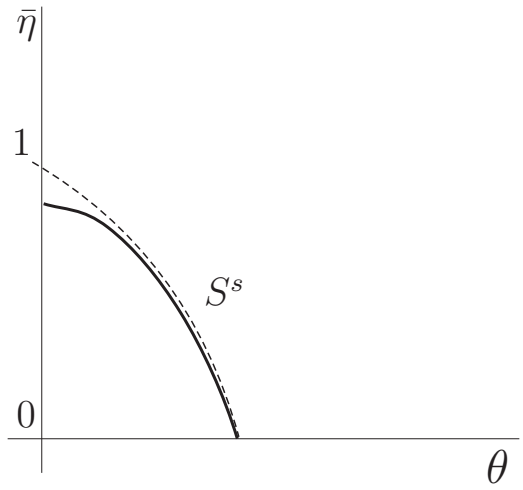


Figure 2.12: The slow curve (the dashed line) and the trajectory (the solid line) in the case of slow combustion regime with nonessential initial heating

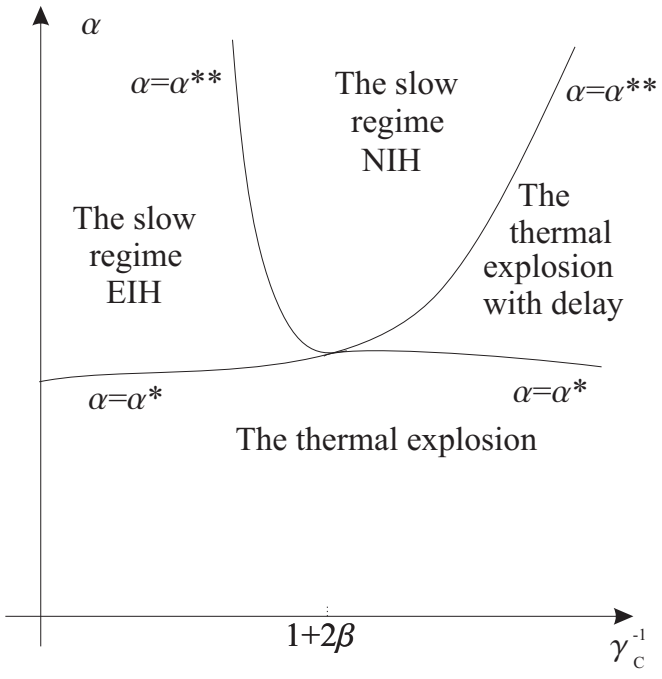


Figure 2.13: The domains of parameters and the associated types of combustion regimes

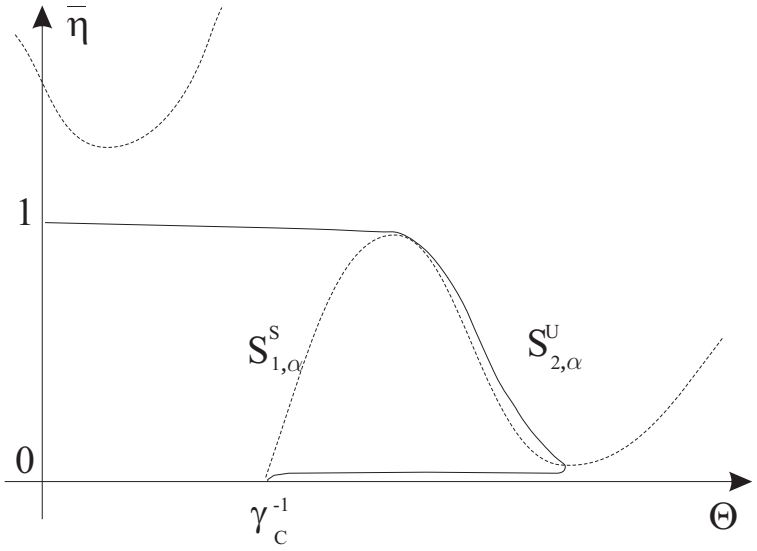


Figure 2.14: The slow curve (the dashed line) and the canard (the solid line) in the case of the first critical regime

$$\alpha^{**} = \exp\left(\frac{\gamma_c^{-1}}{1+\beta\gamma_c^{-1}}\right)\left[\gamma_c - \varepsilon\big(2+\gamma_c^{-1}+\beta(4-2\gamma_c^{-1})\big)\right] + o(\varepsilon+\beta).$$

If we investigate the system in a more general case ($\delta \neq 0$) we can construct a black swan which consists of canards simulating the second type of critical regimes.

Let us take $\gamma_c(\Theta,\varepsilon)$ as control function. Then it and the black swan $\Theta_c = \Theta_c(\bar\eta,\Theta,\varepsilon)$ have asymptotic expansions of the form:

$$\gamma_c = \Gamma_0(\Theta) + \varepsilon\Gamma_1(\Theta) + O(\varepsilon^2),$$

$$\Theta_c = P_0(\bar\eta,\Theta) + \varepsilon P_1(\bar\eta,\Theta) + O(\varepsilon^2),$$

where

$$P_0(\bar\eta,\Theta) = (\delta\Theta - \bar\eta e^{\Theta})/\alpha + \Theta,$$

$$P_1(\bar\eta,\Theta) = -\delta\Theta\bar\eta e^{\Theta}/(\alpha+\delta-\delta\Theta),$$

$$\Gamma_0(\Theta) = \alpha\frac{\alpha+\delta-\delta\Theta}{(\alpha+\delta)e^{\Theta}},$$

$$\Gamma_1(\Theta) = -\frac{\alpha^2\delta\Theta\big[(\alpha+\delta-\delta\Theta)(\alpha\delta\Theta-\alpha-\delta)+\alpha\delta(\alpha+\delta)\big]}{(\alpha+\delta)^2(\alpha+\delta-\delta\Theta)^2}.$$

In the case when δ is a control function (it means that we control the combustion process by regulating the external heat dissipation) we get the following asymptotic expansion for and δ [33]

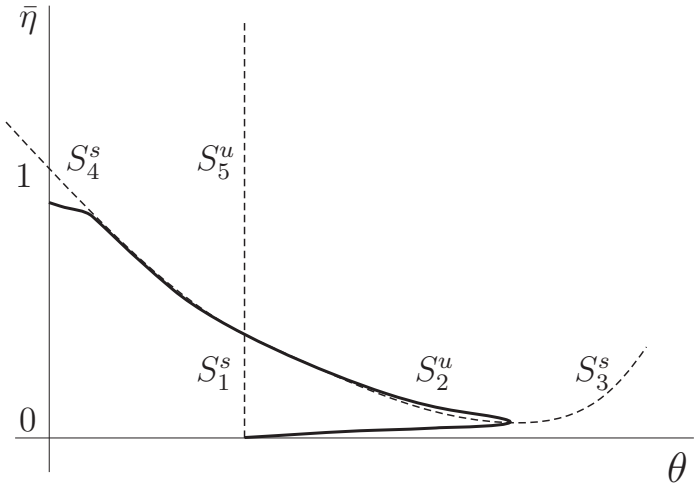


Figure 2.15: The slow curve (the dashed line) and the canard (the solid line) in the case of the second critical regime

$$\delta = \delta(\Theta, \varepsilon) = \Theta^{-1}\Big[\alpha\frac{\left(\Theta - \ln\alpha\gamma_c^{-1} - 1\right)e^{\Theta} + \alpha\gamma_c^{-1}}{\alpha\gamma_c^{-1} - e^{\Theta}} + \\ + \varepsilon(\alpha\gamma_c^{-1} - e^{\Theta}) + O(\varepsilon^2)\Big]$$

corresponding to the black swan $\Theta_c = \Theta_c(\bar{\eta}, \Theta, \varepsilon)$ of the system.

For the fixed point $\Theta = \Theta^*$ of the breakdown curve we can find the value δ^* from the last expression which corresponds to the canard of the system. This trajectory passes through the point Θ^* of the breakdown curve and simulates the critical regime. It should be noted that the choice of the gluing point Θ^* is equivalent to the choice the starting point $\Theta(0)$ of the trajectory. For example, with $\Theta(0) = 0$, $\gamma_c = 1/6$, $\varepsilon = 0.01$, $\alpha = 2.34$ the critical regime corresponds to $\delta^* = 1.10797$.

Chapter 3

Modelling of critical phenomena for ignition of metal particles

The paper is devoted to the investigation of critical phenomena for ignition of metal particles. Dynamics of heating, ignition, and combustion of metal particles has been widely studied over the past 50 years, and has been reviewed in [10, 47, 48], among others, and more recently in [49]. Ignition and combustion of metal particles are the issues important for various applications, including aerospace and chemical technologies, ground transportation, and industrial safety [2, 18, 23].

The use of metals as high–energy fuel additives is generally compromised by the formation of an oxide film that covers the fuel surface. This film prevents direct interaction between the metal and the gaseous oxidant. Hence, the kinetics laws of metal oxidation are different from the kinetics laws of heterogeneous reactions and depend on the physical properties and the thickness of the oxide film build-up on the metal surface [18, 48, 50]. Heat released on metal oxidation may causes fast self–heating of the metal particles at high temperature. Thus, metal ignition, and therefore the explosion, occurs as a result of thermal self–acceleration of the chemical reaction [32]. In some cases, the heat released at oxidation of particles has time to be removed into the surroundings, and the ignition does not take place. Then the particle temperature reaches a maximum and decays to reach the initial gas temperature (*subcritical regime*). In other cases, heat released in the particle causes self–acceleration of the oxidation reaction, which leads to a rapid increase in particle temperature, thus causing ignition (*supercritical regime*) [8].

In this paper the existence of the critical regime, separating the domain of subcritical regimes from the domain of supercritical ones, is shown. Using the special asymptotic formulae [26] the conditions under which the critical regime takes place in the chemical system are obtained. That approach was applied in [4, 11, 14, 20] to model thermal explosion of gaseous reactants.

3.1 Mathematical model

Taking into consideration a uniform temperature distribution in a particle, a constant particle size and the constant physical properties of both gas and particle, the known dimensionless model of the process has the following form [18]:

$$\begin{aligned} \varepsilon\frac{d\theta}{d\tau} &= \varphi(\eta)\exp\left(\frac{\theta}{1+\beta\theta}\right)-\frac{\theta}{\kappa}, \\ \frac{d\eta}{d\tau} &= \varphi(\eta)\exp\left(\frac{\theta}{1+\theta\beta}\right), \end{aligned} \tag{3.1}$$

with initial conditions

$$\eta(0)=0, \quad \theta(0)=-\theta_i.$$

Here θ is the dimensionless temperature of a metal particle and

$$\theta=\frac{(T-T_0)E}{RT_0^2},$$

where T is the temperature of a metal particle, T_0 is the gas temperature, E is the Arrhenius activation energy, R is the universal gas constant; η is the dimensionless related growth of the thickness of the oxide film and

$$\eta=\frac{\delta-\delta_{in}}{\delta},$$

where δ is the oxide film thickness, δ_{in} is the initial thickness of the film; τ is dimensionless time; the parameters β and ε reflect the temperature sensitivity and the exothermicity of the reaction; κ is a modified Semenov number related to convection heat transfer; $\varphi(\eta)$ is the kinetic function. This paper examines two forms of oxidation kinetics:

$$\varphi(\eta)=(\eta+1)^{-n}, \quad n=1,2,$$

corresponding to the cases of parabolic and cubic laws, respectively.

The initial temperature of a metal particle is either lower than the gas temperature or equal to it. In the fist case, corresponding to cold particles, we have $\theta(0)=-\theta_i<0$, and in the second one, when the metal particles and the gas are heated simultaneously during a very short time, $\theta(0)=0$.

The chemically relevant phase space Δ of the system (3.1) is defined by

$$\Delta:=\{(\theta,\eta)\in R^2:\theta\geq-\theta_i,\eta\geq 0\}.$$

It should be noted that the system (3.1) is similar to the dimensionless model of the thermal explosion of a gas [32, 47, 50]. But in the thermal explosion theory the kinetic function is usually $\varphi(\eta)=(\eta+1)^n$, and η reflects the depth of a gas conversion.

In the case of very small particle size and significant initial thickness of the oxide film the parameter ε is small [18] and, hence, the system (3.1) is singularly perturbed [27, 46]. Thus, it is possible to apply the mathematical apparatus of singular perturbations for the investigation of the critical conditions for ignition of a metal particle in this case.

3.2 Case of parabolic law

In the case of a parabolic law of oxidation kinetics the system (3.1) has the form

$$\begin{aligned} \varepsilon\frac{d\theta}{d\tau} &= (\eta+1)^{-1}\exp\left(\frac{\theta}{1+\beta\theta}\right)-\frac{\theta}{\kappa}, \\ \frac{d\eta}{d\tau} &= (\eta+1)^{-1}\exp\left(\frac{\theta}{1+\theta\beta}\right), \end{aligned} \tag{3.2}$$

with initial conditions

$$\eta(0)=0, \quad \theta(0)=-\theta_i. \tag{3.3}$$

If we put $\varepsilon=0$ in the first equation of (3.2) we get *the degenerate equation*

$$F(\eta,\theta,\kappa)=(\eta+1)^{-1}\exp\left(\frac{\theta}{1+\beta\theta}\right)-\frac{\theta}{\kappa}=0 \tag{3.4}$$

which describes *the slow curve*

$$S=\left\{(\theta,\eta):(\eta+1)^{-1}\exp\left(\frac{\theta}{1+\beta\theta}\right)-\frac{\theta}{\kappa}=0\right\}$$

of the system (3.2) (see, for example, [37]). The subset S^s (S^u) of S with

$$\frac{\partial}{\partial\theta}F(\eta,\theta,\kappa)<0 \ \ (>0) \tag{3.5}$$

is called *the attractive (repulsive)* part of S. A point A on S in which $\partial F/\partial\theta=0$ is called *the jump point* [26, 37].

We take κ as the control parameter with fixed β,ε. For all κ the slow curve of the system (3.2) consists of two branches, which are separated by the asymptote $\eta=-1$, see Figure 3.1. Hence, the lower branch of S in (θ,η)–plane is outside Δ. The second one has two jump points A_1 and A_2 with coordinates (η_1,θ_1) and (η_2,θ_2), respectively, where θ_1,θ_2 are the roots of the equation

$$\theta-(1+\beta\theta)^2=0,$$

i.e.,

$$\theta_1=\frac{1-2\beta-\sqrt{1-4\beta}}{2\beta^2}, \quad \theta_2=\frac{1-2\beta+\sqrt{1-4\beta}}{2\beta^2}, \tag{3.6}$$

and

$$\eta_1=\frac{\kappa}{\theta_1}\exp\left(\frac{\theta_1}{1+\beta\theta_1}\right)-1, \quad \eta_2=\frac{\kappa}{\theta_2}\exp\left(\frac{\theta_2}{1+\beta\theta_2}\right)-1. \tag{3.7}$$

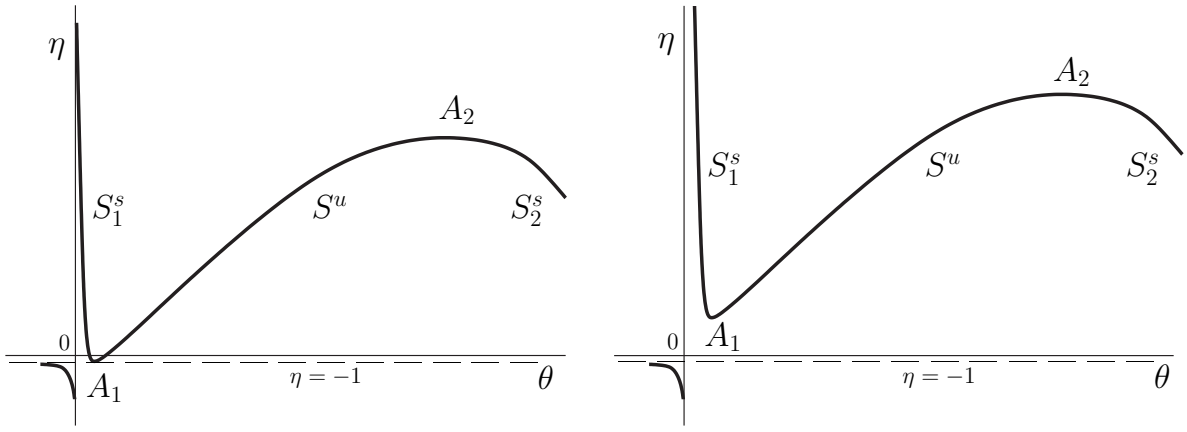


Figure 3.1: The form of the slow curve of the system (3.2): (a) for $\kappa < \kappa_0$, (b) for $\kappa > \kappa_0$, where $\kappa_0 = (1+\beta)/e$, $e = \exp(1)$.

Hence, according to (3.4)–(3.7), the upper branch of the slow curve S consists of two attractive parts S_1^s and S_2^s and the repulsive one S^u, where

$$\begin{aligned} S_1^s &:= \{(\theta,\eta) \in S:\ \eta > -1,\ \ 0 < \theta < \theta_1\}, \\ S_2^s &:= \{(\theta,\eta) \in S:\ \eta > -1,\ \ \theta > \theta_2\}, \\ S^u &:= \{(\theta,\eta) \in S:\ \eta > -1,\ \ \theta_1 < \theta < \theta_2\}. \end{aligned}$$

Since the parameter β is small (for real chemical systems, see, for example, [18, 50]), from (3.6) we have $\theta_1 = 1 + 2\beta + O(\beta^2)$, $\theta_2 = \beta^{-2}\left(1 - 2\beta + O(\beta^2)\right)$ as $\beta \to 0$. Hence, the part S_2^s corresponds to a very high values of the metal temperature and this means in practice the destruction of the reactant vessel. So, to analyze the behavior of the system (3.2), we will concentrate our attention on S_1^s and S^u only.

In the case $\kappa < \kappa_0 = (1+\beta)/e$, where $e = \exp(1)$, some part of set S_1^s of the slow curve lies below the η–axis, see Figures 3.1(a) and 3.2. The trajectory of the system starting from the initial point rapidly tends to S_1^s and then follows the attractive set S_1^s at the tempo of the slow variable, see Figure 3.3. This behavior corresponds to *the slow regime* with low temperatures (subcritical regime).

In the case $\kappa > \kappa_0$ the branch of the slow curve with $\eta > 0$ is situated above the θ–axis entirely, see Figures 3.1(b) and 3.4. The trajectory of the system in this case, starting from the initial point, passes by the slow curve at the tempo of the fast variable. Theoretically the trajectory of (3.2) reaches the attractive set S_2^s of the slow curve and then follows it at the tempo of the slow variable up to the point A_2. After this moment the trajectory loses its connection with the slow curve: a jump of the trajectory of the slow curve occurs. Then the trajectory rapidly tends to the attractive set S_1^s. However, due to a very high temperature the explosion causes long before the trajectory reaches S_2^s, see Figure 3.5. This behavior corresponds to *the ignition* (supercritical regime).

In the case $\kappa = \kappa_0$ we have $\eta_1 = 0$, see Figure 3.6. In a neighborhood of κ_0 it is possible to

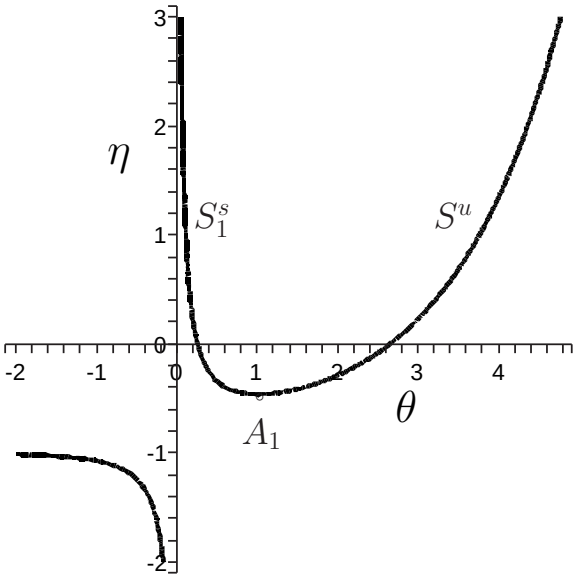


Figure 3.2: The slow curve of the system (3.2) for $\beta = 0.01$, $\kappa = 0.2 < \kappa_0$, $\theta < 5$.

find the value $\kappa = \kappa^*$ corresponding to *the critical regime*. The trajectory of the system with $\kappa = \kappa^*$ starting from the initial point rapidly tends to a very small vicinity of the point A_1 and then follows the repulsive part S^u of the slow curve, up to a point J from which the solution "jumps" towards the attractive component S_1^s and then follows it, see Figure 3.7(a).

To find the value $\kappa = \kappa^*$, which corresponds to a trajectory modelling the critical regime in the chemical system, we use the techniques proposed in [26]. The idea of this approach consists of the following. If we reverse the time in the system (3.2) by $\tau = -t$, the repulsive part S^u of slow curve becomes the attractive one for the system

$$\begin{aligned} \varepsilon\frac{d\theta}{dt} &= -(\eta+1)^{-1}\exp\left(\frac{\theta}{1+\beta\theta}\right) + \frac{\theta}{\kappa} = f(\eta,\theta), \\ \frac{d\eta}{dt} &= -(\eta+1)^{-1}\exp\left(\frac{\theta}{1+\theta\beta}\right) = g(\eta,\theta) \end{aligned}$$

(3.8)

with the new time t. A trajectory of the system (3.8) starting from any point in the basin of attraction of the set S^u, after a short time follows the attractive set S^u at the tempo of the slow variable up to the point A_1, see Figure 3.8. This part of the trajectory is the part of slow motions and the trajectory here has the asymptotic representation [26]

$$\eta(\theta,\varepsilon) = h_0(\theta) + \varepsilon h_1(\theta) + O(\varepsilon^2).$$

When the trajectory reaches the point A_1, it jumps off the slow curve and rapidly tends to the final point. Note, that the final point of the system (3.8) corresponds to the initial point (3.3) of the system (3.2). This part of the trajectory is the part of fast motions and the trajectory

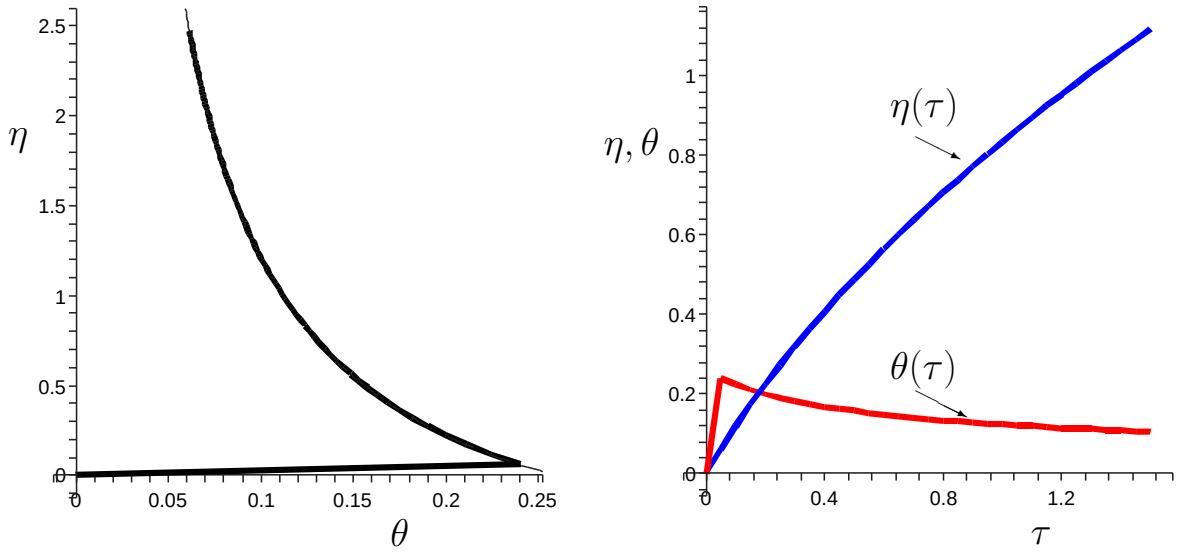


Figure 3.3: (a) The slow curve (the thin line) and the trajectory (the thick line) of the system (3.2) for $\beta = 0.01$, $\varepsilon = 0.01$, $\kappa = 0.2$, $\theta_i = 0$. (b) The η– and θ–components of the solution in the case of the slow regime for $\beta = 0.01$, $\varepsilon = 0.01$, $\kappa = 0.2$, $\theta_i = 0$.

here has the asymptotic representation [26]

$$\eta(\theta,\varepsilon) = \eta_1 + b^0_{0,0}\Gamma^{2/3}\,\mathrm{sign}\,g(\eta_1,\theta_1)\,\varepsilon^{2/3} + \frac{1}{3}b^1_{0,1}\Gamma\,\mathrm{sign}\,g(\eta_1,\theta_1)\,\varepsilon\ln\frac{1}{\varepsilon} + O(\varepsilon), \tag{3.9}$$

where

$$b^0_{0,0} = \Omega_0 = 2.338107,\ \ b^1_{0,1} = \frac{\Gamma'_\xi}{\Gamma},$$

$$\Gamma = \sqrt{\frac{2}{|f_{\theta\theta}(\eta_1,\theta_1)f_\eta(\eta_1,\theta_1)|}}\ |g(\eta_1,\theta_1)|,$$

$$\Gamma'_\xi = \frac{6f_{\theta\theta}(\eta_1,\theta_1)g_\theta(\eta_1,\theta_1) - 2f_{\theta\theta\theta}(\eta_1,\theta_1)g(\eta_1,\theta_1)}{3f^2_{\theta\theta}(\eta_1,\theta_1)}.$$

Recall, η_1 and θ_1 here are the coordinates of the jump point A_1 and, using $\beta \ll 1$, we have from (3.6) and (3.7)

$$\eta_1 = \kappa e(1-\beta) - 1 + O(\beta^2), \quad \theta_1 = 1 + 2\beta + O(\beta^2).$$

With this η_1, θ_1 and (3.3), (3.8), (3.9) we obtain the equation for κ:

$$0 = \kappa e(1-\beta) - 1 + \Omega_0(2\kappa e)^{1/3}\left(1 + \frac{5}{2}\beta\right)^{2/3}\varepsilon^{2/3} + \frac{4(1+6\beta)}{9}\varepsilon\ln\frac{1}{\varepsilon} + O(\varepsilon+\beta^2). \tag{3.10}$$

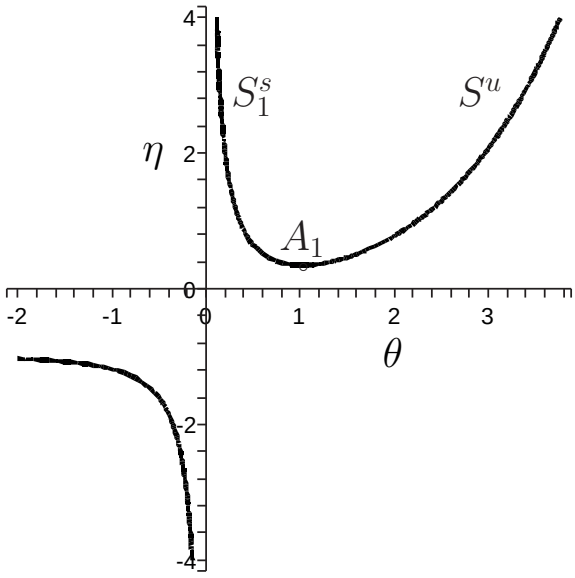


Figure 3.4: The slow curve of the system (3.2) for $\beta = 0.01$, $\kappa = 0.5 > \kappa_0$, $\theta < 4$.

From the equation (3.10) it follows that the critical value of the parameter κ can be found in the asymptotic representation

$$\kappa = \kappa^* = \kappa_0 + \kappa_1 \varepsilon^{2/3} + \kappa_2 \varepsilon \ln \frac{1}{\varepsilon} + O(\varepsilon).$$

By substituting this series into (3.10) and equating the coefficients we get

$$\kappa^* = \frac{1}{e}\left[1 + \beta - \Omega_0 \sqrt[3]{2}(1+3\beta)\varepsilon^{2/3} - \frac{4}{9}(1+7\beta)\varepsilon \ln \frac{1}{\varepsilon}\right] + O(\varepsilon + \beta^2).$$

The critical regime corresponding to $\kappa = \kappa^*$ separates the region of slow regimes ($\kappa < \kappa^*$) which are characterized by low temperatures and the region of the ignition ($\kappa > \kappa^*$). During the critical regime the temperature attains a high value but without the ignition, at the tempo of slow variable of the system, see Figure 3.7(b).

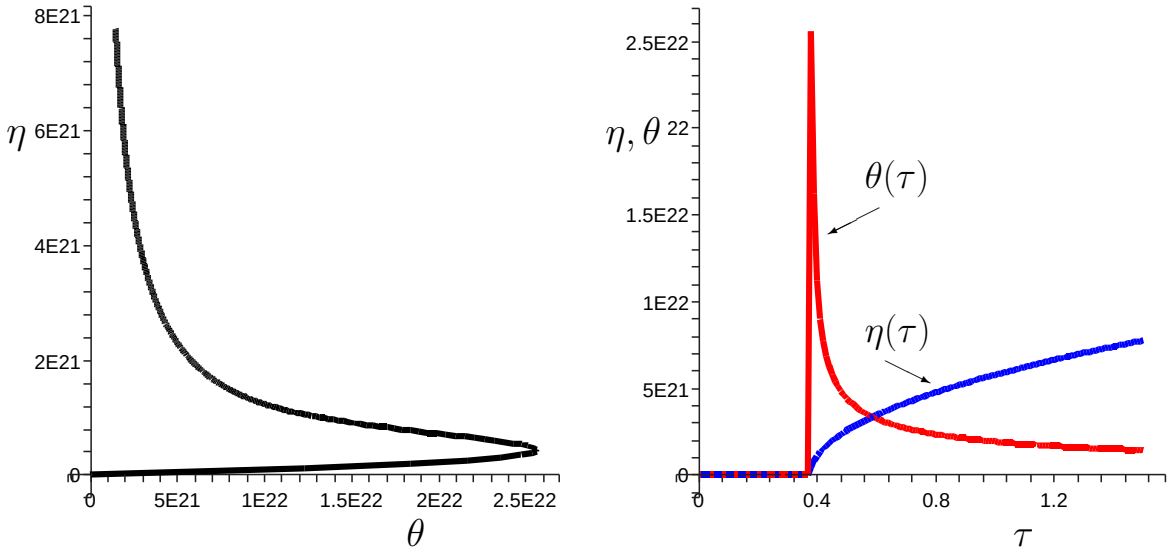
3.3 Case of cubic law

In the case of a cubic law of oxidation kinetics the system (3.1) has the form

$$\begin{aligned} \varepsilon \frac{d\theta}{d\tau} &= (\eta+1)^{-2} \exp\left(\frac{\theta}{1+\beta\theta}\right) - \frac{\theta}{\kappa}, \\ \frac{d\eta}{d\tau} &= (\eta+1)^{-2} \exp\left(\frac{\theta}{1+\theta\beta}\right), \end{aligned} \tag{3.11}$$

with initial conditions

$$\eta(0) = 0, \quad \theta(0) = -\theta_i. \tag{3.12}$$



(a) (b)

Figure 3.5: (a) The trajectory of the system (3.2) for $\beta = 0.01$, $\varepsilon = 0.01$, $\kappa = 0.5$, $\theta_i = 0$. (b) The η– and θ–components of the solution in the case of the ignition for $\beta = 0.01$, $\varepsilon = 0.01$, $\kappa = 0.5$, $\theta_i = 0$.

The degenerate equation

$$F(\eta, \theta, \kappa) = (\eta + 1)^{-2} \exp\left(\frac{\theta}{1 + \beta\theta}\right) - \frac{\theta}{\kappa} = 0 \tag{3.13}$$

describes the slow curve

$$S = \left\{(\theta, \eta) : (\eta + 1)^{-2} \exp\left(\frac{\theta}{1 + \beta\theta}\right) - \frac{\theta}{\kappa} = 0\right\}$$

of the system (3.11).

As in previous section we take κ as a control parameter with fixed β, ε. For all κ the slow curve of the system (3.11) consists of two branches which are described by the equations

$$\eta = -1 + \sqrt{\frac{\kappa}{\theta} \exp\left(\frac{\theta}{1 + \beta\theta}\right)}$$

and

$$\eta = -1 - \sqrt{\frac{\kappa}{\theta} \exp\left(\frac{\theta}{1 + \beta\theta}\right)}.$$

From the last equation it follows that one branch of S (namely, the lower one in (θ, η)–plane) is outside Δ, see Figure 3.9. The upper branch of S has two jump points A_1 and A_2 with coordinates (η_1, θ_1) and (η_2, θ_2), respectively, where θ_1 and θ_2 are the roots of the equation

$$\theta - (1 + \beta\theta)^2 = 0,$$

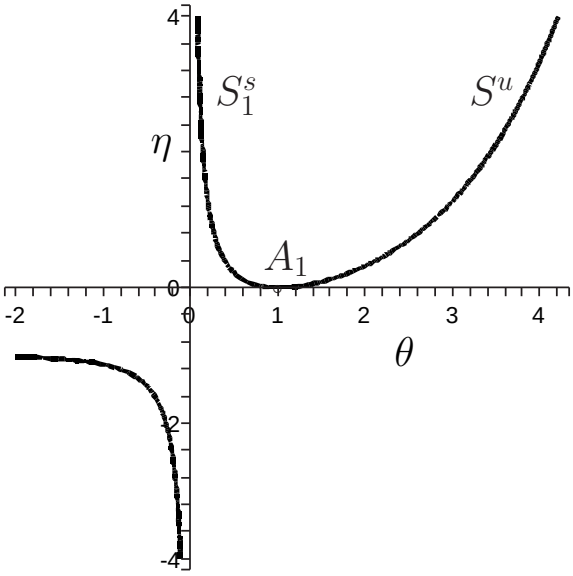
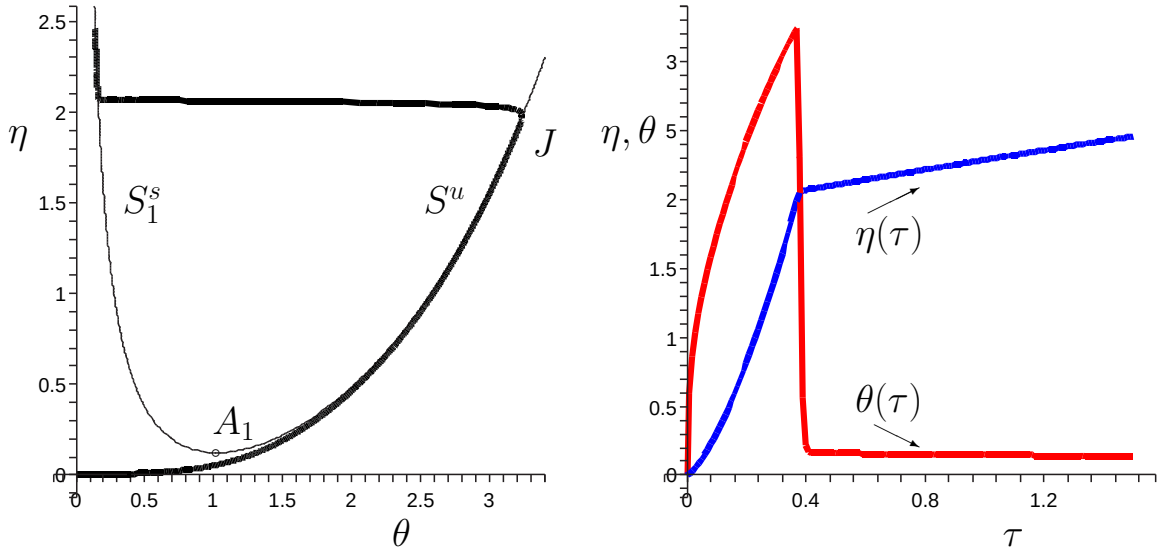


Figure 3.6: The slow curve of the system (3.2) for $\beta = 0.01$, $\kappa = \kappa_0 = 0.3716$, $\theta < 4$.



(a) (b)

Figure 3.7: (a) The slow curve (the thin line) and the trajectory (the thick line) of the system (3.2) in the case of critical regime. (b) The η– and θ–components of the solution in the case of the critical regime for $\beta = 0.01$, $\varepsilon = 0.01$, $\theta_i = 0$, $\kappa = \kappa^* \approx 0.41767$.

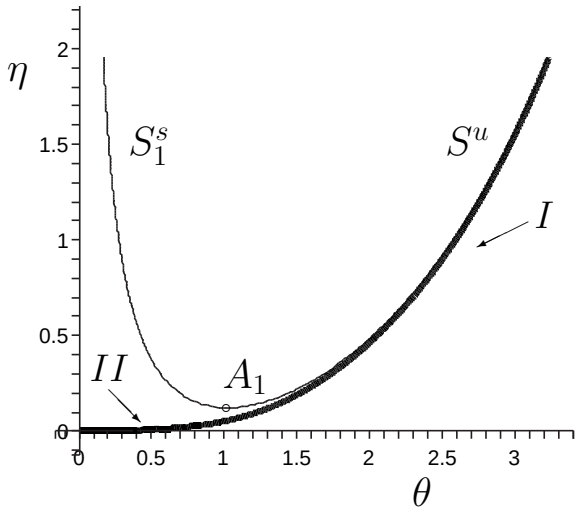
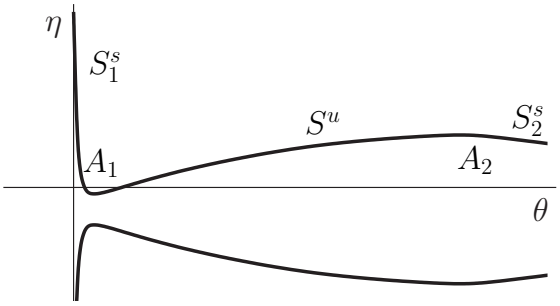
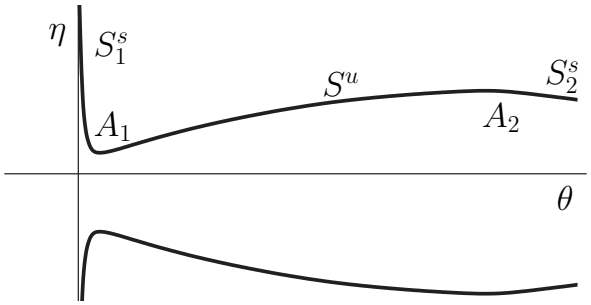


Figure 3.8: The slow curve (the thin line) and the trajectory (the thick line) of the system (3.8) for $\kappa = \kappa^*$. The trajectory contains the part of slow motions (I) and the part of fast motions (II).



(a)



(b)

Figure 3.9: The form of the slow curve of the system (3.11): (a) for $\kappa < \kappa_0$, (b) for $\kappa > \kappa_0$, where $\kappa_0 = (1+\beta)/e$, $e = \exp(1)$.

i.e.,

$$\theta_1 = \frac{1 - 2\beta - \sqrt{1-4\beta}}{2\beta^2}, \quad \theta_2 = \frac{1 - 2\beta + \sqrt{1-4\beta}}{2\beta^2}, \tag{3.14}$$

and

$$\eta_1 = -1 + \sqrt{\frac{\kappa}{\theta_1} \exp\left(\frac{\theta_1}{1+\beta\theta_1}\right)}, \quad \eta_2 = -1 + \sqrt{\frac{\kappa}{\theta_2} \exp\left(\frac{\theta_2}{1+\beta\theta_2}\right)}. \tag{3.15}$$

Hence, according to (3.5), (3.13)–(3.15), the upper branch of the slow curve S consists of two attractive parts S_1^s and S_2^s and the repulsive S^u, where

$$\begin{aligned} S_1^s &:= \{(\theta,\eta) \in S:\ \eta > -1,\ \ 0 < \theta < \theta_1\}, \\ S_2^s &:= \{(\theta,\eta) \in S:\ \eta > -1,\ \ \theta > \theta_2\}, \\ S^u &:= \{(\theta,\eta) \in S:\ \eta > -1,\ \ \theta_1 < \theta < \theta_2\}. \end{aligned}$$

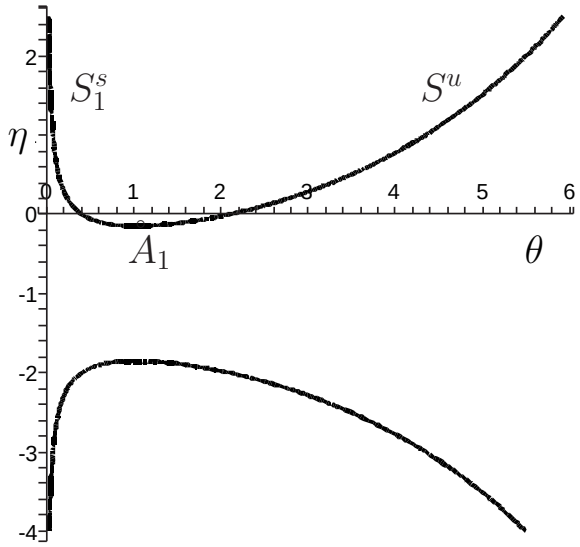


Figure 3.10: The slow curve of the system (3.11) for $\beta = 0.01$, $\kappa = 0.27 < \kappa_0$, $\theta \leq 6$.

Taking into account that $\beta \ll 1$, from (3.14) we have $\theta_1 = 1 + 2\beta + O(\beta^2)$, $\theta_2 = \beta^{-2}\left(1 - 2\beta + O(\beta^2)\right)$ as $\beta \to 0$. By the foregoing, we confine our attention to the behavior of the solution of (3.11) near S_1^s and S^u only.

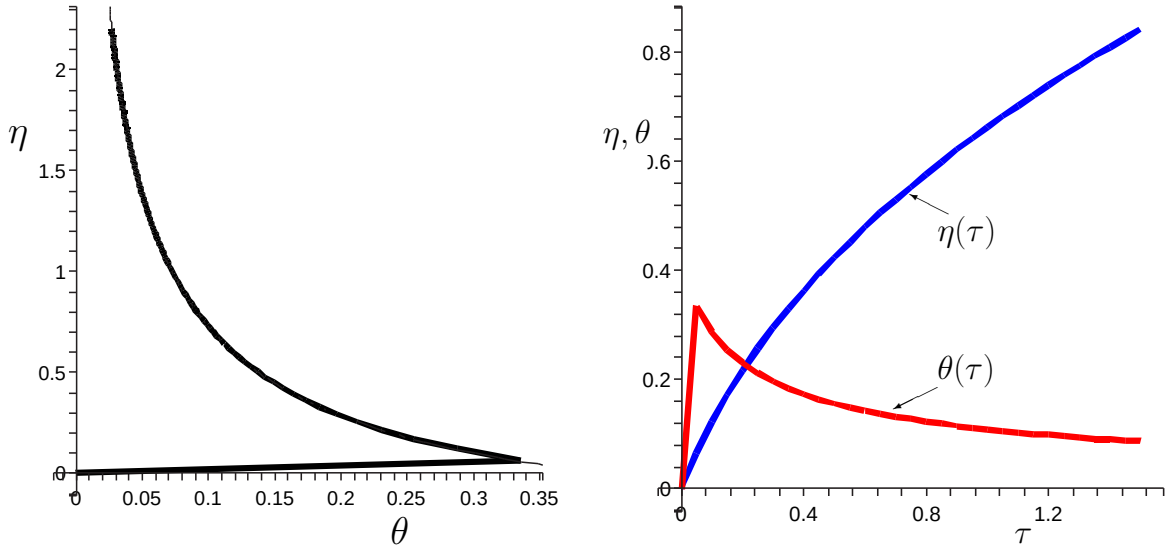
Similar to the case of parabolic law of oxidation kinetics, the form of S depends on the value of the parameter κ and, consequently, depending on its value the chemical reaction either changes to a slow regime with decay of the reaction, or goes into a regime of self–acceleration which leads to an ignition.

In the case $\kappa < \kappa_0$ some part of set S_1^s of the slow curve lies below the η–axis, see Figures 3.9(a) and 3.10. After the part of the fast motion from the initial point up to S_1^s, which corresponds to the initial heating of the chemical system, the trajectory of the system follows the attractive set S_1^s at the tempo of the slow variable, see Figure 3.11. This behavior corresponds to the slow regime with low temperatures (subcritical regime).

In the case $\kappa > \kappa_0$ the branch of the slow curve with $\eta > 0$ lies above the θ–axis entirely, see Figures 3.9(b) and 3.12. The trajectory of the system in this case passes beyond the slow curve and then describes the fast regime. The trajectory of (3.11) reaches the attractive set S_2^s and then follows it at the tempo of the slow variable up to the point A_2. After this moment the trajectory jumps off the slow curve and rapidly tends to the attractive set S_1^s, see Figure 3.13. This behavior corresponds to the ignition characterizing a very high temperature, see Figure 3.13.

Figure 3.14 shows the slow curve in the case $\kappa = \kappa_0$. In a neighborhood of κ_0 it is possible to find the value $\kappa = \kappa^*$ corresponding to the critical regime. In Figure 3.15(a) the trajectory of the system with $\kappa = \kappa^*$, starting from the initial point, rapidly tends to a very small vicinity of the point A_1 and then follows the repulsive part S^u of the slow curve, up to a point J from which the solution "jumps" towards the attractive component S_1^s and then follows it.

To find the value $\kappa = \kappa^*$ which corresponds to a trajectory modelling the critical regime in the chemical system by Mishchenko–Rozov asymptotics we reverse the time in the system (3.11) by $\tau = -t$. As the result we obtain the system



(a) (b)

Figure 3.11: (a) The slow curve (the thin line) and the trajectory (the thick line) of the system (3.11) for $\beta = 0.01$, $\varepsilon = 0.01$, $\kappa = 0.27$, $\theta_i = 0$. (b) The η– and θ–components of the solution in the case of the slow regime for $\beta = 0.01$, $\varepsilon = 0.01$, $\kappa = 0.27$, $\theta_i = 0$.

$$\begin{aligned} \varepsilon\frac{d\theta}{dt} &= -(\eta+1)^{-2}\exp\left(\frac{\theta}{1+\beta\theta}\right) + \frac{\theta}{\kappa} = f(\eta,\theta), \\ \frac{d\eta}{dt} &= -(\eta+1)^{-2}\exp\left(\frac{\theta}{1+\theta\beta}\right) = g(\eta,\theta). \end{aligned} \tag{3.16}$$

The attractive set of the slow curve of the system (3.16) coincides with the repulsive S^u of the system (3.11), and the repulsive set of S of the system (3.16) coincides with S^s of the system (3.11). Hence, a trajectory of the system (3.16) starting from any point from the basin of attraction of the set S^u, after a short time follows the attractive set S^u at the tempo of the slow variable up to the point A_1. This part of the trajectory corresponds to the slow motions and the trajectory here has the asymptotic representation

$$\eta(\theta,\varepsilon) = h_0(\theta) + \varepsilon h_1(\theta) + O(\varepsilon^2).$$

When the trajectory reaches the point A_1, it jumps off the slow curve and rapidly tends to the final point with coordinates $\eta = 0$, $\theta = -\theta_i$. This part of the trajectory corresponds to the part of fast motions and the trajectory here has the asymptotic representation (3.9) with the functions f and g from the system (3.16), and η_1 and θ_1 given by (3.14), (3.15).

Using the fact that $\beta \ll 1$, from (3.14) and (3.15) we have

$$\eta_1 = \sqrt{\kappa e}\left(1 - \frac{\beta}{2}\right) - 1 + O(\beta^2), \quad \theta_1 = 1 + 2\beta + O(\beta^2).$$

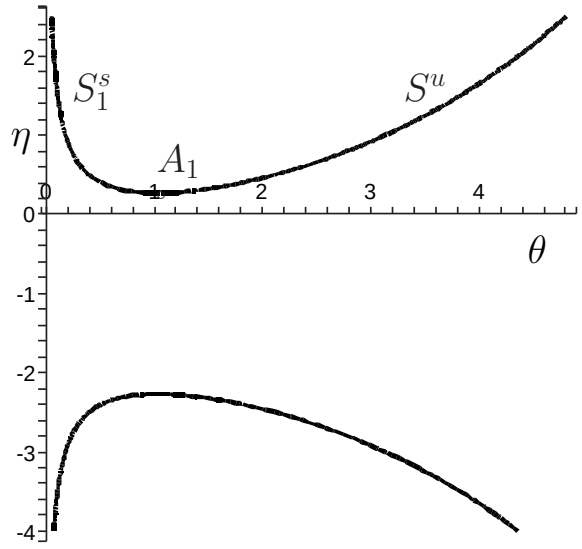


Figure 3.12: The slow curve of the system (3.11) for $\beta = 0.01$, $\kappa = 0.45 > \kappa_0$, $\theta < 5$.

Then from (3.9), (3.12), and (3.16) we obtain the equation

$$0 = \sqrt{\kappa e}\left(1 - \frac{\beta}{2}\right) - 1 + \Omega_0(\kappa e)^{1/6}\left(1 + \frac{11}{4}\beta\right)^{2/3}\varepsilon^{2/3} + \frac{4(1+6\beta)}{9}\varepsilon\ln\frac{1}{\varepsilon} + O(\varepsilon + \beta^2), \quad (3.17)$$

where κ has the asymptotic representation

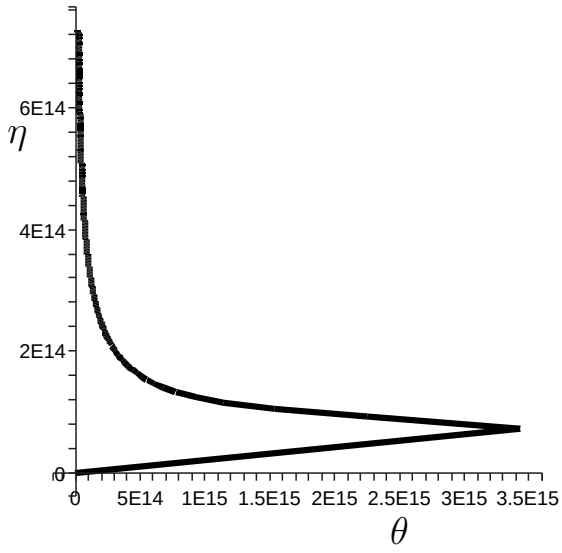
$$\kappa = \kappa^* = \kappa_0 + \kappa_1\varepsilon^{2/3} + \kappa_2\varepsilon\ln\frac{1}{\varepsilon} + O(\varepsilon).$$

By substituting this series into (3.17) and equating the coefficients we get the critical value of the parameter κ

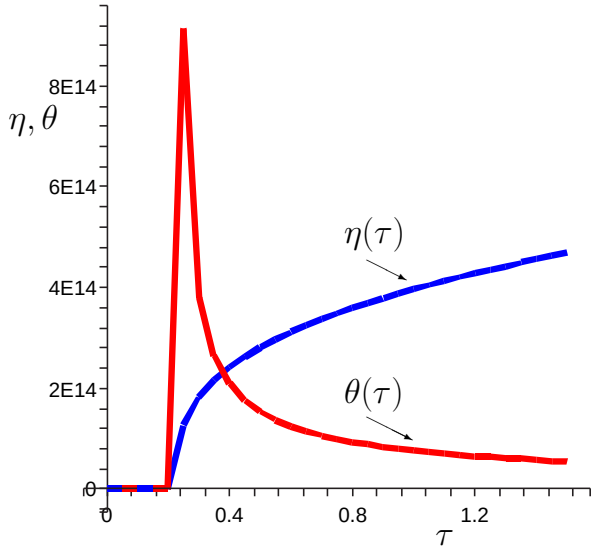
$$\kappa^* = \frac{1}{e}\left[1 + \beta - 2\Omega_0(1+3\beta)\varepsilon^{2/3} - \frac{8}{9}(1+7\beta)\varepsilon\ln\frac{1}{\varepsilon}\right] + O(\varepsilon + \beta^2),$$

which corresponds to the critical regime in the chemical system in the case of cubic law of oxidation kinetics.

As in the previous case the critical regime separates the region of slow regimes ($\kappa < \kappa^*$) which are characterized by low temperatures and the region of the ignition ($\kappa > \kappa^*$). During the critical regime the temperature attains a high value but without ignition, at the tempo of slow variable of the system, see Figure 3.15(b).



(a)



(b)

Figure 3.13: (a) The trajectory of the system (3.11) for $\beta = 0.01$, $\varepsilon = 0.01$, $\kappa = 0.45$, $\theta_i = 0$. (b) The η– and θ–components of the solution in the case of the ignition for $\beta = 0.01$, $\varepsilon = 0.01$, $\kappa = 0.45$, $\theta_i = 0$.

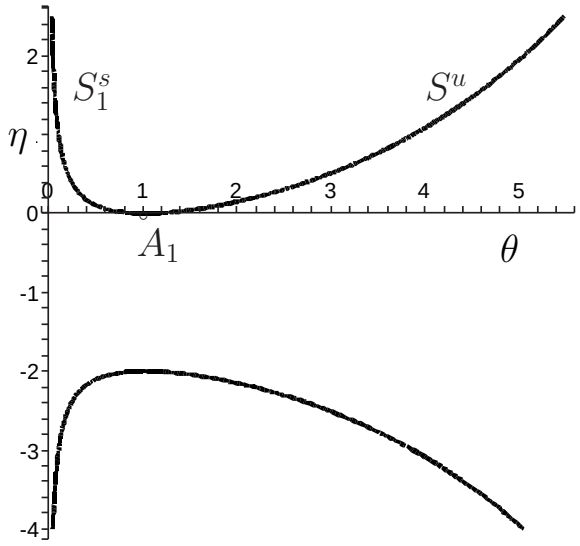


Figure 3.14: The slow curve of the system (3.11) for $\beta = 0.01$, $\kappa = \kappa_0 = 0.3716$, $\theta < 5.5$.

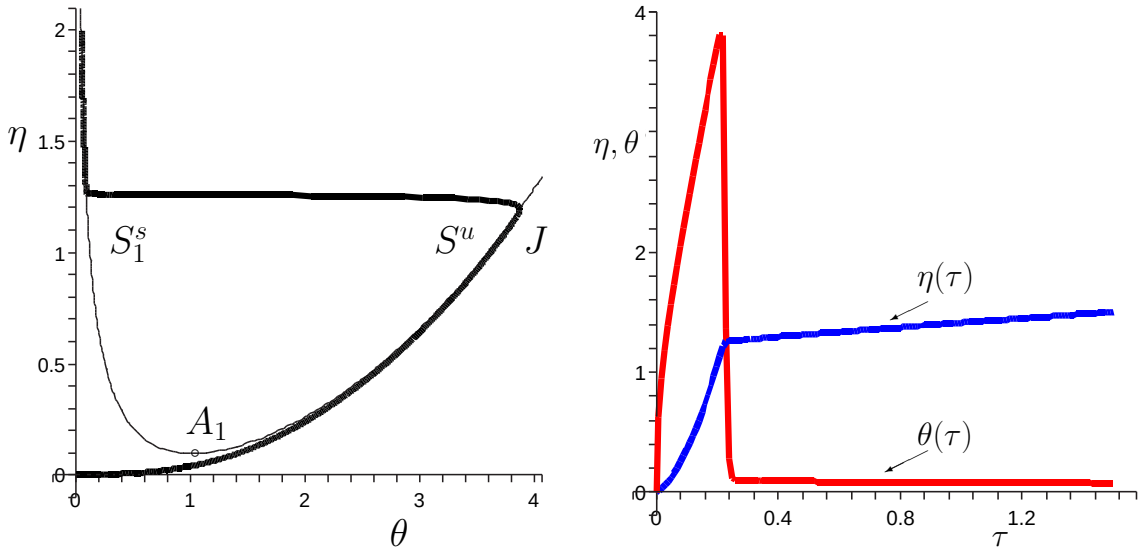


Figure 3.15: (a) The slow curve (the thin line) and the trajectory (the thick line) of the system (3.11) for $\beta = 0.01$, $\varepsilon = 0.01$, $\theta_i = 0$, $\kappa = \kappa^* \approx 0.44720$. (b) The η– and θ–components of the solution in the case of the critical regime for $\beta = 0.01$, $\varepsilon = 0.01$, $\theta_i = 0$, $\kappa = \kappa^* \approx 0.44720$.

Chapter 4

Canards and black swan in a model of a 3-D autocatalator

The mathematical model of a 3-D autocatalator is studied using the geometric theory of singular perturbations, namely, the *black swans* and *canards* techniques.

Critical regimes are modeled by *canards* (one–dimensional stable–unstable slow integral manifolds). The meaning of criticality here is as follows. The critical regime corresponds to a chemical reaction which separates the domain of self–accelerating reactions from the domain of slow reactions.

A two–dimensional stable–unstable slow integral manifold (*black swan*) consisting entirely of canards, which simulate the critical phenomena for different initial data of the dynamical system, is constructed. It is shown that this procedure leads to the phenomenon of auto-oscillations in the chemical system.

The geometric approach combined with asymptotic and numerical methods permits us to explain the strong parametric sensitivity and to obtain asymptotic representations of the critical behavior of the chemical system.

To explain the situation which will be arise in the model of a 3-D autocatalator we give the following examples.

Example 8.

Consider the van der Pol equation in the form of a plane system with an additional parameter α:

$$\dot{x} = z - \alpha, \quad \varepsilon\dot{z} = -1/3z^3 + z - x. \tag{4.1}$$

The jump points $(-2/3, -1)$ and $(2/3, 1)$ divide the slow curve $x = -1/3z^3+z$ into stable ($z < -1$ and $z > 1$) and the unstable ($-1 < z < 1$) parts, and we can observe the canard phenomenon near first jump point with $\alpha = -1 + \varepsilon/8 + \varepsilon^2 \ldots$ or near second one with $\alpha = 1 - \varepsilon/8 + \varepsilon^2 \ldots$.

Example 9.

Consider now the 3-D modification of system (4.1):

$$\dot{x} = z - \alpha, \quad \dot{y} = -0.3y, \quad \varepsilon\dot{z} = -1/3z^3 + z - x. \tag{4.2}$$

The system (4.2) has the black swan. This black swan is a cylindrical attractive surface, see Figure 4.1. All trajectories on this surface are the canards, but only one of them is a cycle on the plane $y = 0$. We can observe a similar situation in a 3-D autocatalator model.

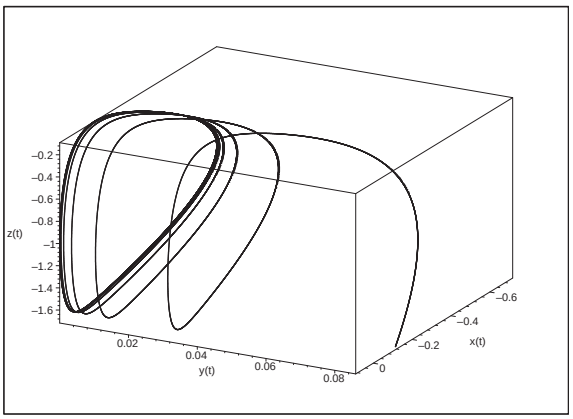


Figure 4.1: The trajectory of the system (4.2) with $\varepsilon = 0.1$ and initial point $x = 0.02$, $y = 0.1$, $z = -0.2$.

4.1 3-D autocatalator

The application of black swans consisting entirely of canards to the modelling of critical phenomena permits us to take into account small perturbations in the chemical systems. Moreover we can use black swans for the modelling of critical phenomena in chemical problems without fixed initial conditions.

As an illustration let us consider a model of the three–dimensional autocatalator [28, 29]:

$$\begin{aligned} \frac{dx}{d\tau} &= \mu(5/2 + y) - xz^2 - x, \\ \frac{dy}{d\tau} &= z - y, \\ \varepsilon\frac{dz}{d\tau} &= xz^2 + x - z, \end{aligned} \tag{4.3}$$

where

$$x \geq 0, \quad y \geq 0, \quad z \geq 0, \quad 0 \leq \mu < 1. \tag{4.4}$$

The system (4.3) simulates a sort of the Belousov–Zhabotinsky reaction. The variables x, y and z represent dimensionless concentrations of three chemical reagents, ε is a small positive parameter, μ is a bifurcation parameter. Note that this and similar models have been studied in [7, 38] and others.

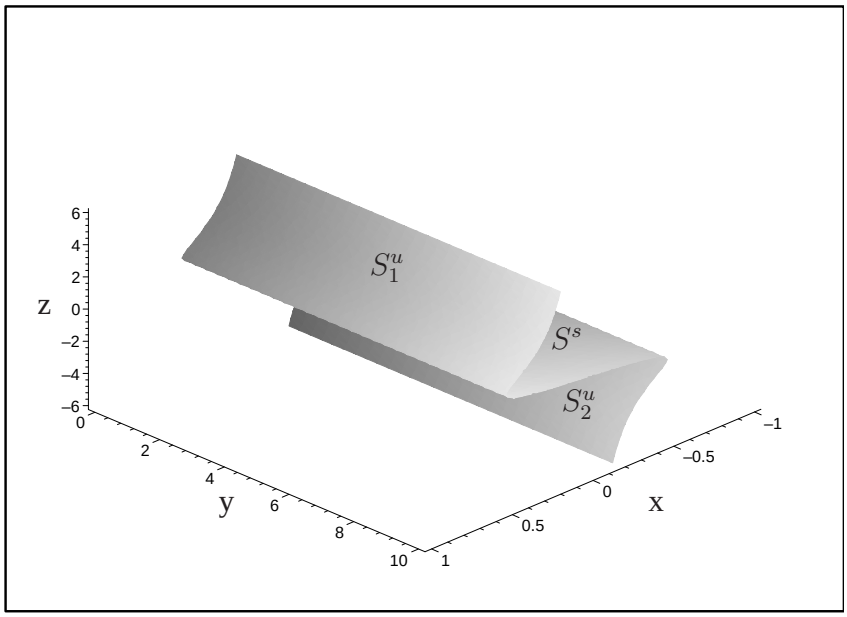


Figure 4.2: The slow surface of the system (4.3).

The slow surface (see Figure 4.2) of the system (4.3) is described by the equation

$$F(x, y, z) = xz^2 + x - z = 0.$$

The breakdown surface, which is described by

$$F = 0, \quad \frac{\partial F}{\partial z} = 2xz - 1 = 0,$$

consists of two straight lines, but only one of them

$$x = 0.5, \quad z = 1 \tag{4.5}$$

has physical meaning. The breakdown surface divides the slow surface into three leaves S_1^u ($z > 1$), S_2^u ($z < 1$), S^s ($|z| < 1$, see Figure 4.2), which are zeroth order approximations for the corresponding slow integral manifolds $S_{1,\varepsilon}^u$, $S_{2,\varepsilon}^u$ and S_ε^s. Manifolds $S_{1,\varepsilon}^u$ and $S_{2,\varepsilon}^u$ are unstable and S_ε^s is stable. Note, that the part of S_ε^s with $0 \le x < 0.5$ and $S_{1,\varepsilon}^u$ are situated in the domain of interest to us (4.4).

A detailed analysis of system under is presented in [36].

Note, the initial data for the system (4.3) are not fixed. With concrete initial data we can glue the stable and unstable slow integral manifold at one point on the breakdown line (4.5). The canard passes through this point and corresponds to the initial value problems for the system under consideration. Thus, a canard is a result of gluing stable and unstable slow integral manifolds at one point of the breakdown surface.

Let $\mu = \mu(y, \varepsilon)$ be considered as a control function. Then the gluing of the stable and unstable parts of slow integral manifolds can be realized at all points of the breakdown line (4.5) at the same time. This permits us to construct slow integral manifolds with changing stability (black swan) consisting entirely of canards. Each simulates the critical regime corresponding to the specified initial data and passes through a definite point on the breakdown line.

4.2 Black swan construction

Let us take $\mu = \mu(y, \varepsilon)$ as incomplete feedback control function. Then it and the black swan $x = x(y, z, \varepsilon)$ have asymptotic expansions of the form:

$$\mu = \mu(y, \varepsilon) = \mu_0(y) + \varepsilon\mu_1(y) + \varepsilon^2\mu_2(y) + \dots ,$$
$$x = x(y, z, \varepsilon) = x_0(y, z) + \varepsilon x_1(y, z) + \varepsilon^2 x_2(y, z) + \dots .$$

Substituting these expansions into the equation

$$\frac{\partial x(y,z,\varepsilon)}{\partial z}\varepsilon^{-1}(x(y,z,\varepsilon)z^2 + x(y,z,\varepsilon) - z) + \frac{\partial x(y,z,\varepsilon)}{\partial y}(z-y)$$
$$= \mu(y,\varepsilon)(5/2+y) - x(y,z,\varepsilon)z^2 - x(y,z,\varepsilon),$$

which follows from (4.3), and using the slow surface equation

$$x_0 z^2 + x_0 - z = 0, \tag{4.6}$$

we obtain

$$\left(\frac{\partial x_0}{\partial z} + \varepsilon\frac{\partial x_1}{\partial z} + \varepsilon^2\frac{\partial x_2}{\partial z} + \dots\right)(x_1 + \varepsilon x_2 + \dots)(1+z^2)$$
$$+\left(\frac{\partial x_0}{\partial y} + \varepsilon\frac{\partial x_1}{\partial y} + \varepsilon^2\frac{\partial x_2}{\partial y} + \dots\right)(z-y) =$$
$$= \left(\mu_0 + \varepsilon\mu_1 + \varepsilon^2\mu_2 + \dots\right)(5/2+y) - \left(x_0 + \varepsilon x_1 + \varepsilon^2 x_2 + \dots\right)z^2 -$$
$$-x_0 - \varepsilon x_1 - \varepsilon^2 x_2 - \dots . \tag{4.7}$$

Setting $\varepsilon = 0$ in (4.7) and taking (4.6) into account, we get

$$\frac{\partial x_0}{\partial z}(1+z^2)x_1 = \mu_0(5/2+y) - z. \tag{4.8}$$

Note, that the relationship

$$\frac{\partial x_0}{\partial z} = 0$$

holds on the breakdown line (4.5). By continuity of the function $x_1 = x_1(z, c)$ we require the following condition:

$$\mu_0 = \frac{1}{(5/2+y)}.$$

From this and (4.8) we have

$$x_1(y,z) = \frac{1+z^2}{1+z}. \tag{4.9}$$

Equating coefficients in ε in (4.7), we obtain

$$\frac{\partial x_1}{\partial y}(z-y) + \frac{\partial x_1}{\partial z}(1+z^2)x_1 + \frac{\partial x_0}{\partial z}(1+z^2)x_2 = \mu_1(5/2+y) - x_1(1+z^2). \tag{4.10}$$

To avoid a discontinuity in the function $x_2 = x_2(y,z)$ on the breakdown line we require the following condition:

$$\mu_1 = \frac{3}{(5/2+y)}.$$

Applying (4.6), (4.9) and (4.10) yields

$$x_2(y,z) = \frac{\left[3(1+z)^3 - 2z(2+z)(1+z^2)^2\right](1+z^2)}{(1+z)^3(1-z^2)}.$$

Thus, we obtain the approximations to the black swan

$$x(y,z,\varepsilon) = \frac{z}{1+z^2} + \varepsilon\frac{1+z^2}{1+z} + \varepsilon^2\frac{\left[3(1+z)^3 - 2z(2+z)(1+z^2)^2\right](1+z^2)}{(1+z)^3(1-z^2)} + O(\varepsilon^3),$$

and corresponding gluing function

$$\mu(y,\varepsilon) = \frac{\alpha(\varepsilon)}{(5/2+y)}, \quad \alpha(\varepsilon) = 1 + 3\varepsilon + O(\varepsilon^2). \tag{4.11}$$

We can construct higher approximations to the functions $x = x(y,z,\varepsilon)$ and $\mu = \mu(y,\varepsilon)$ in a similar way, if it is necessary.

For a given point $y = y^*$ on the breakdown line we can find the value $\mu^* = \mu(y^*,\varepsilon)$ from expression (4.11) which corresponds to the canard of the system. This trajectory lies on the black swan $x = x(y,z,\varepsilon)$ and passes through the point $y = y^*$ of the breakdown line.

It should be noted that the choice of the gluing point $y = y^*$ is equivalent to the choice the starting point of the trajectory.

Note that gluing the stable and unstable slow integral manifolds reduces the original system (4.3) to the following form

$$\frac{dx}{d\tau} = \alpha(\varepsilon) - xz^2 - x, \tag{4.12}$$

$$\varepsilon\frac{dz}{d\tau} = xz^2 + x - z, \tag{4.13}$$

$$\frac{dy}{d\tau} = z - y. \tag{4.14}$$

The system (4.12)–(4.14) has a black swan, which is a cylindrical surface, see Figure 4.4. All trajectories on this surface are canards, but only one of them is a limit cycle. This cycle is asymptotically orbitally stable.

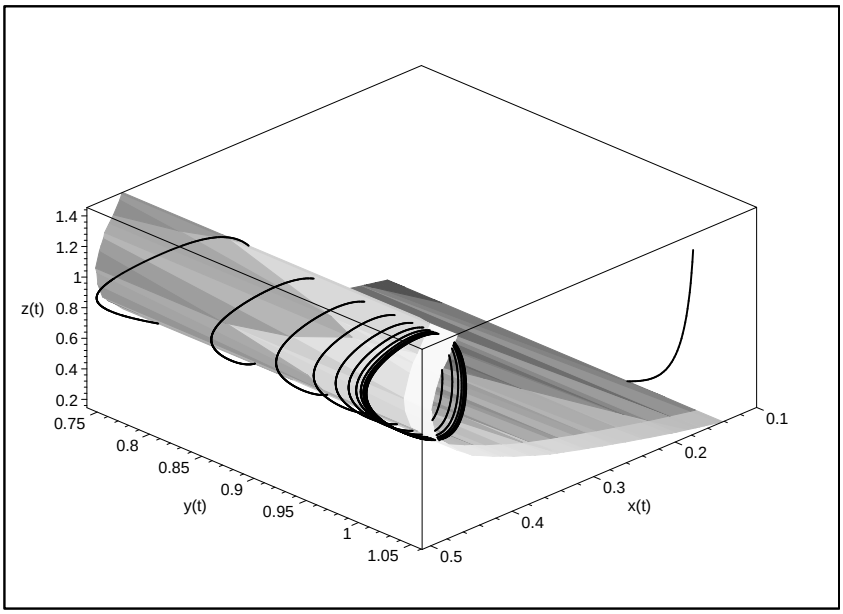


Figure 4.3: The slow surface and the canard of the system (4.12)–(4.14) with $\varepsilon = 0.01$ and initial point $x = 0.1$, $y = 1$, $z = 1$.

Conclusion

The singularly perturbed systems of differential equations describing thermal explosion are analyzed. Critical and transient regimes are modelled by means of geometric theory of singular perturbations methods. The mathematical objects are introduced for the first order reactions and for autocatalytic case. These objects make it possible to follow the continuous transition of reaction from the slow regime to the explosive one. The critical regime is modelled by the mathematical object called canard in the modern mathematical literature. Such trajectories pass from the stable slow invariant manifold to the unstable one. Systems' trajectories, passing some part of its way along critical trajectories, belong to the transient regimes. Thus the transient region is separated into the region of slow transient regimes and the region of the explosive transient regimes. The asymptotic formulae for the calculation of the critical values of heat loss parameter were obtained.

A realistic time scale is used such that rapid motions of the temperature appear against a background of the slow changing of the related growth of the thickness of the oxide film. This clearly demonstrated the possibility of using the singular perturbation theory to investigate reactions of this sort.

For two form of oxidation kinetics (parabolic and cubic laws) the asymptotic formulae are obtained, specifying the critical value of the parameter κ reflecting the convection heat transfer in the metal ignition model. The approach to the modelling of critical phenomena is suggested. The critical trajectory is identified with the trajectory passing along the unstable part of slow curve. This approach was extended on the PDE combustion models [15, 19]. It should be noted that such approach was used in [30] to describe the canard travelling waves.

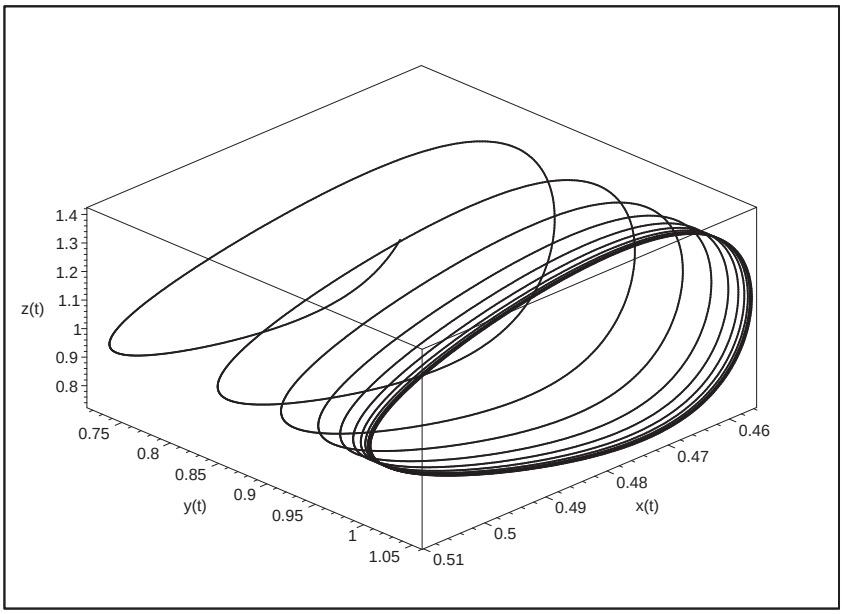


Figure 4.4: The black swan of the system (4.12)–(4.14).

We investigate a singularly perturbed model of a sort of Belousov–Zhabotinsky reaction. The basic types of chemical reaction are defined by means of integral manifold theory. It was shown that the critical regimes, separating the domains of self–accelerating reactions and domains of slow processes, are modelled by canards. The asymptotic formulae for the calculation of the critical values of bifurcation parameter of the system were obtained.

The procedure for constructing the two–dimensional slow integral manifold with changing stability consisting entirely of canards, each of which simulates the critical regime corresponding to specified initial data of the dynamic system, is described. The application of a black swan permits us to take into account small perturbations in the chemical systems.

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Bibliography

[1] V. I. Arnold, V. S. Afraimovich, Yu. S. Il'yashenko and L. P. Shil'nikov. Theory of Bifurcations. V. Arnold, ed., in *Dynamical Systems, 5. Encyclopedia of Mathematical Sciences*, Springer Verlag, New York, 1994.

[2] K. A. Avdeev, F. S. Frolov, S. M. Frolov and B. Basara 2006 *Effect of Transient Heat Transfer on Metal Particle Ignition* (Turbulence, Heat and Mass Transfer vol 5) ed K Hanjalice *et al* (New York: Begell Hous Publ.) pp 581–584.

[3] V. I. Babushok, V. M. Goldshtein, A. S. Romanov and V. S. Babkin, Thermal Explosion in an Inert Porous Medium, *Fizika Gorenia i Vzryva*, 1992, vol. 28, 4, pp 3–10.

[4] V. I. Babushok, V. M. Goldshtein, and V. A. Sobolev 1990 Critical condition for the thermal explosion with reactant consumption *Combust. Sci. and Tech.* **70** p 81.

[5] E. Benoit, J. L. Callot, F. Diener, M. Diener, Chasse au canard, *Collect. Math.*, 1981–1982, vol. 31–32 (1–3), pp 37–119.

[6] M. Brøns, K. Bar–Eli, Asymptotic Analysis of Canards in the EOE Equations and the Role of the Inflaction Line, *Proc. London Roy Soc.*, Ser. A, 1994, vol. 445, pp 305–322.

[7] M. Brøns, K. Bar–Eli 1991 Canard explosion and excitation in a model of the Belousov–Zhabotinsky reaction *Journal of Physical Chemistry* **95** p 8706.

[8] El–Sayed S A 1996 Ignition characteristics of metal particles in thermal explosion theory *J. Loss Prev. Process Ind.* **9** p 393.

[9] D. A. Frank-Kamenetsky *Diffusion and heat transfer in chemical kinetics*, Moscow: Nauka, 1967.

[10] I. Glassman 1996 *Combustion* (Orlando: Academic Press)

[11] V. M. Gol'dshtein and V. A. Sobolev 1992 Integral manifolds in chemical kinetics and combustion *Singularity Theory and Some Problems of Functional Analysis* ed S. Gindikin (AMS Translations 2 vol 153) pp 73–92.

[12] V. Gol'dshtein, A. Zinoviev, V. Sobolev, E. Shchepakina, Criterion for Thermal Explosion with Reactant Consumption in a Dusty Gas, *Proc. London Roy. Soc.*, Ser. A, 1996, vol. 452, pp 2103–2119.

[13] G. N. Gorelov, V. A. Sobolev, Duck-trajectories in a Thermal Explosion Problem, *Appl. Math. Lett.,* 1992, vol. 5, 6, pp 3–6.

[14] G. N. Gorelov, V. A. Sobolev, Mathematical Modeling of Critical Phenomena in Thermal Explosion Theory, *Combust. Flame,* 1991, vol. 87, pp 203–210.

[15] G. N. Gorelov, E. A. Shchepakina and V. A. Sobolev, Canards and critical behavior in autocatalytic combustion models *J Eng Math* (2006) 56, pp 143-160.

[16] B. F. Gray, Critical Behaviour in Chemical Reacting Systems: 2. An Exactly Soluble Model, *Combust. Flame,* 1973, vol. 21, pp 317–325.

[17] D. Henry. *Geometrical Theory of Semilinear Parabolic Equations.* Lecture Notes in Mathematics, vol. 840, Springer Verlag, New York, 1981.

[18] B. I. Khaikin, V. N. Bloshenko and A. G. Merzhanov 1970 On ignition of metal particles *J. Combustion, Explosion and Shock Waves* **6** p 412.

[19] E. V. Kitaeva and V. A. Sobolev, Numerical Determination of Bounded Solutions to Discrete Singularly Perturbed Equations and Critical Combustion Regimes, *Computational Mathematics and Mathematical Physics* **45**, No. 1, January 2005, pp 52–82.

[20] A. Linan and D. K. Kassoy 1978 The influence of reacting consumption on the critical conditions for homogeneous thermal explosion *A. J. Mech. Appl. Math. Electron.* **31** p 99.

[21] P. De Maesschalck, F. Dumortier, Time and entryexit relation near a planar turning point *C. R. Acad. Sci. Paris*, Ser. I 339 (2004) pp 359-364.

[22] P. De Maesschalck, F. Dumortier, Canard solutions at non-generic turning points, *Trans. of AMS*, **358**, No 5 (2005) pp 2291-2334.

[23] A. G. Merzhanov 1975 Thermal theory of metal particle ignition *AIAA Journal* **13** p 209.

[24] A. G. Merzhanov, F. I. Dubovitsky, Quasi–stationary Theory of the Thermal Explosion of a Self–accelerating Reaction, *Zhurnal Fizichaskoi Khimii*, 1960, vol. XXXIV, 10, pp 2235–2244.

[25] A. G. Merzhanov, F. I. Dubovitsky, The Modern State of the Theory of Thermal Explosion, *Uspekhi Khimii,* 1966, vol. 35, 4, pp 656–683.

[26] E. F. Mishchenko, N. Kh. Rozov, Differential Equations with Small Parameters and Relaxation Oscillations. Plenum Press, New York, 1980.

[27] R. E. O'Malley 1991 *Singular Perturbation Methods for Ordinary Differential Equations* (Appl. Math. Sci. vol 89) (New-York: Springer–Verlag).

[28] B. Peng, V. Gáspár and K. Showalter 1991 False bifurcations in chemical systems: Canards *Phil. Trans. R. Soc. Lond.* A **337** p 275.

[29] V. Petrov, S. K. Scott and K. Showalter 1992 Mixed–mode oscillations in chemical systems *Journal of Chemical Physics* **97** p 6191.

[30] K. Schneider, E. Shchepakina, V. Sobolev, A New Type of Travelling Wave, *Mathematical Methods in the Applied Sciences*, 2003, vol. 26, pp 1349–1361.

[31] N. N. Semenov, *On Some Problems of Chemical Kinetics of Reactional Capacity.* Moscow: AN SSSR, 1959.

[32] N. N. Semenov, Zur Theorie des Verbrennungsprozesses, *Z. Physik. Chem.*, 1928, vol. 48, pp 571–581.

[33] E. Shchepakina and V. Sobolev 2001 Integral manifolds, canards and black swans *Nonlinear Analysis* A **44** p 897.

[34] E. A. Shchepakina and V. A. Sobolev 1998 Standard chase on black swans and canards *Preprint of Weierstraß–Institut für Angewandte Analysis und Stochastik, Berlin* 426.

[35] E. Shchepakina, Black Swans and Canards in Self–ignition Problem, *Nonlinear Anal.: Real World Appl.*, 2003, vol. 4, 1, pp 45–50.

[36] E. A. Shchepakina, Canards and black swans in a model of a 3-D autocatalator, 2005 *J. Phys.: Conf. Ser.* 22, pp 194–207.

[37] E. Shchepakina and V. Sobolev 2005 Black Swans and Canards in Laser and Combustion Models *Singular Perturbation and Hysteresis* ed M P Mortell *et al* (Philadelphia: SIAM) pp 207–255.

[38] P. Smolyan and M. Wechselberger, Canards in R^3, *J. Diff. Equations*, 177(2) (2001), pp. 419–453.

[39] V. A. Sobolev, Integral Manifolds and Decomposition of Singularly Perturbed System, *System and Control Lett.*, 1984, 5, pp 169–179.

[40] V. A. Sobolev, E. A. Shchepakina, Duck Trajectories in a Problem of Combustion Theory, *Differential Equations*, 1996, vol. 32, pp. 1177–1186, translation from *Differ. Uravn.*, 1996, vol. 32, pp 1175-1184.

[41] V. A. Sobolev, E. A. Shchepakina, Self–ignition of Laden Medium, *J. Combustion, Explosion and Shock Waves*, 1993, vol. 29, 3, pp 378–381.

[42] V. V. Strygin and V. A. Sobolev, Asymptotic methods in the problem of stabilization of rotating bodies by using passive dampers, *Mechanics of Solids*, 5 (1977), pp 19–25.

[43] V. V. Strygin and V. A. Sobolev, *Effect of geometric and kinetic parameters and energy dissipation on orientation stability of satellites with double spin*, Cosmic Research, 14(3) (1976), pp 331–335.

[44] O. M. Todes, P. V. Melent'ev, The Theory of Thermal Explosion, *Journal of physical chemistry*, 1939, vol. 13, 7, pp 52–58.

[45] F. Xiea, M. Hanb, W. Zhangc, Existence of canard manifolds in a class of singularly perturbed systems Nonlinear Analysis 64 (2006) p 457 - 470.

[46] A. B. Vasilieva, V. F. Butuzov and L. V. Kalachev 1995 *The Boundary Function Method for Singular Perturbation Problems* (Series in Applied Mathematics vol 14) (Philadelphia: SIAM).

[47] F. A. Williams 1985 *Combustion Theory* (Redwood City, CA: Addison–Wesley).

[48] F. A. Williams 1997 Some Aspects of Metal Particle Combustion *Physical and Chemical Aspects of Combustion: A Tribute to Irv Glassman* ed F L Dryer and R F Sawyer (The Nederlands: Gordon and Breach) pp 267–289.

[49] R. A. Yetter and F. L. Dryer 2001 Metal Particle Combustion and Classification *Microgravity Combustion: Fire in Free Fall* ed H Ross (Academic Press) pp 419–478.

[50] Ya. B. Zeldovich, G. I. Barenblatt , V. B. Librovich and G. M. Makhviladze 1985 *The Mathematical Theory of Combustion and Explosions* (New York: Consultants Bureau).