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Jumping behavior in singularly perturbed systems modelling bimolecular reactions

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Abstract. Singular singularly perturbed systems of ordinary differential equations modelling the dynamics of fast bimolecular reactions are considered.
The asymptotic behavior of the solution of the initial value problem on a finite time interval is studied under conditions (change of stability) which are not treated in the usual standard theory. The application of the obtained results to the model under consideration yields conditions under which the reaction rate jumps. This behavior has to be taken into account for identification problems in chemical process modelling.

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1. Introduction

In modelling reaction kinetics a systematic approach consists in the decomposition of the stoichiometric overall reaction into a system of subreactions [6]. This approach leads to very large systems of stiff differential equations of the form

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$$\begin{aligned} \frac{dx_1}{dt} &= r_1(x_1, x_2, t), \\ \varepsilon \frac{dx_2}{dt} &= r_2(x_1, x_2, t) \end{aligned} \tag{1.1}$$

where $x_1 \in R^{n_1}$, $x_2 \in R^{n_2}$, $0 < \varepsilon \ll 1$. Here x_1 is the vector of the concentrations of the slowly reacting species involved in the reaction system, x_2 is the corresponding vector of the fast reacting species, r_1 is the vector of the slow subreactions taking place in the system, and r_2 is the vector of the fast subreactions. Generally we have $n_1 \ll n_2$. The reaction equations (1.1) can be solved numerically by means of suitable solvers. If the fast reactions are much faster than the slow reactions then chemically the fast reactions can be assumed to be in a quasi-stationary state. That means system (1.1) will be replaced by the diffential algebraic system

$$\begin{aligned} \frac{dx_1}{dt} &= r_1(x_1, x_2, t), \\ 0 &= r_2(x_1, x_2, t). \end{aligned} \tag{1.2}$$

This procedure is well established as the QSSA method in chemical engineering and can be justified by singular perturbation theory. There are, however, reactive systems containing fast and slow reactions which do not satisfy the assumptions of the QSSA method. Then the reduction of the differential system to an differential-algebraic system fails and the fast reactions have to be considered explicitly.

This problem is of practical relevance as the fast reactions normally contribute to the observable reaction kinetics only by determining the form of the invariant manifold of (1.1). Their dynamic response on external disturbances is too rapid to be relevant for the dynamical response of the observable reaction system. Therefore, the observable dynamical response of the system is dominated by the time scale of the slow reactions only. Moreover, the reduction of a large reaction system to a small one by elimination of fast reactions is of great importance for the qualitative and quantitative treatment of reaction systems [10] and can be performed numerically [10] provided the QSSA - conditions are satisfied.

The simplest example for a reactive system not satisfying the QSSA - assumptions is a bimolecular system. Therefore, in this paper a bimolecular reaction system of the form

$$\begin{aligned} A &\rightarrow C_1 \quad (\bar{r}_1(x)), \\ B &\rightarrow C_2 \quad (\bar{r}_2(y)), \\ A + B &\rightarrow C \quad (\bar{r}(x, y)) \end{aligned} \tag{1.3}$$

will be studied. $\bar{r}_1, \bar{r}_2$ and $\bar{r}$ are the fast reaction rates depending on the concentrations x and y of the species A and B respectively. To express this fact we represent these reaction rates in the form $\bar{r}_1 = r_1/\varepsilon, \bar{r}_2 = r_2/\varepsilon, \bar{r} = r/\varepsilon$ where ε is a small positive parameter. The time evolution of the concentrations are governed by the differential equation system

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon \left(I_a(t) - g_1(x) \right) - \left(r_1(x) + r(x,y) \right) \\ \varepsilon \frac{dy}{dt} &= \varepsilon \left(I_b(t) - g_2(y) \right) - \left(r_2(y) + r(x,y) \right). \end{aligned} \tag{1.4}$$

$I_a(t)$ and $I_b(t)$ are the input flows of the species A and B respectively, g_1 and g_2 are reaction rates of the slow reactions which usually exist.

We assume the following hypothesis to be satisfied.

(I). The scalar functions $I_a, I_b, g_1, g_2, r_1, r_2, r$ are sufficiently smooth, nonnegative and satisfy

$$I_a(t) > 0,\ I_b(t) > 0 \quad for\ t \geq 0,$$

$$r_i(z) > 0,\ g_i(z) > 0 \quad for\ z > 0, \quad r_i(0) = g_i(0) = 0 \quad for\ i = 1, 2,$$

$$r(x,y) > 0 \quad for \quad x > 0, \quad y > 0, \quad r(0,y) = r(x,0) = 0 \quad for\ x \geq 0, \quad y \geq 0,$$

ε is a small positive parameter.

Hypothesis (I) implies that any solution of (1.4) starting in the positive quadrant remains positive for $t \geq 0$. From a chemical point of view the invariance of the positive orthant under the time-increasing flow of (1.4) is a necessary condition for (1.4) to be a chemically relevant model.

System (1.4) is in general nonautonomous as the "slowly" varying input flows I_a and I_b depend on time. This fact is not only relevant for chemical processes with variable input feed rates but it reflects also the possibility that the reactions (1.3) can be subreactions of a more complex reaction system. Then the input rates of the species A and B are the overall reaction rates of all reactions producing A and B, respectively. As these reaction rates vary with time, the analysis of (1.4) is valid for reactions of this type embedded in complex autonomous reaction systems.
If the species A and B are chemically reactive then the fast unimolecular reactions expressed by the reaction rates $\bar{r}_1(x)$ and $\bar{r}_2(y)$ do not vanish and the QSSA can be applied. A different situation, however, occurs if the unimolecular reaction rates $\bar{r}_1, \bar{r}_2$ vanish. This can be the case if the species are not reactive by themselves and if the bimolecular reaction r is only fast by the catalysis with a highly specific catalyst. Thus, the concentrations of the species A and B are not necessarily small and there may occur an enrichment of one species. Then the invariant manifold containing the slow reactions can change its stability which can leads to a jump in the production rate of the product species C. This phenomenon is very important for the analysis of such reaction kinetic systems, as the overall reaction kinetics of such reaction systems may change qualitatively near the jump points. Moreover, since fast bimolecular reactions of nonreactive species catalysed by highly specific catalysts are typical for biochemical reactions, such jumps in the reaction rates may trigger biological systems.

In this paper the change of stability of the invariant manifold in reaction systems of the type (1.4) will be analyzed in detail. It will be shown that the critical times, when the change of stability occurs can be calculated using the slow reactions only.

In what follows we study for system (1.4) the initial value problem

$$x(0,\varepsilon) = x^0,\ y(0,\varepsilon) = y^0. \tag{1.5}$$

The theory for initial value problems of singularly perturbed systems of ordinary differential equations is primarily due to Tikhonov [21, 22] and Levinson [13], for further developments see also [7, 9, 16, 17, 20, 23, 24]. Following this approach we have to consider first the corresponding degenerate system (also called the reduced system) which we obtain by setting $\varepsilon = 0$. In case of (1.4) we get

$$\begin{aligned} r_1(x) + r(x,y) &= 0, \\ r_2(y) + r(x,y) &= 0. \end{aligned} \tag{1.6}$$

Under hypothesis (I) the origin $x = y = 0$ is a solution of (1.6). If we assume that the origin is the unique solution of (1.6) satisfying some stability hypotheses (see Theorem A and Theorem B in the Appendix for details) then we can apply asymptotic methods to treat (1.4). The analysis gets more complicated if we assume that either r_1 or r_2 or both are identically zero. This situation arises when we study (1.4) in the cases of a fast pure bimolecular reaction or a fast unimolecular reaction. Here, the solution of (1.6) is not unique, and even not isolated. System (1.1) is called critical or singular singularly perturbed if the degenerate system has a family of solutions. Under some additional stability assumptions this case was studied in [8, 12, 24].

We get a further complication of our problem if we admit a change of stability of the equilibria of the associated system (for definition see the Appendix). In that case, the theory developed in [8, 12, 24] cannot be applied.

In section 2 we present a treatment of singular singularly perturbed systems with change of stability which benefits from ideas in [3, 4, 12] and [5]. Our approach consists of two steps: firstly we reduce the singular singularly perturbed system to a regular singularly perturbed system, then we derive a result about the asymptotic behavior of the solution of the corresponding initial value problem by applying either Theorem B (in case of no change of stability) or Theorem C (in case of change of stability).

In sections 3 - 5 we apply the obtained results to the initial value problem (1.4), (1.5). The main results are conditions under which a transition layer (jumping behavior) can be observed in the time behavior of the reaction rate $\bar{r}$.

For convenience of the reader we have added an appendix containing fundamental results about the asymptotic treatment of initial value problems for singularly perturbed systems.

2. Mathematical Preliminaries

We consider the singularly perturbed differential system

$$\begin{aligned} \varepsilon \frac{dz_1}{dt} &= \varepsilon\, \varphi_1(z_1, z_2, t, \varepsilon) + \eta_1(z_1, z_2), \\ \varepsilon \frac{dz_2}{dt} &= \varepsilon\, \varphi_2(z_1, z_2, t, \varepsilon) + \eta_2(z_1, z_2) \end{aligned} \tag{2.1}$$

with $z_1 \in R^n, z_2 \in R^m$. System (2.1) is said to be a *singular singularly perturbed system* if the corresponding degenerate system (for definition see the Appendix)

$$\begin{aligned} \eta_1(z_1, z_2) &= 0, \\ \eta_2(z_1, z_2) &= 0 \end{aligned} \tag{2.2}$$

has a continuum of zeros, or equivalently, if the corresponding Jacobi matrix vanishes identically on some subset of $R^n \times R^m$.

Our first aim is to ask for conditions such that (2.1) can be reduced to a (regular) singularly perturbed system. To this end we assume

(A_1). *The functions $\varphi_1, \varphi_2, \eta_1, \eta_2$ are sufficiently smooth in all variables in the domain of interest.*

(A_2). *The associated system*

$$\begin{aligned} \frac{dz_1}{d\tau} &= \eta_1(z_1, z_2), \\ \frac{dz_2}{d\tau} &= \eta_2(z_1, z_2) \end{aligned} \tag{2.3}$$

has a first integral of the form

$$z_2 - \Phi(z_1) = c. \tag{2.4}$$

Hypothesis (A_2) implies

$$\eta_2(z_1, z_2) \equiv \Phi'(z_1)\, \eta_1(z_1, z_2). \tag{2.5}$$

Thus, under assumption (A_2) the degenerate system (2.2) reads

$$\begin{aligned} \eta_1(z_1, z_2) &= 0, \\ \Phi'(z_1)\eta_1(z_1, z_2) &= 0 \end{aligned} \tag{2.6}$$

and has in general no isolated solution. Consequently, under the assumption (A_2) system (2.1) is a singular singularly perturbed system. The following lemma plays an important role in our investigations.

Lemma 1. *Assume hypothesis (A_2) to be valid. Then there is a coordinate transformation*

$$\sigma = z_2 - \Phi(z_1) \tag{2.7}$$

reducing the singular singularly perturbed system (2.1) to the (regular) singularly perturbed system

$$\begin{aligned} \varepsilon \frac{dz_1}{dt} &= \varepsilon\, \varphi_1(z_1, \sigma + \Phi(z_1), t, \varepsilon) + \eta_1(z_1, \sigma + \Phi(z_1)) := g^*(z_1, \sigma, t, \varepsilon), \\ \frac{d\sigma}{dt} &= \varphi_2(z_1, \sigma + \Phi(z_1), t, \varepsilon) - \Phi'(z_1)\varphi_1(z_1, \sigma + \Phi(z_1), t, \varepsilon) := f^*(z_1, \sigma, t, \varepsilon). \end{aligned} \tag{2.8}$$

Proof. From (2.7) and (2.1) we get

$$\varepsilon \frac{d\sigma}{dt} = \varepsilon \frac{dz_2}{dt} - \Phi'(z_1)\, \varepsilon \frac{dz_1}{dt} = \varepsilon\Big(\varphi_2 - \Phi'(z_1)\varphi_1\Big) + \eta_2 - \Phi'(z_1)\eta_1.$$

Taking into account (2.5) we obtain the second equation in (2.8). The first equation follows immedeately by substituting (2.7) into (2.1).

Remark 2.1 *The transformation (2.7) is not unique. The transformation $\sigma = \phi(z_1) - z_2$ yields also a (regular) singularly perturbed system.*

Now we study for system (2.1) the initial value problem for system

$$z_1(0) = z_1^0, \; z_2(0) = z_2^0 \tag{2.9}$$

on the interval $0 < t \leq T$. The initial value problem (2.1), (2.9) is equivalent to the initial value problem

$$z_1(0) = z_1^0 \,, \; \sigma(0) = \sigma^0 := z_2^0 - \Phi(z_1^0) \tag{2.10}$$

for (2.8). We are interested in the asymptotic behavior of the solution of (2.1), (2.9) with respect to the small parameter ε under the hypotheses (A_1) and (A_2). It is clear that this behavior depends on the solutions of the equation $\eta_1(z_1, \sigma + \Phi(z_1)) = 0$. Therefore, we additionally assume:

(A_3). *The equation*

$$\eta_1(z_1, \sigma + \Phi(z_1)) = 0 \tag{2.11}$$

has a solution $z_1 = z_1^*(\sigma)$, and the initial value problem

$$\begin{aligned} \frac{d\sigma}{dt} &= \varphi_2(z_1^*(\sigma), \sigma + \Phi(z_1^*(\sigma)), t, 0)) - \Phi'(z_1^*(\sigma))\varphi_1(z_1^*(\sigma), \sigma + \Phi(z_1^*(\sigma)), t, 0), \\ \sigma(0) &= \sigma^0 := z_2^0 - \Phi(z_1^0) \end{aligned} \tag{2.12}$$

has a unique solution $\bar\sigma(t, \sigma^0)$ defined on [0,T].

(A_4). *The solution $\tilde{z}_1(\tau, z_1^0)$ of the initial value problem*

$$\frac{dz_1}{d\tau} = \eta_1(z_1, \sigma^0 + \Phi(z_1)), \quad z_1(0) = z_1^0$$

exists for $\tau \geq 0$ and tends to $z_1^*(\sigma^0)$ as $\tau \to \infty$.

(A_5). *All eigenvalues $\lambda_i(t)$ of the Jacobian*

$$\frac{\partial \eta_1}{\partial z_1}(z_1^*(\bar{\sigma}(t,\sigma^0)), \bar{\sigma}(t,\sigma^0)) + \frac{\partial \eta_1}{\partial z_2}(z_1^*(\bar{\sigma}(t,\sigma^0)), \bar{\sigma}(t,\sigma^0))\Phi'(z_1^*(\bar{\sigma}(t,\sigma^0)))$$

satisfy

$$Re\lambda_i(t) < 0 \quad on \quad 0 \leq t \leq T.$$

By means of Theorem B in the Appendix we get the following result

Theorem 2.1. *We assume the hypotheses $(A_1) - (A_5)$ to be valid. Let $(Z_n^1(t,\varepsilon), \Sigma_n(t,\varepsilon))$ be the truncated asymptotic expansion of the solution to the initial value problem (2.8), (2.10) obtained by the method of boundary layer functions* (see [23] for details). *Then there is a sufficiently small ε_0 and a constant $c = c(\varepsilon_0)$ such that for $0 < \varepsilon < \varepsilon_0$ the initial value problem (2.1), (2.9) has a unique solution $(z_1(t,\varepsilon), z_2(t,\varepsilon))$ on $[0,T]$ satisfying*

$$|z_1(t,\varepsilon) - Z_n^1(t,\varepsilon)| \leq c\,\varepsilon^{n+1},$$

$$|z_2(t,\varepsilon) - \Sigma_n(t,\varepsilon) + \Phi(Z_n^1(t,\varepsilon))| \leq c\,\varepsilon^{n+1}.$$

In particular, for $n = 0$ we have

$$z_1(t,\varepsilon) = z_1^*(\bar{\sigma}(t,\sigma^0)) + \Pi_0 z_1(\tau) + O(\varepsilon),$$

$$z_2(t,\varepsilon) = \bar{\sigma}(t,\sigma^0) + \Phi(z_1^*(\bar{\sigma}(t,\sigma^0))) + O(\varepsilon).$$

Theorem 2.1 is related to the situation when the solution $z_1^*(\sigma)$ of (2.11) does not change its stability (see assumption (A_5)). Now we study the case when (2.11) has two solutions which intersect in such a way that the corresponding angular solution changes its stability (for a definition see the Appendix). The following approach requires $n = 1$, that is, z_1 is a scalar variable. Instead of the assumptions $(A_3), (A_5)$ we now assume

(A_3^*). *The equation (2.11) has two solutions $z_1^1(\sigma)$ and $z_1^2(\sigma)$ with the same smoothness as g^*. The initial value problem*

$$\begin{aligned} \frac{d\sigma}{dt} &= \varphi_2(z_1^1(\sigma), \sigma + \Phi(z_1^1(\sigma)), t, 0)) - \Phi'(z_1^1(\sigma))\varphi_1(z_1^1(\sigma), \sigma + \Phi(z_1^1(\sigma)), t, 0), \\ \sigma(0) &= \sigma^0 := z_2^0 - \Phi(z_1^0) \end{aligned}$$

has a unique solution $\bar{\sigma}_1(t,\sigma^0)$ defined on $[0,T]$. The initial value problem

$$\begin{aligned} \frac{d\sigma}{dt} &= \varphi_2(z_1^2(\sigma), \sigma + \Phi(z_1^2(\sigma)), t, 0)) - \Phi'(z_1^2(\sigma))\varphi_1(z_1^2(\sigma), \sigma + \Phi(z_1^2(\sigma)), t, 0), \\ \sigma(t_0) &= \sigma^1 := \bar{\sigma}_1(t_0, \sigma^0) \end{aligned}$$

has a unique solution $\bar{\sigma}_2(t,\sigma^1)$ defined on $[0,T]$.

(A_4^*) *The curves* $z_1 = \psi_1(t) := z_1^1(\bar{\sigma}_1(t,\sigma^0))$ *and* $z_1 = \psi_2(t) := z_1^2(\bar{\sigma}_2(t,\sigma^1))$ *intersect for* $t = t_0 \in (0,T)$ *with different slopes where* $\psi_1(t)$ *is stable for* $[0,t_0)$ *and* $\psi_2(t)$ *is stable for* $(t_0,T]$. *Thus,*

$$\frac{\partial\eta_1}{\partial z_1}(\psi_1(t),\bar{\sigma}_1(t,\sigma^0)) + \frac{\partial\eta_1}{\partial z_2}(\psi_1(t),\bar{\sigma}_1(t,\sigma^0))\Phi'(\psi_1(t)) < 0 \text{ for } t \in [0,t_0)$$

and

$$\frac{\partial\eta_1}{\partial z_1}(\psi_2(t),\bar{\sigma}_2(t,\sigma^1)) + \frac{\partial\eta_1}{\partial z_2}(\psi_2(t),\bar{\sigma}_2(t,\sigma^1))\Phi'(\psi_2(t)) < 0 \text{ for } t \in (t_0,T].$$

According to the definition in the Appendix we call $(\hat{z}_1(t),\hat{\sigma}(t))$ defined by

$$\hat{z}_1(t) := \begin{cases} \psi_1(t) & 0 \le t \le t_0 \\ \psi_2(t) & t_0 \le t \le T \end{cases}, \hat{\sigma}(t) := \begin{cases} \bar{\sigma}_1(t,\sigma^0) & 0 \le t \le t_0 \\ \bar{\sigma}_2(t,\sigma^1) & t_0 \le t \le T \end{cases}$$

the angular solution to the degenerate system of (2.8) belonging to the solutions $z_1^1(\sigma)$ and $z_1^2(\sigma)$ of (2.11). Furthermore, we assume

(A_5^*). The solution $\tilde{z}_1(\tau,z_1^0)$ of the initial value problem

$$\frac{dz_1}{d\tau} = \eta_1(z_1,\sigma^0+\Phi(z_1)), \quad z_1(0) = z_1^0$$

exists for $\tau \ge 0$ and tends to $z_1^1(\sigma^0)$ as $\tau \to \infty$.

(A_6^*) $g^*_{z_1 z_1}(\hat{z}_1(t_0),\hat{\sigma}(t_0),t_0,0) < 0$.

Let $I_\nu := t_0 - \nu \le t \le t_o + \nu$.

(A_7^*) *For* $i = 1,\ldots n$, $0 < \varepsilon < \varepsilon^*$ *and* $t \in I_\nu f_i^*(z_1,\sigma_1,\ldots,\sigma_{i-1},\hat{\sigma}_i(t),\sigma_{i+1},\ldots,\sigma_n,t,\varepsilon)$ *is nondecreasing in* $(z_1,\sigma_1,\ldots,\sigma_{i-1},\sigma_{i+1},\ldots,\sigma_n)$ *and* $g^*(\hat{z}_1(t),\sigma_1,\ldots,\sigma_n,t,\varepsilon)$ *is nondecreasing in* $(\sigma_1,\ldots,\sigma_n)$ *in the region defined by* $\sigma_k \in [\hat{\sigma}_k(t),\hat{\sigma}_k(t)+s\varepsilon]$, $z_1 \in [\hat{z}_1(t)\ ,\hat{z}_1(t)+s\varepsilon]$ *where* s *is a sufficiently large constant independent of* ε *and* z_1 *is a scalar variable*

(A_8^*) *For* $t \in (0,t_0+\nu)$, *where* ν *is any given small positive number, we have*

$$\begin{aligned} \varepsilon\frac{d\hat{z}_1}{dt} &\le \varepsilon\,\varphi_1(\hat{z}_1,\hat{\sigma}+\Phi(\hat{z}_1),t,\varepsilon)+\eta_1(\hat{z}_1,\hat{\sigma}+\Phi(\hat{z}_1)), \\ \frac{d\hat{\sigma}}{dt} &\le \varphi_2(\hat{z}_1,\hat{\sigma}+\Phi(\hat{z}_1),t,\varepsilon)-\Phi'(\hat{z}_1)\varphi_1(\hat{z}_1,\hat{\sigma}+\Phi(\hat{z}_1),t,\varepsilon) \end{aligned} \tag{2.13}$$

At $t = t_0$ *the inequalities must be fulfilled for the corresponding left and right derivatives.*

By means of Theorem C in the Appendix we get the result

Theorem 2.2. *We assume the hypotheses* $(A_1), (A_2), (A_3^*), (A_4^*) - (A_8^*)$ *to be valid. Then there is a sufficiently small* $\varepsilon_0 = \varepsilon_0(\nu)$ *such that for* $0 < \varepsilon < \varepsilon_0(\nu)$ *the initial value problem (2.8),(2.10) with* $z_1^0 \geq \psi_1(0)$ *(and consequently also (2.1),(2.9)) has a unique solution* $(z_1(t,\varepsilon), \sigma(t,\varepsilon))$*, satisfying*

$$\begin{aligned} \lim_{\varepsilon \to 0} z_1(t,\varepsilon) &= \hat{z}_1(t) \quad for \quad 0 < t \leq T, \\ \lim_{\varepsilon \to 0} \sigma(t,\varepsilon) &= \hat{\sigma}(t) \quad for \quad 0 \leq t \leq T. \end{aligned}$$

Moreover, we have

$$\sigma(t,\varepsilon) = \hat{\sigma}(t) + 0(\varepsilon), \qquad for \quad 0 \leq t \leq T$$

$$z_1(t,\varepsilon) = \begin{cases} \hat{z}_1(t) + \Pi_0 z_1(\tau) + O(\varepsilon) & for \quad 0 \leq t \leq t_0 - \nu, \\ \hat{z}_1(t) + O(\varepsilon^{\frac{1}{2}}) & for \quad t_0 - \nu \leq t \leq t_0 + \nu, \\ \hat{z}_1(t) + O(\varepsilon) & for \quad t_0 + \nu \leq t \leq T \end{cases}$$

where $\Pi_0 z_1(\tau)$ *is the zeroth order boundary layer function.*

Remark 2.1.1. *For the case* $z_1^0 < \psi_1(0)$ *we can apply to (2.8) Theorem* C^*.

3. The purely bimolecular reaction

In what follows we shall apply the results of section 2 to special cases of system (1.4). First we consider the case $g_i \equiv 0 \equiv r_i$, $i = 1, 2$. That means system (1.4) describes a purely bimolecular reaction and reads

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon\, I_a(t) - r(x,y), \\ \varepsilon \frac{dy}{dt} &= \varepsilon\, I_b(t) - r(x,y). \end{aligned} \tag{3.1}$$

We suppose hypothesis (I) in the introduction to be valid. If we consider (3.1) as a special case of (2.1) then the validity of hypothesis (I) implies that assumption (A_1) holds. Since the Jacobian of the degenerate system to (3.1) has two identical rows its determinant vanishes identically for all x, y. Thus, according to the notation introduced in section 2, system (3.1) is a singular singularly perturbed system.
The associated system to (3.1) reads

$$\begin{aligned} \frac{dx}{d\tau} &= -r(x,y), \\ \frac{dy}{d\tau} &= -r(x,y). \end{aligned}$$

It has the first integral $y - x = c$ and thus hypothesis (A_2) in section 2 is fulfilled. By means of the coordinate transformation

$$x = x, \; y = x + \sigma \tag{3.2}$$

we can reduce the singular singularly perturbed system (3.1) to the regular singularly perturbated system

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon\, I_a(t) - r(x, x+\sigma), \\ \frac{d\sigma}{dt} &= I_b(t) - I_a(t). \end{aligned} \tag{3.3}$$

Now we study to (3.1) the initial value problem

$$x(0,\varepsilon) = x^0, \quad y(0,\varepsilon) = y^0 \tag{3.4}$$

on the interval $0 < t \leq T$. By introducing

$$I(t) = \int_0^t (I_b(s) - I_a(s))ds \tag{3.5}$$

we get from (3.2), (3.4) and the second equation in (3.3)

$$\bar{\sigma}(t, \sigma^0) = \sigma^0 + I(t) \tag{3.6}$$

where

$$\sigma^0 := y^0 - x^0. \tag{3.7}$$

Hence, the initial value problem (3.1), (3.4) is equivalent to the initial value problem

$$\begin{aligned} \varepsilon \frac{dx}{dt} = \varepsilon\, I_a(t) &- r(x, x+\sigma^0 + I(t)), \\ x(0,\varepsilon) &= x^0. \end{aligned} \tag{3.8}$$

The degenerate equation to (3.8) reads

$$r(x, x + \sigma^0 + I(t)) = 0, \tag{3.9}$$

the associated system is

$$\frac{dx}{d\tau} = -r(x, x + \sigma^0 + I(t)). \tag{3.10}$$

From assumption (I) it follows that (3.9) has two solutions

$$x^1(t) \equiv 0 \text{ and } x^2(t) \equiv -\sigma^0 - I(t). \tag{3.11}$$

First we consider the case where these roots do not intersect for $t \in [0, T]$.

(B_1). $I(t) \neq x^0 - y^0 \quad \forall t \in [0, T]$.

This case is within the scope of Theorem 2.1 if we assume, for definiteness, that the root $x^1(t)$ is stable. The stability of the root $x^1(t)$ is expressed by

(B_2). $r_x(0, \sigma^0 + I(t)) + r_y(0, \sigma^0 + I(t)) > 0$ *for all* $t \in [0, T]$.

In addition, also B_3 has to hold

(B_3). The point x^0 is in the domain of attraction of $x^1(t)$.

Hypotheses (B_2) and (B_3) imply the validity of the assumptions $(A_3) - (A_5)$ of Theorem 2.1.

Since we are looking for an asymptotic expansion of the solution $x(t, \varepsilon)$ of (3.8) near $x^1(t)$ we represent $x(t, \varepsilon)$ in the form

$$x(t, \varepsilon) = \bar{x}(t, \varepsilon) + \Pi x(\tau, \varepsilon) \tag{3.12}$$

where $\bar{x}(t, \varepsilon)$ is the regular part of the asymptotics, that is

$$\bar{x}(t, \varepsilon) = \sum_{i=0}^{\infty} \varepsilon^i \bar{x}_i(t),$$

and $\Pi x(\tau, \varepsilon)$ is the boundary layer correction near $t = 0$,

$$\Pi x(\tau, \varepsilon) = \sum_{i=0}^{\infty} \varepsilon^i \Pi_i x(\tau)$$

where τ is the stretched variable $\tau = t/\varepsilon$. According to the formulae given in the Appendix we get for the zeroth order approximation of (3.12) $\bar{x}_0(t) \equiv x^1(t) \equiv 0$, while $\Pi_0 x$ is determined by

$$\frac{d\Pi_0 x}{d\tau} = -r(\Pi_0 x, \Pi_0 x + \sigma^0), \quad \Pi_0 x(0) = x^0.$$

By assumptions (B_2), (B_3) $\Pi_0 x$ is exponentially decaying. According to Theorem 2.1 we get the following result:

Theorem 3.1 *Suppose that the hypotheses* $(I), (B_1) - (B_3)$ *hold. Then for sufficiently small* ε *the inital value problem (3.8) has a unique solution* $x(t, \varepsilon)$ *satisfying*

$$x(t, \varepsilon) = \Pi_0 x(\tau) + O(\varepsilon)$$

on $0 \le t \le T$.

Remark 3.1.1. *Under the assumptions of Theorem 3.1 the initial value problem (3.1), (3.4) has a unique solution* $(x(t, \varepsilon), y(t, \varepsilon))$ *where*

$$y(t, \varepsilon) = x(t, \varepsilon) + y^0 - x^0 + I(t).$$

Remark 3.1.2. *Obviously, a similar result holds for the case when* $x^2(t) \equiv -\sigma^0 - I(t)$ *is the stable root.*

Corollary 3.1. *Under the assumptions of Theorem 3.1 there exists for any given small* ν *an* $\varepsilon_0 = \varepsilon_0(\nu)$ *such that for* $0 < \varepsilon < \varepsilon_0$, $t \geq \nu$ *the reaction rate* $r(x(t,\varepsilon), y(t,\varepsilon))/\varepsilon$ *satisfies*

$$\frac{r(x(t,\varepsilon), y(t,\varepsilon))}{\varepsilon} = I_a(t) + O(\varepsilon)$$

that is, the reaction rate does not jump for $t \geq \nu$.

Next we treat the case when $x^1(t)$ and $x^2(t)$ intersect for $t = t_0 \in (0,T)$. In order to be able to apply Theorem 2.2 we check the validity of its hypotheses. Assumption (I) implies the hypotheses (A_1) and (A_3^*) of Theorem 2.2 are valid. We note that the corresponding initial value problems can be solved explicitely. Assumption (A_2) is obviously fulfilled for system (3.1). To satisfy (A_5^*) we suppose

(C_1). *There is a* $t_0 \in (0,T)$ *such that* $x^2(t)$ *has exactly one zero in* $[0,T]$ *at* $t = t_0$ *where* $dx^2/dt(t_0) = I_b(t_0) - I_a(t_0) > 0$.

(C_2).

$$r_x(-\sigma^0 - I(t), 0) + r_y(-\sigma^0 - I(t), 0) > 0 \quad \textit{for all} \quad t \in [0, t_0)$$

and

$$r_x(0, \sigma^0 + I(t)) + r_y(0, \sigma^0 + I(t)) > 0 \quad \textit{for all} \quad t \in (t_0, T]$$

Hypotheses (C_1) and (C_2) mean that $x^2(t)$ changes its sign at t_0 (from positive to negative values) and is stable on $0 \leq t < t_0$, while $x^1(t)$ is stable on $t_0 < t \leq T$.

Now we define the corresponding angular solution by

$$\hat{x}(t) = \begin{cases} -\sigma^0 - I(t), & 0 \leq t \leq t_0, \\ 0, & t_0 \leq t \leq T \end{cases} \tag{3.13}$$

To fulfill hypotheses (A_4^*) and (A_6^*) we assume

(C_3). *The point* x^0 *is in the domain of attraction of* $x^2(t)$.

(C_4). $r_{xx}(0,0) + 2r_{xy}(0,0) + r_{yy}(0,0) > 0$.

Assumption (A_7^*) is trivially fulfilled since the right hand side of (3.8) does not depend on σ.

Concerning system (3.1) assumption (A_8^*) on the fast component reads as follows

$$\varepsilon \frac{d\hat{x}}{dt} \leq \varepsilon\, I_a(t) \quad - \quad r(\hat{x}, \hat{x} + \sigma^0 + I(t))) \tag{3.14}$$

for all $t \in [0,T]$ except $t = t_0$. Substituting (3.13) into (3.14) and taking (3.5) into account we get

$$\varepsilon\,(I_a(t) - I_b(t)) \le \varepsilon\, I_a(t) \quad \text{for} \quad 0 \le t < t_0,$$
$$0 \le \varepsilon\, I_a(t) \quad \text{for} \quad t_0 < t \le T.$$

That means if we assume $I_a(t) \ge 0, I_b(t) \ge 0$ for $t \in [0,T]$ then assumption (A_8^*) is valid. But this assumption is already contained in hypothesis (I). Consequently, we get from Theorem 2.2 the following result

Theorem 3.2 *Suppose that assumptions $(I), (C_1) - (C_4)$ hold. Then for sufficiently small ε the solution $x(t,\varepsilon)$ of the initial value problem (3.8) satisfies*

$$x(t,\varepsilon) = \begin{cases} \hat{x}(t) + \Pi_0 x(\tau) + O(\varepsilon) & for \quad 0 \le t \le t_0 - \nu, \\ \hat{x}(t) + O(\varepsilon^{\frac{1}{2}}) & for \quad t_0 - \nu \le t \le t_0 + \nu, \\ \hat{x}(t) + O(\varepsilon) & for \quad t_0 + \nu \le t \le T \end{cases}$$

where $\hat{x}(t)$ is given by (3.13) and $\Pi_0 x$ is determined by

$$\frac{d\Pi_0 x}{d\tau} = -r(-\sigma^0 + \Pi_0 x, \Pi_0 x), \quad \Pi_0 x(0) = x^0 + \sigma^0 = y^0.$$

Remark 3.2.1. *Under the assumptions of Theorem 3.2 the initial value problem (3.1), (3.4) has a unique solution $(x(t,\varepsilon), y(t,\varepsilon))$ where*

$$y(t,\varepsilon) = x(t,\varepsilon) + \sigma^0 + I(t).$$

Remark 3.2.2. *It is obvious that a similar result holds when the angular solution has the form*

$$\hat{x}(t) = \begin{cases} 0, & 0 \le t \le t_0, \\ -\sigma^0 - I(t), & t_0 \le t \le T \end{cases} \tag{3.15}$$

Corollary 3.2 *Under the assumptions of Theorem 3.2 the reaction rate has a "jump" near t_0 (transition layer), this means that to any given small $\nu > 0$ we have*

$$r(x(t,\varepsilon), y(t,\varepsilon))/\varepsilon = I_a(t) + 0(\varepsilon), \quad t \in [\nu, t_0 - \nu]$$

and

$$r(x(t,\varepsilon), y(t,\varepsilon))/\varepsilon = I_b(t) + 0(\varepsilon), \quad t \in [t_0 + \nu, T]$$

Proof. The proof of this result follows from Corollary C1 from the Appendix, Theorem 3.2 and system (3.1).

We illustrate our results by considering two examples.

Example 3.1. We investigate system (3.1) in the case

$$r(x,y) \equiv xy, \; I_a(t) \equiv 0, \; I_b(t) \equiv 1.$$

The corresponding system reads

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= -xy, \\ \varepsilon \frac{dy}{dt} &= \varepsilon - xy. \end{aligned} \tag{3.16}$$

We consider in the positive orthant the initial value problem

$$x(0,\varepsilon) = x^0 \; , \; y(0,\varepsilon) = y^0 \tag{3.17}$$

to (3.16) on the interval $0 < t \leq T$ under the additional conditions

$$x^0 - y^0 = 1 \; , \; T > 1. \tag{3.18}$$

This problem can be solved exactly. From (3.16) – (3.18) we get

$$y(t,\varepsilon) = x(t,\varepsilon) + t \tag{3.19}$$

such that the initial value problem (3.16) – (3.18) is equivalent to

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= -x[x-(1-t)] \\ x(0,\varepsilon) &= x^0. \end{aligned} \tag{3.20}$$

We note that this problem can be solved explicitely

$$x(t,\varepsilon) = x^0 \left\{ e^{[(1-t)^2-1]/2\varepsilon} + \frac{1}{\varepsilon} x^0 \int_{1-t}^{1} e^{[(1-t)^2-s^2]/2\varepsilon} ds \right\}^{-1}.$$

It requires some effort (asymptotic expansion in ε) to see that $x(t,\varepsilon)$ has an initial layer near $t = 0$ and satisfies

$$\lim_{\varepsilon \to 0} x(t,\varepsilon) = 1 - t \quad \text{for } 0 < t \leq 1$$

$$\lim_{\varepsilon \to o} x(t,\varepsilon) = 0 \quad \text{for } 1 \leq t \leq T.$$

Now we show that we get the same results in a simpler way by applying Theorem 2.2. The degenerate equation to (3.20) reads

$$x[x-(1-t)] = 0.$$

This equation has the solutions $x^1(t) \equiv 0$ and $x^2(t) \equiv 1-t$. The root $x^2(t) \equiv 1-t$ is stable for $t \in [0,1)$, the root $x^1(t) \equiv 0$ is stable for $t \in (1,T]$. Then, by applying Theorem 2.2 we get the same result as above.
Since we are interested in the asymptotic expansion of $x(t,\varepsilon) = \bar{x}(t,\varepsilon) + \Pi(t,\varepsilon)$ we have to distinguish between $0 < t < 1$ and $1 < t \leq T$. For $0 < t < 1$, we get according to the procedure described in the Appendix

$$\bar{x}_0(t) = 1-t,\ \bar{x}_1(t) = \frac{1}{1-t},\ \bar{x}_2(t) = -\frac{2}{(1-t)^3}, \cdots.$$

hence we have

$$\bar{x}(t,\varepsilon) = 1 - t + \varepsilon\frac{1}{1-t} - \varepsilon^2\frac{2}{(1-t)^3} + \cdots.$$

Concerning the zeroth order boundary layer correction we have to solve the initial value problem

$$\begin{aligned} \frac{d\Pi_0}{d\tau} &= -\Pi_0(\Pi_0+1) \\ \Pi_0(0) &= x^0 - \bar{x}_0(0) = y^0. \end{aligned} \tag{3.21}$$

This problem can be solved explicitely, we get

$$\Pi_0(\tau) = (ke^\tau - 1)^{-1}$$

where k is defined by

$$k = (1+y^0)/y^0.$$

Therefore, we have for $0 < t < 1$

$$x(t,\varepsilon) = 1 - t + \left(\frac{1+y^0}{y^0}e^{t/\varepsilon} - 1\right)^{-1} + O(\varepsilon)$$

For $t > 1$ we get that the regular part of asymptotic expansion is identically zero. To determine what happens near $t = 1$ we use the known procedure of matching (for example see [17]).

To do so we set $x(t,\varepsilon) =: \varepsilon^{\frac{1}{2}}\omega(\xi,\varepsilon)$ where $\xi = (t-1)/\varepsilon^{\frac{1}{2}}$. From (3.20) we get that ω has to obey the differential equation

$$\frac{d\omega}{d\xi} = -\omega(\omega + \xi) \tag{3.22}$$

moreover, $\varepsilon^{\frac{1}{2}}\omega(\xi,\varepsilon)$ must match the outer solution

$$\bar{x}(t,\varepsilon) = \varepsilon^{\frac{1}{2}}(-\xi - \frac{1}{\xi} + \frac{2}{\xi^3} + \cdots)$$

as $\xi \to -\infty$, and ω must tend to 0 as $\xi \to \infty$. Taking into account this conditions we obtain from (3.22)

$$\omega(\xi,\varepsilon) = e^{-\xi^2/2} \Bigg/ \left(\int_{\infty}^{\xi} e^{-s^2/2} ds \right).$$

The function $\omega(\xi)$ describes a transition layer between the reduced solutions $\bar{x}_0(t) = 1-t$ and $\bar{x}_0 = 0$ and it can be used for describing the nonuniform convergence of dx/dt from -1 to 0 as t passes through 1.

Remark. *In this case it is easy to prove the correctness of our matching procedure since we have an exact solution. In general, it can be very complicated. As mentioned in [17] there is a lot of possibilties for matching procedures but it is a hard problem to choose the correct one.*

Example 3.2 Now we study system (3.1) in the case

$$r(x,y) \equiv xy, \quad I_a(t) \equiv 1, \quad I_b(t) = 1 + \cos t, \tag{3.23}$$

that means, we consider the initial value problem

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon - xy, \\ \varepsilon \frac{dy}{dt} &= \varepsilon\,(1+\cos t) - xy, \\ x(0,\varepsilon) &= x^0, \quad y(0,\varepsilon) = y^0, \end{aligned} \tag{3.24}$$

on the interval $0 < t \leq T$.

Problem (3.24) is equivalent to the initial value problem for the singularly perturbed scalar Riccati equation

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon - x[x + \sigma^0 + \sin t], \quad t \in [0,T], \\ x(0,\varepsilon) &= x^0 \end{aligned} \tag{3.25}$$

where $\sigma^0 = y^0 - x^0$. The degenerate equation to (3.25) reads

$$x[x + \sigma^0 + \sin t)] = 0 \tag{3.26}$$

and it has two roots

$$x^1(t) \equiv 0 \quad , \quad x^2(t) \equiv -\sigma^0 - \sin t. \tag{3.27}$$

For $-\sigma^0 > 1$ $x^1(t)$ and $x^2(t)$ have no common point. If we consider t as a parameter then we get that $x^1(t)$ and $x^2(t)$ are equilibria of the associated system to (3.25)

$$\frac{dx}{d\tau} = -x[x + \sigma^0 + \sin t] \tag{3.28}$$

It is easy to show that $x^2(t)$ is an asymptotically stable equilibrium point of (3.28) for all t and $x^1(t)$ is an unstable one. The basin of attraction of $x^2(t)$ is the whole positive line. Therefore, all assumptions of Theorem 3.1 are fulfilled and we obtain the following result:
For $-\sigma^0 > 1$ the solution $(x(t,\varepsilon), y(t,\varepsilon))$ of (3.24) satisfies for $0 < t \leq T$

$$\lim_{\varepsilon \to 0} x(t,\varepsilon) = x^2(t) \equiv -\sigma^0 - \sin t,$$

$$\lim_{\varepsilon \to o} y(t,\varepsilon) = 0.$$

Thus, as a consequence we get that the reaction rate $x(t,\varepsilon)y(t,\varepsilon)/\varepsilon$ has no internal layer on any interval $[\nu, T]$ where ν is any fixed small positive number.

With respect to the asymptotic expansion of the solution $x(t,\varepsilon)$ we get for the first coefficients of the regular part

$$\bar{x}_0(t) = -\sigma^0 - \sin t, \quad \bar{x}_1(t) = \frac{\cos t + 1}{-\sigma^0 - \sin t}.$$

Concerning the boundary layer correction we determine the main term $\Pi_0 x$. For this term we get the initial value problem

$$\begin{aligned} \frac{d\Pi_0 x}{d\tau} &= -\Pi_0 x(\Pi_0 x - \sigma^0), \\ \Pi_0 x(0) &= x^0 - \bar{x}_0(0) = x^0 + \sigma^0 = y^0. \end{aligned}$$

This problem has the exact solution

$$\Pi_0 x(\tau) = \frac{1}{k \exp(-\sigma^0 \tau) + \sigma^{0^{-1}}}$$

where k is defined by

$$k = \frac{-x^0}{y^0\,\sigma^0}.$$

It follows that $\Pi_0 x(\tau)$ is the exponentially decaying function.

Now we consider the case $0 < -\sigma^0 < 1$. The equation $-\sigma^0 - \sin t = 0$ has the zeros $0 < t_1 < t_2 < \ldots$. In these points the equilibria $x^2(t) \equiv -\sigma^0 - \sin t$ and $x^1(t) \equiv 0$ of (*) changes their stability. In the interval $0 < t < t_1$ $x^2(t)$ is stable while $x^1(t)$ is unstable. In the next interval $t_1 < t < t_2$ $x^1(t)$ is stable while $x^2(t)$ is unstable, and so on. All assumptions of the Theorem 3.2 can be easily verified. Therefore, for $0 < -\sigma^0 < 1, t_1 < T < t_2$, the solution $x(t,\varepsilon)$ of the problem (3.25) satisfies pointwise for $t > 0$

$$\lim_{\varepsilon \to 0} x(t,\varepsilon) = \hat{x}(t),$$

where $\hat{x}(t)$ defined by

$$\hat{x}(t) = \begin{cases} -\sigma^0 - \sin t, & 0 \leq t \leq t_1, \\ 0, & t_1 \leq t \leq T. \end{cases}$$

From Corollary 3.2 we get that the reaction rate $x(t,\varepsilon)y(t,\varepsilon)/\varepsilon$ has "jumps" (transition layer behavior) near the points $t_1, t_2 \dots$, for example we have

$$x(t,\varepsilon)y(t,\varepsilon)/\varepsilon = 1 + \cos t + O(\varepsilon),\ \nu < t < t_1 - \nu$$

and

$$x(t,\varepsilon)y(t,\varepsilon)/\varepsilon = 1 - O(\varepsilon),\ t_1 + \nu < t < t_2 - \nu$$

where ν is any small positive number and $t_1 = \arcsin(-\sigma^0)$, $t_2 = \pi - \arcsin(-\sigma^0)$.

4. Fast bimolecular reaction with unimolecular slow reaction

In this section we shall apply the results of section 2 to system (1.4) for the case that $r_1 \equiv r_2 \equiv 0$. This means that system (1.4) describes a fast bimolecular reaction including slow unimolecular reactions and is given by

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon\,(I_a(t) - g_1(x)) - r(x,y), \\ \varepsilon \frac{dy}{dt} &= \varepsilon\,(I_b(t) - g_2(y)) - r(x,y). \end{aligned} \tag{4.1}$$

We suppose hypothesis (I) to be valid. The degenerate and the associated system to (4.1) are the same as for system (3.1). Thus, (4.1) is a singular singularly perturbed system which can be reduced by means of the coordinate transformation $x = x,\ y = x - \sigma$ to the (regular) singularly perturbed system

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon\,(I_a(t) - g_1(x)) - r(x, x-\sigma), \\ \frac{d\sigma}{dt} &= I_a(t) - I_b(t) + g_2(x-\sigma) - g_1(x). \end{aligned} \tag{4.2}$$

Now we study to (4.2) the initial value problem

$$x(0,\varepsilon) = x^0,\ \sigma(0,\varepsilon) = \sigma^0 := x^0 - y^0 \tag{4.3}$$

on the interval $0 < t \le T$. The degenerate equation to (4.2) reads

$$r(x, x-\sigma) = 0. \tag{4.4}$$

By assumption (I) equation (4.4) has the solutions

$$x^{(1)}(\sigma) \equiv 0,\ x^{(2)}(\sigma) \equiv \sigma.$$

In order to be able to apply Theorem 2.1 we have to fulfil the hypotheses $(A_3) - (A_5)$. First we consider the solution $x^{(1)}(\sigma) \equiv 0$. Concerning this solution the assumptions $(A_3) - (A_5)$ read as follows:

$(\bar{A}_3)$. *The initial value problem*

$$\begin{aligned} \frac{d\sigma}{dt} &= I_a(t) - I_b(t) + g_2(-\sigma), \\ \sigma(0) &= \sigma^0 \end{aligned}$$

has a unique solution $\bar{\sigma}(t, \sigma^0)$ *on* $[0, T]$.

$(\bar{A}_4)$. *The initial value problem*

$$\frac{dx}{d\tau} = -r(x, x - \sigma^0), \quad x(0) = x^0$$

has a unique solution for $\tau \geq 0$ *which tends to zero as* $\tau \to \infty$.

$(\bar{A}_5)$.

$$\frac{\partial r}{\partial x}(0, -\bar{\sigma}(t, \sigma^0)) + \frac{\partial r}{\partial y}(0, -\bar{\sigma}(t, \sigma^0)) > 0 \quad for \quad 0 \leq t \leq T.$$

Applying Theorem 2.1 we get the result

Theorem 4.1. *Suppose the hypotheses* $(I), (\bar{A}_3) - (\bar{A}_5)$*hold. Then there is a sufficiently small* $\varepsilon_0 > 0$ *such that for* $0 < \varepsilon < \varepsilon_0$ *the initial value problem (4.1), (4.3) has a unique solution* $(x(t, \varepsilon), y(t, \varepsilon))$ *on* $[0, T]$ *satisfying*

$$\begin{aligned} x(t, \varepsilon) &= \Pi_0 x(\tau) + O(\varepsilon), \\ y(t, \varepsilon) &= \Pi_0 x(\tau) - \bar{\sigma}(t, \sigma^0) + O(\varepsilon) \end{aligned}$$

where the boundary layer function $\Pi_0 x(\tau)$ *is defined by*

$$\frac{d\Pi_0 x}{d\tau} = -r(\Pi_0 x, \Pi_0 x - \sigma^0) \ , \ \Pi_0 x(0) = x^0.$$

Corollary 4.1.1. *Under the assumptions of Theorem 4.1 there is to any given small positive* ν *an* $\varepsilon_0 = \varepsilon_0(\nu)$ *such that for* $0 < \varepsilon < \varepsilon_0$, $t \geq \nu$ *the reaction rate* $r(x(t, \varepsilon), y(t, \varepsilon))/\varepsilon$ *satisfies*

$$\frac{r(x(t, \varepsilon), y(t, \varepsilon))}{\varepsilon} = I_a(t) + O(\varepsilon)$$

that is, the reaction rate has no jump for $t \geq \nu$.

Remark 4.1.1 *A similar result holds with respect to the root* $x^2(\sigma) \equiv \sigma$.

Now we consider the case when the solutions $x^1(\sigma)$ and $x^2(\sigma)$ intersect and change their stability. In order to be able to apply Theorem 2.2 we reformulate some hypotheses of this theorem.

$(\bar{A}_3{}^*)$. *The initial value problems*

$$\begin{aligned}\frac{d\sigma}{dt} &= I_a(t) - I_b(t) + g_2(-\sigma), \quad \sigma(0) = \sigma^0,\\ \frac{d\sigma}{dt} &= I_a(t) - I_b(t) - g_1(\sigma), \quad \sigma(t_0) = \sigma^1 := \bar{\sigma}_1(t_0, \sigma^0)\end{aligned}$$

have a unique solution $\bar{\sigma}_1(t, \sigma^0)$ *and* $\bar{\sigma}_2(t, \sigma^1)$ *respectively defined on* $[0, T]$.

$(\bar{A}_5{}^*)$. *There is a* $t_0 \in (0, T)$ *such that* $\bar{\sigma}_2(t, \sigma^1)$ *has a unique zero* $t = t_0$ *in (0,T) and such that*

$$\begin{aligned}&\frac{d\bar{\sigma}_2}{dt}(t_0, \sigma^1) = I_a(t_0) - I_b(t_0) > 0,\\ &\frac{\partial r}{\partial x}(0, -\bar{\sigma}_1(t, \sigma^0)) + \frac{\partial r}{\partial y}(0, -\bar{\sigma}_1(t, \sigma^0)) > 0 \qquad \text{for} \quad t \in [0, t_0),\\ &\frac{\partial r}{\partial x}(\bar{\sigma}_2(t, \sigma^1), 0) + \frac{\partial r}{\partial y}(\bar{\sigma}_2(t, \sigma^1), 0) > 0 \qquad \text{for} \quad t \in (t_0), T].\end{aligned}$$

By means of the functions $\psi_1(t) \equiv 0$ and $\psi_2(t) = \bar{\sigma}_2(t, \sigma^1)$ we define the angular solution $(\hat{x}(t), \hat{\sigma}(t))$ of (4.2) associated to the solutions $x^1(\sigma) \equiv 0$ and $x^2(\sigma) \equiv \sigma$ of (4.4).

$$\hat{x}(t) = \begin{cases} 0 & 0 \le t \le t_0 \\ \bar{\sigma}_2(t, \sigma^1) & t_0 \le t \le T \end{cases}, \hat{\sigma}(t) = \begin{cases} \bar{\sigma}_1(t, \sigma^0) & 0 \le t \le t, \\ \bar{\sigma}_2(t, \sigma^1) & t_0 \le t \le T \end{cases}$$

Moreover, we assume (compare to (A_6^*),(A_7^*))

$(\bar{A}_6^*)$. $r_{xx}(0,0) + 2r_{xy}(0,0) + r_{yy}(0,0) > 0$.

$(\bar{A}_7^*)$. *The function* $-r(\hat{x}(t), \hat{x}(t) - \sigma)$ *is a quasi-monotone function of* σ *(for definition see the Appendix) in* $[\hat{\sigma}(t), \hat{\sigma}(t) + d\varepsilon]$, *and the function* $g_2(x - \hat{\sigma}(t)) - g_1(x)$ *is a quasi-monotone function of* x *in* $[\hat{x}(t), \hat{x}(t) + d\varepsilon]$ *where* d *is a sufficiently large constant independent of* ε.

The validity of assumption (A_8^*) follows from hypotheses (I) and (A_5^*). Thus, by means of Theorem 2.2 the following result holds.

Theorem 4.2 *Assume the hypotheses* $(I), (\bar{A}_3^*), (\bar{A}_4), (\bar{A}_5{}^*) - (\bar{A}_7{}^*)$ *hold. Then there is a sufficiently small* $\varepsilon_0 > 0$ *such that for* $0 < \varepsilon < \varepsilon_0$ *the initial value problem (4.1), (4.3) has a unique solution* $(x(t, \varepsilon), y(t, \varepsilon))$ *satisfying*

$$\begin{aligned}\lim_{\varepsilon \to 0} x(t, \varepsilon) &= \hat{x}(t) \quad \text{for} \quad 0 < t \le T,\\ \lim_{\varepsilon \to 0} y(t, \varepsilon) &= \hat{x}(t) - \hat{\sigma}(t) \quad \text{for} \quad 0 \le t \le T.\end{aligned}$$

Moreover, we have

$$\begin{aligned} x(t,\varepsilon) &= \hat{x}(t) + \Pi_0 x(\tau) + O(\varepsilon), \\ y(t,\varepsilon) &= \hat{x}(t) - \hat{\sigma}(t) + \Pi_0 x(\tau) + O(\varepsilon) \end{aligned}$$

for $0 \le t \le T$.

Corollary 4.2.1. *Under the assumptions of Theorem 4.2 the reaction rate has a jump near* t_0 *(transition layer), this means, for any small* $\nu > 0$ *we have*

$$r(x(t,\varepsilon), y(t,\varepsilon))/\varepsilon = I_a(t) + O(\varepsilon), \quad t \in [\nu, t_0 - \nu]$$

and

$$r(x(t,\varepsilon), y(t,\varepsilon))/\varepsilon = I_b(t) + O(\varepsilon), \quad t \in [t_0 + \nu, T].$$

We illustrate our results by considering the following example.

Example 4.1. We study system (4.1) in the case

$$g_1(x) \equiv x, \;\; g_2(y) \equiv y, \;\; r(x,y) \equiv xy.$$

By means of the coordinate transformation $x = x, y = x - \sigma$ we get the regular singularly perturbed system

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon\,(I_a(t) - \; x) - x\,(x - \sigma), \\ \frac{d\sigma}{dt} &= I_a(t) - I_b(t) + \sigma(t), \\ x(0) &= x^0, \;\; \sigma(0) = \sigma^0. \end{aligned} \tag{4.5}$$

From the last equation we obtain

$$\bar{\sigma}(t_0, \sigma^0) = e^t \bigg(\sigma^0 + \int_0^t e^{-s}(I_a(s) - I_b(s))ds \bigg). \tag{4.6}$$

Consequently, if $\bar{\sigma}(t,\sigma^0)$ does not change its sign in [0,T] then Theorem 4.1 can be applied. It is easily checked that $x^1(t) \equiv 0$ is stable if $\bar{\sigma}(t,\sigma^0) < 0$ for $t \in [0,T]$ and $x^2(t) \equiv -\sigma$ is stable if $\bar{\sigma}(t,\sigma^0) > 0$ for $t \in [0,T]$. From Corollary 4.1.1 we obtain that the reaction rate does not jump for $t \in [0,T]$.

If $\bar{\sigma}(t,\sigma^0)$ changes its sign on $0 < t < T$, say, at the point t_0 then we have an angular solution and the reaction rate jumps by Corollary 4.2.1. To illustrate this we consider the special case that

$$I_a(t) \equiv 1 \;,\; I_b(t) \equiv 1 + \cos t.$$

In this situation we get from (4.6) for $\bar{\sigma}(t,\sigma^0)$

$$\bar{\sigma}(t,\sigma^0) \;\; = \;\; \left(\sigma^0 - \frac{1}{2}\right) e^t + \frac{\cos t - \sin t}{2}. \tag{4.7}$$

For $0 < \sigma^0 < \frac{1}{2}$ and $T = \frac{5}{4}\pi$ the equation

$$\left(\sigma^0 - \frac{1}{2}\right) e^t - \frac{\cos t - \sin t}{2} = 0 \tag{4.8}$$

has a unique solution $t = t_0$ in $\left[0, \frac{5}{4}\pi\right]$. It can be easily shown that $x^2(t) \equiv -\bar{\sigma}(t, \sigma^0)$ is stable for $[0, t_0)$ and $x^1(t)$ is stable for $(t_0, \frac{5}{4}\pi]$. Consequently, there is the angular solution

$$\hat{x}(t) = \begin{cases} \left(\frac{1}{2} - \sigma^0\right) e^t + \frac{\sin t - \cos t}{2} & , \ 0 \le t \le t_0, \\ 0 \ , \ t_0 \le t \le \frac{5\pi}{4}. \end{cases}$$

It follows from Corollary 4.2.1 that the reaction rates jumps near the point $t = t_0$. The asymptotic behavior of the reaction rate on the interval $[\nu, t_0 - \nu]$ is given by

$$\frac{x(t,\varepsilon)y(t,\varepsilon)}{\varepsilon} = 1 + O(\varepsilon),$$

on the interval $[t_0 + \nu, T]$ it behaves like

$$\frac{x(t,\varepsilon)y(t,\varepsilon)}{\varepsilon} = 1 + \cos t + O(\varepsilon).$$

5. The Case of Fast Bimolecular and One Fast Unimolecular Reaction

For $g_1 \equiv g_2 \equiv 0$, $r_1 \equiv 0$, system (1.4) describes a fast bimolecular reaction coupled with a fast unimolecular reaction. We consider the initial value problem

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= \varepsilon I_a(t) - r(x,y), \\ \varepsilon \frac{dy}{dt} &= \varepsilon I_b(t) - r_2(y) - r(x,y), \\ x(0,\varepsilon) &= x^0, \quad y(0,\varepsilon) = y^0, \quad 0 < t \le T. \end{aligned} \tag{5.1}$$

Under hypothesis (I) it is easy to verify that system (5.1) is a singular singularly perturbed system and that any solution of (5.1) which starts in the positive orthant remains there for all future times. In order to be able to reduce (5.1) to a (regular) singularly perturbed system we have to assume that the corresponding associated system

$$\begin{aligned} \frac{dx}{d\tau} &= -r(x,y), \\ \frac{dy}{d\tau} &= -r_2(y) - r(x,y) \end{aligned} \tag{5.2}$$

has a first integral. In contrast to the cases studied in sections 3 and 4, the structure of system (5.2) by itself does not imply the existence of a first integral. Therefore, we will study system (5.1) in the positive orthant for the special case

$$r(x,y) \equiv k_1\, xy,\ r_2(y) \equiv k_2\, y,\quad k_1, k_2 > 0 \tag{5.3}$$

which is important for applications. In that case, (5.1) reads

$$\begin{aligned} \varepsilon\frac{dx}{dt} &= \varepsilon I_a(t) - k_1\, xy, \\ \varepsilon\frac{dy}{dt} &= \varepsilon I_b(t) - k_2\, y - k_1\, xy \end{aligned} \tag{5.4}$$

and the corresponding associated system has for $x > 0$, $y > 0$ the first integral

$$y - k\ \ln\ x - x = c,$$

where $k = k_2/k_1 > 0$. Thus, hypothesis (A_2) in Section 2 is fulfilled. By means of the coordinate transformation

$$x = x\ ,\quad y = \sigma + x + k\ \ln x$$

we can reduce the singular singularly perturbed system (5.4) to the regular singularly perturbed system

$$\begin{aligned} \varepsilon\,\frac{dx}{dt} &= \varepsilon\, I_a(t) - k_1 x(\sigma + x + k\ \ln x), \\ \frac{d\sigma}{dt} &= I_b(t) - \left(1 + \frac{k}{x}\right)\, I_a(t), \\ x(0,\varepsilon) &= x^0,\quad \sigma(0,\varepsilon) = \sigma^0,\quad 0 < t \le T. \end{aligned} \tag{5.5}$$

The degenerate equation to (5.5)

$$x(\sigma + x + k\ \ln x) = 0 \tag{5.6}$$

has for $x > 0$ the unique solution $x = x^*(\sigma)$ which is implicitely defined by

$$\sigma + x + k\ \ln x = 0.$$

In order to be able to apply Theorem 2.1 we shall verify that its assumptions are fulfilled for (5.4) with respect to $x^*(\sigma)$. First we note that the positivity of $x^*(\sigma)$ and k and assumption (I) imply that the initial value problem

$$\begin{aligned} \frac{d\sigma}{dt} &= I_b(t) - \left(1 + \frac{k}{x^*(\sigma)}\right)\, I_a(t), \\ \sigma(0) &= \sigma^0 = y^0 - x^0 - k\ \ln\, x^0. \end{aligned} \tag{5.7}$$

has a unique solution $\bar{\sigma}(t, \sigma^0)$ defined for $t \in [0, T]$. That means assumption (A_3) holds. The positivity of $x = x^*(\sigma)$ also implies that the stability assumption (A_5) and assumption (A_4) are valid.

According to the Appendix we get for the zeroth order approximation $X_0(t, \varepsilon) = \bar{x}_0(t) + \Pi_0 x(\tau)$ of the solution $x(t, \varepsilon)$ of (5.5) $\bar{x}_0(t) \equiv x^*(\bar{\sigma}(t, \sigma^0))$, and $\Pi_0 x(\tau)$ is determined by

$$\begin{aligned} \frac{d\Pi_0 x}{d\tau} &= -(x^*(\sigma^0) + \Pi_0 x)\left(\sigma^0 + x^*(\sigma^0) + \Pi_0 x + k\ln(x^*(\sigma^0) + \Pi_0 x)\right), \\ \Pi_0 x(0) &= x^0 - x^*(\sigma^0). \end{aligned} \tag{5.8}$$

It follows that $\Pi_0 x = 0$ is the only stable equilibrium point of (5.8) and that $\Pi_0 x(\tau)$ is exponentially decaying.

According to Theorem 2.1 we get the following result:

Theorem 5.1 *For sufficiently small ε the initial value problem (5.1) has in the case (5.3) a unique solution $(x(t, \varepsilon), y(t, \varepsilon))$ satisfying*

$$\begin{aligned} x(t, \varepsilon) &= x^*(\bar{\sigma}(t, \sigma^0)) + \Pi_0 x(\tau) + O(\varepsilon), \\ y(t, \varepsilon) &= \bar{\sigma}(t, \sigma^0) + x^*(\bar{\sigma}(t, \sigma^0)) + \Pi_0 x(\tau) + k\ln(x^*(\bar{\sigma}(t, \sigma^0)) + \Pi_0 x(\tau)) + O(\varepsilon) \end{aligned}$$

on $0 \leq t \leq T$.

By using Theorem 5.1 and Corollary B2 we get immediately from (5.4)

Corollary 5.1.1. *Under the assumptions of Theorem 5.1 there is to any given small ν an $\varepsilon_0(\nu)$ such that for $0 < \varepsilon \leq \varepsilon_0(\nu)$, $t \geq \nu$ the bimolecular reaction rate $r(x(t, \varepsilon), y(t, \varepsilon))/\varepsilon$ satisfies*

$$\frac{r(x(t, \varepsilon), y(t, \varepsilon))}{\varepsilon} = I_b(t)\frac{x^*(\bar{\sigma}(t, \sigma^0))}{1 + x^*(\bar{\sigma}(t, \sigma^0))} + O(\varepsilon)$$

and the unimolecular reaction rate $r_2(y(t, \varepsilon))/\varepsilon$ satisfies

$$\frac{r_2(y(t, \varepsilon))}{\varepsilon} = \frac{I_b(t)}{1 + x^*(\bar{\sigma}(t, \sigma^0))} + O(\varepsilon) \tag{5.9}$$

that is, the reaction rates have no jump for $t \geq \nu$.

Remark. From (5.9) we get for $t \geq \nu$

$$y(t, \varepsilon) = \frac{I_b(t)}{1 + x^*(\bar{\sigma}(t, \sigma^0))}\varepsilon + O(\varepsilon^2).$$

From Theorem 5.1 we only obtain $y(t, \varepsilon) = O(\varepsilon)$.

6. Appendix

We consider the singularly perturbed system

$$\begin{aligned} \frac{d\sigma}{dt} &= f(\sigma, z, t, \varepsilon), \\ \varepsilon \frac{dz}{dt} &= g(\sigma, z, t, \varepsilon) \end{aligned} \tag{6.1}$$

where $\sigma \in R^n$, $z \in R^m$, and ε is a small parameter belonging to the interval $J := \{\varepsilon \in R : 0 \leq \varepsilon \leq \varepsilon^* \ll 1\}$. Concerning the regularity of the right hand side of (6.1) we assume

($\tilde{V}_1$). *$f : R^n \times R^m \times R \times J \to R^n$ and $g : R^n \times R^m \times R \times J \to R^m$ are continuous and continuously differentiable with respect to the first three variables.*

If we set $\varepsilon = 0$ in (6.1) then the corresponding system

$$\begin{aligned} \frac{d\sigma}{dt} &= f(\sigma, z, t, 0), \\ 0 &= g(\sigma, z, t, 0) \end{aligned} \tag{6.2}$$

is called degenerate.

For (6.1) we shall study the initial value problem

$$\sigma(0, \varepsilon) = \sigma^0, \; z(0, \varepsilon) = z^0 \tag{6.3}$$

on the interval $0 < t \leq T$ under the following assumptions.

(V_2). *For $0 \leq t \leq T$ the equation*

$$g(\sigma, z, t, 0) = 0 \tag{6.4}$$

has a solution $z = \varphi(\sigma, t)$, and the corresponding initial value problem

$$\frac{d\sigma}{dt} = f(\sigma, \varphi(\sigma, t), t, 0), \quad \sigma(0) = \sigma^0$$

has a unique solution $\bar{\sigma}(t, \sigma^0)$ on [0, T].

Beside the degenerate system (6.2) we consider the associated system to the second equation of (6.1)

$$\frac{dz}{d\tau} = g(\sigma, z, t, 0) \tag{6.5}$$

where σ and t are considered as parameters. By the assumption (V_2), $z = \varphi(\sigma, t)$ is an equilibrium point of (6.5). With respect to its stability we assume

($\tilde{V}_3$). *$z = \varphi(\sigma, t)$ is an asymptotically stable equilibrium point of the associated system (6.5) uniformly for all σ and t in the domain of interest.*

Finally we assume

(V_4). *The initial value problem*

$$\frac{dz}{d\tau} = g(\sigma^0, z, 0, 0), \quad z(0) = z^0$$

has a unique solution $\tilde{z}(\tau, z^0)$ *which exists for* $\tau \geq 0$ *and tends to* $\varphi(\sigma^0, 0)$ *as* $\tau \to \infty$.

The following theorem is essentially due to A.N. Tikhonov [22].

Theorem A. *Suppose the hypotheses* $(\tilde{V}_1),(V_2),(\tilde{V}_3),(V_4)$ *hold. Then there exists a sufficiently small* $\varepsilon_0 \leq \varepsilon^*$ *such that for* $0 < \varepsilon \leq \varepsilon_0$ *the initial value problem (6.1), (6.3) has a unique solution* $(\sigma(t,\varepsilon), z(t,\varepsilon))$ *satisfying*

$$\begin{aligned} \lim_{\varepsilon \to 0} \sigma(t,\varepsilon) &= \bar{\sigma}(t,\sigma^0) \quad \text{for} \quad 0 \leq t \leq T, \\ \lim_{\varepsilon \to 0} z(t,\varepsilon) &= \varphi(\bar{\sigma}(t,\sigma^0), t) \quad \text{for} \quad 0 < t \leq T. \end{aligned}$$

Remark. *Theorem A can be applied also to systems of the form (6.1) which are independent of the* σ*-variable, that means to systems of the form*

$$\varepsilon \frac{dz}{dt} = g(z, t, \varepsilon). \tag{6.6}$$

In order to formulate the next theorem, which is due to A.B. Vasiljeva [23], we introduce the concept of an asymptotic expansion of the solution $(\sigma(t,\varepsilon), z(t,\varepsilon))$ of (6.1), (6.3).

An asymptotic expansion of the solution of (6.1), (6.3) is a representation of $\sigma(t,\varepsilon)$ and $z(t,\varepsilon)$ in the form

$$x_a(t,\varepsilon) = \bar{x}(t,\varepsilon) + \Pi x(\tau,\varepsilon) \tag{6.7}$$

where x is a placeholder for σ and z respectively, $\bar{x}(t,\varepsilon)$ is the regular part of the asymptotics, that is,

$$\bar{x}(t,\varepsilon) := \sum_{i=0}^{\infty} \varepsilon^i \bar{x}_i(t), \tag{6.8}$$

and $\Pi x(\tau,\varepsilon)$ is the boundary layer correction near $t = 0$,

$$\Pi x(\tau,\varepsilon) := \sum_{i=0}^{\infty} \varepsilon^i \Pi_i x(\tau) \tag{6.9}$$

where τ is the stretched variable $\tau = t/\varepsilon$. We denote by $X_k(t,\varepsilon)$ the truncated part of (6.7)

$$X_k(t,\varepsilon) = \sum_{i=0}^{k} \varepsilon^i (\bar{x}_i(t) + \Pi_i x(\tau)).$$

By means of the representation (6.7) we may rewrite $F(x_a, t, \varepsilon)$ in the form

$$F(x_a(t,\varepsilon),t,\varepsilon) = F(\bar{x}(t,\varepsilon),t,\varepsilon) + F(x_a(\tau\varepsilon,\varepsilon),\tau\varepsilon,\varepsilon) - F(\bar{x}(\tau\varepsilon,\varepsilon),\tau\varepsilon,\varepsilon) =: \bar{F} + \Pi F \tag{6.10}$$

where

$$\bar{F} := F(\bar{x}(t,\varepsilon),t,\varepsilon),\ \Pi F := F(x_a(\tau\varepsilon,\varepsilon),\tau\varepsilon,\varepsilon) - F(\bar{x}(\tau\varepsilon,\varepsilon),\tau\varepsilon,\varepsilon). \tag{6.11}$$

In order to compute the coefficients $\bar{x}_i(t)$ and $\Pi_i x(\tau)$ we substitute (6.7) - (6.9) into (6.1), (6.3) and use the representation (6.10), (6.11). By equating expressions with the same power of ε (separately for t and τ) we obtain equations which let us determine the unknown coefficients of the asymptotic expansion. In particular, if our conditions are satisfied then $\bar{\sigma}_0(t)$ and $\bar{z}_0(t)$ are uniquely determined by the degenerate system (6.2) and the initial value σ^0. Note that $\Pi\sigma_0(\tau)$ and $\Pi z_0(\tau)$ are determined by the initial value problems (see [23])

$$\begin{aligned} \frac{d\Pi_0 z}{d\tau} &= \Pi_0 g(\bar{\sigma}_0(0) + \Pi_0\sigma(\tau), \bar{z}_0(0) + \Pi_0 z(\tau), 0, 0), \quad \Pi_0 z(0) = z^0 - \bar{z}_0(0), \\ \frac{d\Pi_0\sigma}{d\tau} &= 0, \quad \Pi_0\sigma(0) = 0. \end{aligned} \tag{6.12}$$

Finally, we strengthen the assumptions ($\tilde{V}_1$) and ($\tilde{V}_3$) as follows.

(V_1). *The functions f and g are $(k+2)$-times continuously differentiable with respect to all variables in the domain of interest.*

(V_3). *All eigenvalues $\lambda_i(t)$ of the Jacobian $g_z(\bar{\sigma}(t,\sigma^0), \varphi(\bar{\sigma}(t,\sigma^0),t),t,0)$ satisfy*

$$\text{Re } \lambda_i(t) < 0 \quad \text{for} \quad 0 \le t \le T, \quad 1 \le i \le m.$$

Theorem B. *We assume the hypotheses $(V_1) - (V_4)$ to hold. Let $(\Sigma_k(t,\varepsilon), Z_k(t,\varepsilon))$ be the truncated parts of the asymptotic expansion of the solution of problem* (6.1), (6.3) *obtained by the method of boundary layer functions* (see [23], [25] for details). *Then there exists a sufficiently small ε_0 and a constant $c = c(\varepsilon_0)$ such that for $0 < \varepsilon \le \varepsilon_0$ the initial value problem* (6.1), (6.3) *has a unique solution $(\sigma(t,\varepsilon), z(t,\varepsilon))$ for $0 \le t \le T$ satisfying*

$$\begin{aligned} |\sigma(t,\varepsilon) - \Sigma_k(t,\varepsilon)| &\le c\,\varepsilon^{k+1}, \\ |z(t,\varepsilon) - Z_k(t,\varepsilon)| &\le c\,\varepsilon^{k+1}. \end{aligned}$$

In particular, we have for $n = 0$:

$$z(t,\varepsilon) = \bar{z}_0(t) + \Pi_0 z(\tau) + O(\varepsilon),\ \sigma(t,\varepsilon) = \bar{\sigma}_0(t) + O(\varepsilon)$$

where $\Pi_0 z$ is defined by (6.12).

Corollary B.1. *Let ν be any small positive number. Then under the assumptions of Theorem B there is an $\varepsilon_0 = \varepsilon_0(\nu)$ such that for $0 < \varepsilon < \varepsilon_0(\nu)$, $\nu \le t \le T$*

$$z(t,\varepsilon) = \bar{z}_0(t) + O(\varepsilon). \tag{6.13}$$

Concerning the time derivative we have the result:

Corollary B.2. *Under the assumptions of Theorem B the following estimates hold for $\nu \le t \le T$, where ν is any small positive number*

$$\frac{d}{dt}\Big(z(t,\varepsilon) - \bar{Z}_k(t,\varepsilon)\Big) = O(\varepsilon^{k+1}), \tag{6.14}$$

$$\frac{d}{dt}\Big(\sigma(t,\varepsilon) - \bar{\Sigma}_k(t,\varepsilon)\Big) = O(\varepsilon^{k+1}). \tag{6.15}$$

Here $\bar{Z}_k(t,\varepsilon)$ and $\bar{\Sigma}_k(t,\varepsilon)$ are the truncated regular parts of the asymptotic expansion of $z(t,\varepsilon)$ and $\sigma(t,\varepsilon)$, that is,

$$\bar{Z}_k(t,\varepsilon) = \sum_{i=0}^{k} \varepsilon^i \bar{z}_i(t), \quad \bar{\Sigma}_k(t,\varepsilon) = \sum_{i=0}^{k} \varepsilon^i \bar{\sigma}_i(t).$$

Proof. Let $\sigma(t,\varepsilon) = \Sigma_{k+1}(t,\varepsilon) + \eta(t,\varepsilon)$, $\quad z(t,\varepsilon) = Z_{k+1}(t,\varepsilon) + \zeta(t,\varepsilon)$. We have

$$\begin{aligned} \frac{d\eta}{dt} &= f(\Sigma_{k+1} + \eta, Z_{k+1} + \zeta, t, \varepsilon) - \frac{d\Sigma_{k+1}(t,\varepsilon)}{dt} = \\ & f(\Sigma_{k+1} + \eta, Z_{k+1} + \zeta, t, \varepsilon) - f(\Sigma_{k+1}, Z_{k+1}, t, \varepsilon) \\ & + f(\Sigma_{k+1}, Z_{k+1}, t, \varepsilon) - \frac{d\Sigma_{k+1}(t,\varepsilon)}{dt}. \end{aligned} \tag{6.16}$$

From assumption (V_1) and Theorem B we get

$$f(\Sigma_{k+1} + \eta, Z_{k+1} + \zeta, t, \varepsilon) - f(\Sigma_{k+1}, Z_{k+1}, t, \varepsilon) = O(\varepsilon^{k+2}). \tag{6.17}$$

By [23] we have

$$f(\Sigma_{k+1}, Z_{k+1}, t, \varepsilon) - \frac{d\Sigma_{k+1}(t,\varepsilon)}{dt} = O(\varepsilon^{k+2}). \tag{6.18}$$

Hence, from (6.16) – (6.18) it follows

$$\frac{d\eta}{dt} = \frac{d}{dt}\Big(\sigma(t,\varepsilon) - \Sigma_{k+1}(t,\varepsilon)\Big) = O(\varepsilon^{k+2}) \text{ for } t \in [0,T]. \tag{6.19}$$

From this relation we get (6.15).

Concerning $\zeta(t,\varepsilon)$ we have

$$\varepsilon \frac{d\zeta}{dt} = g(\Sigma_{k+1} + \eta, Z_{k+1} + \zeta, t, \varepsilon) - \varepsilon \frac{dZ_{k+1}(t,\varepsilon)}{dt}.$$

In the same way as above we get

$$\frac{d\zeta}{dt} = \frac{d}{dt}\Big(z(t,\varepsilon) - Z_{k+1}(t,\varepsilon)\Big) = O(\varepsilon^{k+1}).$$

Using the relation

$$z(t,\varepsilon) - Z_{k+1}(t,\varepsilon) = z(t,\varepsilon) - Z_k(t,\varepsilon) + \varepsilon^{k+1}(\Pi_{k+1}z(\tau) + \bar{z}_k(t)) \tag{6.20}$$

where $\Pi_{k+1}z(\tau)$ is a boundary layer function to $t = 0$ which exponentially decays and $\bar{z}_k(t)$ is continuously differentiable on $(0,T)$ we obtain from (6.20) the estimate (6.14).

In what follows we study the case when (6.4) has more than one solution which intersect at some points. To this end we consider the initial value problem (6.1), (6.3) under the condition $m = 1$, that means, the fast equation is scalar. We assume the following hypotheses:

(D_1). *Let g be a scalar function and the equation $g(\sigma, z, t, 0) = 0$ have exactly two solutions $z_1 = \varphi_1(\sigma, t)$ and $z_2 = \varphi_2(\sigma, t)$ with the same smoothness as g in the domain of interest.*

(D_2). *The initial value problem*

$$\begin{aligned} \frac{d\sigma}{dt} &= f(\sigma, \varphi_1(\sigma,t), t, 0), \\ \sigma(0) &= \sigma^0 \end{aligned}$$

has a unique solution $\bar{\sigma}^1(t,\sigma^0)$ defined on $[0,T]$.
The initial value problem

$$\begin{aligned} \frac{d\sigma}{dt} &= f(\sigma, \varphi_2(\sigma,t), t, 0), \\ \sigma(t_0) &= \bar{\sigma}^1(t_0,\sigma^0) = \sigma^1 \end{aligned}$$

has a unique solution $\bar{\sigma}^2(t,\sigma^1)$ defined on $[0,T]$.

(D_3). *The curves $z = \psi_1(t) := \varphi_1(\bar{\sigma}^1(t,\sigma^0), t)$ and $z = \psi_2(t) := \varphi_2(\bar{\sigma}^2(t,\sigma^1), t)$ intersect for $t = t_0 \in (0,T)$ such that*

$$\frac{d\psi_1}{dt}(t_0) < \frac{d\psi_2}{dt}(t_0)$$

where $\psi_1(t)$ is stable for $[0,t_0)$ and $\psi_2(t)$ is stable for $(t_0,T]$. The stability is expressed by

$$g_z(\bar{\sigma}^1(t,\sigma^0), \psi_1(t), t, 0) < 0 \text{ for } t \in [0,t_0)$$

and

$$g_z(\bar{\sigma}^2(t,\sigma^1), \psi_2(t), t, 0) < 0 \text{ for } t \in (t_0,T].$$

Definition. *Under the assumptions $(D_1) - (D_3)$ the function $(\hat{\sigma}(t), \hat{z}(t))$ defined by*

$$\hat{\sigma}(t) = \begin{cases} \bar{\sigma}^1(t,\sigma^0) & 0 \le t \le t_0 \\ \bar{\sigma}^2(t,\sigma^1) & t_0 \le t \le T \end{cases}, \quad \hat{z}(t) = \begin{cases} \psi_1(t) & 0 \le t \le t_0 \\ \psi_2(t) & t_0 \le t \le T \end{cases}$$

is referred to as the angular solution of (6.2) with respect to $\psi_1(t), \psi_2(t)$.

For any fixed small positive ν let I_ν be the interval $[t_0 - \nu, t_0 + \nu]$. By I_ν^- and I_ν^+ we denote the intervals $[t_0 - \nu, t_0]$ and $[t_0, t_0 + \nu]$, respectively. For $\varepsilon \in J$ and $t \in I_\nu$ we define the functions $(\beta^\sigma(t,\varepsilon), \beta^z(t,\varepsilon))$ by

$$\beta^\sigma(t,\varepsilon) := \hat{\sigma}(t) + \varepsilon e^{\lambda t}\ ,\ \beta^z(t,\varepsilon) := \hat{z}(t) + \varepsilon^{\frac{1}{2}}\gamma, \tag{6.21}$$

where the positive constants λ and γ will be chosen later such that these functions form an upper solution for some initial value problem of (6.1) on I_ν.

$(\tilde{V}_4)$. *The initial value problem*

$$\frac{dz}{d\tau} = g(\sigma^0, z, 0, 0), \quad z(0) = z^0$$

has a unique solution $\tilde{z}(\tau, z^0)$ which exists for $\tau \geq 0$ and tends to $\varphi_1(\sigma^0, 0)$ as $\tau \longrightarrow \infty$.

(V_5). $g_{zz}(\hat{\sigma}(t_0), \hat{z}(t_0), t_0, 0) < 0$.

(V_6). *For $i = 1, \ldots n, \varepsilon \in J$ and $t \in I_\nu$ the function $f_i(\sigma_1, \ldots, \sigma_{i-1}, \hat{\sigma}_i(t), \sigma_{i+1}, \ldots, \sigma_n, z, t, \varepsilon)$ is non-decreasing in $(\sigma_1, \ldots, \sigma_{i-1}, \sigma_{i+1}, \ldots, \sigma_n, z)$ and the scalar function $g(\sigma_1, \ldots, \sigma_n, \hat{z}(t), t, \varepsilon)$ is non-decreasing in $(\sigma_1, \ldots, \sigma_n)$ in the region defined by $\sigma_k \in [\hat{\sigma}_k(t), \beta_k^\sigma(t,\varepsilon)]\,, k = 1, ..., n,\ z \in [\hat{z}(t)\ ,\ \beta^z(t,\varepsilon)]$.*

Remark. *Assumption (V_6) implies that system (6.1) is quasi-monotone in the domain of interest [14].*

(V_7). *For $t \in (0, t_0 + \nu)$, where ν is any given small positive number, we have*

$$\begin{aligned} \frac{d\hat{\sigma}}{dt} &\leq f(\hat{\sigma}(t), \hat{z}(t), t, \varepsilon), \\ \varepsilon\frac{d\hat{z}}{dt} &\leq g(\hat{\sigma}(t), \hat{z}(t), t, \varepsilon) \end{aligned}$$

where at $t = t_0$ the corresponding left and right derivatives have to be used.

Theorem C. *Assume the hypotheses $(V_1), (\tilde{V}_4), (V_5) - (V_7)$ to hold. Then there exists a sufficiently small $\varepsilon_0 = \varepsilon_0(\nu)$ such that for $0 < \varepsilon \leq \varepsilon_0(\nu)$ the initial value problem (6.1), (6.3) with $z^0 \geq \psi_1(0)$ has a unique solution $(\sigma(t,\varepsilon), z(t,\varepsilon))$ for $t \in [0,T]$ satisfying*

$$\begin{aligned} \lim_{\varepsilon \to 0} \sigma(t,\varepsilon) &= \hat{\sigma}(t) \quad \textit{for}\ t \in [0,T], \\ \lim_{\varepsilon \to 0} z(t,\varepsilon) &= \hat{z}(t) \quad \textit{for}\ t \in (0,T]. \end{aligned}$$

Moreover, we have

$$\sigma(t,\varepsilon) = \hat{\sigma}(t) + O(\varepsilon) \quad \textit{for} \quad t \in [0,T],$$

$$z(t,\varepsilon) = \begin{cases} \hat{z}(t) + \Pi_0 z(\tau) + O(\varepsilon) & \text{for} \quad 0 \le t \le t_0 - \nu, \\ \hat{z}(t) + O(\varepsilon^{\frac{1}{2}}) & \text{for} \quad t \in I_\nu, \\ \hat{z}(t) + O(\varepsilon) & \text{for} \quad t_0 + \nu \le t \le T \end{cases}$$

where $\Pi_0 z(\tau)$ *is the zeroth order boundary layer function.*

Proof. For simplicity we consider the case that σ is also a scalar. The proof proceeds in three steps. In the first step we consider (6.1), (6.3) on the interval $[0, t_0 - \nu]$ and apply Theorem B. Thereby we prove the existence of the solution $(\sigma(t,\varepsilon), z(t,\varepsilon))$ of (6.1), (6.3) on the interval $[0, t_0 - \nu]$ with asymptotic behavior as described above. Let

$$\sigma_\nu^- := \sigma(t_0 - \nu, \varepsilon), \ z_\nu^- := z(t_0 - \nu, \varepsilon). \tag{6.22}$$

Next we consider the initial value problem (6.1), (6.22) on the interval I_ν. We prove the existence of a unique solution to this problem by applying the method of lower and upper solutions. Following [5], [14], [1] we call the functions $(\alpha^\sigma(t,\varepsilon),\ \alpha^z(t,\varepsilon))$ and $(\beta^\sigma(t,\varepsilon), \beta^z(t,\varepsilon))$ the lower and upper solutions of the problem (6.1), (6.22), respectively, provided they satisfy the following inequalities

$$\alpha^\sigma(t,\varepsilon) \le \beta^\sigma(t,\varepsilon)\ ,\ \alpha^z(t,\varepsilon) \le \beta^z(t,\varepsilon), \tag{6.23}$$

$$\frac{d\alpha^\sigma}{dt} - f(\alpha^\sigma, z, t, \varepsilon) \le 0 \le \frac{d\beta^\sigma}{dt} - f(\beta^\sigma, z, t, \varepsilon), \tag{6.24}$$

$$\varepsilon\,\frac{d\alpha^z}{dt} - g(\sigma, \alpha^z, t, \varepsilon) \le 0 \le \varepsilon\,\frac{d\beta^z}{dt} - g(\sigma, \beta^z, t, \varepsilon) \tag{6.25}$$

for $0 < \varepsilon \le \varepsilon_*$, $\sigma \in [\alpha^\sigma(t,\varepsilon), \beta^\sigma(t,\varepsilon)]$, $z \in [\alpha^z(t,\varepsilon), \beta^z(t,\varepsilon)]$, $t \in I_\nu$, and

$$\alpha^\sigma(t_0 - \nu, \varepsilon) \le \sigma_\nu^- \le \beta^\sigma(t_0 - \nu, \varepsilon),\ \alpha^z(t_0 - \nu, \varepsilon) \le z_\nu^- \le \beta^z(t_0 - \nu, \varepsilon). \tag{6.26}$$

The existence of a lower and an upper solution implies the existence of a solution $(\sigma(t,\varepsilon), z(t,\varepsilon))$ of (6.1), (6.22) satisfying

$$\alpha^\sigma(t,\varepsilon) \le \sigma(t,\varepsilon) \le \beta^\sigma(t,\varepsilon),\ \alpha^z(t,\varepsilon) \le z(t,\varepsilon) \le \beta^z(t,\varepsilon) \ \text{ for } t \in I_\nu.$$

If we assume that (V_6) is valid then the differential inequalities (6.24), (6.25) are fulfilled if the following differential inequalities are satisfied

$$\frac{d\alpha^\sigma}{dt} - f(\alpha^\sigma, \alpha^z(t,\varepsilon), t, \varepsilon) \le 0 \le \frac{d\beta^\sigma}{dt} - f(\beta^\sigma, \beta^z(t,\varepsilon), t, \varepsilon), \tag{6.27}$$

$$\varepsilon\,\frac{d\alpha^z}{dt} - g(\alpha^\sigma, \alpha^z(t,\varepsilon), t, \varepsilon) \le 0 \le \varepsilon\,\frac{d\beta^z}{dt} - g(\beta^\sigma, \beta^z(t,\varepsilon), t, \varepsilon). \tag{6.28}$$

From assumption (V_7) it follows immediately that $(\hat{\sigma}(t), \hat{z}(t))$ is a lower solution of the problem (6.1), (6.22) on I_ν. Now we prove that $\beta^\sigma(t,\varepsilon)$ and $\beta^z(t,\varepsilon)$ defined in (6.21) are an upper solution of (6.1), (6.22) on I_ν. By assumption (V_6) we have

$$
\begin{aligned}
&\varepsilon\frac{d\beta^z}{dt} - g(\beta^\sigma(t,\varepsilon),\beta^z(t,\varepsilon),t,\varepsilon) \geq \varepsilon\frac{d\hat{z}}{dt} - g(\hat{\sigma}(t),\hat{z}(t)+\gamma\varepsilon^{\frac{1}{2}},t,\varepsilon) = \\
&= -g_z(\hat{\sigma}(t),\hat{z}(t),t,0)\,\gamma\,\varepsilon^{\frac{1}{2}} - g_{zz}(\hat{\sigma}(t),\hat{z}(t),t,0)\frac{\gamma^2}{2}\varepsilon + g_\varepsilon(\hat{\sigma}(t),\hat{z}(t),t,0)\varepsilon + o(\varepsilon).
\end{aligned} \tag{6.29}
$$

From the stability assumption (D_3) it follows that the first term in (6.29) can be estimated below by 0. Since $|g_\varepsilon(\hat{\sigma}(t),\hat{z}(t),t,0)|$ is bounded on I_ν, by assumption (V_5) there is some positive constant γ_0 such that for $0<\varepsilon<\varepsilon_0$ and $\gamma>\gamma_0$ the right hand side of (6.29) can be estimated below by 0. In order to check that (β^σ,β^z) defined in (6.21) satisfies condition (6.27) we substitute (6.21) into (6.27). We get

$$
\begin{aligned}
&\frac{d\beta^\sigma}{dt} - f(\beta^\sigma(t,\varepsilon),\beta^z(t,\varepsilon),t,\varepsilon) \geq \frac{d\hat{\sigma}}{dt} + \lambda\varepsilon e^{\lambda t} - f(\hat{\sigma}(t)+\varepsilon e^{\lambda t},\hat{z}(t),t,\varepsilon) \\
&= \lambda\varepsilon e^{\lambda t} - f_\sigma(\hat{\sigma}(t),\hat{z}(t),t,0)\varepsilon e^{\lambda t} - f_\varepsilon(\hat{\sigma}(t),\hat{z}(t),t,0)\varepsilon + o(\varepsilon) \\
&= \varepsilon e^{\lambda t}\big(\lambda - f_\sigma(\hat{\sigma}(t),\hat{z}(t),t,0) - f_\varepsilon(\hat{\sigma}(t),\hat{z}(t),t,0)e^{-\lambda t} + o(1)\big).
\end{aligned} \tag{6.30}
$$

Thus, there is a constant $\lambda_0>0$ such that for $\lambda>\lambda_0$ and $0<\varepsilon<\varepsilon_0$ the right hand side of (6.30) can be estimated below by 0. Consequently, we have proved the existence of a lower and an upper solution of (6.1), (6.22) on I_ν which implies the existence of a unique solution of (6.1), (6.22) on I_ν satisfying the estimate of Theorem C. Let

$$
\sigma^+_{\nu/2} := \sigma(t_0+\nu/2,\varepsilon),\ z^+_{\nu/2} := z(t_0+\nu/2,\varepsilon). \tag{6.31}
$$

Finally we apply Theorem B to (6.1), (6.31) on the interval $[t_0+\nu/2,T]$, where we assume that $\varepsilon_0(\nu)$ is so small that $\sigma^+_{\nu/2}$ is in the domain of attraction of the stable root φ_2 and the corresponding boundary layer is contained in $(t_0+\nu/2,t_0+\nu)$ for $0<\varepsilon\leq\varepsilon_0(\nu)$. This completes the proof of Theorem C.

Corollary C1. *Under the assumptions of Theorem C the following estimates on the derivative of the solution of (6.1), (6.3) hold for $t\in[\nu,T]\backslash I^-_\nu$ where ν is any small positive number*

$$
\begin{aligned}
\frac{d}{dt}\Big(z(t,\varepsilon)-\hat{z}(t,\varepsilon)\Big) &= O(\varepsilon), \\
\frac{d}{dt}\Big(\sigma(t,\varepsilon)-\hat{\sigma}(t,\varepsilon)\Big) &= O(\varepsilon).
\end{aligned} \tag{6.32}
$$

The proof of Corollary C1 follows from Corollary B2 and an application of Theorem B for $t\in[\nu,T]\backslash I^-_\nu$ (compare the proof of the Theorem C).

Now we consider the case $z^0<\psi_1(0)$. To this end we assume

(V_7^*). *For $t\in I_\nu$, where ν is any given small positive number we have*

$$\frac{d\bar{\sigma}^2}{dt} \leq f\left(\bar{\sigma}^2(t), \psi_2(t), t, \varepsilon\right),$$
$$\varepsilon\frac{d\psi_2}{dt} \leq g\left(\bar{\sigma}^2(t), \psi_2(t), t, \varepsilon\right).$$

Theorem C^*. *Assume the hypotheses* $(V_1), (\tilde{V_4}), (V_5), (V_6), (V_7^*)$ *to be valid. Then there exists a sufficiently small* $\varepsilon_0 = \varepsilon(\nu)$ *such that for* $0 < \varepsilon \leq \varepsilon_0(\nu)$ *the initial value problem (6.1), (6.3) with* $z^0 < \psi_1(0)$ *has a unique solution* $(\sigma(t,\varepsilon), z(t,\varepsilon))$ *for* $t \in [0,T]$ *satisfying*

$$\lim_{\varepsilon\to 0}\sigma(t,\varepsilon) = \hat{\sigma}(t) \text{ for t} \in [0,\mathrm{T}]\backslash \mathrm{I}_\nu^-,$$
$$\lim_{\varepsilon\to 0} z(t,\varepsilon) = \hat{z}(t) \text{ for t} \in (0,\mathrm{T}]\backslash \mathrm{I}_\nu^-.$$

Moreover, we have

$$\sigma(t,\varepsilon) = \hat{\sigma}(t) + O(\varepsilon), \qquad \text{for } \in [0,\mathrm{T}]\backslash \mathrm{I}_\nu^-,$$

$$z(t,\varepsilon) = \begin{cases} \hat{z}(t) + \Pi_0 z(\tau) + O(\varepsilon) & \text{for} \quad 0 \leq t \leq t_0 - \nu, \\ \hat{z}(t) + O(\varepsilon^{\frac{1}{2}}) & \text{for} \quad t_0 \leq t \leq t_0 + \nu, \\ \hat{z}(t) + O(\varepsilon) & \text{for} \quad t_0 + \nu \leq t \leq T, \end{cases}$$

where $\Pi_0 z(\tau)$ *is the zeroth order boundary layer function.*

The proof of Theorem C^* is essentially the same as of Theorem C, when $(\bar{\sigma}^2(t,\sigma^1), \psi_2(t))$ in used as a lower solution of (6.1), (6.22) on I_ν^-.

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