Calculation of Separatrices in Multistable Chemical Reaction Systems

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In multistable chemical reaction systems the space of variables is partitioned by separatrices into different cells which are the domains of attraction of the respective critical points. By numerically solving an initial value problem, which is based on the particular stability properties of separatrix manifolds, we achieve a direct approximation of the stability boundaries in the phase space. The method is principally applicable to nonlinear systems of any number of variables and, other than the direct method of Liapunov, also in regions of the phase space which are far from the critical points.

1. Introduction

Homogeneous chemical reaction systems with nonlinear kinetics may be non-unique in their final state, or, in the notation of dynamical systems theory, may have more than one asymptotically stable limit set. In such systems, besides the limit sets themselves, the corresponding regions of attraction and their boundary hypersurfaces, so-called separatrices, are of interest. These hypersurfaces, consisting of orbitally unstable trajectories, are characterized as the stable manifolds of unstable limit sets.

Together with the limit sets, the separatrices of a dynamical system uniquely define its topological structure [1]. An exhaustive presentation of this topic with respect to systems in the phase plane has been given by Andronov et al. [2].

Beyond this theoretical aspect in problems concerning practical stability of dynamical systems, the separatrices provide exact information about those perturbations which eventually shift the system away from a locally asymptotically stable state.

Separatrix manifolds can be treated analytically only in exceptional cases (e.g. [3]), which are seldom of practical relevance. Therefore, when dealing with most concrete problems one has to resort to purely numerical methods.

2. Notation

We shall use the following notation.

D   A dynamical system defined by a set of ordinary differential equations:

$$\dot{x} = f(x), \quad x \in \mathbb{R}^n \tag{1}$$

($\dot{x}$ — derivative with respect to t)

f is a vector valued function. The components of x represent chemical concentrations, partial pressures, temperature and so on. $\mathbb{R}^n$ denotes the n-dimensional phase space.

$x(x_0, t)$ A solution of (1) with initial value x_0, $0 \leq t \leq +\infty$, or the corresponding trajectory (path) of **D**.

Λ A (positive) limit set of **D**, i.e., the set of all limit points for some $x_0 \in \mathbb{R}^n$ and $t \to +\infty$. We call Λ an attractor if it is asymptotically stable.

RAS   Region of asymptotic stability of a given Λ, i.e., the set of all initial values $x_0 \in \mathbb{R}^n$ for which Λ is an attractor.

Σ A separatrix of **D** defined as follows: We call $\Sigma \subset \mathbb{R}^n$ a separatrix of **D** if for $s_0 \in \Sigma$ and every x_0 in an ε-neighborhood of s_0, $x_0 \notin \Sigma$, the limit sets of x_0 and s_0 are different for every ε.

3. Application of Liapunov's Direct Method

Problems of computing regions of asymptotic stability have most often been treated using Liapunov's direct method which, however, provides only sufficient conditions for stability. This is a serious shortcoming whenever one tries to obtain true estimates of a RAS by these techniques, as for nonlinear systems the results may strongly depend on the local properties at the critical point. Consequently we often have very conservative estimates of the RAS, especially with increasing dimension of the system [4]. As a further point, Liapunov methods by definition yield stability boundaries which are closed shells around the attractor. This may lead us

to qualitatively wrong predictions if the RAS under investigation is an open region in the phase space (see example 5 b).

There have been some efforts to overcome the local nature of the results provided by Liapunov methods, e.g. by involving Krasovskii's theorem [4, 5] or via Zubov's construction [6, 7] but no constructive method of general value could be worked out, especially with regard to systems of dimension > 2.

In fact, Liapunov methods have found the most widespread application in the analysis of two-dimensional systems. This, however, is often at the cost of reducing the higher dimensional problem to a model in the phase plane, as for example in many chemical engineering problems. Obviously, valuable information may hereby be lost.

4. Calculation of Separatrix Manifolds

As indicated above, in many cases it seems reasonable to apply techniques which allow for a direct calculation of separatrix manifolds, e.g. if one is interested only in a picewise but correct description of separatrices. We now outline some contributions to this topic.

a) Separatrices in the Phase Plane

In this case there are only two possible types:

i) Paths which have a critical point as an attractor. These critical points are saddle points of the system **D**.

ii) Closed orbits, i.e. paths which are identical with their limit set, hence unstable limit cycles in **D**.

In both cases single trajectories of **D** must be calculated. This can be done by standard numerical integration methods, since a special technique proposed for one-dimensional Σ seems not to be worthwhile [7].

As a first step, an initial point $s_0 \in \Sigma$ has to be found. The integration should be done in negative time direction. Thus, the orbitally unstable separatrix paths change to be asymptotically stable, whereby stability problems in the computation process are avoided, i.e. s_0 may be chosen with moderate accuracy without detraction from the numerical result. For separatrices of type i), for example, s_0 in a small neighborhood of a saddle point will give a solution which is a good approximation to Σ after few integration steps.

b) Separatrices in a Phase Space of Dimension $n \geqq 3$

For higher dimensional systems with separatrices Σ of dimension $\geqq 2$ the description via integration of single trajectories would be a wasteful method, since there clearly exists no local criterion indicating wether or not a path of **D** belongs to Σ.

Here, however, we can use some results taken from the qualitative theory of dynamical systems, and with two reasonable assumptions we solve an initial value problem which yields the plane tangential to Σ in every given point $s_0 \in \Sigma$.

Premises:

i) Theorem: A separatrix Σ is an invariant set of **D** [8]. This means that for every $s_0 \in \Sigma$ the whole path $x(s_0, t)$ is in Σ.

ii) If an invariant set, say, Σ of **D**, has the dimension $m < n$, we can define a dynamical system **D*** on Σ [8].

iii) We assume: **D*** on Σ has an attractor Λ^*.

iv) Theorem: If Λ^* is a minimal set, then all paths $x(s_0, t)$, $s_0 \in \Sigma$, are asymptotically stable [8]. We assume Λ^* of Σ to be minimal.

Note on iii): The assumption holds if **D*** is compact [8], which is normally fulfilled by a chemical system.

Note on iv): A set is minimal if it is closed, invariant, and has no proper subset with these qualities. It consists of one trajectory which has to be at least recurrent [8]. The simplest minimal limit sets are critical points and limit cycles. Some precaution with our assumption is indicated in regard to so called chaotic systems, as they contain attractors which are no minimal sets. Examples for such systems, which may be interpreted in chemical terms, have recently been published [9, 10].

Consider a system **D** defined by (1) which has a separatrix Σ with an attractor Λ^*, say, a critical point (this would correspond to a saddle point of **D** with one unstable and $n-1$ stable eigenvectors, by linearization at the critical point).

If we have $s_0 \in \Sigma$, then

$$\lim_{t \to \infty} x(s_0, t) = \Lambda^* \,.$$

For a trajectory in the neighborhood of $x(s_0, t)$ denoted by $z(z_0, t) = x(s_0, t) + y(y_0, t)$ with $z_0 = s_0 + y_0$, we can write

$$\dot{z} = \dot{x} + \dot{y} \,,$$

the linearization of which is

$$\dot{z} = f(x) + J(x) \cdot y + \cdots$$

with $J(x)$ denoting the Jacobian of $f(x)$ in x. This leads to

$$\dot{y} = J(x) \cdot y = J(s_0, t) \cdot y, \tag{2}$$

a linear differential equation with variable coefficients whose solution is given by

$$y(y_0, t) = Y(s_0, t) \cdot y_0,$$

where $Y(s_0, t)$ is the fundamental matrix of system (2) with $Y(s_0, 0) = I$ (unity matrix).

Because of assumption iv) we now have for $y_0 \in \Sigma$

$$\lim_{t \to \infty} y(y_0, t) = 0$$

or

$$Y(s_0, t = \infty) \cdot y_0 = 0. \tag{3}$$

Eventually, the solution of the homogeneous Eq. (3), i.e., $\mathrm{Ker}(Y(s_0, t = \infty))$ yields the span of the plane tangential to Σ in s_0. As $\dim(\Sigma) = n - 1$, the condition: $\mathrm{rank}(Y(s_0, t)) = 1$ gives a criterion for the breakoff of the numerical process.

In practice, we first have to find a starting point s_0 by trial and error. $Y(s_0, t)$ is then calculated by simultaneous integration of $\dot{x}$ and the fundamental system $\dot{Y} = J(x) \cdot Y$, using a Runge Kutta method or Gear's method. To save computing time, $\dot{Y}$ may be substituted by a system with piecewise constant coefficients, which allows for a drastically simpler method in the integration of the fundamental system. When the basis of the tangential space in s_0 has been calculated, a new point s_1 in the neighborhood of s_0 can be found and the process may be repeated until a sufficient description of the hypersurface Σ is attained.

Application of the procedure sketched above was made by incorporating it into a computer program which generates a description of separatrices as a series of niveau curves in a given region of the phase space [11]. Some examples of the program's output are presented below.

5. Simple Examples of Three Dimensional Systems

We now give some simple examples of three dimensional systems which may demonstrate the influence of separatrix structure on the stability properties of reaction systems.

a) The mechanism depicted in Fig. 1 has been proposed as a model for the formation of pure
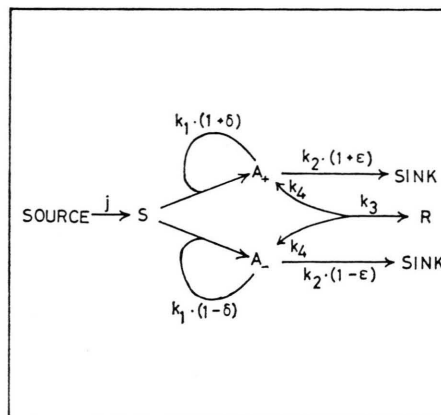

Fig. 1. Scheme of the reaction mechanism in example 5a). S-achiral substrate, A_+, A_--optical active products, R-product of A_+ and A_-, j-feed rate of S, k_i-rate constants, δ and ε-asymmetry parameters.
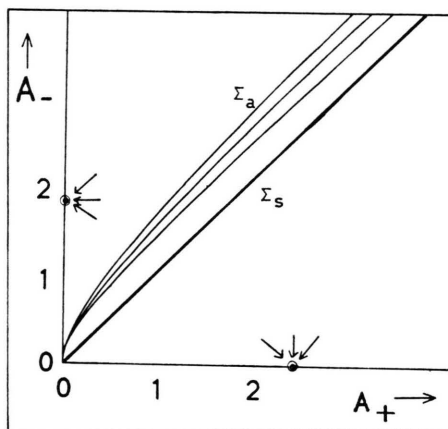

Fig. 2. Phase space of example 5a) projected onto the A_+/A_--plane. Σ_s-separatrix for $\delta, \varepsilon = 0$. Σ_a-level lines of the separatrix for $\delta = 0.25$, $\varepsilon = -0.15$ and constant values of $S = 1, 2, 3$ (from right to left). $\odot$ steady states.

optical antipodes from an achiral substrate on the basis of an autocatalytic reaction step [12]. This system has two asymptotically steady states, at each of which the concentration of one of the antipodes A_+ or A_- is close to zero. In the symmetrical system where both of the asymmetry parameters δ and ε are zero, the separatrix is the plane spanned by the S-axis and the bisector of the A_+/A_- plane, i.e., both steady states have an RAS of equal amount (see Figure 2). When we admit nonzero δ and ε, the separatrix is deformed and shifted somewhat with the whole RAS of the "right" steady state being slightly enlarged. Near the origin, however, we now have strong predominance of the "right" RAS, as can be seen from the position of

the separatrix in this region. In this case, therefore, the system starting at zero concentrations of the products will probably produce pure A_+. This effect is further enhanced by increasing the initial concentration of the substrate S.

b) The model given in Fig. 3 describes a non adiabatic continuous stirred tank reactor in which two products are formed consecutively. This system has strong nonlinearities because of the Arrhenius type temperature dependence of the kinetic constants and may show up to five steady states of which three are stable. We chose here a set of parameters for which there are two stable steady states, i.e., one low temperature-low production state and one high temperature-high production state. The separatrix of the system together with the stable stationary points is depicted in Figure 4.
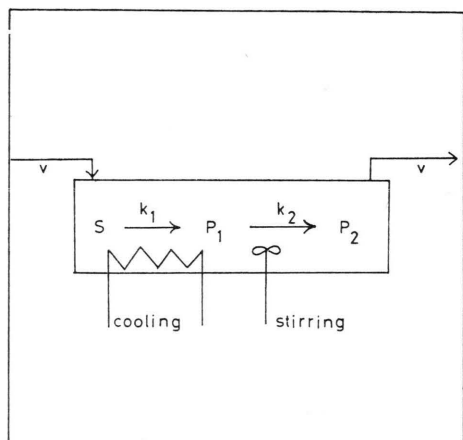

Fig. 3. Scheme of the continuous stirred tank reactor in example 5b). S, P_1, P_2, v, k_i refer to the substrate, both products, the volumetric flow rate and the temperature dependent rate parameters, respectively. For details see [11].
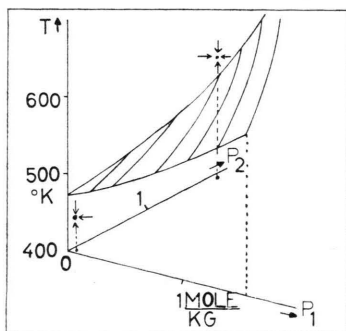

Fig. 4. Parallel projection of the phase space in example 5b) with the two asymptotically stable critical points (⊙) and the separatrix surface.
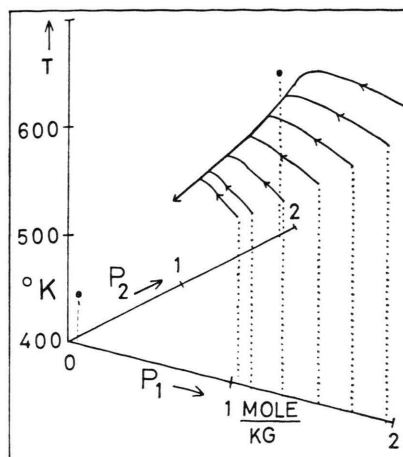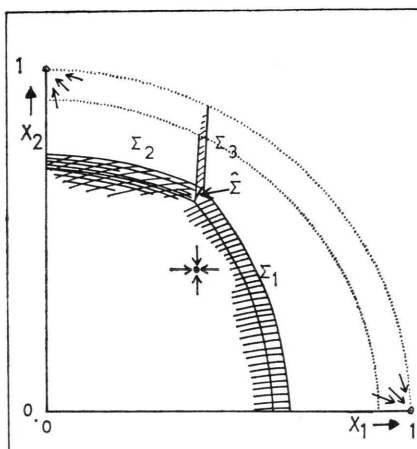

Fig. 5. Trajectories in the separatrix of example 5b).

Fig. 6. Phase space of the system given by:
$$\dot{x}_1 = 0.5 - 1.5\,x_1 + x_1{}^2\,,$$
$$\dot{x}_2 = 1.5\,(x_1 - x_2) - x_1 x_2 + x_2{}^2\,,$$
$$\dot{x}_3 = x_3(x_1 + x_2 - 2.2 - x_3(x_1 + x_2))\,.$$

The representation is in homogeneous coordinates (see e.g. [3]) the dotted level lines refering to boundary "at infinity". The shaded areas denote two-dimensional separatrices, $\hat{\Sigma}$ is a one dimensional separatrix.

We notice the following features: both steady states are sensitive to sufficient disturbances of temperature. Furthermore, a small pulse, e.g. in the concentration of P_1 (approx. 0.1 mole/kg) only will lead out of the upper RAS. The lower steady state, however, is completely stable against perturbation in the chemical concentrations. This result could not have been achieved by Liapunov methods. In Fig. 5 we notice that the paths in the separatrix of this system converge far away from the saddle point so that the numerical integration process for $Y(s_0, t)$ may be broken off early.

c) The third example sketched briefly lacks direct chemical interpretation but may serve to demonstrate a more complicated separatrix structure (see Figure 6). The system has only one finite stable steady state. If either Σ_1 or Σ_2 is passed over, either x_1 or x_2 grows to infinity with the RAS's of the two "infinite" states being separated by Σ_3. The three separatrices Σ_1 to Σ_3 are separated by a one dimensional separatrix $\hat{\Sigma}$. In order to treat this system numerically, homogeneous coordinates were introduced (see e.g. [3]).

6. Conclusion

Besides the simple case of systems in the phase plane, where standard integration methods are indicated, we proposed for systems of dimension $\geqq 3$ the solution of an initial value problem and the calculation of the planes tangential to separatrices as a reasonable approximation method for stability boundaries in dynamical systems. This is on the basis of the special stability properties of trajectories in separatrices, which, being orbitally unstable, are attracting sets within the separatrix subsystem.

The numerical method outlined may be applied in principle to systems of any dimension and for arbitrary analytical form of the rate functions which define the system under investigation. Some examples for a graphic representation of separatrix hypersurfaces were given. It should be noted, however, that in many cases the calculation of the tangential hyperplanes in few separatrix points may give a sufficient answer to stability questions or initial value problems of interest.

We feel that in the analysis of multistable chemical reaction systems the methods presented may serve as a useful tool for stability boundary problems where Liapunov methods, being apt to give sufficient conditions for local stability, in fact would be overtaxed.

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