



# Optimization of chemical batch reactors using temperature control

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# Optimization of chemical batch reactors using temperature control

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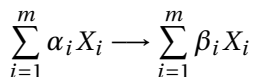
*joint work with B. Bonnard (INRIA & UBFC)*

# Chemical Networks with mass action kinetics

## Graph Model :

Species  $\{X_1, \dots, X_m\}$ .

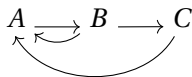
Notations :  $\mathcal{R}$  is the set of reactions of the form :



$\alpha_i, \beta_i$  are stoichiometric coefficients.

Feinberg-Horn-Jackson graph

- Vertices :  $\mathbf{y} = (\alpha_1, \dots, \alpha_m)^\top$ ,  $\mathbf{y}' = (\beta_1, \dots, \beta_m)^\top$
- Orientation :  $\mathbf{y} \rightarrow \mathbf{y}'$



(1)

## Rate dynamics $\mathbf{y} \rightarrow \mathbf{y}'$ (Mass kinetics)

$$K(\mathbf{y} \rightarrow \mathbf{y}') = k(T) c^{\mathbf{y}}$$

- $k(T) = A \exp(-\frac{E}{RT})$  : Arrhenius law  
 $E, A$  parameters,  $T$  temperature and  $R$  is the gas constant
- $\mathbf{c} = (\mathbf{c}_1, \dots, c_m)^\top$   
 $c_i$  : concentrations of the species  $X_i$  with

$$c^{\mathbf{y}} = \mathbf{c}_1^{\alpha_1} \dots c_m^{\alpha_m}$$

$\Rightarrow K(\mathbf{y} \rightarrow \mathbf{y}')$  depends only on  $\mathbf{y}$ .

# Dynamics for the network

$$\dot{\mathbf{c}}(\mathbf{t}) = F(\mathbf{c}(\mathbf{t}), T) = \sum_{\mathbf{y} \rightarrow \mathbf{y}' \in \mathcal{R}} K(\mathbf{y} \rightarrow \mathbf{y}') (\mathbf{y}' - \mathbf{y})$$

The dynamics is defined by the graph.

More explicit representation of the dynamics.

- **Stoichiometric subspace**

$$S = \text{span} \{ \mathbf{y}' - \mathbf{y}, \mathbf{y} \rightarrow \mathbf{y}' \in \mathcal{R} \}$$

- **Positive class** (strict if  $> 0$ )

$$(\mathbf{c}(\mathbf{0}) + S) \cap \mathbb{R}_{\geq 0}^m$$

## Lemma

The class  $(\mathbf{c}(\mathbf{0}) + S) \cap \mathbb{R}_{> 0}^m$  is **invariant** for the dynamics.

## Notations

- **Complex matrix** :  $Y = (y_1, \dots, y_n)$  ( $n$  : number of complexes).
- **Incidence connectivity matrix** :  $A = (a_{ij})_{ij}$   
with for instance  $a_{21} = k_1$  indicating a reaction with constant  $k_1$  from the first node of the graph to the second.
- **Laplacian matrix** :

$$\tilde{A} = A - \text{diag} \left( \sum_{i=1}^n a_{i1}, \dots, \sum_{i=1}^n a_{in} \right)$$

One has

$$\dot{\mathbf{c}}(\mathbf{t}) = f(\mathbf{c}(\mathbf{t}), T) = Y \tilde{A} \mathbf{c}^Y$$

where  $\mathbf{c}^Y = (c^{y_1}, \dots, c^{y_n})^\top$ .

# Zero deficiency theorem

## Definition (Deficiency)

*Feinberg and Horn-Jackson : articles in Archive Rational Mechanics*

**Graph concept** : deficiency :  $\delta = n - l - s$  where

- $n$  : number of vertices
- $l$  : number of connecting components
- $s$  : dimension of the stoichiometric subspace

## Definition

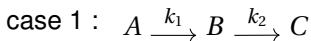
The network is **weakly reversible** if  $\forall$  vertices  $(i, j)$  such that  $\exists$  oriented path joining  $i$  to  $j$ , there exists an oriented path joining  $j$  to  $i$ .

Assumption  $\delta = 0$  (Zero deficiency assumption)

## Theorem

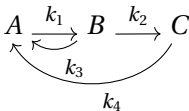
- 1 If the network is **not weakly reversible** then for arbitrary kinetics, the differential equation **cannot have a positive equilibrium nor a positive periodic trajectory**.
- 2 If the network is **weakly reversible**, there exists within each strictly positive compatibility class precisely **one equilibrium**  $c^*$ , this equilibrium is locally asymptotically stable with (pseudo-Helmholtz) Lyapunov function  $V(c, c^*) = \sum_i [c_i (\ln(c_i) - \ln(c_i^*)) - 1] + c_i^*$ .  
Moreover there is non trivial periodic orbit.

## Application : Test bed cases :



$\delta = 3 - 1 - 2 = 0$  : not weakly reversible

case 2 : (**McKeithan network**)



$\delta = 3 - 1 - 2 = 0$  : one single equilibrium  
globally asymptotically stable



# Equilibrium for the McKeithan network

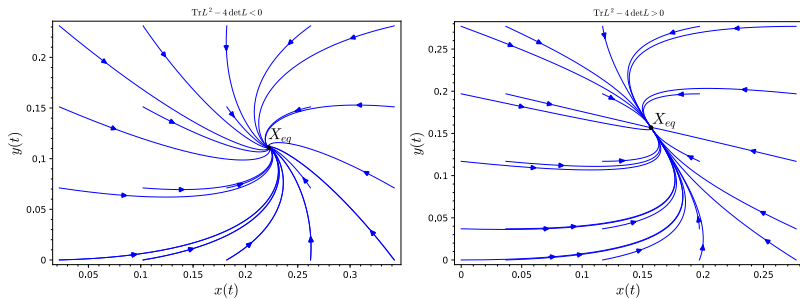


FIGURE – Phase portrait for the McKeithan model. (left) Focus ; (right) Node.

# Geometric Optimal Control

# Optimal Control Problem

$$\frac{d\mathbf{c}}{dt} = f(\mathbf{c}, T), \quad \frac{dT}{dt} = u, \quad u \in [u_-, u_+]$$

$u(\cdot)$  tracked the derivative of the temperature (related to the Goh Transformation).

Single input  $C^\omega$ -control system :

$$\begin{cases} \dot{\mathbf{q}} = F(\mathbf{q}) + u G(\mathbf{q}), & |u| \leq 1, \\ \mathbf{q} = (\mathbf{c}, T) \in \mathbb{R}^n \end{cases}$$

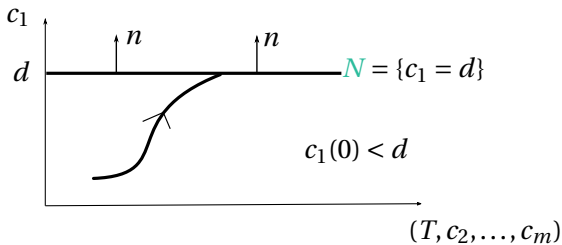
## Formulation :

$$\max c_1(t_f) \quad t_f : \text{time batch duration}$$

Formulated as

$$\begin{cases} \min t_f, & |u| \leq 1 \\ c_1(t_f) = d \text{ is a desired quantity} \end{cases}$$

$N$  : terminal manifold of codimension 1.



# Necessary optimality conditions Pontryagin Maximum Principle (1956)

**Statement :**

$$\begin{cases} \dot{\mathbf{q}} = F(\mathbf{q}) + uG(\mathbf{q}), & |u| \leq 1, \\ \min t_f, & \mathbf{q}(t_f) \in \mathbf{N} \end{cases}$$

- $H(\mathbf{q}, p, u) = p \cdot (F(\mathbf{q}) + uG(\mathbf{q}))$ ,  $p \in \mathbb{R}^n \setminus \{0\}$  : adjoint vector
- $H$  : pseudo-Hamiltonian and the maximized Hamiltonian is

$$M(\mathbf{q}, p) = \max_{|u| \leq 1} H(\mathbf{q}, p, u), \quad \mathbf{q}, p \text{ are fixed}$$

## Theorem

Assume  $(q^*(\cdot), p^*(\cdot))$  is a time minimal solution on  $[0, t_f^*]$  then there exists  $p^*(\cdot)$  such that a.e. on  $[0, t_f^*]$  :

$$\dot{q}^*(\cdot) = \frac{\partial H}{\partial p}(q^*(t), p^*(t), u^*(t)), \quad \dot{p}^*(\cdot) = -\frac{\partial H}{\partial q}(q^*(t), p^*(t), u^*(t)) \quad (2)$$

the maximization condition is satisfied

$$H(q^*(t), p^*(t), u^*(t)) = M(q^*(t), p^*(t)).$$

Moreover

- $t \mapsto M(q^*(t), p^*(t))$  is constant and  $\geq 0$  and at the final time one has the transversality condition :

$$p^*(t_f) \perp T_{q^*(t_f)}\mathbf{N} \quad (3)$$

**Extremals** are solutions of (2). BC-extremal : transversality condition (4) satisfied.

## Maximization condition

- *regular* :

$$u(t) = \text{sign} p(t) \cdot G(\mathbf{q}(t)) \text{ a.e.}$$

Finite number of switches : **Bang-Bang**

- *singular* :

$$p(t) \cdot G(\mathbf{q}(t)) = 0 \quad \forall t$$

**Exceptional extremals** :  $M = 0$ .

Moreover

- $t \mapsto M(q^*(t), p^*(t))$  is **constant** and  $\geq 0$ .
- *Transversality condition* :

$$p^*(t_f) \perp T_{q^*(t_f)}\mathbf{N} \quad (4)$$

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**Exceptional extremals** :  $M = 0$ .



# Computations of singular extremals and properties

**Notation :**  $X, Y$  : two vector fields on  $\mathbb{R}^n$

*Lie bracket :*

$$[X, Y](q) = \frac{\partial X}{\partial q} Y(q) - \frac{\partial Y}{\partial q} X(q)$$

$z = (q, p)$   $H_X(z) = p \cdot X(q)$

*Poisson bracket :*

$$\{H_X, H_Y\}(z) = p \cdot [X, Y](q)$$

**Computations**  $H_G(z) = p \cdot G(q) = 0$

Differentiating twice w.r.t. time gives the two equations

$$\frac{d}{dt} H_G(z) = dH_G \cdot \dot{z} = \{H_G, H_F + u H_G\} = \{\mathbf{H}_G, \mathbf{H}_F\} = \mathbf{0}$$

$$\{\{\mathbf{H}_G, \mathbf{H}_F\}, \mathbf{H}_F\}(z) + u \{\{\mathbf{H}_G, \mathbf{H}_F\}, \mathbf{H}_G\}(z) = \mathbf{0}$$

Then if  $\{\{H_G, H_F\}, H_G\}(z) \neq 0$  then we compute  $\hat{u}$  and plug it in  $H$  to obtain the *true Hamiltonian*.

## Generalized Legendre-Clebsch condition

$$\{\{H_G, H_F\}, H_F\}(z) \geq 0$$

⇒ necessary optimality condition (High Order Maximum Principle, Krener).

## Strict Legendre-Clebsch condition

$$\{\{H_G, H_F\}, H_F\}(z) > 0$$

## Classification of singular extremals

$M = H_F$  : constant value

- $M = 0$  : **Exceptional case**
- $M > 0$  :  $\{\{H_G, H_F\}, H_G\}(z) > 0$  : **Hyperbolic case (fast)**
- $M > 0$  :  $\{\{H_G, H_F\}, H_G\}(z) < 0$  : **Elliptic case (slow)**

## Classification of regular extremals (Ekeland - IHES, Kupka - TAMS)

Denote :

- $\sigma_+$  : bang arc with  $u = +1$
- $\sigma_-$  : bang arc with  $u = -1$
- $\sigma_s$  : singular arc  $u = u_s \in ]-1, 1[$

$\sigma_1\sigma_2$  is the arc  $\sigma_1$  followed by  $\sigma_2$ .

### Switching surface :

- $\Sigma : \{p \cdot G(q) = 0\}$

$\Phi(t) = p(t) \cdot G(\mathbf{q}(t))$  is the **switching function**.

$$\dot{\Phi}(t) = p(t) \cdot [G, F](\mathbf{q}(t))$$

$$\ddot{\Phi}(t) = p(t) \cdot ([ [G, F], F](\mathbf{q}(t)) + u(t) [ [G, F], G](\mathbf{q}(t)) )$$

**Ordinary Switching time** :  $t \in ]0, t_f[$  such that  $\Phi(t) = 0$  and  $\dot{\Phi}(t) \neq 0$

### Lemma

Near  $z(t)$  every extremal solution projects onto  $\sigma_+ \sigma_-$  if  $\dot{\Phi}(t) < 0$  and  $\sigma_- \sigma_+$  if  $\dot{\Phi}(t) > 0$

**Fold case** : If  $\Phi(t) = \dot{\Phi}(t) = 0$  then  $z(t) \in \Sigma'$

$$\ddot{\Phi}_\varepsilon(z(t)) = p(t) \cdot ([G, F], F)(\mathbf{q}(t)) + \varepsilon [[G, F], G](\mathbf{q}(t)), \quad \varepsilon = \pm 1$$

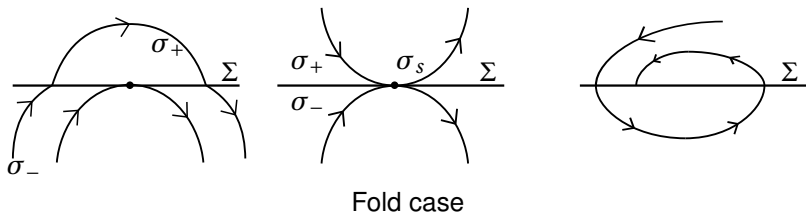
*Assumption* :  $\Sigma'$  : surface of codimension two,  $\ddot{\Phi}_\varepsilon(z(t)) \neq 0$  for  $\varepsilon = \pm 1$ .

$z(t)$  : fold point

- Case 1 : **parabolic case**  $\ddot{\Phi}_+(t)\ddot{\Phi}_-(t) > 0$
- Case 2 : **hyperbolic case**  $\ddot{\Phi}_+(t) > 0$  and  $\ddot{\Phi}_-(t) < 0$
- Case 3 : **elliptic case**  $\ddot{\Phi}_+(t) < 0$  and  $\ddot{\Phi}_-(t) > 0$

$u_s$  is the singular control defined by

$$p(t) \cdot ([G, F], F)(\mathbf{q}(t)) + u_s(t) [[G, F], G](\mathbf{q}(t)) = 0$$



In the parabolic case  $|u_0| > 1$  and the singular arc is not admissible.

## Theorem

*Kupka TAMS* In the neighborhood of  $z(t)$  every extremal projects onto :

- *Parabolic case* :  $\sigma_+ \sigma_- \sigma_+$  or  $\sigma_- \sigma_+ \sigma_-$
- *Hyperbolic case* :  $\sigma_{\pm} \sigma_s \sigma_{\pm}$
- *Elliptic case* : every extremal is of the form  $\sigma_+ \sigma_- \sigma_+ \sigma_- \dots$  (Bang-Bang) but the number of switches is not uniformly bounded.

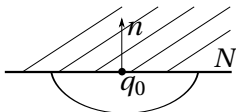
# **Application to Chemical Networks**

## Time minimal synthesis for chemical systems

$$\begin{cases} \min t_f & |u| \leq 1 \\ \dot{\mathbf{q}} = F(\mathbf{q}) + uG(\mathbf{q}) \\ \mathbf{c}_1(t_f) \in \mathbf{N} = \{\mathbf{c}_1 = d\} \end{cases}$$

*Methods* : Two steps :

- 1 Calculation of the time minimal syntheses near the terminal manifold
- 2 Bounds on the number of switches



Step 1: Take  $q_0 \in \mathbf{N}$ ,  $z_0 = (q_0, n(q_0))$  where  $n(q_0)$  is the normal vector of  $\mathbf{N}$  at  $q_0$ .

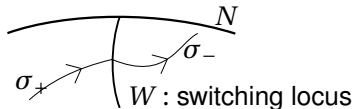
Find, in a small neighborhood  $U$  of  $q_0$ , the time minimal closed loop control  $u^*(q)$  to reach  $\mathbf{N}$  starting from  $\mathbf{q}$  in minimal time.

**Computations** :  $\dot{\mathbf{q}} = F(\mathbf{q}) + uG(\mathbf{q})$ ,  $q(t_f) \in \mathbf{N}$

*Synthesis* :  $u^*(\mathbf{q})$  means

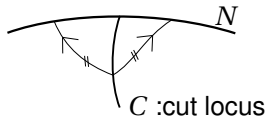
- determine the **switching locus**

Ex. :



- determine the **splitting locus** or the **cut locus**  $C$  where two distinct optimal trajectories occur.

Ex. :





**Tools** : Singularity theory  $\mathbf{N} = \{f^{-1}(0)\}$

- *expand* at  $q_0$  with Taylor series : jet spaces.
- *compute* : Normal form to estimate  $W, C$  near  $q_0$ . The tools are simple but the classification is complicated.

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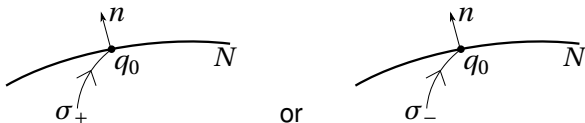
- *expand* at  $q_0$  with Taylor series : jet spaces.
- *compute* : Normal form to estimate  $W, C$  near  $q_0$ . The tools are simple but the classification is complicated.

Ex. : *Two reactions only.*  $(C, T) \in \mathbb{R}^3$   $\dot{\mathbf{q}} = F + uG$  and  $\mathbf{N} = f^{-1}(0)$ .

**Generic case**  $z_0 = (q_0, n(q_0))$ .

**G is tangent to N** : Then  $p \cdot G = 0$  so  $p$  is normal to  $\mathbf{N}$ .

Using classification of extremals at a point such that  $p \cdot G(\mathbf{q}) = 0$ ,  
 $p \cdot [G, F](\mathbf{q}) \neq 0$  :



depending on the sign of  $p \cdot [G, F](q_0)$ .

... but there are more complicated situations

Define :

$\mathcal{S}$  the singular locus :  $\{\mathbf{q} \in \mathbf{N}; n \cdot [G, F](\mathbf{q}) = 0\}$

$\mathcal{E}$  the exceptional locus :  $\{\mathbf{q} \in \mathbf{N}; n \cdot F(\mathbf{q}) = 0\}$

For  $\mathcal{S}$  : from the classification near a fold point one has :

- *Hyperbolic* case
- *Elliptic* case
- *Parabolic* case

To make the analysis we construct a semi-normal form :  $\mathbf{q} = (x, y, z)$  near 0

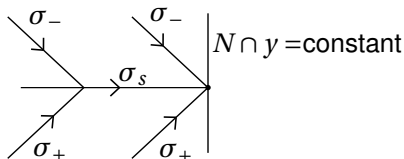
$$\begin{cases} \dot{x} = 1 + a(x) z^2 + 2b(x) yz + c(x) y^2 + \dots \\ \dot{y} = d(x) y + e(0) + \dots \\ \dot{z} = (u - \hat{u}(x)) + f(x)y + g(0)z + \dots \end{cases}$$

with

- $\mathbf{N}$  is identified to  $x = 0$
- the singular arc is identified to  $\sigma_s : t \rightarrow (t, 0, 0)$  with singular control  $\hat{u}$ .
- $a(0) < 0$  hyperbolic if  $|\hat{u}| < 1$ .
- $a(0) > 0$  : elliptic if  $|\hat{u}| < 1$ .
- parabolic if  $|\hat{u}| > 1$ .

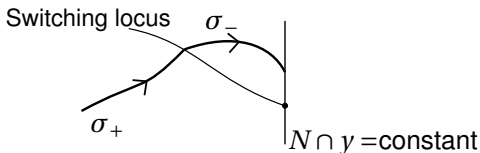
*Synthesis* : There exists a  $C^0$ -foliation by planes such that in each plane the synthesis is :

Case : Hyperbolic.

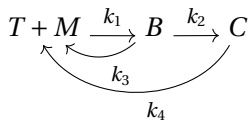


Note that the synthesis is  $\sigma_+ \sigma_s \sigma_-$  hence the temperature is not constant.

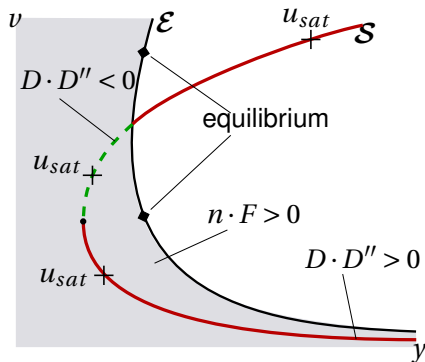
Case : Parabolic. For instance, a synthesis is



# The McKeithan network



Stratification of the terminal manifold :



## Bridge phenomenon

**Local (planar) simplified model** (inspired from the saturation problem in Magnetic Resonance Imaging) :

$$\min_{u(\cdot)} t_f \quad \dot{q}(t) = F(q(t)) + u G(q(t)), \quad t \in [0, t_f]$$

where

$$q = (x, y), \quad F = (1 - x^2 y) \frac{\partial}{\partial y}, \quad G = -(y - 1) \frac{\partial}{\partial x} + x \frac{\partial}{\partial y}.$$

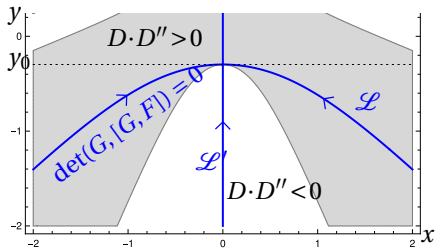
**Singular lines**  $\mathcal{L} : \det(G, [G, F])(q) = 0$

- **fast** if  $D(q) \cdot D''(q) > 0$
- **slow** if  $D(q) \cdot D''(q) < 0$

where  $D(q) = \det(G(q), [G, F](q), [[G, F], G](q))$

and  $D'(q) = \det(G(q), [G, F](q), [[G, F], F](q))$

## Singular sets

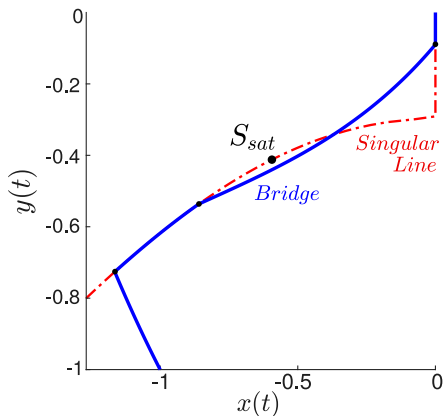


The **Singular control** along  $\mathcal{L}$  is

$$u_s(q) = -\frac{D'(q)}{D(q)}$$

and is not bounded.

## Trajectories : bridge



Bridge connecting two switching points of the singular set.



# Conclusion

General techniques to handle complicated networks :

**Geometric approach** : Find coordinates to analyze the syntheses

→ applicable to general networks

## Details :

T. Bakir, B. Bonnard, J. Rouot *Geometric Optimal Control Techniques to Optimize the Production of Chemical Reactors using Temperature Control* (submitted 2019)

B. Bonnard, G. Launay, M. Pelletier,

*Classification générique de synthèses temps minimales avec cible de codimension un et applications,*

Annales de l'I.H.P. Analyse non linéaire **14** no.1 (1997) 55–102.

Even a simple network  $A \rightarrow B \rightarrow C$  can give complex optimal solution : work in progress on the *McKeithan network*.