Université catholique de Louvain
Ecole Polytechnique de Louvain

Thermodynamics and Process Control

Thèse présentée par
Audrey FAVACHE
en vue de l'obtention du grade de
Docteur en Sciences de l'Ingénieur

Jury:

Promoteurs:	
Pr. Denis DOCHAIN	Université catholique de Louvain
Pr. Bernhard MASCHKE	Université Lyon 1
Président:	
Pr. Christian BAILLY	Université catholique de Louvain
Autres membres:	
Pr. Antonio ALONSO	Instituto de Investigaciones Marinas (CISC)
Pr. Georges BASTIN	Université catholique de Louvain
Pr. Joseph WINKIN	Facultés Notre Dame de la Paix
Pr. B.Erik YDSTIE	Carnegie Mellon University

Septembre 2009

Acknowledgements

I would like to thank my advisors Denis Dochain and Bernhard Maschke for their support and help. They gave me a great liberty for my research, and at the same time provided me much useful advice and many ideas. I am also very grateful for their careful reading of my thesis.

I would also like to thank the other members of my thesis committee, Christian Jallut for his useful explanations about thermodynamics, and Joseph Winkin for his help in differential geometry. I am grateful to all the members of the jury for their reading of the thesis, their questions and comments, that helped me to improve the manuscript.

I do not forget in my acknowledgements all the other persons who helped me in my research and with who I had very interesting discussions: Damien Eberard, Françoise Couenne, Yann Le Gorrec, Laurent Lefèvre, Pierre Rouchon... Special thanks go to Valérie Dos Santos whose advice was very useful for the writing of an article and of one chapter of my thesis.

I enjoyed very much my stays at LAGEP in Lyon, and I thank heartily all the people who welcomed me nicely. My gratitude goes also to Nadia Chapel who cared about the hotel reservations.

My thesis gave me the opportunity attending several conferences and congresses and I would like to thank Isabelle Hisette for her help in organizing the travel and accommodation. She made easier for me many administrative tasks by her effective advice.

It has been a great pleasure to work at IMAP. I spent very good time with all of the people working there, and especially with those who shared my office, Mickey and Danielle. It has been enriching to mix with people studying quite different scientific domains, and coming from a large variety of countries. Even if my office was located in IMAP, I have always been welcomed at CESAME, so I am very grateful to all CESAME members, too. I greatly appreciated the help from Julien who spared me a lot of tedious making up of this thesis by allowing me to reuse his thesis LaTeXstyle file.

Finally, this thesis would probably never have come into being without the support of my family and of my friends. Therefore I would like to express my

profound thanks more particularly to my parents and to Laurent, who always remained on my side.

The sinews of war This thesis was funded by a F.S.R. grant from the UCL during one year. Since October 2006 it is funded by a grant of aspirant of Fonds National de la Recherche Scientifique (Belgium). I also acknowledge the Interuniversity Attraction Poles Programme, initiated by the Belgian State, Science Policy Office for its contribution to several travel expenses. Finally I acknowledge the financial support of the Hubert Curien collaborative project TOURNESOL n° 18091VJ of the Communauté française de Belgique allowing exchanges between the Université Lyon 1 and the Université catholique de Louvain.

Contents

Introduction **1**

1 Thermodynamic fundamentals **9**

1.1 The fundamental principles 11

1.1.1 Some preliminary notions 11

1.1.2 The first principle of thermodynamics 13

1.1.3 The second principle of thermodynamics 14

1.2 The state of a thermodynamic system 15

1.2.1 The thermodynamic equilibrium states 15

1.2.2 The state equations 17

1.3 Evolution of the state of a system 18

1.3.1 The balance equations 18

1.3.2 Quasi-static processes 19

1.3.3 Gibbs' relation 21

1.3.4 The dynamical model of a thermodynamic system . . . 26

I Physics based approach **29**

2 The CSTR case study **35**

2.1 The dynamical model 36

2.1.1 Description and general assumptions 36

2.1.2 The balance equations 41

2.2 Analysis of the dynamical behaviour 44

2.2.1 The equilibrium points 45

2.2.2 Stability of the equilibrium points 51
2.3 Internal energy balance versus temperature equation 55
2.4 Conclusion 57

3 A thermodynamic point of view 59
3.1 Stability analysis based on the linearized model of the CSTR . 61
3.2 Stability analysis based on the Lyapunov's second method . . . 63
3.2.1 Entropy-based stability analysis 63
3.2.2 Energy-based stability analysis 76
3.3 Conclusion 83

4 The power-shaping approach 87
4.1 Power-shaping control 89
4.1.1 The Brayton-Moser equations 89
4.1.2 Controller design 90
4.2 The Brayton-Moser PDE for a general simplified CSTR 92
4.2.1 The dynamical model 92
4.2.2 Integrability condition 94
4.3 The Brayton-Moser formulation of the CSTR 97
4.3.1 The dynamical model 97
4.3.2 The Brayton-Moser matrix and the potential function . 98
4.3.3 Stability analysis using the Brayton-Moser formulation . 102
4.4 Controller design via the power-shaping approach 107
4.4.1 Controller design 107
4.4.2 Global convergence of the closed-loop system 115
4.4.3 Analysis of the convergence rate 123
4.4.4 Robustness analysis 124
4.5 Extension to more complex systems 134
4.6 Conclusion 136

5 Conclusion 139

II Differential geometric approach 143

6 A geometric approach of the thermodynamics 149
6.1 The thermodynamic model 150
6.2 The system dynamics 156
6.3 The contact model of thermodynamic systems 159
6.3.1 Simple thermodynamic systems 159
6.3.2 Interconnected thermodynamic systems 163
6.4 Conclusion 173

7 Some properties of port contact systems 177
7.1 Expression of the dynamical properties 178
7.1.1 Equivalent contact Hamiltonian functions 178
7.1.2 Equilibrium points 182
7.1.3 Sufficient stability condition 185
7.2 Physical interpretation of the stability condition 190
7.3 Conclusion 195

8 Alternative formal approaches 197
8.1 The GENERIC formalism 198
8.1.1 Representation of isolated systems 199
8.1.2 Extension to open systems 201
8.1.3 Contact formulation of the GENERIC model 205
8.2 The Matrix formalism 205
8.2.1 Definition 206
8.2.2 Contact formulation of the Matrix model 207
8.3 Case study : the adiabatic piston 208
8.3.1 Contact formulation 210
8.3.2 The GENERIC model 214
8.3.3 The Matrix model 218
8.4 Conclusion 219

9 Conclusion 221

General conclusion **227**

Bibliography **232**

Appendixes **241**

A List of publications **243**

B Calculation details for (3.11) **245**

C Numerical values used for the simulations **249**

D The CSTR: some particular cases **251**
D.1 Parallel reactions 252
D.2 Reaction with 2 reactants 258
D.3 Consecutive reactions 261

E Some elements of differential geometry **267**
E.1 Manifolds and tangent spaces 267
E.1.1 Manifolds and submanifolds 267
E.1.2 Tangent vectors and tangent space 273
E.2 Differential forms 277
E.2.1 Cotangent fibre bundle 277
E.2.2 Exterior product 278
E.2.3 Pfaffian equation 279
E.3 Contact manifolds 281

List of Figures

1.1 Balance of the extensive quantity X_{ext} 19
1.2 Illustration of $\mathscr{S}$ and of a quasi-static process 20

2.1 Schematic view of the CSTR 37
2.2 Shape of $n_A^{eq}(T)$ 49
2.3 Shape of the function $\Delta^{eq}(T)$ 50

3.1 Representation of the intuitive approach 77
3.2 Graph of $(\Delta^{eq}(T))^2$ 78
3.3 Domains of decreasing $(\Delta^{eq}(T))^2$ 81
3.4 Trajectory directions in the CSTR with irreversible kinetics . . 84

4.1 Level curves of $\mathscr{P}(n_A, T)$ 104
4.2 Possible configurations for $\Delta_0(T)$ 119
4.3 Influence of ω on $\Delta(T)$ 119
4.4 Level curves of $\mathscr{P}_d(n_A, T)$ (local convergence) 121
4.5 Level curves of $\mathscr{P}_d(n_A, T)$ (global convergence) 121
4.6 Temperature evolution with saturated input 122
4.7 Influence of ω on the convergence rate 125
4.8 Influence of α on the convergence rate 125
4.9 Influence of the modelling error in $k(T)$ 128
4.10 Influence of the measurement error 132
4.11 Cancellation of the static error 132

6.1 Intuitive construction of the Legendre submanifold 154

7.1 Contact Hamiltonian function for Example 7.1 185

8.1 Case study: the adiabatic piston 209

E.1 Chart 269
E.2 North pole stereographic projection 269
E.3 Tangent curves and tangent vectors 274

List of Tables

2.1 Notations for the CSTR case study 38

3.1 Sign of $\frac{d(\Delta^{eq})^2}{dt}$ 79

4.1 Determination of the sign of $\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*, T^*\right)$ 111

Notations

Standard notation has been used as much as possible throughout this text. This list contains the important symbols and their definition. Symbols used only once, or within a single chapter are not listed.

Physical quantities

Symbol	*Meaning*
C_j	concentration of component j
C_p	molar heat capacity at constant pressure
C_v	molar heat capacity at constant volume
$\mathscr{C}_p$	total volumetric constant pressure heat capacity of a mixture
$\mathscr{C}_v$	total volumetric constant volume heat capacity of a mixture
d_F	degrees of freedom of a system
E	total energy (i.e. internal, kinetic and potential energy)
E^{kin}	kinetic energy
E^{pot}	potential energy
N_c	number of components
P	pressure
$\dot{Q}$	heat exchange flow rate
R	ideal gaz constant
S	entropy
T	temperature
T_w	cooling fluid temperature

Symbol	*Meaning*
T_0	reference temperature
U	internal energy
V	volume
h	molar enthalpy
h_{0_j}	reference molar enthalpy of component j
$k\,(T)$	kinetic coefficient
n_j	quantity of component j (number of moles)
n	vector of the quantities of the components
q	momentum
q_l	volume flow rate
r	reaction rate
s	molar entropy
s_{0_j}	reference molar entropy of component j
t	time
u	molar internal energy
$\Delta_r H$	reaction heat
α, β, γ	real constants
κ	heat transfer coefficient
μ_j	chemical potential of component j
μ	vector of the chemical potentials
ξ	estimation error
σ_Y	production rate of the quantity Y

Subscripts and Superscripts

Symbol	*Meaning*
in	inlet
tot	total, i.e. of the whole system
out	outlet
$\bar{y}$	equilibrium value of the variable y

Mathematical objects

Symbol	*Meaning*
F	generating function of some Legendre submanifold
I, J, K, L	subsets of the indices
X	state vector
f	contact Hamiltonian function
p	local coordinates
x	local coordinates
x_0	local coordinates
$\boldsymbol{\mathcal{H}}(w)$	Hessian matrix of the scalar function w
$\mathscr{L}$	Legendre submanifold
$\mathscr{P}$	Brayton-Moser potential function
$\mathscr{P}_a$	$\mathscr{P}_d - \mathscr{P}$
$\mathscr{P}_d$	desired Brayton-Moser potential function
$\boldsymbol{Q}$	matrix in the Brayton-Moser formulation
$\mathcal{T}$	thermodynamic phase space
$\boldsymbol{\Lambda}$	matrix of a linearized system
λ	eigenvalue of a matrix

Notation conventions

Transpose of a vector or a matrix : the transpose of a vector or a matrix y is denoted as y^t.

Vectors : all vectors (including the gradient of a scalar function) are column vectors.

Derivative of a vector function : Let $f(x) = [f_1(x), \ldots, f_n(x)]^t$ be a m-dimensional vector function of a n-dimensional variable x. The derivative

matrix is denoted as $\frac{\partial f}{\partial x}$. The entries of $\frac{\partial f}{\partial x}$ are defined as follows:

$$\left(\frac{\partial f}{\partial x}\right)_{ij} = \frac{\partial f_i}{\partial x_j}$$

where $\left(\frac{\partial f}{\partial x}\right)_{ij}$ is the entry in position (i, j).

Introduction

> *A theory is the more impressive the greater the simplicity of its premises, the more varied the kinds of things that it relates and the more extended the area of its applicability. Therefore classical thermodynamics have made a deep impression on me. It is the only physical theory of universal content which I am convinced, within the areas of the applicability of its concepts, that it will never been overthrown.*
>
> *Albert Einstein, 1949*

The above assertion is indeed of great interest, in particular since it comes from the one who has overthrown the classical Newtonian theory and the notions of space and time.

The universal character of classical thermodynamics comes from the fact that it does not deal with a restricted class of systems and does not depend on any model nor assumptions on the structure of matter. Unlike other branches of classical science (such as for instance mechanics or electromagnetics), thermodynamics does not try to explain the consequences of some formulated laws (as it is the case with the Newton's laws or the Maxwell's equations). The classical thermodynamic theory relates concepts that seem to be very different such as heat and work, and it explains equally well the working of a combined-cycle gas turbine power plant, of a fridge or of a car engine. Even in biology, thermodynamics shows up to be of primary importance. Indeed most of the exchanges in the human body are based on thermodynamic equilibria (e.g. the essential

role of osmotic pressure for the kidneys). Yet let us mention that the first outstanding results of thermodynamics go back to the end of the XVIIIth century, i.e. when the theories about the structure of matter were only at their early beginnings.

One of the core quantities that is considered in thermodynamics is the energy of the considered system. Indeed as its name indicates (from the ancient Greek $\theta\epsilon\rho\mu o\varsigma$, *thermos*: heat and $\delta u\nu\alpha\mu\iota\kappa o\varsigma$, *dynamikos*: powerful), thermodynamics is concerned with the transformations of energy between its different forms. For example let us consider a perfectly isolated vessel that contains some reacting mixture. Due to reaction, chemical bonds are either broken or created. The breaking of a chemical bond releases energy whereas its creation consumes energy. The total energy is conserved (first principle of thermodynamics) and hence the energy from the chemical bonds is either transmitted to the reacting mixture by increasing its temperature or withdrawn from it by decreasing it, respectively. In other words, the energy of the system is transformed from a chemical form into a thermal form, or conversely. The evolution of the system state (e.g. the temperature, the concentration of each species) is directly linked to the energy transformations that are taking place. Beside the conservation of energy, another important feature in thermodynamics is the so-called second law of thermodynamics. It restricts the set of possible evolutions of a system. As a consequence energy considerations and the second law allow to predict the evolution of the state of the system.

In chemical engineering, thermodynamics plays a central role in the modelling of chemical processes. Indeed typical phenomena that are going on in chemical reactors are heat transfers, chemical reactions, mass transfers... These all are phenomena that can be explained and modelled by the thermodynamics. Process control is a particular domain of chemical engineering which is concerned with the design of systems that act on the inputs of the process (e.g. the flow rate of the cooling fluid in a heat exchanger) so as to maintain the process at a desired operating point. In other words, process control is concerned with the dynamical behaviour of the process state.

Actually process control gathers two engineering domains. Beside chemical engineering, process control uses also mathematics and more precisely dynam-

ical system theory. Dynamical system theory offers the tools for the analysis and the control of the dynamical behaviour of some system, given a mathematical model. But the mathematical tools that are used in system theory introduce abstract concepts such as the Lyapunov functions in the Lyapunov theory [63] or the storage functions in the case of the so-called passive systems [96]. In the case of chemical processes the link between the abstract objects of system theory and the underlying physical system is far from being obvious. The interpretation of these abstract concepts of system theory by the chemical engineer is often quite difficult because he cannot relate them to the physical understanding of the process. After the step of modelling the chemical process using the thermodynamics, the underlying phenomena are more or less pushed aside, and the rest of the analysis of the dynamical behaviour is based on the mathematical model. Although process control gathers chemical engineering and system theory, in practice the link between the two domains is rather tenuous. As already mentioned the evolution of the state of a chemical process can be modelled by using the thermodynamic theory. The goal of a controller is to act on the process so as to modify its dynamical behaviour. The controller acts on the process via physical quantities (e.g. a heat flow) which modify the dynamical behaviour of the system as predicted by the thermodynamics. It is therefore straightforward that there should exist a link between process control and thermodynamics.

Chemical processes differ in this point from electro-mechanical systems. Indeed in these domains, the abstract concepts of system theory can be related to the physics of the system. In electromechanical systems this link has been made by considering their Lagrangian or Hamiltonian formulation [95]. Lyapunov functions can be related to the total energy, passivity can be related to energy dissipation [104][105]. It is also possible to develop a network approach where electromechanical systems are considered as a network of more simple subsystems exchanging energy.

For the past decade a new approach for the analysis and control of physical systems has been receiving a growing interest. This approach is based on the physics of the systems. It uses the relations between the physics and the mathematical tools to develop physics based control systems. This has led

to the development for instance of energy-shaping control [54][70][82][83] or of power-shaping control [55][56][80]. These approaches use considerations on the energy of the system or on the dissipated power to control the dynamical behaviour. One of the main interests of this approach is that it allows an easy handling of interconnected systems. This is of course of utmost interest for chemical processes which are typically an interconnection of unit operations.

In this framework, the aim of this study is to introduce physical insight into dynamical system theory when applied to chemical processes for process control. Like it has been done for electromechanical systems we want to develop a physics based approach for the analysis and control of chemical systems. Due to the central role of energy transfers and transformations and of the second law on the evolution of the process state and hence on its dynamical behaviour, we want to interpret system theory results for chemical processes in terms of energy and entropy considerations.

This work lies within the scope of a research area that has received a growing interest in the past years, namely the link between thermodynamics and system theory. This research domain started with the embryonic work of Aris and Amundson [7] up to more recent studies such as the work of A. Alonso, B.E. Ydstie and coworkers [2][84][106], of H. Ramírez and coworkers [87], or of H. Hoang and coworkers [51]. Indeed this approach should lead to a better understanding of the influence of the physical phenomena on the characteristics of the dynamical behaviour of the system (e.g. equilibrium points, stability) and consequently allow to develop more efficient control systems that can act more specifically on the sources of the undesired behaviour.

Since the thermodynamics is the central tool that is used in this study we shall start in Chapter 1 with a brief summary of the fundamentals of thermodynamics. Then the thesis shall be divided into two parts. Indeed we want to link together the scientific fields of chemical engineering and of system theory and we can either start from the first one and move to the second one, or the other way we can start from the second one and move into the first one. In Part I we shall present the first approach: we shall start from classical chemical engineering considerations on the physics of the process, and try to interpret some physical quantities in terms of objects of system theory. This study shall

be led using a case study. Then in Part II we shall apply the second approach: we shall develop a formal mathematical framework for the expression of the dynamical behaviour of thermodynamic system. This mathematical formalism uses objects of differential geometry and is at the same time in the direct continuity of Gibbs' work. Finally we shall show how the introduced mathematical objects can be interpreted in terms of physical quantities such as e.g. the entropy, the internal energy, the heat flows.

Key contributions[1]

The contribution of this thesis can be summarized as the study of different ways of introducing physical understanding into the analysis of the dynamical behaviour of chemical processes. We have distinguished two different approaches: the first one is based on the expression of the balance equations and the thermodynamic properties of the chemical reactors, and the second one starts from a differential-geometric formulation of the dynamics adapted to thermodynamic systems.

Part I

Several contributions can be found in the first part of this thesis. First we have used a dynamical model for the CSTR that differs from the usual model used in classical literature. More precisely we have used the internal energy as a state variable instead of the temperature, which gives us a more general model of the CSTR. We have re-demonstrated the well-known stability results using this more correct model (from a thermodynamic point of view) instead of the usual model. Then we have used several existing thermodynamic results for deriving thermodynamics based Lyapunov function candidates. Finally we have applied the power-shaping approach, which had previously only be applied to electrical and mechanical systems, to the CSTR. There our main contribution is the Brayton-Moser formulation of the CSTR dynamics. This has led to a Lyapunov function for the simplified CSTR case. We have also designed a controller for the temperature control of the CSTR by applying the power-shaping approach on the Brayton-Moser formulation of the dynamics.

Part II

In the second part of this thesis we have used a particular formalism for the modelling of thermodynamic systems, namely the contact formalism. This formalism itself is not new, but it has not been used yet in a systematic way

[1] A list of our publications can be found in Appendix A.

for modelling the dynamical behaviour of thermodynamic systems. Our contribution is the development of a methodology that allows to model complex thermodynamic system composed of an interconnection of simple subsystems using the contact formalism, starting from the balance equations on the internal energy, the volume and the quantity of each component. Departing from previous work, we have used the entropy form of the Gibbs' relation instead of the internal energy form. We have also related some dynamical properties of the system (equilibrium points, local stability) to its contact formulation, and more precisely to the contact Hamiltonian function and to the generating function of the Legendre submanifold. We have related the stability criterion to physical considerations. Finally we have compared the contact formalism with two other existing formalisms and, based on a study case, we have shown that the contact formalism seems to be better appropriated for control purposes of chemical processes.

Chapter 1

Thermodynamic fundamentals

Thermodynamics aims at predicting the evolution of a system with a given structure, in a defined environment and with interactions with the environment that follow known physical laws. The prediction of the evolution of a system can be very complex due to its structure and to the numerous interactions with its environment. Nevertheless the underlying thermodynamic laws that combine the structure with the interactions of the system in order to predict its evolution are of a great simplicity. Beside the well known conservation of mass, the evolution is constrained by the conservation of energy (first principle of thermodynamics) and by a preferred direction of change (e.g. heat goes spontaneously only from the warm to the cold, or a gas from the compartment with a higher pressure to the one with a lower one, and never in the other direction). The latter feature is explained by the second principle of thermodynamics. As we shall see in this chapter, these concepts are the only ones that are needed to characterize the evolution of a system.

The golden age of thermodynamics was the end of the XVIIIth century and the first half of the XIXth century when the two fundamental principles of thermodynamics have been formulated. Nonetheless let us mention that

some embryonic results had already been obtained since the first half of the XVIIth century, such as for instance Francis Bacon who suggested that heat was related to movement. Numerous famous researchers contributed to the development of the thermodynamic theory and their names went down to posterity, for instance under the form of units (e.g. Joule or Kelvin) and relations (e.g. the Gibbs' relation, the Maxwell relations and the Clapeyron equation).

In this work we used the classical thermodynamic theory. It adopts a macroscopic viewpoint, in the sense that the nature of the individual particles that make up the substance and their interactions are not taken into account. Consequently the general laws of classical thermodynamics are based on macroscopic measurements (e.g. the temperature, the pressure, the density). The key to the simplicity of the macroscopic description lies in the fact that macroscopic measurements are extremely slow on the atomic scale of time, and they are extremely coarse on the atomic scale of distance [19]. Let us mention that there exists another method for the study of thermodynamic properties and energy relationships: the statistical thermodynamics. Contrary to classical thermodynamics, it adopts a microscopic point of view of matter. It postulates that the macroscopic measurements reflect some sort of statistical average of the behaviour of the tremendous number of particles.

Even if the thermodynamics have been studied for more than 150 years it is still a living scientific domain. Indeed, the theory for the description of systems in equilibrium, or thermostatics, is unique and well known. But there exist nearly as much theories than scientists working on it to describe non-equilibrium systems. The theory of non-equilibrium thermodynamics was born in the thirties, with the work of Lars Onsager, and then later with the work of Ilya Prigogine. They developed the so-called classical irreversible thermodynamics (CIT) which is based on the assumption of local equilibrium. It is also worth to mention the abstract mathematical approach of C. Truesdell in the fifties, the rationale thermodynamics, which adopts a more axiomatic point of view. The main characteristics of Truesdell's approach are firstly, that the existence of the entropy and of the temperature are considered as primitive concepts, without any physical interpretation and thus any link with the experimental definition of the temperature, and secondly that the state of the

system depends on the history. Finally let us also mention the theory of extended irreversible thermodynamics (EIT) developed by D. Jou, G. Lebon and J. Casas-Vázquez which is intermediate to the classical irreversible thermodynamic theory and the rationale thermodynamic theory [62]. Indeed, it takes the variables of classical irreversible thermodynamics, and adds new variables to them, that take into account the dissipative fluxes and hence extends the classical irreversible thermodynamics, without attaining the degree of abstraction of Truesdell's approach.

The aim of this chapter is to give an overview of the main elements of classical thermodynamics that will be used in this thesis[1]. Thermodynamics is based on two fundamental principles that are presented in Section 1.1 after a brief overview of some preliminary notions. Since the centre of interest of thermodynamics is the system, we shall then explain in Section 1.2 how the state of a system can be defined. The second governing feature of thermodynamics are the transformations that take place in the system, and in particular the transformations of energy. The way these transformations result in the change of the system state is presented in Section 1.3.

1.1 The fundamental principles

The central issue of thermodynamics is to predict the new thermodynamic equilibrium state of a system in which transformations take place. The possible state transformations are constrained by two fundamental principles that are presented here.

1.1.1 Some preliminary notions

Like any other scientific domain, thermodynamics has its own vocabulary. We shall first introduce some definitions.

[1]This chapter gives only a broad overview of the fundamentals of thermodynamics. For a more detailed presentation the reader can refer to textbooks on thermodynamics such as for instance [19][25][91][103].

As already mentioned the centre of interest of thermodynamics is the system. A *system* is a set of material objects that are made distinct from the rest of the universe (called the *environment* of the system) by some fictitious or real boundary. Depending on the nature of the interaction of the system with its environment, systems can be:

- *isolated*: it cannot exchange energy nor matter with its environment (e.g. a vacuum flask).

- *closed*: it can exchange energy but no matter with its environment (e.g. a pressure cooker).

- *open*: it can exchange energy and matter with its environment (e.g. the human body).

In order to analyze the behaviour of a system, we have to describe its state. In the thermodynamic formalism this is done by a set of macroscopic coordinates representing physical properties of the system, the *state variables*. These are, among others, the internal energy U, the volume V, the quantity of each chemical component n_i (where the subscript i refers to the species i), the temperature T, the pressure P and the chemical potential of each component μ_i[1]. In fact these quantities can be divided into two categories. Indeed let us take two identical systems (for example two identical glasses of water at the same temperature) and let us put them together. In the new system, some of the above mentioned quantities (the volume, the internal energy, the quantity of each component, the entropy), the *extensive* quantities, are doubled, whereas the others (the temperature, the pressure, the chemical potential of each component), the *intensive* quantities, remain unchanged. More formally, the extensive quantities depend on the amount of matter in the system, whereas the intensive quantities do not.

[1] In the sequel, we will denote respectively n and μ the vectors containing the number of moles and the chemical potential. The i^{th} entry corresponds to the component i .

1.1.2 The first principle of thermodynamics

The first principle of thermodynamics deals with the conservation of energy. The historic development towards the statement of the principle of thermodynamics is a complex issue. To put it in a nutshell, let us mention that one of the most important contributions was made by Robert Mayer and James Joule in the middle of the XIXth century. Based on experimental results, they both established the equivalence between heat and work. Even if Joule's formulation was more precise, Mayer is considered as the spiritual father of the first principle of thermodynamics.

The first principle of thermodynamics can indeed be formulated under several different forms. The development of Joule's approach leads to the following statement:

> *If a closed system undergoes a cyclic set of transformations the amount of heat transferred from the system to the environment is equal to the amount of work exerted by the environment on the system.*

But the first principle of thermodynamics goes much further than the above formulation and is based on a wide range of experiments. A more general formulation of the first principle is the following one [91][103]:

> *In any change of state, the total energy (i.e. the sum of internal, kinetic and potential energy), heat and work is conserved.*

or to say it in a more concise form:

> *Energy is neither created nor destroyed, but may change form.*

One may note the similarity with Lavoisier's famous statement about matter (nearly a century before Joule's work): *"Nothing is lost, nothing is created, all is transformed"*. It applies indeed also to energy and is an adequate statement for the first principle of thermodynamics.

1.1.3 The second principle of thermodynamics

Experience has shown that not all processes that satisfy the energy conservation principle are possible. For example, heat will never spontaneously flow from a cold body to a warmer one. This example and many others show that each process has a preferred direction of change. This cannot be explained by any conservation principle and suggests that another law is needed to determine the set of possible processes. Furthermore, several experiments show that energy exists under several forms and they all do not have the same ability to produce work. The way energy is degraded and the direction of change of spontaneous processes is explained by the so-called second law or second principle of thermodynamics.

It was a long and winding road that led to the statement of the second principle of thermodynamics. The very first formulation of the second principle is due to Sadi Carnot in the first half of the XIXth century who was working on vapour engines. Let us mention that in that time, heat was considered as a fluid, and that Carnot used this concept in his work even if he was doubtful about the idea. Carnot prematurely died in 1832, but his work was taken over by other prestigious researchers, such as Joule, Thompson, Kelvin, Clausius, Rankine, Boltzmann and Gibbs. The concept of entropy was introduced by Clausius, and Gibbs showed that entropy was a fundamental property of matter. Maxwell managed in particular to define clearly the notions of equilibrium and potential thanks to Gibbs' work.

Historically, the second principle of thermodynamics was formulated in two equivalent statements [103]:

Kelvin's statement:

> *It is impossible to convert completely heat into work.*

Clausius' statement:

> *It is impossible to operate any device in such a manner that the sole effect is to transfer heat from a cold source to a hot one.*

The introduction of the concept of entropy by Clausius allows to express the second principle of thermodynamics in terms of state variables, and more precisely as an inequality.

Definition 1.1 (Entropy [91])**.** The entropy S is an extensive quantity and a state variable. In a system in which there are heat flows across the boundaries, the heat flow $\dot{Q}$ causes a change in the entropy of the system. The rate of entropy change is $\frac{\dot{Q}}{T}$ where T is the temperature of the system.

Using the notion of entropy, it can be shown that the second principle of thermodynamics can also be stated as follows:

> *During a process, the rate of internal generation of entropy σ_S within a system is always positive:* $\sigma_S \geq 0$.

A process is said to be *irreversible* if $\sigma_S > 0$ and *reversible* if $\sigma_S = 0$.

The notion of entropy is linked to the quality of the energy of a system, i.e. its ability to produce work. An irreversible entropy production is always accompanied by a degradation of energy. But entropy is also linked to the disorder in the system as for example in a mixing process which also increases the entropy of the system.

1.2 The state of a thermodynamic system

1.2.1 The thermodynamic equilibrium states

As already mentioned the state of the system can change due to the interactions with the environment. Nevertheless a system is said to be at *thermodynamic equilibrium with its environment* if [91]:

- the state of the system does not change with time.
- the state of the system is uniform in space (i.e. no temperature, velocity, pressure or concentration gradients), or can be decomposed into subsystems that are uniform in space.

- the matter, heat and work exchanges with the environment are equal to zero.
- the net rate of all chemical reactions is equal to zero.

It is of the utmost importance not to confuse the notion of thermodynamic equilibrium and that of equilibrium or steady state used in dynamical system theory. Indeed a system can be at equilibrium in the sense of dynamical system theory without being at thermodynamic equilibrium with its environment as it is illustrated in Example 1.1. In order to avoid confusion in the sequel, we shall always specify whenever we refer to the thermodynamic equilibrium. If not specified otherwise explicitly, we refer to the equilibrium in the sense of dynamical system theory.

Example 1.1. *Let us consider a tank fed with a liquid at some constant flow rate. The liquid leaves the tank through a hole at the bottom of the tank due to the weight of the liquid in the tank. After some time the volume of water in the tank will remain constant, when the inlet and outlet flow rates are equal. The system is at equilibrium in the sense of dynamical system theory. But the system is not at thermodynamic equilibrium since the third condition cited previously is obviously not fulfilled.*

A state of a system is said to be a *thermodynamic equilibrium state* if it is the state of the system when it is in thermodynamic equilibrium with some environment. In other words, one can find some environment such that when the system is at the considered state, it is in thermodynamic equilibrium with it.

Remark 1.1. *Thermodynamic equilibrium states are independent of the history of the system. Therefore the thermodynamic equilibrium states are characterized by intrinsic properties of the system [19].*

Despite the universal nature of thermodynamics, we shall restrict ourselves to a particular class of systems. First let us define a simple thermodynamic system.

Definition 1.2 (Simple thermodynamic system)**.** A simple thermodynamic system is a thermodynamic system that is macroscopically homogeneous, isotropic and uncharged. The surface effects can be neglected.

In this work we shall only consider systems that are simple thermodynamic systems, or an interconnection of simple thermodynamic systems that exchange energy and matter. In other words, we assume that the diffusion and mixing processes are sufficiently fast so that homogeneity takes place in the subsystems. This restriction implies that we do not have spatial gradients and that the dependence on space of the state variables has not to be considered.

Remark 1.2. *Simple thermodynamic systems are homogeneous systems (i.e. systems with a single phase). Multiphase systems can be considered as an interconnection of simple systems that are exchanging matter (i.e. a set of simple subsystems exchanging flows of extensive quantities) and energy, where each phase is a simple thermodynamic system.*

1.2.2 The state equations

As already mentioned in Section 1.1.1, the state of a system can be described by some state variables. The thermodynamic equilibrium states of a system depend only on intrinsic properties of the system. More precisely the values of all the state variables of a thermodynamic equilibrium state are not independent. The number of degrees of freedom d_F of a system (i.e. the number of independent state variables) is a direct consequence of Gibbs' phase rule:

> *Consider a simple thermodynamic system with N_c different chemical species. Then a thermodynamic equilibrium state of the system is completely described by $d_F = N_c + 2$ state variables.*

An example of a set of independent state variables is given by Callen's first postulate in [19]: the internal energy U, the volume V and the vector of the quantities of each species n. But this choice is not unique.

Since there are only d_F independent state variables, all the other state variables are related to them by a relation of the following type:

$$f\left(X_{dep}, X_{indep}\right) = 0$$

where X_{dep} and X_{indep} are respectively dependent and independent state variables. Such a relation is called a *state equation*. The most famous, and also historically one of the first, state equation was discovered by Boyle and Mariotte in the second half of the XVIIth century and then improved by Charles and Gay-Lussac in the end of the XVIIIth century: the ideal gas relation $pV = nRT$ where $R = 8.3145\,{}^{\mathrm{J}}/_{\mathrm{mol\cdot K}}$ is the ideal gas constant.

1.3 Evolution of the state of a system

1.3.1 The balance equations

The evolution of the extensive quantities can always be determined from a balance equation. Consider a system and some extensive quantity X_{ext}. The quantity of X_{ext} contained in the system changes because some amount of X_{ext} is going in or out of the system (for example by convection or diffusion) and because some X_{ext} is created inside the system, as illustrated in Figure 1.1. This can be written more formally as follows:

$$\frac{dX_{ext}}{dt} = \mathcal{F}^{in}_{X_{ext}} - \mathcal{F}^{out}_{X_{ext}} + \sigma_{X_{ext}} \tag{1.1}$$

where $\mathcal{F}^{in}_{X_{ext}}$ and $\mathcal{F}^{out}_{X_{ext}}$ are the ingoing and outgoing flow rates of X_{ext}, respectively, and $\sigma_{X_{ext}}$ is the production rate of X_{ext} inside the system. By convention the production term $\sigma_{X_{ext}}$ is negative if X_{ext} is consumed inside the system.

It is worth noting that there exists a particular class of extensive quantities, the conservative quantities, as defined below.

Definition 1.3 (Conservative quantity)**.** An extensive quantity X_{ext} is said to be conservative if its production rate is always equal to zero: $\sigma_{X_{ext}} = 0$.

A consequence of the mass and energy conservation is that both quantities are conservative whereas entropy is not a conservative quantity (due to the second principle).

Remark 1.3. *The production term for the mass balance is equal to zero only if the total mass of the system is considered, but this is not true if the mass*

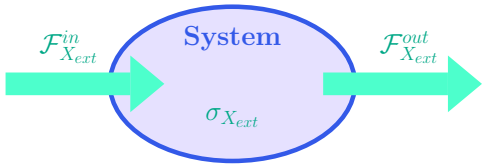


Figure 1.1: Balance of the extensive quantity X_{ext}

(or the mole number) of each individual species is considered. Indeed if there is a chemical reaction, molecules of some species (the reactants) "disappear" and molecules of other species (the products) "appear". Nevertheless since a chemical reaction can be seen as a recombination of atoms, the amount of each atom is conserved and so is the total mass:

$$\sum_{i=1}^{N_c} M_i \sigma_{n_i} = 0$$

where N_c is the number of chemical components of the system, M_i is the molar weight of component i and σ_{n_i} is the molar production/consumption rate of the species i. But σ_{n_i} can be non-zero.

1.3.2 Quasi-static processes

As explained in Section 1.2.2, all equilibrium states of a system are described by $N_c + 2$ state variables. A possible choice for these state variables is the set $(U, V, n_1, ..., n_{N_c})$. This means that if the values of U, V, n_1,... and n_{N_c} are fixed, the value of all other state variables for this thermodynamic equilibrium state are also fixed. As a consequence, there exists a value for the entropy S for each set of values $(U, V, n_1, ..., n_{N_c})$, or in other words there exists a function $\tilde{S}\,(U, V, n_1, ..., n_{N_c})$ that gives the value of the entropy at each equilibrium state:

$$S = \tilde{S}\,(U, V, n_1, ..., n_{N_c}) \tag{1.2}$$

Remark 1.4. *It can be shown that the entropy function $\tilde{S}\,(U, V, n_1, ..., n_{N_c})$ has to be a monotonically increasing function of the internal energy. Furthermore*

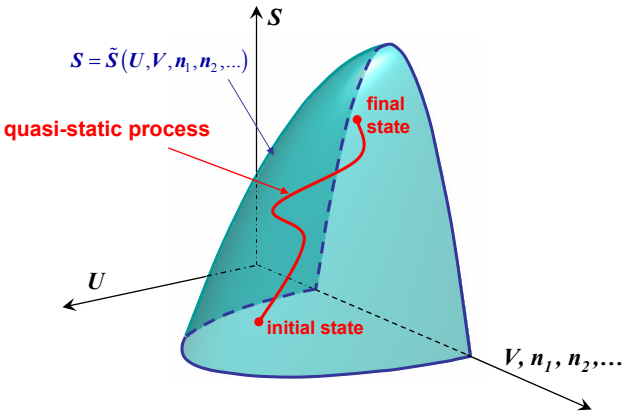


Figure 1.2: Illustration of $\mathscr{S}$ and of a quasi-static process

the entropy function has to be a concave function in order to fulfill the second principle.

Remark 1.5. *The fundamental relations are homogeneous first-order functions of their extensive arguments [19].*

In order to describe and characterize the thermodynamic equilibrium states, let us consider the thermodynamic configuration space defined as follows:

Definition 1.4 (Thermodynamic configuration space)**.** The thermodynamic configuration space is the abstract space spanned by coordinate axes that correspond to the entropy and to the parameters U, V, n_1,... and n_{N_c} of the system.

The function $\tilde{S}(U, V, n_1, ..., n_{N_c})$ can be represented by a hypersurface $\mathscr{S}$ in the thermodynamic configuration space as shown in Figure 1.2. By definition, each point of this hypersurface represents a thermodynamic equilibrium state. The function $\tilde{S}(U, V, n_1, ..., n_{N_c})$ is an intrinsic property of the system that is not depending on the processes that the system has undergone in the past.

Let us now consider a system that is in equilibrium with its environment. The initial state of this system is therefore an equilibrium state and can be represented as a point of $\mathscr{S}$. Now suppose that the environment is changing.

The system is no more in equilibrium with its environment and its state will change until a new state in thermodynamic equilibrium with the new environment is reached. The final state is also a thermodynamic equilibrium state on $\mathscr{S}$. But during the process, the intermediate states of the system could be non-equilibrium states, i.e. states that are not on the hypersurface. Nevertheless one can define a particular class of processes, namely *quasi-static processes* that are defined as follows:

Definition 1.5 (Quasi-static process [19])**.** A quasi-static process is a process where all the intermediate states are thermodynamic equilibrium states.

A quasi-static process can be represented as a curve on the hypersurface of $\tilde{S}\left(U, V, n_1, ..., n_{N_c}\right)$ as shown in Figure 1.2.

Assumption 1.1. In this thesis all considered thermodynamic processes are assumed to be quasi-static processes. In the case of interconnection of simple thermodynamic subsystems, we shall assume that each simple subsystem evolves by following a quasi-static process.

Remark 1.6. *In the case of spatially distributed systems where the variables are also space dependent, the above assumption corresponds to the hypothesis of local equilibrium (HLE) [62].*

1.3.3 Gibbs' relation

Let us consider a closed system evolving along some process. The application of the first principle of thermodynamics to this process can be written down as follows:

$$U_{final} - U_{init} = Q + W \tag{1.3}$$

where U_{init} and U_{final} are the initial and final internal energy of the system, Q is the total heat that has been transferred to system during the process and W is the total work applied on the system. Since the internal energy is a state function of the system, (1.3) can be written in the differential form as follows:

$$\mathrm{d}U = đQ + đW \tag{1.4}$$

where the symbol đ means that đQ and đW are not exact differentials since they depend on the process. Nevertheless, for quasi-static processes, it can be shown that the work đW due to forces exerted on the system can be expressed as follows:

$$đW = \sum_i X^i_{int} \mathrm{d}X^i_{ext}$$

where X^i_{int} is an intensive quantity and X^i_{ext} is an extensive quantity. For instance, the work due to pressure is equal to $-P\mathrm{d}V$. In the same manner, đQ can be expressed in a similar way. Indeed from the definition of entropy (Definition 1.1), we can write:

$$đQ = T\mathrm{d}S$$

As a consequence, (1.4) for a closed system can be written as follows:

$$\mathrm{d}U = T\mathrm{d}S + \sum_i X^i_{int} \mathrm{d}X^i_{ext} \tag{1.5}$$

Without any loss of generality we shall only consider the effects due to compression/dilation of the system, such that the second term reduces to $-P\mathrm{d}V$. For open system a term has to be added in order to take into account the variation of the internal energy due to the change in mass. It can be shown that the more general form of (1.5) is simply:

$$\mathrm{d}U = T\mathrm{d}S + \sum_i X^i_{int} \mathrm{d}X^i_{ext} + \sum_{i=1}^{N_c} \mu_i \mathrm{d}n_i$$

where μ_i is the chemical potential of species i. This relation is known as the Gibbs' relation and describes the relations between the variables of a system at thermodynamic equilibrium. Since in this work we consider only the work due to compression/dilation, we shall use the following form of the Gibbs' relation:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu^t \mathrm{d}n \tag{1.6}$$

The above form of the Gibbs' relation is called the internal energy form.

Remark 1.7. *Above we have only considered the effects due to compression or dilation of the system. Indeed the work due to compression/dilation is frequently*

the most important contribution compared to other effects in the case of a large number of chemical processes. However other effects (e.g. magnetic effects, elastic deformation) can be easily included by adding the related terms in the Gibbs' relation (1.6)*. Their treatment is similar to the treatment of the term related to the compression/dilation term.*

In this thesis we shall prefer the following form of the Gibbs' relation, namely the entropy form[1]:

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \frac{\mu^t}{T}\mathrm{d}n \tag{1.7}$$

The Gibbs' relation can be used to predict the time evolution of the variables along a quasi-static process. Indeed, we have:

$$\frac{dU}{dt} = T\frac{dS}{dt} - P\frac{dV}{dt} + \mu^t\frac{dn}{dt} \tag{1.8}$$

The Gibbs' relation exhibits particular pairs of variables. These are the so-called conjugated variables. When considering the entropy form of the Gibbs' relation (1.7) the pairs of conjugated variables are: $\left(\frac{1}{T}, U\right)$, $\left(\frac{P}{T}, V\right)$ and $\left(-\frac{\mu}{T}, n\right)$. Let us note that a pair of conjugated variables always combines an intensive quantity and an extensive one, and also a dependent variable and an independent one. The "standing alone" variable is called the *thermodynamic potential* associated to the Gibbs' relation.

Besides let us remember that we have assumed a quasi-static process. At each time the state of the system is on the hypersurface of the function $\tilde{S}\left(U, V, n_1, ..., n_{N_c}\right)$. As a consequence, the following relation can also be written:

$$\mathrm{d}S = \left(\frac{\partial\tilde{S}}{\partial U}\right)_{V,n}\mathrm{d}U + \left(\frac{\partial\tilde{S}}{\partial V}\right)_{U,n}\mathrm{d}V + \left(\frac{\partial^t\tilde{S}}{\partial n}\right)_{U,V}\mathrm{d}n \tag{1.9}$$

By identifying (1.7) with (1.9), the following relations are obtained:

$$\frac{1}{T} = \left(\frac{\partial\tilde{S}}{\partial U}\right)_{V,n} \quad \frac{P}{T} = \left(\frac{\partial\tilde{S}}{\partial V}\right)_{U,n} \quad -\frac{\mu_i}{T} = \left(\frac{\partial\tilde{S}}{\partial n_i}\right)_{U,V,n_{j\neq i}} \tag{1.10}$$

[1]The division by T is allowed since $T > 0$ according to Nernst's theorem which states that the absolute zero is not accessible.

In other words, the value of the dependent variables can be derived from the function $\tilde{S}(U, V, n_1, ..., n_{N_c})$. Hence the knowledge of the entropy function $\tilde{S}(U, V, n_1, ..., n_{N_c})$ of a system is sufficient to characterize the entire state of some thermodynamic equilibrium state. Graphically, this means that the intensive variables $\frac{1}{T}$, $\frac{P}{T}$ and $\frac{\mu}{T}$ at a thermodynamic equilibrium state are given by the tangent plane of the hypersurface $\mathscr{S}$ at the corresponding point [43].

The function $\tilde{S}(U, V, n_1, ..., n_{N_c})$ is in fact a particular case of the so-called *fundamental relations* of a system, defined as follows:

Definition 1.6 (Fundamental relation [11])**.** A fundamental relation is the thermodynamic potential of some form of Gibbs' relation expressed as a function of the independent variables of the latter.

The fundamental relation contains all thermodynamic information about a system, contrary to the state equations defined in Section 1.2.2. A fundamental relation can be found by combining together several state equations [19]. There exist several fundamental relations for a given system. For example $U = \tilde{U}(S, V, n_1, ..., n_{N_c})$ is the fundamental relation associated to the internal energy form of Gibbs' relation (1.6).

Example 1.2. *Let us consider an ideal gas. The Boyle-Mariotte relation $PV = nRT$ is an equation of state but is not a fundamental relation since it does not allow to determine the internal energy U of the system, for instance. Nevertheless additional state equations can be considered:*

$$\begin{aligned} U &= n\left(C_v\left(T - T_0\right) + u_0\right) \\ S &= n\left[s_0 + \left(C_p \ln\left(\frac{T}{T_0}\right) - R\ln\left(\frac{P}{P_0}\right)\right)\right] \end{aligned}$$

where C_v is the molar constant volume heat capacity, T_0 is a reference temperature, u_0 and s_0 are the reference internal energy and entropy, respectively, $C_p = C_v + R$ is the molar constant volume heat capacity and P_0 is a reference pressure. By considering these three state equations, one can determine a fundamental relation of the ideal gas as follows:

$$\tilde{S}(U, V, n) = n\left[s_0 + \left(C_v \ln\left(\frac{U - n\left(u_0 - C_v T_0\right)}{nC_v T_0}\right) - R\ln\left(\frac{nRT_0}{VP_0}\right)\right)\right]$$

It is easy to check that this relation fulfills (1.10).

Note that the fundamental relations can be obtained one from each other by Legendre transforms[1]. The Legendre transforms of the internal energy are the usual thermodynamic potentials such as the Helmholtz energy or the Gibbs' free energy whereas the Legendre transforms of the entropy are the so-called Massieu-Planck potentials which are also related to the usual potentials.

Example 1.3. *In this example we shall show that the Gibbs' free energy G can also be a thermodynamic potential. The Gibbs' free energy is defined as follows:*

$$G = U + PV - TS$$

This relation can be differentiated:

$$\mathrm{d}G = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P - T\mathrm{d}S - S\mathrm{d}T$$

By inserting the internal energy form of Gibbs' relation (1.6) *in this equation, it becomes:*

$$\mathrm{d}G = \mu^t \mathrm{d}n + V\mathrm{d}P - S\mathrm{d}T$$

This relation is the Gibbs' free energy form of Gibbs' relation. Now let us consider the function $\tilde{G}(n,T,P)$ that gives the Gibbs' free energy as a function of n, T and P for a given system. According to Definition 1.6, $\tilde{G}(n,T,P)$ is a fundamental relation and thus the Gibbs free energy is a thermodynamic potential. Moreover $\tilde{G}(n,T,P)$ is the Legendre transform of the internal energy since we have:

$$\tilde{G}(n,T,P) = \tilde{U}(S,V,n) - \frac{\partial \tilde{U}}{\partial V}V - \frac{\partial \tilde{U}}{\partial S}S$$

As stated in Remark 1.5, the fundamental relations are homogeneous first-order functions of their extensive arguments. A consequence of this property is the so-called Gibbs-Duhem equation [19]:

$$S\mathrm{d}T - V\mathrm{d}P + n^t \mathrm{d}\mu = 0 \tag{1.11}$$

[1] see Definition E.24 in Appendix E

Remark 1.8. *Up to now we have only considered simple thermodynamic systems. Nevertheless this study can be easily extended to complex systems that are an interconnection of simple thermodynamic systems. The state of the whole system is given by the set of the states of all the subsystems. Since the thermodynamic equilibrium states of each subsystem are given by N_c+2 state variables, the state of the whole system is given by $m\,(N_c+2)$ where m is the number of interconnected subsystems. For each subsystem j (with $j=1,...,m$) we have:*

$$S^{(j)} = \tilde{S}^{(j)}\left(U^{(j)}, V^{(j)}, n^{(j)}\right)$$

The Gibbs' relation (1.7) *and the relations* (1.10) *are of course still true for each subsystem individually. It can be shown easily that the following relation:*

$$S = \tilde{S}\left(U^{(1)},...,U^{(m)},V^{(1)},...,V^{(m)},n^{(1)},...,n^{(m)}\right) = \sum_{j=1}^{m}\tilde{S}^{(j)}\left(U^{(j)},V^{(j)},n^{(j)}\right)$$

is a fundamental relation for the interconnected system. The Gibbs' relation for the interconnected system is the following:

$$\mathrm{d}S = \sum_{j=1}^{m}\left(\frac{1}{T^{(j)}}\mathrm{d}U^{(j)} + \frac{P^{(j)}}{T^{(j)}}\mathrm{d}V^{(j)} - \frac{\mu^{(j)^t}}{T^{(j)}}\mathrm{d}n^{(j)}\right)$$

1.3.4 The dynamical model of a thermodynamic system

The state of a thermodynamic system changes because of the interactions between the system and its environment. These interactions are flows of extensive quantities that are entering or leaving the system. The first step to model the dynamical behaviour of a thermodynamic system consists therefore in writing balance equations. Usually the ingoing and outgoing flows of the extensive quantities of the system are known. Moreover the kinetics of the chemical reactions that are taking place are also assumed to be known. Since mass and energy are conserved quantities, one can write the balance equation for the internal energy (see [91]) and for each chemical species as follows:

$$\frac{dU}{dt} = \sum_{j=1}^{N_F}\left(\mathcal{F}_N^j h^j\right) + \dot{Q} - P\frac{dV}{dt} \tag{1.12}$$

and

$$\frac{dn_i}{dt} = \sum_{j=1}^{N_F} \left(\mathcal{F}_{n_i}^j\right) + \sigma_{n_i} \tag{1.13}$$

where $\mathcal{F}_N^j$ is molar flowrate of the inlet/outlet mass flow j, N_F is the number of inlet/outlet flows, h^j is the molar enthalpy of the mass flow j, $\dot{Q}$ is the net inlet heat transfer rate, $\mathcal{F}_{n_i}^j$ is the molar inlet flow rate of i in flow j and σ_{n_i} is the production rate of i due to chemical reactions. $-P\frac{dV}{dt}$ is in fact the mechanical work in the case of quasi-static processes. The volume change of the system can be modelled by considering the behaviour of the boundary of the system.

This means that considering the interaction between a simple thermodynamic system and the environment leads to $N_c + 2$ balance equations (or $m\,(N_c + 2)$ equations in the case of an interconnection of m simple systems). But, as explained in Section 1.2.2, this number of variables is sufficient to characterize the thermodynamic equilibrium states of the system. Due to Assumption 1.1, all intermediate states are also thermodynamic equilibrium states. As a consequence the balance equations obtained here above are sufficient to characterize the dynamical behaviour of all the variables of the system. Indeed the other variables are linked to the internal energy, the volume and the quantity of each component by the fundamental relation (1.2). As an example, the temperature variation is given by the following relation:

$$\frac{d}{dt}\left(\frac{1}{T}\right) = \frac{d}{dt}\left(\frac{\partial \tilde{S}}{\partial U}\right) = \frac{\partial^2 \tilde{S}}{\partial U^2}\frac{dU}{dt} + \frac{\partial^2 \tilde{S}}{\partial U \partial V}\frac{dV}{dt} + \sum_{i=1}^{N_c} \frac{\partial^2 \tilde{S}}{\partial U \partial n_i}\frac{dn_i}{dt}$$

It can also be important to consider the entropy balance equation since it allows to deduce the entropy production term σ_S which is always non-negative. The entropy balance equation can be obtained directly considering the entropy form of Gibbs' relation (1.7):

$$\frac{dS}{dt} = \frac{1}{T}\frac{dU}{dt} + \frac{P}{T}\frac{dV}{dt} - \frac{\mu^t}{T}\frac{dn}{dt}$$

Since the inlet and outlet entropy flows $\mathcal{F}_S^{in}$ and $\mathcal{F}_S^{out}$ are known by considering the interactions of the system with its environment, the entropy production term can be directly deduced from the preceding equation:

$$\sigma_S = \frac{dS}{dt} - \left(\mathcal{F}_S^{in} - \mathcal{F}_S^{out}\right) \geq 0 \tag{1.14}$$

The expression of σ_S allows to determine which phenomena occurring in the system are sources of entropy and are hence irreversible.

Part I

Physics based approach

The main topic of this thesis is to integrate physical considerations into the analysis and the design of process control systems. This task involves two scientific fields: chemical engineering and system theory. Two approaches can correspondingly be considered so as to achieve the desired objective: either we start from the first domain and move into the latter one, or we do it the other way round. In this part, we have chosen the first approach, i.e. we shall start from physical considerations on the process system and then try to interpret the observed dynamical behaviour based on these considerations. The second approach shall be explored in the second part of this document.

Even reformulated in this way, the task remains challenging due to a too general statement. For this reason, in a first step we shall narrow the scope of our research and consider a particular subclass of process systems, and more precisely a particular case study. The aim is to get a better insight of the links between the physical phenomena and the observed dynamical behaviour in this particular case, and then to extend the conclusions to thermodynamic process systems in general.

We have now to select the adequate case study among the huge diversity of thermodynamic process systems. It should be simple enough so as to be modelled and analyzed easily, but at the same time it should undergo different physical phenomena and show a sufficiently complex dynamical behaviour. An example of a process system that fulfills those requirements and that shall be investigated in this part is the Continuous Stirred Tank Reactor (CSTR).

A CSTR is a tank into which reactants flow and out of which the products are withdrawn, and in which a stirring mechanism keeps the content as uniform as possible. A heat exchange coil or a heating or cooling jacket may also be added in order to allow heat exchanges. It is an idealized reactor and an actual reactor will depart from this idealized extreme to some degree. Nonetheless the CSTR, together with the ideal tubular reactor, is widely encountered in chemical engineering. Its study is worthwhile since it is the basis for the design of actual reactors and it emphasizes important features of their behaviour. Actual CSTRs are widely used in the industry, especially in the organic chemical industry [86]. Among many examples, let us mention the production of caprolactam (monomer for Nylon), of ethyl acetate (solvent used for example

in nail polish removers or for the decaffeination of coffee beans and tea leaves), of phenol (used in the pharmaceutical industry e.g. as starting material for aspirin, as a strong antiseptic in medical environment and for the production of synthetic resins such as Bakelite) and of nitrobenzene (intermediary product in the production of aniline which is a dye component and the starting product of many drugs such as paracetamol). CSTRs are also used in polymerization processes, as for example in the production process of PVC (flexible hoses and tubing, flooring, roofing membranes, electrical cable insulation...) or of polystyrene (disposable cutlery, plastic models, CD and DVD cases, packing materials, foam drink cups...).

As it appears from the above description, different phenomena occur in the CSTR: mass and energy convection, mixing, chemical reaction and heat transfer. The uniformity of its content makes it a simple thermodynamic system, as defined in Chapter 1. Consequently no spatial dependence of the state has to be considered. Due to its simplicity the CSTR is easy to model by using mass and energy balances. On the other hand, despite its simplicity, the dynamical model of the CSTR is nonlinear and its dynamical behaviour can be rather complex, as for instance the multiplicity of steady states with among them an unstable one. The control of such reactors is of great interest, for example for security reasons (e.g. by avoiding an increase of temperature) or for productivity reasons (e.g. by maintaining the operating point that maximizes the selectivity with respect to by-products). Beside being a cornerstone in chemical reactor design [6][67], the CSTR is also widely used in system theory, and more precisely in process control, as an example for nonlinear dynamical systems. Hence the CSTR case study is a particularly suitable benchmark example in chemical engineering as well as in system theory, i.e. in the two scientific fields we wish to connect.

The analysis of the dynamical behaviour and the control of the non-isothermal CSTR has been considered since the first half of the XX^{th} century. The literature on this subject is much too wide to be exhaustively cited. Therefore we shall restrict ourselves to some important contributions that are particularly relevant to this research. Concerning the open-loop behaviour of an exothermic CSTR, let us first mention Aris, Amundson and coworkers who have discussed

the stability of the CSTR using Lyapunov's first and second method in a series of papers in 1958 [7][8] and in 1964 [101][102]. The presence of an unstable steady state and the behaviour of the system around it has been studied by Bilous [13] and later by Berger and Perlmutter [12] as well as Sabo [90]. Finally let us cite the work from Uppal and Ray who analyzed the influence of the parameters on the dynamical behaviour and more precisely the number and the nature of equilibrium states [93][94].

In addition to the high nonlinearity of the model, the practical applicability of the control system makes the CSTR even more difficult to control. Indeed we have to take into account that the whole state is often not available for measurements since concentrations are usually not measurable on-line. Furthermore the controller must be sufficiently robust against modelling errors, since the expression of the reaction kinetics are based on experiments and often only partially known. Various techniques have been applied for controlling the exothermic CSTR: conventional PID controllers [7][8], state feedback, use of state observers,... Viel, Jadot and coworkers proposed a state feedback control law that takes into account uncertainty about reaction kinetics [99][100], the problem of partial state measurements and also control input saturation [53].

But most of the studies on the CSTR do not take into account the underlying physical phenomena beyond the step of modelling. The controllers are designed only on the basis of the mathematical equations of the model. As a consequence the conclusions of those works cannot be extended and exploited for the control of other thermodynamics systems in which similar physical phenomena occur (e.g., an interconnection of several CSTRs). Nevertheless some work have already linked thermodynamics and system theory [24][42][92]. More recently, Alonso, Ydstie and coworkers have been quite active in exploring this research area, resulting in very insightful works on the control design of process systems, while Rouchon and Creff provided important results about the flash dynamics [88].

In the approach that Alonso, Ydstie and coworkers have proposed for the control of process systems, the process system is controlled by the so-called inventory control. Inventories are non-negative extensive quantities [34] so as for example the mass or the energy. The control objective of inventory control is

to make some selected process inventories to follow their respective set points. The inventory control is achieved by using the dissipativity and passivity theory of nonlinear control [106][107]. The passivity properties of the system are derived from the convexity of the entropy function and the considered storage function is closely related to the availability of the system[1]. This inventory control approach has been applied to distributed process systems [2][3][4][89] and to process networks [34][57][58]. In [5], the inventory control has been used to stabilize the mass and the energy of the plant so as to guarantee that the state converges to a convex region. The entropy is then used as a Lyapunov function inside this region. Based on this, the control structure is complemented so that the intensive variables also converge to the desired state. The availability has also been used directly as a Lyapunov function for the design of a control system for the CSTR [51]. Besides in [84] an entropy-like function is used as a Lyapunov function for the analysis and control of isothermal reactors in which a complex reaction network takes place. Another example where thermodynamic considerations are used for process control purposes is given in [59] and [78]. A controller for a plug-flow reactor is designed so as to maximize the energy efficiency, i.e. the controller minimizes the entropy production rate in the reactor.

The objective of this part of the thesis is to present several old and new results that aim at linking the thermodynamics and the system theory via the exothermic CSTR case study. First we shall present the CSTR model and its open-loop dynamical behaviour in Chapter 2. Then Chapter 3 is dedicated to some thermodynamic considerations on the CSTR. More precisely, different Lyapunov function candidates related to the thermodynamics, more specifically based on the entropy, the entropy production and the internal energy, are considered. In Chapter 4, we shall apply a recent approach for the "physics-based control" of systems to our CSTR case study, namely the power shaping approach that was developed recently for electromechanical systems. Finally the main results of this part shall be recalled and summarized up in Chapter 5.

[1]Roughly, the availability is the difference between the entropy of the system and a plane that is tangent to the entropy function at some given reference state [3], and is related to the available energy in the system.

Chapter 2

The CSTR case study

This chapter is dedicated to the modelling and the description of the dynamical behaviour of the CSTR. The physical approach aims at explaining physically the dynamical behaviour of the CSTR to obtain a dynamical model for the CSTR case study.

Chemical reactors are thermodynamic systems and hence their dynamical model are obtained by considering balance equations. In most chemical engineering textbooks the balance equations are derived from the principles of thermodynamics (see e.g. [67][91]). But when considered in system theory the dynamical models are often simplified versions of those derived directly from the balance equations. For instance, the heat capacity of the mixture is usually assumed to be constant, or the dependence of the reaction heat in the temperature is neglected. What is usually presented as the "heat-balance equation" is in reality the temperature evolution equation. The derivation of the temperature evolution equation from the internal energy balance is done by considering simplifying assumptions, which are sometimes passed over. Furthermore in many cases, irreversible reactions are considered, which are only an approximation from a thermodynamic point of view. The consequences of these approximations are a loss of physical information and a loss of generality.

Contrary to most researches on the CSTR, we shall work here with a dynamical model that is more exact from a thermodynamic point of view, i.e.

it will be derived from the balance equations with as less modelling assumptions as possible. We shall then analyze the dynamical behaviour of the CSTR based on this model. We show that the results obtained with the more simplified model (such as for instance in [93]) are also valid for the more general case.

This chapter is organized as follows. First the dynamical model is derived in Section 2.1. After a brief description of the case study and the modelling assumptions, the balance equations are used to obtain two equivalent dynamical models. All the steps of the development are justified on the basis of the thermodynamic principles and/or of the modelling assumptions. Then the dynamical behaviour of the CSTR is analyzed in Section 2.2. We shall first calculate the equilibrium points of the system and then analyze their stability features. The differences and similarities with the usual simplified approach in system theory shall be emphasized in Section 2.3.

2.1 The dynamical model

2.1.1 Description and general assumptions

Here we consider a CSTR in which an exothermic reaction takes place. The reactor is equipped with a jacket in which a cooling fluid at a constant temperature T_w is circulating. A schematic view of the CSTR is presented in Figure 2.1 and the main notations used in this case study are listed in Table 2.1. The chemical reaction takes place in a liquid medium and involves two chemical species, A and B as follows:

$$A \rightleftharpoons \beta B$$

where β is a stoichiometric coefficient. Besides there is also an inert component I in the mixture. The inlet stream contains only A and I.

The choice of a liquid phase CSTR instead of a gaseous CSTR is driven by the motivation to consider a system that is close to the system considered in the classical literature. Indeed in liquid phase CSTR, no pressure effects have to be taken into account. However the present study should be generally

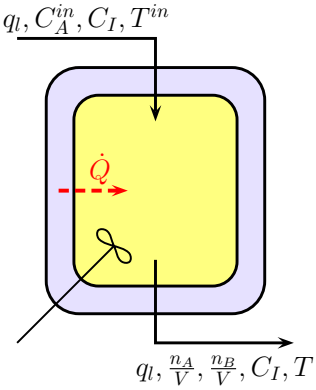


Figure 2.1: Schematic view of the CSTR

applicable also to gaseous CSTRs since these ones have a similar dynamical behaviour [23].

As it shall be shown in the sequel, an endothermic reaction leads to a dynamical behaviour with a single asymptotically stable equilibrium point whereas an exothermic reaction can lead to multiple equilibrium points, some of them being unstable. This makes the exothermic reaction choice more interesting from a system analysis point of view. Nevertheless most of the results obtained in the exothermic reaction case are in fact also valid for the endothermic reaction case, or can be easily adapted.

Moreover let us consider the following modelling assumptions:

Assumption 2.1. The reactor is perfectly mixed.

This assumption is underlying to the fact that we consider an ideal CSTR. This allows to neglect any spatial gradient and as a consequence the CSTR is a simple thermodynamic system (see Definition 1.2).

Assumption 2.2. The inlet and outlet volume flow rates are equal:

$$q_l^{in} = q_l^{out} = q_l$$

Assumption 2.3. The concentrations of A and B in the reactor and in the inlet flow are very low compared to the concentration of the inert I so that only

Symbol	*Meaning*
A, B, I	chemical components
C_i	concentration of component i
C_i^{in}	inlet concentration of component i
C_{p_i}	molar constant pressure heat capacity of component i
C_{v_i}	molar constant volume heat capacity of component i
$\mathscr{C}_p$	volumetric constant pressure heat capacity of the mixture
$\mathscr{C}_p^{in}$	volumetric constant pressure heat capacity of the inlet stream
$\mathscr{C}_v$	volumetric constant volume heat capacity of the mixture
H	enthalpy of the mixture
$\dot{Q}$	heat exchange flow rate
R	ideal gas constant
S	entropy of the mixture
T	temperature inside the reactor
T^{in}	inlet temperature
T_0	reference temperature
T_w	cooling fluid temperature
U	internal energy of the mixture
V	liquid volume
h_i	molar enthalpy of component i
h_{0_i}	molar enthalpy of component i at T_0
n_i	quantity of component i
n	vector of the quantities of the components
q_l	volume flowrate
r	reaction rate per volume unit
t	time
u_i	molar internal energy of component i
$\Delta_r H$	reaction heat
κ	heat transfer coefficient

Table 2.1: Notations for the CSTR case study

the molar volume v_I of I has to be taken into account for the determination of the total volume:

$$V = v_I n_I = \frac{n_I}{C_I}$$

where C_I is the concentration of I. The molar volume $v_I = \frac{1}{C_I}$ is constant and in particular it is independent of the quantity of the dissolved species A and B or of the temperature.

As it shall be shown in the sequel, Assumptions 2.2 and 2.3 allow to have constant volume. Assumption 2.3 is valid in a large number of practical cases, and especially in the cases where the reactants are sufficiently dilute.

Assumption 2.4. The heat exchange is proportional to the temperature difference between the cooling fluid and the liquid in the reactor as follows:

$$\dot{Q} = \kappa\,(T_w - T)$$

where $\dot{Q}$ is positive if heat is extracted from the cooling fluid into the reactor, with κ the heat exchanger coefficient. κ is independent of the temperature and of the composition of the mixture.

This assumption is valid if the interval of considered temperatures is sufficiently narrow so as to neglect the temperature dependence of κ.

Assumption 2.5. The dynamics of the cooling fluid are sufficiently fast compared to the reactor temperature dynamics so that the temperature of the cooling fluid T_w can be assumed to be constant.

Assumption 2.6. The molar constant pressure and constant volume heat capacities C_{p_i} and C_{v_i} of each species are constant.

This assumption is valid if the interval of considered temperatures is sufficiently narrow so as to neglect the temperature dependence of the heat capacities.

Assumption 2.7. The thermodynamic model considered for the liquid is that of an ideal liquid mixture.

Assumption 2.8. The global reaction rate r depends only on the temperature T of the mixture, and on the concentration of the involved species, i.e. A and B. More precisely the reaction rate is in fact composed of two individual reaction rates, one for the forward reaction ($A \rightarrow \beta B$), r_f, and one for the backward reaction ($\beta B \rightarrow A$), r_b. The global reaction rate is given by $r(\cdot) = r_f(\cdot) - r_b(\cdot)$. $r > 0$ if the net reaction is such that A is consumed, whereas $r < 0$ if A is produced. The case $r = 0$ corresponds to the chemical equilibrium. Each reaction rate is a strictly increasing function of the concentration of its reactant, i.e. A for the forward reaction and B for the backward reaction, but it does not depend on the concentration of its respective product. The reaction rates are equal to zero if the concentration of their reactant is equal to zero.

The functions $r_f(\cdot)$ and $r_b(\cdot)$ are continuously differentiable functions of their arguments.

Assumption 2.9. Each individual reaction rate (i.e. r_f and r_b) is strictly increasing with the temperature and tends to zero as the temperature tends to zero for any value of the concentration of A and B. For any fixed value of the reactant concentration, the reaction rates are upper-bounded with respect to the temperature. From Assumption 2.8, these upper bounds are increasing functions of the concentration of A or of B.

The assumptions on the reaction kinetics imply that we consider reversible reactions as well as irreversible ones. Indeed by setting $r_b = 0$ the reaction kinetics become those of an irreversible reaction. For the sake of coherence with thermodynamics, we shall consider a reversible reaction in the CSTR although the classical CSTR model often considers an irreversible reaction: this point will further discussed at the end of Section 3.2.1 in Chapter 3.

Assumption 2.8 is usual for simple reversible reactions. This means in particular that each individual reaction is not auto-catalytic and without inhibition by the reaction product. A possible expression for the individual reaction rates that fulfills the above-mentioned assumption is given by the mass action law. Assumption 2.9 is also very classical for reaction kinetics. It is fulfilled by most actual reactions, and in particular by the Arrhenius law.

Assumption 2.10. Since we have assumed a liquid medium, we can safely assume that the partial molar enthalpies and internal energies are equal [91], i.e. $h_i = u_i$, where h_i and u_i are the partial molar enthalpy and the partial molar internal energy of component i. As a consequence the constant volume molar heat capacities $C_{v_i} = \frac{\partial u_i}{\partial T}$ and the constant pressure molar heat capacities $C_{p_i} = \frac{\partial h_i}{\partial T}$ of each component are equal.

Furthermore let us recall that Assumption 1.1 is still valid, i.e. the time evolution of the CSTR is a quasi-static process.

2.1.2 The balance equations

As explained in Section 1.3.4, the state evolution of the system is determined by the balance equations the number of moles of each species n_A, n_B and n_I, the volume V and the internal energy U. Since T_w is constant, the dynamics of the jacket do not have to be considered.

The balance equations for each species

The balance equation for A, B and I can be written directly by applying the concepts of Section 1.3.1, and more precisely of Remark 1.3.

Inlet flows From Assumption 2.2, the molar inlet flow $\mathcal{F}_i^{in}$ of the component i (where $i = A, B, I$) is given by the following relation:

$$\mathcal{F}_i^{in} = C_i^{in} q_l^{in} = C_i^{in} q_l$$

where C_i^{in} is the concentration of i in the inlet stream and $C_B^{in} = 0$.

Outlet flows Assumption 2.1 implies that the composition of the outlet flow is equal to the composition inside the reactor. Using Assumption 2.2, the molar outlet flow rate $\mathcal{F}_i^{out}$ of the component i (where $i = A, B, I$) is given by the following relation:

$$\mathcal{F}_i^{out} = q_l^{out} \frac{n_i}{V} = q_l \frac{n_i}{V}$$

Reaction terms The inert species I does not intervene in the reaction and thus the production/consumption rate σ_I of I is equal to zero: $\sigma_I = 0$. The production/consumption rate σ_A and σ_B of the components A and B are given by the reaction rate r and by taking into account the stoichiometry of the reaction, the following expressions are obtained:

$$\begin{cases} \sigma_A &= -rV \\ \sigma_B &= \beta rV \end{cases}$$

Finally by gathering these considerations together in equation (1.1), the following mass balance equations are obtained:

$$\begin{cases} \frac{dn_A}{dt} &= \mathcal{F}_A^{in} - \mathcal{F}_A^{out} + \sigma_A &= \frac{q_l}{V}\left(C_A^{in}V - n_A\right) - rV \\ \frac{dn_B}{dt} &= \mathcal{F}_B^{in} - \mathcal{F}_B^{out} + \sigma_B &= -\frac{q_l}{V}n_B + \beta rV \\ \frac{dn_I}{dt} &= \mathcal{F}_I^{in} - \mathcal{F}_I^{out} + \sigma_I &= \frac{q_l}{V}\left(C_I^{in}V - n_I\right) \end{cases} \tag{2.1}$$

But Assumption 2.3 implies $C_I^{in} = C_I$ and $n_I = C_I V$, such that the balance equation on the species I simply reduces to the following expression:

$$\frac{dn_I}{dt} = \frac{q_l}{V}\left(C_I^{in}V - n_I\right) = \frac{q_l}{V}\left(C_I V - C_I V\right) = 0 \tag{2.2}$$

The volume balance equation

The volume balance equation is in fact a consequence of the total mass balance since the volume is linked to the molar volume of the components of the mixture. By taking Assumption 2.3 into account, the volume evolution is given by the following relation:

$$\frac{dV}{dt} = \frac{d\left(v_I n_I\right)}{dt} = v_I \frac{dn_I}{dt}$$

By inserting (2.2) in this equation, we are finally led to the conclusion that the volume remains constant:

$$\frac{dV}{dt} = 0$$

Remark 2.1. *The reaction rate r is a function of the temperature T and the concentrations of A and B, i.e. $\frac{n_A}{V}$ and $\frac{n_B}{V}$. But the volume is constant and hence the concentrations of A and B are proportional to the quantity of matter n_A and n_B. For the sake of notation simplicity, we shall therefore denote*

the dependence of the reaction rate as $r(T, n_A, n_B)$ $(= r_f(T, n_A) - r_b(T, n_B))$ *instead of the usual way that would be* $r\left(T, \frac{n_A}{V}, \frac{n_B}{V}\right)$*. In the sequel,* V *and* n_I *shall be considered as parameters of the system since they are constant.*

The internal energy balance equation

The internal energy balance is given by (1.12) as follows:

$$\frac{dU}{dt} = \mathcal{F}_H^{in} - \mathcal{F}_H^{out} + \dot{Q} - P\frac{dV}{dt}$$

where $\mathcal{F}_H^{in}$ and $\mathcal{F}_H^{out}$ are the inlet and outlet enthalpy flow rate and $\dot{Q}$ is the transferred heat.

Assumption 2.7 implies that the inlet enthalpy flow rate can be written as follows:

$$\mathcal{F}_H^{in} = \sum_{i=A,B,I} \left(q_l C_i^{in} h_i^{in}\right) = \sum_{i=A,I} \left[q_l C_i^{in} \left(C_{p_i}\left(T^{in} - T_0\right) + h_{0_i}\right)\right]$$

where h_i^j is the partial molar enthalpy of component i in the flow j and C_i^j is the concentration of i in flow j, C_{p_i} is the molar constant pressure heat capacity of component i, T_0 is the reference temperature and h_{0_j} is the reference molar enthalpy of component i (i.e. at the temperature T_0). Due to Assumption 2.1, the outlet enthalpy flow rate is simply given by the following expression:

$$\mathcal{F}_H^{out} = \frac{q_l}{V} H$$

Using also Assumption 2.4 and the volume "balance" equation previously obtained, the final expression for the internal energy balance can finally be written as follows:

$$\frac{dU}{dt} = q_l \mathscr{C}_p^{in}\left(T^{in} - T_0\right) + q_l\left(C_A^{in} h_{0_A} + C_I h_{0_I}\right) - \frac{q_l}{V} H - \kappa\left(T - T_w\right) \tag{2.3}$$

where the inlet volumetric constant pressure heat capacity $\mathscr{C}_p^{in}$ has been defined as follows:

$$\mathscr{C}_p^{in} = C_A^{in} C_{p_A} + C_I C_{p_I} \tag{2.4}$$

The dynamical model

The volume and the quantity of I do not vary so that their balance equations do not have to be considered in the dynamical model. Hence the dynamical model of the CSTR is simply given by (2.1) and (2.3) as follows:

$$\begin{cases} \dfrac{dU}{dt} = q_l \mathscr{C}_p^{in} \left(T^{in} - T_0\right) + q_l \left(C_A^{in} h_{0_A} + C_I h_{0_I}\right) \\ \qquad\qquad - \dfrac{q_l}{V} \tilde{H}\left(\tilde{T}\left(U, n_A, n_B\right), n_A, n_B\right) - \kappa\left(\tilde{T}\left(U, n_A, n_B\right) - T_w\right) \\ \dfrac{dn_A}{dt} = \dfrac{q_l}{V}\left(C_A^{in} V - n_A\right) - r\left(\tilde{T}\left(U, n_A, n_B\right), n_A, n_B\right) V \\ \dfrac{dn_B}{dt} = -\dfrac{q_l}{V} n_B + \beta r\left(\tilde{T}\left(U, n_A, n_B\right), n_A, n_B\right) V \end{cases} \tag{2.5}$$

where $T = \tilde{T}\left(U, n_A, n_B\right)$ and $H = \tilde{H}\left(\tilde{T}\left(U, n_A, n_B\right), n_A, n_B\right)$. These notations are used to emphasize that the coordinates of this representation are $(U, n_{_A}, n_B)$ and hence the temperature and the enthalpy are functions of U, n_A and n_B. (2.5) has to be completed with the expression of $\tilde{T}\left(U, n_A, n_B\right)$ and $\tilde{H}\left(T, n_A, n_B\right)$ by considering the thermodynamic model of the mixture.

2.2 Analysis of the dynamical behaviour

In this section we shall describe the dynamical behaviour of the CSTR based on the previously obtained model. First we shall derive the equilibrium points of the system and then we shall analyze their (in)stability properties by using the Lyapunov's first method.

2.2.1 The equilibrium points

The equilibrium points[1] $\left(\bar{U}, \bar{n}_A, \bar{n}_B\right)$ of (2.5) are the solution of the following equation system:

$$\begin{cases} 0 = q_l \mathscr{C}_p^{in} \left(T^{in} - T_0\right) + q_l \left(C_A^{in} h_{0_A} + C_I h_{0_I}\right) - \kappa \left(\bar{T} - T_w\right) \\ \qquad - \dfrac{q_l}{V} \tilde{H} \left(\bar{T}, \bar{n}_A, \bar{n}_B\right) \\ 0 = \dfrac{q_l}{V} \left(C_A^{in} V - \bar{n}_A\right) - r \left(\bar{T}, \bar{n}_A, \bar{n}_B\right) V \\ 0 = -\dfrac{q_l}{V} \bar{n}_B + \beta r \left(\bar{T}, \bar{n}_A, \bar{n}_B\right) V \end{cases} \tag{2.6}$$

where $\bar{T} = \tilde{T}\left(\bar{U}, \bar{n}_A, \bar{n}_B\right)$. Let us consider the first relation of (2.6):

$$\begin{aligned} 0 &= q_l \mathscr{C}_p^{in} \left(T^{in} - T_0\right) + q_l \left(C_A^{in} h_{0_A} + C_I h_{0_I}\right) - \kappa \left(\bar{T} - T_w\right) \\ &\quad - \frac{q_l}{V} \tilde{H} \left(\bar{T}, \bar{n}_A, \bar{n}_B\right) \\ &= q_l \mathscr{C}_p^{in} \left(T^{in} - T_0\right) + q_l \left(C_A^{in} h_{0_A} + C_I h_{0_I}\right) - \kappa \left(\bar{T} - T_w\right) \\ &\quad - \frac{q_l}{V} \tilde{H} \left(\bar{T}, \bar{n}_A, \bar{n}_B\right) \\ &\quad - \bar{h}_A \left(\frac{q_l}{V} \left(C_A^{in} V - \bar{n}_A\right) - r \left(\bar{T}, \bar{n}_A, \bar{n}_B\right) V\right) \\ &\quad - \bar{h}_B \left(-\frac{q_l}{V} \bar{n}_B + \beta r \left(\bar{T}, \bar{n}_A, \bar{n}_B\right) V\right) \end{aligned} \tag{2.7}$$

where $\bar{h}_i$ is the partial molar enthalpy of component i at the equilibrium temperature $\bar{T}$:

$$\bar{h}_i = C_{p_i} \left(\bar{T} - T_0\right) + h_{0_i}$$

By inserting this expression into (2.7), one obtains the following relation:

$$0 = \kappa \left(T_w - \bar{T}\right) + q_l \mathscr{C}_p^{in} \left(T^{in} - \bar{T}\right) + r \left(T, \bar{n}_A, \bar{n}_B\right) V \left(-\Delta_r H\right) \left(\bar{T}\right)$$

where $\left(-\Delta_r H\right)(T)$ is the reaction enthalpy:

$$\left(-\Delta_r H\right)(T) = h_A - \beta h_B = \left[C_{p_A} \left(T - T_0\right) + h_{0_A}\right] - \beta \left[C_{p_B} \left(T - T_0\right) + h_{0_B}\right]$$

[1] in the sense of system theory, see Section 1.2.1

The following system is equivalent to (2.6):

$$\begin{cases} 0 = \kappa\left(T_w - \bar{T}\right) + q_l \mathscr{C}_p^{in}\left(T^{in} - \bar{T}\right) + r\left(T, \bar{n}_A, \bar{n}_B\right) V \left(-\Delta_r H\right)\left(\bar{T}\right) \\ 0 = \dfrac{q_l}{V}\left(C_A^{in} V - \bar{n}_A\right) - r\left(\bar{T}, \bar{n}_A, \bar{n}_B\right) V \\ 0 = -\dfrac{q_l}{V}\bar{n}_B + \beta r\left(\bar{T}, \bar{n}_A, \bar{n}_B\right) V \end{cases} \tag{2.8}$$

From the two last equations, we get:

$$\begin{cases} \bar{n}_B &= \beta\left(C_A^{in} V - \bar{n}_A\right) \\ \frac{q_l}{V} C_A^{in} V &= r\left(\bar{T}, \bar{n}_A, \bar{n}_B\right) V + \frac{q_l}{V}\bar{n}_A \end{cases} \tag{2.9}$$

Using Assumption 2.8, the last relation finally reduces to:

$$r_f\left(\bar{T}, \bar{n}_A\right) V - r_b\left(\bar{T}, \beta\left(C_A^{in} V - \bar{n}_A\right)\right) V + \frac{q_l}{V}\bar{n}_A = \frac{q_l}{V} C_A^{in} V \tag{2.10}$$

By analogy with (2.9) and (2.10), let us define the following two functions $n_A^{eq}(T)$ and $n_B^{eq}(T)$:

$$\frac{q_l}{V} C_A^{in} V = r\left(T, n_A^{eq}(T), \beta\left(C_A^{in} V - n_A^{eq}(T)\right)\right) V + \frac{q_l}{V} n_A^{eq}(T) \tag{2.11a}$$

$$n_B^{eq}(T) = \beta\left(C_A^{in} V - n_A^{eq}(T)\right) \tag{2.11b}$$

The above defined function $n_A^{eq}(T)$ (and consequently $n_B^{eq}(T)$) is indeed well defined, i.e. for a given value of T, there exists a unique value $n_A = n_A^{eq}(T)$ such that the following relation is fulfilled:

$$r_f\left(T, n_A\right) V - r_b\left(T, \beta\left(C_A^{in} V - n_A\right)\right) V + \frac{q_l}{V} n_A - \frac{q_l}{V} C_A^{in} V = 0 \tag{2.12}$$

In other words, the function $n_A^{eq}(T)$ is the solution of the above equation for a fixed T. From Assumption 2.8, the left-hand term is continuous. At $n_A = 0$, the left-hand term is negative definite and at $n_A = C_A^{in} V$, the left-hand-term is positive definite. Using Bolzano's therorem, this implies that (2.12) has a solution in the interval $\left]0, C_A^{in} V\right[$. This solution is unique because the left-hand term is strictly increasing with increasing n_A (from Assumption 2.8). As a consequence the function $n_A^{eq}(T)$, which is implicitly defined in the above definition, is well defined. Furthermore $0 < n_A^{eq}(T) < C_A^{in} V$.

In the sequel we shall also use the following notation:

$$r^{eq}(T) = r\left(T, n_A^{eq}(T), n_B^{eq}(T)\right)$$

The functions $n_A^{eq}(T)$ and $n_B^{eq}(T)$ defined in (2.11a) and (2.11b) correspond in fact to the equilibrium values of n_A and n_B if the CSTR was isothermal.

Remark 2.2. *An explicit expression of the function $n_A^{eq}(T)$ can be found by considering explicit kinetic expressions. For example, if $\beta = 1$ and the kinetics follow the mass action law, i.e. $r(T, n_A, n_B) = k_f(T)\, n_A - k_b(T)\, n_B$, then the expression of $n_A^{eq}(T)$ is as follows:*

$$n_A^{eq}(T) = \frac{\left(\frac{q_l}{V} + k_b(T)\right) C_A^{in} V}{k_f(T) + k_b(T) + \frac{q_l}{V}}$$

Lemma 2.1 (Shape of $n_A^{eq}(T)$)**.** *The derivative of $n_A^{eq}(T)$ with respect to the temperature is given by the following relation:*

$$\frac{dn_A^{eq}}{dT} = \frac{-R_T^{eq}(T)}{R_A^{eq}(T) - \beta R_B^{eq}(T) + \frac{q_l}{V}} \tag{2.13}$$

where the following notation has been introduced:

$$R_T^{eq}(T) = \left(\frac{\partial(rV)}{\partial T}\right)\left(T, n_A^{eq}(T), n_B^{eq}(T)\right)$$

and

$$R_Y^{eq}(T) = \left(\frac{\partial(rV)}{\partial n_Y}\right)\left(T, n_A^{eq}(T), n_B^{eq}(T)\right) \quad \text{with } Y = A, B$$

The limits for T tending towards zero and infinity can be computed to provide the following values:

$$\lim_{T\to 0} n_A^{eq}(T) = C_A^{in} V \quad \textit{and} \quad \lim_{T\to\infty} n_A^{eq}(T) = n_{A_\infty}^{eq} = C_A^{in} V - r_\infty^{eq} V \leq C_A^{in} V$$

where

$$r_\infty^{eq} V = \lim_{T\to\infty} r^{eq}(T)$$

Proof. The derivative with respect to T of (2.11a) is given by the following relation:

$$0 = \frac{\partial(r^{eq}V)}{\partial T} + \frac{q_l}{V}\frac{dn_A^{eq}}{dT} = R_T^{eq}(T) + R_A^{eq}(T)\frac{dn_A^{eq}}{dT} - \beta R_B^{eq}(T)\frac{dn_A^{eq}}{dT} + \frac{q_l}{V}\frac{dn_A^{eq}}{dT}$$

where the above defined notations have been used. By reorganizing the terms, one directly obtains (2.13) and also $\frac{dr^{eq}}{dT} = -\frac{q_l}{V}\frac{dn_A^{eq}}{dT}$. The limit of T towards zero of (2.11a) is given by the following relation:

$$\frac{q_l}{V} C_A^{in} V = \lim_{T\to 0} r\left(T, n_A^{eq}(T), n_B^{eq}(T)\right) V + \frac{q_l}{V} \lim_{T\to 0} n_A^{eq}(T)$$

From Assumption 2.9:

$$\forall n_A, n_B \geq 0,\ \lim_{T\to 0} r\left(T, n_A, n_B\right) = 0 \text{ and } \lim_{T\to 0} \frac{\partial r}{\partial T} = 0$$

This is in particular true for $n_A = n_A^{eq}\left(T\right)$ and $n_B = n_B^{eq}\left(T\right)$ such that:

$$\lim_{T\to 0} r^{eq}\left(T\right) = 0 \text{ and } \lim_{T\to 0} R_T^{eq}\left(T\right) = 0$$

As a consequence

$$\lim_{T\to 0} n_A^{eq}\left(T\right) = C_A^{in} V$$

and

$$\lim_{T\to 0} \frac{dn_A^{eq}}{dT} = -\frac{q_l}{V} \lim_{T\to 0} \frac{dr^{eq} V}{dT} = 0$$

$n_A^{eq}\left(T\right)$ and $r^{eq}\left(T\right)$ have a horizontal asymptote for T tending towards infinity. Let us denote by $n_{A_\infty}^{eq}$ and r_∞^{eq} the values of the asymptotes. By taking the limit towards infinity of (2.11a), one directly obtains:

$$\lim_{T\to \infty} n_A^{eq}\left(T\right) = n_{A_\infty}^{eq} = C_A^{in} V - \frac{r_\infty^{eq}}{q_l} \qquad \square$$

Remark 2.3. *The above result is in agreement with the physical intuition. Indeed no reaction occurs at very low temperature, and hence no A is consumed and no B is produced. The composition of the mixture at equilibrium will have the same composition than the inlet stream.*

Remark 2.4. *Note that in the case of irreversible reaction kinetics,* $n_{A_\infty}^{eq} = 0$.

The shape of the function $n_A^{eq}\left(T\right)$ is shown in Figure 2.2.

By analogy with the first relation of (2.8), let us also define the following function:

$$\Delta^{eq}\left(T\right) = \kappa\left(T_w - T\right) + q_l \mathscr{C}_p^{in}\left(T^{in} - T\right) + r^{eq}\left(T\right) V\left(-\Delta_r H\right)\left(T\right) \qquad (2.14)$$

The set of the equilibrium points of (2.5) are finally obtained by inserting the definitions of $n_A^{eq}\left(T\right)$ and $n_B^{eq}\left(T\right)$ in (2.6):

$$\left\{ \left(\bar{T}, \bar{n}_A, \bar{n}_B\right) \middle| \Delta^{eq}\left(\bar{T}\right) = 0, \bar{n}_A = n_A^{eq}\left(\bar{T}\right), \bar{n}_B = n_B^{eq}\left(\bar{T}\right) \right\} \qquad (2.15)$$

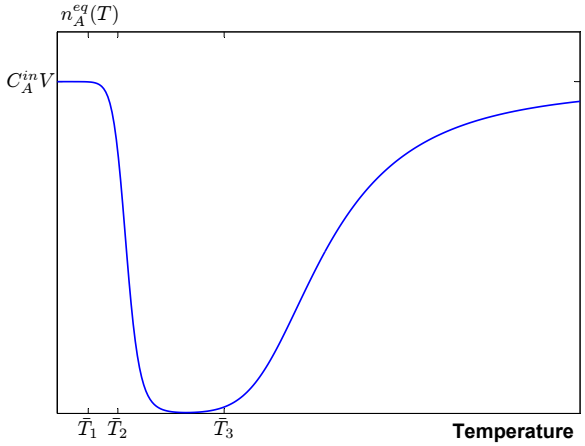


Figure 2.2: Shape of $n_A^{eq}(T)$

From the previous relations, we can conclude:

$$\begin{aligned} \lim_{T\to 0} \Delta^{eq}(T) &= \kappa T_w + q_l \mathscr{C}_p^{in} > 0 \\ \lim_{T\to \infty} \Delta^{eq}(T) &= -\infty \end{aligned}$$

As a consequence, the function $\Delta^{eq}(T)$ has at least one zero, and hence there exists at least one equilibrium point in (2.15).

The derivative of the function $\Delta^{eq}(T)$ is given by the following expression:

$$\frac{d\Delta^{eq}}{dT} = -\kappa - q_l \mathscr{C}_p^{in} + r^{eq}(T) V \frac{d(-\Delta_r H)}{dT} + (-\Delta_r H) V \frac{dr^{eq}}{dT} \tag{2.16}$$

The last term of (2.16) tends to zero at low and high temperatures so that we can deduce the following relation:

$$\lim_{T\to 0} \frac{d\Delta^{eq}}{dT} = -\kappa - q_l \mathscr{C}_p^{in} < 0 \tag{2.17a}$$

$$\lim_{T\to \infty} \frac{d\Delta^{eq}}{dT} = -\kappa - q_l \mathscr{C}_p^{in} + r_\infty^{eq} V \left(\lim_{T\to \infty} \frac{d(-\Delta_r H)}{dT} \right) \tag{2.17b}$$

Usually $(-\Delta_r H)$ does not vary much on small temperature ranges, i.e. $\frac{d(-\Delta_r H)}{dT}$ is usually small. Therefore the last term of (2.17b) can be neglected with

respect to the two first ones. As a consequence, we have:

$$\lim_{T\to\infty} \frac{d\Delta^{eq}}{dT} < 0$$

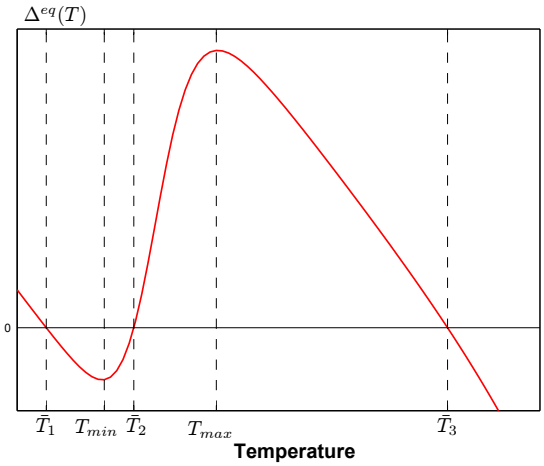


Figure 2.3: Shape of the function $\Delta^{eq}(T)$

At intermediate temperatures, nothing can be said in general, since the sign of $\frac{dr^{eq}}{dT}$ has not been determined up to now. From Assumption 2.8, $R_A^{eq} \geq 0$ and $R_B^{eq} \leq 0$. Thus the sign of $\frac{dr^{eq}}{dT}$ is the same as the one of

$$R_T^{eq} = \left.\frac{\partial r_f}{\partial T}\right|_{T,\left(n_A^{eq}(T)\right)} - \left.\frac{\partial r_b}{\partial T}\right|_{T,\left(n_B^{eq}(T)\right)}$$

The sign of this quantity is strongly dependent on the form of the kinetics. Indeed if the temperature increases, both $r_f(T, n_A)$ and $r_b(T, n_B)$ increase so that there is some kind of competition between the forward and the backward reaction. $\lim_{T\to 0} n_A^{eq}(T) \geq \lim_{T\to\infty} n_A^{eq}(T)$ so that there exists at least one range of temperature such that $\frac{dn_A^{eq}}{dT} < 0$ and thus $\frac{dr^{eq}}{dT} > 0$. In that temperature range the last term of (2.16) is positive. Depending on the reaction kinetics and the values of the system parameters, it can become large enough so that $\frac{d\Delta^{eq}}{dT} > 0$ for some temperature interval. Then the function $\Delta^{eq}(T)$ has two extrema at the limits of this interval: a minimum at the lower bound and a maximum

at the upper bound. Depending of the value of this minimum and maximum, $\Delta^{eq}(T)$ can have up to two additional zeros for each interval where $\frac{d\Delta^{eq}}{dT} > 0$. In the most common cases (for instance with Arrhenius type kinetics), there is only one interval where $\frac{d\Delta^{eq}}{dT} > 0$. Then $\Delta^{eq}(T)$ has up to three zeros. This case is shown in Figure 2.3. However since we have assumed more general kinetics, we cannot exclude the cases where there are two or more intervals where $\frac{d\Delta^{eq}}{dT} > 0$. The maximal number of zeros of $\Delta^{eq}(T)$ is then equal to $2\omega + 1$ where ω is the number of intervals where $\frac{d\Delta^{eq}}{dT} > 0$. As a consequence, depending on the values of the parameters and the kinetics, the system (2.5) can have up to $2\omega + 1$ equilibria.

Assumption 2.11. The values of the parameters of the CSTR and the form of the reaction kinetics are such that the system (2.5) has three distinct equilibria.

We do not loose any generality with this assumption as it shall be seen in Remark 2.8.

Remark 2.5. *The conditions on the parameters in order to have three equilibria can be found in [93] for the simplified CSTR model with a first-order irreversible reaction.*

Remark 2.6. *In the case of an irreversible endothermic reaction, there is only one single equilibrium. Indeed the last term of* (2.16) *is always negative since* $\frac{dr^{eq}}{dT} = -\frac{q_l}{V}\frac{dn_A^{eq}}{dT} > 0$. *In the case of a reversible reaction, there can exist an interval where* $\frac{dr^{eq}}{dT} = -\frac{q_l}{V}\frac{dn_A^{eq}}{dT} < 0$ *so that the last term can become positive so that there could be multiple equilibrium points.*

2.2.2 Stability of the equilibrium points

The stability of the three equilibrium points can be analyzed by using Lyapunov's first theorem. The analysis is based on a linearization of the system around the equilibrium points. Indeed the trajectories of the system around hyperbolic equilibria are topologically equivalent to those of the linearized system. Therefore let us take the Jacobian matrix of the system (2.5) around each of the equilibrium points $\left(\bar{U}, \bar{n}_A, \bar{n}_B\right)$.

From Assumption 2.7, we have:

$$\mathrm{d}U = \mathscr{C}_v V \mathrm{d}T + \sum_{i=A,B,I} u_i \mathrm{d}n_i$$

where $u_i = \left(\frac{\partial U}{\partial n_i}\right)_{V,T}$ is the partial molar internal energy of component i and $\mathscr{C}_v$ is the volumetric constant volume heat capacity of the mixture:

$$\mathscr{C}_v V = \sum_{i=A,B,I} n_i C_{v_i}$$

with C_{v_i} the constant volume molar heat capacity of component i. As a consequence:

$$\frac{\partial \tilde{T}}{\partial U} = \frac{1}{\mathscr{C}_v V} \quad \text{and} \quad \frac{\partial \tilde{T}}{\partial n_i} = -\frac{u_i}{\mathscr{C}_v V}$$

Furthermore we have:

$$\frac{\partial \tilde{H}}{\partial T} = \mathscr{C}_p V$$

so that:

$$\frac{\partial \tilde{H}}{\partial U} = \frac{\partial \tilde{H}}{\partial T}\frac{\partial \tilde{T}}{\partial U} = \frac{\mathscr{C}_p}{\mathscr{C}_v}$$

From Assumption 2.10, we have $C_{p_i} = C_{v_i}$ and thus $\mathscr{C}_p = \mathscr{C}_v$ such that finally:

$$\frac{\partial \tilde{H}}{\partial U} = 1$$

Hence the Jacobian matrix $\mathbf{\Lambda}$ of (2.5) around the equilibrium points $\left(\bar{U}, \bar{n}_A, \bar{n}_B\right)$ is given by the following expression, evaluated at $\left(\bar{U}, \bar{n}_A, \bar{n}_B\right)$:

$$\mathbf{\Lambda} = \begin{pmatrix} -\frac{q_l}{V} - \frac{\kappa}{\mathscr{C}_v V} & \kappa\frac{u_A}{\mathscr{C}_v V} & \kappa\frac{u_B}{\mathscr{C}_v V} \\ \frac{-R_T}{\mathscr{C}_v V} & -\frac{q_l}{V} - R_A + R_T\frac{u_A}{\mathscr{C}_v V} & -R_B + R_T\frac{u_B}{\mathscr{C}_v V} \\ \beta\frac{R_T}{\mathscr{C}_v V} & -\beta\left(R_T\frac{u_A}{\mathscr{C}_v V} - R_A\right) & -\frac{q_l}{V} - \beta\left(-R_B + R_T\frac{u_B}{\mathscr{C}_v V}\right) \end{pmatrix} \tag{2.18}$$

where the following notation has been introduced:

$$R_T = \left(\frac{\partial\left(rV\right)}{\partial T}\right)$$

and

$$R_Y = \left(\frac{\partial\left(rV\right)}{\partial n_Y}\right) \quad \text{with } Y = A, B$$

From Assumption 2.10 we have:

$$(-\Delta_r H)(T) = h_A - \beta h_B = u_A - \beta u_B$$

As a consequence it can be shown that the characteristic polynomial of $\mathbf{\Lambda}$ is given by the following expression:

$$P_c(\lambda) = \left(\frac{q_l}{V} + \lambda\right)\left[\left(\frac{q_l}{V} + \lambda\right)^2 + \frac{\kappa}{\bar{\mathscr{C}_v} V}\left(\bar{R}_A - \beta \bar{R}_B\right) + \left(\frac{q_l}{V} + \lambda\right)\left(\frac{\kappa}{\bar{\mathscr{C}_v} V} + \left(\bar{R}_A - \beta \bar{R}_B\right) - \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V}\bar{R}_T\right)\right]$$

and the eigenvalues of $\mathbf{\Lambda}$ are equal to:

$$\lambda_1 = -\frac{q_l}{V} \tag{2.19a}$$

$$\lambda_2 = -\frac{q_l}{V} + \frac{1}{2}\left[-\frac{\kappa}{\bar{\mathscr{C}_v} V} - \left(\bar{R}_A - \beta \bar{R}_B\right) + \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V}\bar{R}_T + \sqrt{\varphi}\right] \tag{2.19b}$$

$$\lambda_3 = -\frac{q_l}{V} + \frac{1}{2}\left[-\frac{\kappa}{\bar{\mathscr{C}_v} V} - \left(\bar{R}_A - \beta \bar{R}_B\right) + \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V}\bar{R}_T - \sqrt{\varphi}\right] \tag{2.19c}$$

where the notation $\bar{Y}$ holds for the value of Y at the equilibrium (with Y a function of U, n_A and n_B). The discriminant φ is equal to:

$$\varphi = \left[\frac{\kappa}{\bar{\mathscr{C}_v} V} + \left(\bar{R}_A - \beta \bar{R}_B\right) - \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V}\bar{R}_T\right]^2 - 4\frac{\kappa}{\bar{\mathscr{C}_v} V}\left(\bar{R}_A - \beta \bar{R}_B\right) \tag{2.20}$$

λ_1 is obviously negative. It is straightforward to note that λ_2 is the first eigenvalue to test to evaluate the (in)stability of each equilibrium point.

The sign of λ_2 is linked to the sign of $\frac{d\Delta^{eq}}{dT}$. First let us consider the intermediate equilibrium point. At this equilibrium point $\frac{d\Delta^{eq}}{dT}$ is positive. Besides from the expression of $(-\Delta_r H)$, we have $\frac{d(-\Delta_r H)}{dT} = C_{p_A} - \beta C_{p_B}$. A simple calculation allows to derive the following relation from (2.6):

$$\frac{d(-\Delta_r H)}{dT}\bar{r}V = \bar{r}V\left(C_{p_A} - \beta C_{p_B}\right) = -q_l \bar{\mathscr{C}_p} + q_l \mathscr{C}_p^{in}$$

At the intermediate equilibrium point $\frac{d\Delta^{eq}}{dT} > 0$ and we have the following

inequality:

$$\begin{aligned} 0 &< -\kappa - q_l \bar{\mathscr{C}_p^{in}} + \bar{r} V \frac{d\left(-\Delta_r H\right)}{dT} + \left(-\overline{\Delta_r H}\right) V \left.\frac{dr^{eq}}{dT}\right|_{\bar{T}} \\ &= -\kappa - q_l \bar{\mathscr{C}_p} + \frac{q_l}{V} \frac{\left(-\overline{\Delta_r H}\right) \bar{R}_T}{\bar{R}_A - \beta \bar{R}_B + \frac{q_l}{V}} \\ 0 &> \left(\kappa + q_l \bar{\mathscr{C}_p}\right) \left(\bar{R}_A - \beta \bar{R}_B + \frac{q_l}{V}\right) - \frac{q_l}{V} \left(-\overline{\Delta_r H}\right) \bar{R}_T \end{aligned} \tag{2.21}$$

λ_2 and λ_3 are the roots of the following polynomial:

$$\begin{aligned} &\left(\frac{q_l}{V} + \lambda\right)^2 + \left(\frac{q_l}{V} + \lambda\right) \left(\frac{\kappa}{\bar{\mathscr{C}_v} V} + \left(\bar{R}_A - \beta \bar{R}_B\right) - \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V} \bar{R}_T\right) \\ &+ \frac{\kappa}{\bar{\mathscr{C}_v} V} \left(\bar{R}_A - \beta \bar{R}_B\right) \\ &= \lambda^2 + \lambda \left(\frac{\kappa}{\bar{\mathscr{C}_v} V} + \left(\bar{R}_A - \beta \bar{R}_B\right) - \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V} \bar{R}_T + 2 \frac{q_l}{V}\right) \\ &+ \frac{\left(\kappa + q_l \bar{\mathscr{C}_p}\right)}{\bar{\mathscr{C}_v} V} \left(\bar{R}_A - \beta \bar{R}_B + \frac{q_l}{V}\right) - \frac{q_l}{V} \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V} \bar{R}_T \end{aligned} \tag{2.22}$$

As already mentioned $\frac{\bar{\mathscr{C}_p}}{\bar{\mathscr{C}_v}} = 1$ and the independent term of this polynomial is equal to the right-hand term of (2.21) divided by $\bar{\mathscr{C}_v} V$. The independent term is equal to the product of the two roots. It is negative and consequently λ_2 and λ_3 are real and have different signs. $\lambda_2 > \lambda_3$ and it is obvious that $\lambda_2 > 0$ and $\lambda_3 < 0$.

A similar development for the extremal equilibrium points leads to analog results. The sign of (2.21) is inverted and thus the independent term of (2.22) is positive. Moreover since we are at the extremal equilibria points, the term $\frac{q_l}{V} \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V} \bar{R}_T$ is assumed to be small compared to the other ones, so that the coefficient of the first-order term is positive, too. As a consequence the extreme equilibrium points are asymptotically stable.

Remark 2.7. *The assumption that the coefficient of the first order term is positive is referred to as the "dynamic" stability condition in [93]. However it is possible that for some values of the parameters or some forms of the kinetics this assumption is not fulfilled. Then more exotic behaviours such as periodic solutions and limit cycles may occur. [93] presents the conditions on the parameters for which the dynamic stability condition is broken in the case of an*

irreversible reaction with first-order Arrhenius type kinetics and the associated behaviour.

Remark 2.8. *The sign of λ_2 is linked to the sign of $\frac{d\Delta^{eq}}{dT}$. Hence the above result can be extended easily to all the cases with an* odd *number of equilibrium points. All the zeros of $\Delta^{eq}(T)$ situated on increasing parts of $\Delta^{eq}(T)$ lead to unstable equilibrium points whereas the zeros which are in the decreasing parts of $\Delta^{eq}(T)$ lead to asymptotically stable equilibrium points. As a direct consequence a CSTR with an irreversible endothermic reaction has a single asymptotically stable equilibrium.*

If the system has an even *number of equilibrium points, then this means that at least one of these is such that $\frac{d\Delta^{eq}}{dT} = 0$. Then one of the eigenvalues of $\mathbf{\Lambda}$ is equal to zero*[1] *and nothing can be said about the stability using Lyapunov's first theorem. This special case shall not be considered in this study. A possible way to study this case could be to use the Centre Manifold Theorem [63][77].*

2.3 Internal energy balance versus temperature equation

In the literature, the most often used model for the CSTR is a simplified version of (2.5). Indeed the temperature is used as a state variable instead of the internal energy.

First let us consider the total enthalpy of the mixture:

$$H = \sum_{i=A,B,I} n_i h_i = \mathscr{C}_p V (T - T_0) + \sum_{i=A,B,I} n_i h_{0_i} \tag{2.23}$$

The time derivative of (2.23) is given by the following expression:

$$\frac{dH}{dt} = \mathscr{C}_p V \frac{dT}{dt} + \sum_{i=A,B,I} \frac{dn_i}{dt} \left[C_{p_i} (T - T_0) + h_{0_i}\right] \tag{2.24}$$

Besides from Assumption 2.10, we can deduce the following equality:

$$\frac{dH}{dt} = \frac{d}{dt}\left(\sum_{i=A,B,I} n_i h_i\right) = \frac{d}{dt}\left(\sum_{i=A,B,I} n_i u_i\right) = \frac{dU}{dt} \tag{2.25}$$

[1] Indeed the 0-order term of (2.22) is equal to zero.

By equating (2.24) and (2.25), one directly obtains:

$$\frac{dU}{dt} = \frac{dH}{dt} = \mathscr{C}_p V \frac{dT}{dt} + \sum_{i=A,B,I} \frac{dn_i}{dt} \left[C_{p_i} \left(T - T_0 \right) + h_{0_i} \right] \tag{2.26}$$

The time derivative of the internal energy U and of the quantity of each species n_i are given by (2.5). By inserting the corresponding expressions into (2.26), one finally obtains the following relation for the temperature evolution:

$$\begin{aligned} \mathscr{C}_p \left(n_A, n_B \right) V \frac{dT}{dt} = \kappa \left(T_w - T \right) + q_l \mathscr{C}_p^{in} \left(T^{in} - T \right) \\ + r \left(T, n_A, n_B \right) V \left(-\Delta_r H \right) \left(T \right) \end{aligned} \tag{2.27}$$

In fact this is equivalent to the following change of variables:

$$T = \tilde{T} \left(U, n_A, n_B \right) = \frac{U - \left(-\mathscr{C}_p V T_0 + \sum_{i=A,B,I} n_i h_{0_i} \right)}{\mathscr{C}_p V} \tag{2.28}$$

(2.28) is a bijection and thus the following system is also a dynamical model for the CSTR that is equivalent to (2.5):

$$\begin{cases} \mathscr{C}_p \left(n_A, n_B \right) V \dfrac{dT}{dt} = \kappa \left(T_w - T \right) + q_l \mathscr{C}_p^{in} \left(T^{in} - T \right) \\ \qquad\qquad + r \left(T, n_A, n_B \right) V \left(-\Delta_r H \right) \left(T \right) \\ \dfrac{dn_A}{dt} = \dfrac{q_l}{V} \left(C_A^{in} V - n_A \right) - r \left(T, n_A, n_B \right) V \\ \dfrac{dn_B}{dt} = -\dfrac{q_l}{V} n_B + \beta r \left(T, n_A, n_B \right) V \end{cases} \tag{2.29}$$

Remark 2.9. *In order to obtain the above system we had to introduce Assumption 2.10 directly. In the previous development the Assumption 2.10 has been introduced only in Section 2.2.2, i.e. for evaluating the stability characteristics of the equilibria. This means that in reality the previous developments, i.e. the model and the number of equilibrium points, are also valid without Assumption 2.10 such as for instance for a gaseous CSTR. This would not be the case if* (2.29) *had been used instead of* (2.5)*.*

Even if (2.29) is very similar to the CSTR model usually used in the literature (see e.g. [13][93][99]), it is worth emphasizing the differences. The model

usually used in the literature is in fact a simplification of (2.29), and more precisely of the temperature differential equation.

Firstly (2.27) is usually referred to as the "heat balance equation" or even sometimes as the energy conservation equation. Although it is a consequence of the internal energy conservation (but also of the mass balance equations as it can be seen in (2.24)), the terminology "energy conservation equation" for (2.27) is inadequate for the energy does not appear explicitly on the left-hand side, and $r\left(T, n_A, n_B\right) V\left(-\Delta_r H\right)(T)$ is a production/consumption term which is paradoxical when talking about a conserved quantity. The term "heat-balance" is also a bit awkward, since heat is something which is transferred and is not a property of the system itself (it has no sense to talk about the heat of the liquid or of the reactor), over which you can make a balance. It would perhaps be better to talk about "thermal energy".

Then, in many papers the reaction heat $(-\Delta_r H)$ is considered to be independent of the temperature. This assumption is only valid if small ranges of temperatures are considered. Furthermore the volume heat capacity of the mixture is assumed to be independent of the composition, i.e. $\mathscr{C}_p^{in} = \mathscr{C}_p$ for all (n_A, n_B).

The risk of these simplifications is to result in a loss of information about the thermodynamic characteristics of the system. Therefore we shall be considering the more general forms (2.5) or (2.29) whenever possible.

Remark 2.10. *By using Assumptions 2.8 and 2.9, it is easy to see in* (2.29) *that the orthant* $\{n_A > 0, n_B > 0, T > 0\}$ *is invariant for the system*[1]*. The states outside of this orthant have no physical meaning. Therefore we shall restrict our analysis to the postive orthant in the sequel of this thesis.*

2.4 Conclusion

This chapter presents well-known results about the dynamical behaviour of the open-loop exothermic CSTR. Nevertheless the results have been obtained using less tight assumptions than in most of the works dedicated to the CSTR control

[1]Indeed $T^{in} > 0$ and $T_w > 0$.

problem. In particular the assumptions on the reaction kinetics can be easily interpreted from a physical point of view (e.g. Assumption 2.8 translates the fact that without reactant there is no reaction, and that the more reactant there is, the faster the reaction) and are valid for a broad range of chemical reactions. Although Arrhenius-type temperature dependence of the reaction rate or mass action law are included in the assumptions, they are not necessary for the study of the dynamical behaviour of the CSTR.

Moreover the study of the dynamical behaviour has not been conducted using the usual state variables (i.e. temperature and concentration). Indeed we have worked with variables representing the extensive quantities and which are in fact those which are actually used for modelling the CSTR. At first sight, this approach only consists in simple change of variable and thus it seems trivial that the same results are obtained. But, as we have explained in this chapter, a closer look shows that the model usually used in the literature (i.e. with the temperature equation instead of the internal energy balance) requires more restricting assumptions, such as Assumption 2.10 (equality of the molar internal energy and the molar enthalpy of the species) for instance. This chapter emphasizes the assumptions that are hidden when using directly the temperature equation (e.g. mixture heat capacity that is independent of the composition, reaction heat that is independent of the temperature, equality of the molar internal energy and the molar enthalpy of the species). These assumptions are not necessary and the results are valid in a more general case.

Chapter 3

A thermodynamic point of view[1]

The analysis and design of control algorithms are largely based on system theory tools, and in particular on the stability "à la Lyapunov" and the passivity. Historically, this has indeed been intrinsically based and justified on energy considerations (e.g. [105]), although now other physical quantities have also been considered. It is therefore natural to consider the thermodynamic theory for the control design of chemical processes. However, if in many situations it is rather easy to describe the Lyapunov theory and passivity in terms of energy for electrical and mechanical systems, this is unfortunately not the case for reaction systems. Hence other physical quantities have to be considered, such as for instance in the passivity based approach of Alonso and Ydstie who used the availability as a storage function [3][4], or the approach in [88] where the entropy production has been used as a Lyapunov function in the case of the flash separator.

The objective of this chapter is to present several old and new results that aim at linking the thermodynamics and the system theory concepts via the CSTR case study. As already shown in the previous chapter, the choice of the

[1]The content of this chapter has been published in [36].
http://dx.doi.org/doi:10.1016/j.jprocont.2008.07.007

CSTR is indeed driven by its simplicity while emphasizing typical important features of reaction system models: it combines energy and mass balances, it is nonlinear and is possibly characterized by multiple steady states, the system state variables (concentration, temperature) are non-negative, it is an open system and the balance equations combine kinetics and hydrodynamics. The CSTR has also been largely studied in the literature, yet the way to systematically link thermodynamics and stability theory even for this apparently simple case study remains an open question. The main reason is probably due to the complexity of the chemical thermodynamics and the difficulty to link its concepts with those of system theory. As a matter of example, the notion of entropy is a priori very attractive to analyze the stability of a reaction system (and therefore of the CSTR model) but, as it will be illustrated in the present chapter, its transcription in terms of Lyapunov based stability is not obvious. It is probably worth noting that the negativeness of the entropy production variation can be emphasized with linear phenomenological laws while no general demonstration is available with nonlinear ones (which corresponds indeed to a large class of chemical systems) (e.g. [25]). Symptomatically, so far the efforts to take advantage of the positivity of the state variables to consider Lyapunov functions that are not the classical quadratic functions (representative of the energy of mechanical and electrical systems, but not of reactions systems) have produced very limited results, the most illustrative one being the logarithm based function suggested by Feinberg [38] for isothermal reactors. Our objective in the present chapter is to clarify as much as possible the reasons that makes the stability analysis with thermodynamic functions so complex. With that respect the paper of Rouchon and Creff [88] dedicated to the flash case study (i.e. without reaction) provides a good basis for an appropriate explanation: the main difficulty for such a thermodynamics based stability analysis arise from the reaction terms in the balance models.

The dynamical equations for the CSTR from mass and energy balances have already been derived in Chapter 2. The core of the chapter is concerned with the physical interpretation of the stability analysis of the CSTR. It shall be performed by considering first the linearized model of the CSTR and the first method of Lyapunov (Section 3.1), then using the second method of

Lyapunov and the related stability theory results (Section 3.2). Several thermodynamics based functions will be considered for the stability analysis. We shall indeed successively consider entropy-based Lyapunov function candidates in Section 3.2.1 (the entropy and the entropy production), and energy-based Lyapunov function candidates in Section 3.2.2.

3.1 Stability analysis based on the linearized model of the CSTR (Lyapunov's first method)

As demonstrated in Section 2.2.1, the CSTR has three equilibrium points. Using Lyapunov's first method we have shown in Section 2.2.2 that the two extreme ones are asymptotically stable whereas the intermediate one is unstable. Yet we have only considered the sign of the real part of the eigenvalues of the linearized system around the equilibria. We did not link the characteristics of the linearized system with any thermodynamic property of the system.

In his paper of 1986 [42], Georgakis has considered extensive thermodynamic variables to analyze and give a physical interpretation of the slow and fast modes of different chemical process case studies, and in particular of an isothermal CSTR and of a simplified adiabatic CSTR. The argument is based on the rewriting of the linearized tangent model by considering the state transformation:

$$z = \Sigma^t \tilde{x}$$

with $\tilde{x} = \left[U - \bar{U}, n_A - \bar{n}_A, n_B - \bar{n}_B\right]^t$ and Σ the eigenvector matrix associated to the transpose of the state matrix of the linearized tangent $\mathbf{\Lambda}^t$ given in (2.18). Then the dynamics in z are equal to:

$$\frac{dz}{dt} = Dz$$

with D the diagonal matrix of the eigenvalues of $\mathbf{\Lambda}$. In his simplified adiabatic reactor example, Georgakis shows that two entries of the vector z are associated to the system reaction invariants (see e.g. [39][41]) while the third

one is associated with the reaction rate and is a mode of the reaction variant subspace. Let us apply this approach to our CSTR example. The variables z are then written as follows:

$$\begin{aligned} z_1 &= \beta\tilde{n}_A + \tilde{n}_B \\ z_2 &= \left(\frac{q_l}{V} + \lambda_2\right)\left(\tilde{U} - \bar{u}_A\tilde{n}_A - \bar{u}_B\tilde{n}_B\right) + \left(\bar{R}_A - \beta\bar{R}_B\right)\tilde{U} \\ &\quad + \left(\bar{R}_B\bar{u}_A - \bar{R}_A\bar{u}_B\right)\left(\beta\tilde{n}_A + \tilde{n}_B\right) \\ z_3 &= \left(\frac{q_l}{V} + \lambda_3\right)\left(\tilde{U} - \bar{u}_A\tilde{n}_A - \bar{u}_B\tilde{n}_B\right) + \left(\bar{R}_A - \beta\bar{R}_B\right)\tilde{U} \\ &\quad + \left(\bar{R}_B\bar{u}_A - \bar{R}_A\bar{u}_B\right)\left(\beta\tilde{n}_A + \tilde{n}_B\right) \end{aligned}$$

where $\tilde{U}$, $\tilde{n}_A$ and $\tilde{n}_B$ are the deviation variables in the linearized tangent model of the system of U, n_A and n_B, respectively. The unstable mode is associated to z_2 while the other two are stable. In the above general case, it is possible to give a physical interpretation to z_1. It is indeed proportional to the total mass in the reactor m_{tot}:

$$\begin{aligned} m_{tot} &= M_A n_A + M_B n_B + M_I n_I \\ &= z_1 M_B + M_I n_I + \left(\beta\bar{n}_A + \bar{n}_B\right) M_B \end{aligned}$$

with M_i the molecular weight of the species i, and by stoichiometry, $M_A = \beta M_B$. n_I is constant and z_1 is therefore proportional to the difference of mass with respect to the mass at equilibrium. Indeed from (2.6) it is easy to see that the total mass is the same for the three equilibria:

$$\begin{aligned} \bar{m}_{tot} &= M_A\bar{n}_A + M_B\bar{n}_B + M_I n_I \\ &= M_I n_I + \left(\beta\bar{n}_A + \bar{n}_B\right) M_B \\ &= M_I n_I + \beta C_A^{in} V M_B \end{aligned}$$

In fact the plane $z_1 = 0$ is the reaction invariant of the system.

In the adiabatic case ($\kappa = 0$), the eigenvalues λ_2 and λ_3 and the associated variables z_2 and z_3 are equal to:

$$\lambda_2 = -\frac{q_l}{V} - \left(\bar{R}_A - \beta\bar{R}_B\right) + \frac{\left(-\overline{\Delta_r H}\right)}{\bar{\mathscr{C}_v} V} \qquad \lambda_3 = -\frac{q_l}{V}$$

$$z_2 = \bar{R}_A\tilde{n}_A + \bar{R}_B\tilde{n}_B + \bar{R}_T\tilde{T} \qquad z_3 = \tilde{U}$$

The result is completely similar to the one in [42], i.e. the three variables z_i ($i = 1, 2, 3$) are related to the deviations to the total mass, the reaction rate, and to the internal energy, respectively. This means that, in line with [42], we can conclude that the stable modes are associated to the total mass and internal energy and the unstable is associated to the reaction rate.

Note that the result is valid by only assuming that the molar internal energies only depend on the temperature, an assumption used to write that

$$\frac{\partial \tilde{T}}{\partial U} = \frac{1}{\mathscr{C}_v V} \quad \text{and} \quad \frac{\partial \tilde{T}}{\partial n_i} = -\frac{u_i}{\mathscr{C}_v V}$$

With that respect, the above result extends that of [42] for less restrictive assumptions on the system dynamics and thermodynamics.

3.2 Stability analysis based on the Lyapunov's second method

3.2.1 Entropy-based stability analysis

Entropy and entropy production

As explained in Section 1.3.4, the Gibbs' relation (1.7) for a quasi-static process provides the basis for calculating the time variation of the entropy :

$$\frac{dS}{dt} = \frac{1}{T}\frac{dU}{dt} - \frac{\mu^t}{T}\frac{dn}{dt} + \frac{P}{T}\frac{dV}{dt} \tag{3.1}$$

In our case $\frac{dV}{dt} = 0$ as shown in Chapter 2. By introducing (1.10) this relation can also be written as follows:

$$\frac{dS}{dt} = \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_X \frac{dX}{dt}$$

where X denotes the state of the system, i.e. $X = [U, n_A, n_B, n_I]$. The balance equations for the energy and the quantity of A and B are given by (1.12) and (1.13) so that the above relation becomes as follows:

$$\frac{dS}{dt} = \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_X \left(\mathcal{F}_X^{in} - \mathcal{F}_X^{out}\right) + \left.\frac{\partial^t \tilde{S}}{\partial n}\right|_X \sigma_n + \left.\frac{\partial \tilde{S}}{\partial U}\right|_X \dot{Q} \tag{3.2}$$

where $\mathcal{F}_X^j = \left[\mathcal{F}_U^j, \mathcal{F}_A^j, \mathcal{F}_B^j, \mathcal{F}_I^j\right]^t$ $(j = in, out)$ represents the inlet and outlet flows of X, and $\sigma_n = [\sigma_A, \sigma_B]^t$ stands for the consumption/production rate of A and B by the chemical reaction, respectively.

By considering the inlet and outlet entropy flow rates by convection $\mathcal{F}_S^{in}$ and $\mathcal{F}_S^{out}$ and the entropy flow rate due to thermal exchange $\frac{\dot{Q}}{T_w}$, the entropy production can be deduced from (3.2) as follows:

$$\begin{aligned}\sigma_S &= \frac{dS}{dt} - \left(\mathcal{F}_S^{in} - \mathcal{F}_S^{out} + \frac{\dot{Q}}{T_w}\right) \\ &= \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_X \left(\mathcal{F}_X^{in} - \mathcal{F}_X^{out}\right) + \left.\frac{\partial^t \tilde{S}}{\partial n}\right|_X \sigma_n + \left(\left.\frac{\partial \tilde{S}}{\partial U}\right|_X - \frac{1}{T_w}\right)\dot{Q} - \mathcal{F}_S^{in} + \mathcal{F}_S^{out}\end{aligned} \tag{3.3}$$

From the homogeneity of the reactor (Assumption 2.1), we have:

$$S = \frac{V}{q_l}\mathcal{F}_S^{out} \quad \text{and} \quad X = \frac{V}{q_l}\mathcal{F}_X^{out} \tag{3.4}$$

Since the entropy is a homogeneous function of degree 1, we can write:

$$S = \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_X X$$

This implies that:

$$\mathcal{F}_S^{out} = \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_X \mathcal{F}_X^{out} \tag{3.5}$$

Moreover since there is only one inlet flow, the above relation (3.5) is also true for the inlet entropy flow rate:

$$\mathcal{F}_S^{in} = \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_{X^{in}} \mathcal{F}_X^{in}$$

The entropy production (3.3) can then be rewritten as follows:

$$\sigma_S = \left(\left.\frac{\partial^t \tilde{S}}{\partial X}\right|_X - \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_{X^{in}}\right)\mathcal{F}_X^{in} + \left.\frac{\partial^t \tilde{S}}{\partial n}\right|_X \sigma_n + \left(\left.\frac{\partial \tilde{S}}{\partial U}\right|_X - \frac{1}{T_w}\right)\dot{Q} \tag{3.6}$$

Let us now concentrate more specifically on the CSTR example. The balance equations for the energy and the quantity of A and B are given by (2.1)

and (2.3). The entropy balance for the CSTR is obtained by introducing those balance equations into (3.1):

$$\begin{aligned}\frac{dS}{dt} &= q_l \mathscr{C}_p^{in} \frac{\left(T^{in} - T_0\right)}{T} + q_l \frac{\left(C_A^{in} h_{0_A} + C_I h_{0_I}\right)}{T} - \frac{q_l}{V}\frac{H}{T} - \kappa \frac{(T - T_w)}{T} \\ &+ \frac{(\mu_A - \beta\mu_B)}{T} rV - \frac{q_l}{V}\frac{1}{T}\left[\left(C_A^{in} V - n_A\right)\mu_A - n_B\mu_B\right]\end{aligned} \tag{3.7}$$

The entropy of an ideal liquid mixture is given by the following relationship [91]:

$$S = \mathscr{C}_p V \ln\left(\frac{T}{T_0}\right) - R \sum_{i=A,B,I} \left[n_i \ln\left(\frac{n_i}{N}\right)\right] + \sum_{i=A,B,I} n_i s_{0_i} \tag{3.8}$$

where $N = n_A + n_B + n_I$ is the total quantity of matter in the liquid and s_{0_i} is the reference molar entropy of component i. The chemical potential μ_i of the species i in an ideal liquid is given as follows[1]:

$$\mu_i = -T\frac{\partial \tilde{S}}{\partial n_i} = -TC_{p_i} \ln\left(\frac{T}{T_0}\right) + RT \ln\left(\frac{n_i}{N}\right) - Ts_{0_i} + C_{p_i}\left(T - T_0\right) + h_{0_i} \tag{3.9}$$

Remark 3.1. *The expression given in* (3.8) *gives a non-zero entropy at the absolute zero temperature. However this fact is not in contradiction with the third law of thermodynamics, which states that the entropy is zero at 0 K for perfect crystalline substances, and an ideal liquid is obviously not a perfect crystalline substance [68][72][91]. Furthermore the expression* (3.8) *is classically used in literature [19][91] and is valid as far as the ration* $\frac{T}{T_0}$ *remains much greater than 1. Since we are working with an exothermic reactor we do not loose much generality by assuming that* $T >> T_0$ *and we are allowed to use* (3.8)*. In a crystal, the Debye theory indicates that the heat capacity is proprtionnal to* T^3 *at low temperatures. This leads to an entropy formulation that fulfills the third principle [68].*

The entropy production can be obtained from the entropy balance (i.e. (3.7) combined with (3.9)) by subtracting the net entropy fluxes coming from the environment:

- by heat transfer: $\mathcal{F}_S^{heat} = \dfrac{\dot{Q}}{T_w} = \kappa \dfrac{T_w - T}{T_w}$

[1] This relation has been obtained by inserting (3.8) into (1.10).

- by convection:

$$\mathcal{F}_S^{conv} = q_l C_A^{in}\left[C_{p_A}\ln\left(\frac{T^{in}}{T_0}\right) - R\ln\left(\frac{C_A^{in}}{C_I+C_A^{in}}\right) + s_{0_A}\right] + q_l C_I\left[C_{p_I}\ln\left(\frac{T^{in}}{T_0}\right) - R\ln\left(\frac{C_I}{C_I+C_A^{in}}\right) + s_{0_I}\right] - \frac{q_l}{V}S$$

Consequently the entropy production rate is equal to:

$$\sigma_S = \kappa\frac{(T-T_w)^2}{TT_w} + \frac{(\mu_A-\beta\mu_B)}{T}rV + q_l R C_I\left[\ln\left(\frac{C_I}{C_I+C_A^{in}}\right) - \ln\left(\frac{n_I}{N}\right)\right] + q_l\mathscr{C}_p^{in}\left[\frac{T^{in}-T}{T} + \ln\left(\frac{T}{T^{in}}\right)\right] + q_l R C_A^{in}\left[\ln\left(\frac{C_A^{in}}{C_I+C_A^{in}}\right) - \ln\left(\frac{n_A}{N}\right)\right] \tag{3.10}$$

It is easy to check that (3.10) corresponds to (3.6) for the particular case of the CSTR. Indeed let us develop the terms of (3.6) in the particular case of the CSTR:

$$\left(\left.\frac{\partial\tilde{S}}{\partial U}\right|_X - \frac{1}{T_w}\right)\dot{Q} = \left(\frac{1}{T}-\frac{1}{T_w}\right)\kappa\left(T_w-T\right) = \kappa\frac{(T-T_w)^2}{TT_w}$$

$$\left.\frac{\partial^t\tilde{S}}{\partial n}\right|_X \sigma_n = \begin{bmatrix} -\frac{\mu_A}{T} & -\frac{\mu_B}{T}\end{bmatrix}\begin{bmatrix} -rV \\ \beta rV\end{bmatrix} = \frac{(\mu_A-\beta\mu_B)}{T}rV$$

It is also possible to show that

$$\left(\left.\frac{\partial^t\tilde{S}}{\partial X}\right|_X - \left.\frac{\partial^t\tilde{S}}{\partial X}\right|_{X^{in}}\right)\mathcal{F}_X^{in} \tag{3.11}$$

$$= \begin{bmatrix} \frac{1}{T}-\frac{1}{T^{in}} \\ -\frac{\mu_A}{T}+\frac{\mu_A^{in}}{T^{in}} \\ -\frac{\mu_B}{T}+\frac{\mu_B^{in}}{T^{in}} \\ -\frac{\mu_I}{T}+\frac{\mu_I^{in}}{T^{in}}\end{bmatrix}^t\begin{bmatrix} q_l\mathscr{C}_p^{in}\left(T^{in}-T_0\right)+q_l\left(C_A^{in}h_{0_A}+C_I h_{0_I}\right) \\ q_l C_A^{in} \\ 0 \\ q_l C_I\end{bmatrix}$$

$$= q_l\mathscr{C}_p^{in}\left[\frac{T^{in}-T}{T}+\ln\left(\frac{T}{T^{in}}\right)\right] + q_l R C_I\left[\ln\left(\frac{C_I}{C_I+C_A^{in}}\right) - \ln\left(\frac{n_I}{N}\right)\right] + q_l R C_A^{in}\left[\ln\left(\frac{C_A^{in}}{C_I+C_A^{in}}\right) - \ln\left(\frac{n_A}{N}\right)\right]$$

but the computation is quite tedious and thus will not be shown here[1]. The different entropy sources can be identified on the basis of (3.10):

- heat transfer: $\kappa \frac{(T-T_w)^2}{TT_w}$
- chemical reaction: $\frac{(\mu_A - \beta\mu_B)}{T} rV$
- heat convection: $q_l \mathscr{C}_p^{in} \left[\frac{T^{in}-T}{T} + \ln\left(\frac{T}{T^{in}}\right) \right]$
- mixing:

$$q_l R C_A^{in} \left[\ln\left(\frac{C_A^{in}}{C_I + C_A^{in}}\right) - \ln\left(\frac{n_A}{N}\right) \right] + q_l R C_I \left[\ln\left(\frac{C_I}{C_I + C_A^{in}}\right) - \ln\left(\frac{n_I}{N}\right) \right]$$

The second law of thermodynamics tells us that the entropy production is always non-negative. Since the above-mentioned effects are independent from each other, the entropy production for each of them has to be non-negative. For the heat transfer, this implies that $\kappa \geq 0$, i.e. the conductive heat transfer has to go from the warm source to the cold source. For the heat convection and for the mixing, it is straightforward to check that the above expressions are non-negative.

For the entropy production due to the reaction, there is indeed an apparent contradiction. $(\mu_A - \beta\mu_B)$ is the affinity of the reaction and r is the reaction rate. On one hand, thermodynamics considers that all reactions are reversible and the equilibrium is reached when the affinity is equal to zero. Therefore if the affinity is positive, the reaction should progress towards a production of B, i.e. $r > 0$, and if the affinity is negative, the reaction should progress towards a production of A, i.e. $r < 0$. This guarantees the positivity of entropy production but excludes the existence of irreversible reactions.

On the other hand, the assumptions of Chapter 2 on the kinetics do not imply that the reaction always evolves in the direction that reduces the affinity. Furthermore, the assumptions allow the existence of irreversible reactions (by choosing $r_b = 0$). Indeed kinetic theory considers the existence of irreversible reactions. Finally the kinetics models usually considered in chemical engineering very often do not depend on the affinity: this is indeed due to the fact that kinetics is largely based on experiments.

[1] For the calculation details, the reader can refer to Appendix B.

Let us calculate the affinity of the reaction:

$$\begin{aligned} Aff &= \mu_A - \beta\mu_B \\ &= -T\left(C_{p_A} - \beta C_{p_B}\right)\ln\left(\frac{T}{T_0}\right) - T\left(s_{0_A} - \beta s_{0_B}\right) \\ &\quad + \left(-\Delta_r H\right)(T) + RT\ln\left(\frac{n_A}{n_B^{\beta}}N^{\beta-1}\right) \end{aligned}$$

Note that only one term depends on the chemical composition of the mixture. At a given temperature, the affinity is positive if:

$$RT\ln\left(\frac{n_A}{n_B^{\beta}}N^{\beta-1}\right) > T\left(-\Delta_r S\right)(T) - \left(-\Delta_r H\right)(T)$$

with

$$\left(-\Delta_r S\right)(T) = \left(C_{p_A} - \beta C_{p_B}\right)\ln\left(\frac{T}{T_0}\right) + \left(s_{0_A} - \beta s_{0_B}\right)$$

the entropy variation of the reaction. If the reaction is highly exothermic (large $(-\Delta_r H)$) and if the reaction is such that $\Delta_r S > 0$ (more "disorder"), the affinity remains positive for very low concentration ratios $\frac{n_A}{n_B}$. This means that thermodynamics foresees a reversible reaction whose equilibrium is largely pushed towards high values of the reaction products. The reaction can then be considered to be practically completed and the entropy production remains positive up to very high conversions that are never reached in practice.

As mentioned in the introduction of Chapter 2, for the sake of coherence with thermodynamics, we shall consider here a reversible reaction. Note however that the results presented in the present manuscript are valid for irreversible reactions which can be considered as a particular case of reversible reactions for which the equilibrium is displaced to very low values of the reactant concentrations.

Remark 3.2. *The mixing (resp. heat convection) term of* (3.10) *represents the entropy creation due to the fact that the inlet flow is not at the same concentration (resp. temperature) as the reactor. The mixing of the inlet flow and the reactor content increases the disorder and this results in an entropy creation.*

In an ideal plug flow reactor these two contributions do not appear. Indeed an ideal plug flow reactor is the extreme ideal case where there is no mixing

and no heat conduction, and the content of the reactor is simply pushed along the reactor, contrary to a CSTR where total mixing is assumed. In a plug flow reactor the total entropy production is given by the following expression:

$$\sigma_S^{tot} = \int_0^A \phi \frac{(T - T_w)^2}{T T_w} \mathrm{d}A + \int_0^V \frac{\mu_A - \beta\mu_B}{T} r \mathrm{d}V$$

where V is the total volume of the reactor, A is the heat exchange area (assumed to be present along the whole reactor), ϕ is the heat transfer coefficient per unit area (i.e. $\kappa = \phi A$).

An ideal plug flow reactor is often represented as an infinite cascade of CSTRs. Let us therefore consider a cascade of m CSTRs in series. From (3.10)*, it is easy to find the total entropy production for the whole cascade:*

$$\begin{aligned}
\sigma_S^{tot} = & \sum_{i=1}^{m} \phi A^{(i)} \frac{\left(T^{(i)} - T_w\right)^2}{T^{(i)} T_w} + \sum_{i=1}^{m} \frac{\mu_A^{(i)} - \beta\mu_B^{(i)}}{T^{(i)}} r^{(i)} V^{(i)} \\
& + \sum_{i=1}^{m} \left[q_l \mathscr{C}_p^{(i-1)} \left(\frac{T^{(i-1)} - T^{(i)}}{T^{(i)}} + \ln\left(\frac{T^{(i)}}{T^{(i-1)}} \right) \right) \right] \\
& + \sum_{i=1}^{m} \sum_{j=A,B,I} q_l R C_j^{(i-1)} \left[\ln\left(\frac{C_j^{(i-1)}}{C^{(i-1)}} \right) - \ln\left(\frac{C_j^{(i)}}{C^{(i)}} \right) \right]
\end{aligned}$$

where the exponent (i) refers to the i^{th} reactor, C_j is the concentration of species j and $C = C_A + C_B + C_I$. By using the definition of the integral as a Riemannian sum, we can write the following relation:

$$\lim_{m\to\infty} \sum_{i=1}^{m} \left[\phi A^{(i)} \frac{\left(T^{(i)} - T_w\right)^2}{T^{(i)} T_w} \right] = \int_0^A \phi \frac{(T - T_w)^2}{T T_w} \mathrm{d}A \qquad \textit{with} \sum_{i=1}^{m} A^{(i)} = A$$

and

$$\lim_{m\to\infty} \sum_{i=1}^{m} \left[\frac{\mu_A^{(i)} - \beta\mu_B^{(i)}}{T^{(i)}} r^{(i)} V^{(i)} \right] = \int_0^V \frac{\mu_A - \beta\mu_B}{T} r \mathrm{d}V \qquad \textit{with} \sum_{i=1}^{m} V^{(i)} = V$$

This indeed corresponds to the two contributions in an ideal plug flow reactor.

Let us now consider the term corresponding to the mixing:

$$\begin{aligned}
\sigma_S^{mix} &= \sum_{i=1}^{m} \sum_{j=A,B,I} q_l R C_j^{(i-1)} \left[\ln\left(\frac{C_j^{(i-1)}}{C^{(i-1)}}\right) - \ln\left(\frac{C_j^{(i)}}{C^{(i)}}\right) \right] \\
&= -\sum_{j=A,B,I} \left[\sum_{i=1}^{m} q_l R C_j^{(i-1)} \left(\ln C_j^{(i)} - \ln C_j^{(i-1)} \right) \right] \\
&\quad + \sum_{i=1}^{m} \left[q_l R \sum_{j=A,B,I} \left(C_j^{(i-1)} \right) \left(\ln C^{(i)} - \ln C^{(i-1)} \right) \right] \\
&= -\sum_{j=A,B,I} \left[\sum_{i=1}^{m} q_l R C_j^{(i-1)} \left(\ln C_j^{(i)} - \ln C_j^{(i-1)} \right) \right] \\
&\quad + \sum_{i=1}^{m} \left[q_l R C^{(i-1)} \left(\ln C^{(i)} - \ln C^{(i-1)} \right) \right]
\end{aligned}$$

Let us now take the limit for an infinite number of CSTRs with $C_j^{(0)} = C_j^{in}$, $C_j^{(m)} = C_j^{out}$ *and* $C_j^{(i-1)} < C_j^{(i)}$*:*

$$\begin{aligned}
&\lim_{m\to\infty} \sum_{j=A,B,I} \left[\sum_{i=1}^{m} q_l R C_j^{(i-1)} \left(\ln C_j^{(i)} - \ln C_j^{(i-1)} \right) \right] \\
&= q_l R \sum_{j=A,B,I} \int_{\ln C_j^{in}}^{\ln C_j^{out}} C_j \mathrm{d}\left(\ln C_j\right) = q_l R \sum_{j=A,B,I} \int_{C_j^{in}}^{C_j^{out}} \mathrm{d}C_j \\
&= q_l R \sum_{j=A,B,I} \left(C_j^{out} - C_j^{in} \right) = q_l R \left(C^{out} - C^{in} \right)
\end{aligned}$$

and

$$\begin{aligned}
&\lim_{m\to\infty} \sum_{i=1}^{m} \left[q_l R C^{(i-1)} \left(\ln C^{(i)} - \ln C^{(i-1)} \right) \right] \\
&= q_l R \int_{\ln C^{in}}^{\ln C^{out}} C \mathrm{d}\left(\ln C\right) = q_l R \int_{C^{in}}^{C^{out}} \mathrm{d}C = q_l R \left(C^{out} - C^{in} \right)
\end{aligned}$$

As a consequence:

$$\lim_{m\to\infty} \sigma_S^{mix} = -q_l R \left(C^{out} - C^{in} \right) + q_l R \left(C^{out} - C^{in} \right) = 0$$

Finally let us consider the contribution due to heat convection:

$$\begin{aligned}\sigma_S^{heat\,conv} &= \sum_{i=1}^{m}\left[q_l\mathscr{C}_p^{(i-1)}\left(\frac{T^{(i-1)}-T^{(i)}}{T^{(i)}}+\ln\left(\frac{T^{(i)}}{T^{(i-1)}}\right)\right)\right]\\ &= \sum_{i=1}^{m}\left[q_l\mathscr{C}_p^{(i-1)}T^{(i-1)}\left(\frac{1}{T^{(i)}}-\frac{1}{T^{(i-1)}}\right)\right]\\ &\quad+\sum_{i=1}^{m}\left[q_l\mathscr{C}_p^{(i-1)}\left(\ln T^{(i)}-\ln T^{(i-1)}\right)\right]\end{aligned}$$

Let us now take the limit for an infinite number of CSTRs with $T^{(0)}=T^{in}$, $T^{(m)}=T^{out}$ *and* $T^{(i-1)}<T^{(i)}$*:*

$$\begin{aligned}&\lim_{m\to\infty}\sum_{i=1}^{m}\left[q_l\mathscr{C}_p^{(i-1)}T^{(i-1)}\left(\frac{1}{T^{(i)}}-\frac{1}{T^{(i-1)}}\right)\right]\\ &=\int_{\frac{1}{T^{in}}}^{\frac{1}{T^{out}}}q_l\mathscr{C}_pT\mathrm{d}\left(\frac{1}{T}\right)=-\int_{T^{in}}^{T^{out}}q_l\mathscr{C}_p\frac{1}{T}\mathrm{d}T\end{aligned}$$

and

$$\begin{aligned}&\lim_{m\to\infty}\sum_{i=1}^{m}\left[q_l\mathscr{C}_p^{(i-1)}\left(\ln T^{(i)}-\ln T^{(i-1)}\right)\right]\\ &=\int_{\ln T^{in}}^{\ln T^{out}}q_l\mathscr{C}_p\mathrm{d}\left(\ln T\right)=\int_{T^{in}}^{T^{out}}q_l\mathscr{C}_p\frac{1}{T}\mathrm{d}T\end{aligned}$$

As a consequence:

$$\lim_{m\to\infty}\sigma_S^{heat\,conv}=-\int_{T^{in}}^{T^{out}}q_l\mathscr{C}_p\frac{1}{T}\mathrm{d}T+\int_{T^{in}}^{T^{out}}q_l\mathscr{C}_p\frac{1}{T}\mathrm{d}T=0$$

This proves indeed that the contribution due to mixing and heat convection vanishes in an ideal plug flow reactor.

The entropy as the Lyapunov function candidate

The second law of thermodynamics suggests that entropy related functions should be a priori good candidates as Lyapunov functions in order to analyze the stability properties of the CSTR model. Since the entropy production is assumed to be positive, one possible option could be to consider the integral

of the trajectories of the entropy production. This function $W(U, n_A, n_B, n_I)$ would be such that:

$$\sigma_S = \frac{\partial^t W}{\partial X} \frac{dX}{dt}$$

with $X = [U, n_A, n_B, n_I]^t$. Such a function exists for an isolated system. The entropy production is indeed given by:

$$\sigma_S = \frac{dS}{dt} = \frac{\partial^t \tilde{S}}{\partial X} \frac{dX}{dt}$$

since the entropy fluxes are equal to zero. Thermodynamics tells us that the stationary state of an isolated system is the one for which the entropy is maximum. Therefore the entropy is an appropriate Lyapunov function for isolated systems. For instance, it can be used as a Lyapunov function in adiabatic batch reactors.

However it is worth noting that the entropy production is not the total derivative of a state function for non-isolated systems. Indeed the entropy production is then not equal to the entropy variation due to the presence of the inlet and outlet entropy flows

$$\sigma_S = \frac{dS}{dt} - \left(\mathcal{F}_S^{in} - \mathcal{F}_S^{out} + \frac{\dot{Q}}{T_w} \right)$$

with $\mathcal{F}_S^{in}$ and $\mathcal{F}_S^{out}$ the inlet and outlet convection flow rates, respectively. The entropy production is not the exact derivative of a state function and it is therefore not possible to deduce a Lyapunov function for the CSTR model by integration of the entropy production.

The entropy production as the Lyapunov function candidate

A consequence of the second principle of thermodynamics is that the entropy is a concave function of the other extensive quantities, i.e. the internal energy, the volume and the number of moles of each species [19]. Based on this, Glansdorff and Prigogine have established a general evolution criterion for all macroscopic systems submitted to time independent boundary conditions [44]. This criterion states that there exist some flows of extensive quantities $\hat{J}_i$ and some associated

thermodynamic forces $\hat{Y}_i$ such that

$$\Psi = \sum_i \hat{J}_i \frac{d\hat{Y}_i}{dt} \leq 0 \tag{3.12}$$

where Ψ is given by the following relation:

$$\Psi = \frac{dU}{dt}\frac{d}{dt}\left(\frac{1}{T}\right) - \sum_{i=1}^{N_c} \frac{dn_i}{dt}\frac{d}{dt}\left(\frac{\mu_i}{T}\right)$$

Note that the total entropy production σ_S can always be written as a sum of some fluxes J_i and thermodynamic forces Y_i:

$$\sigma_S = \sum_i J_i Y_i \tag{3.13}$$

Yet the choice of the expression of these fluxes and thermodynamic forces is not unique. It is also worth noting that in the most general case, the fluxes $\hat{J}_i$ and the thermodynamic forces $\hat{Y}_i$ defined by Glansdorff and Prigogine are not fulfilling (3.13), i.e.:

$$\sigma_S \neq \sum_i \hat{J}_i \hat{Y}_i$$

The equality is fulfilled only in special cases, e.g. for systems for which one particular choice of $\hat{J}_i$ and $\hat{Y}_i$ is such that they fulfill the Onsager reciprocal relations with constant phenomenological coefficients. For those systems, the thermodynamic fluxes appearing in the expression of the entropy production can be written as a linear combination of the thermodynamic forces:

$$J_i = \sum_j L_{ij} Y_j$$

where L_{ij} is a constant symmetric matrix. The time variation of the entropy production is then given by following expression:

$$\frac{d\sigma_S}{dt} = \sum_i \frac{dJ_i}{dt} Y_i + \sum_i J_i \frac{dY_i}{dt} = 2\sum_{i,j} L_{ij} \frac{dY_i}{dt} Y_j = 2\sum_i J_i \frac{dY_i}{dt}$$

It can be shown that for this special case, the entropy production variation is negative, i.e.:

$$\sum_i J_i \frac{dY_i}{dt} = \frac{1}{2}\frac{d\sigma_S}{dt} \leq 0 \tag{3.14}$$

Comparing the above relation (3.14) to (3.12) shows that in this special case $\hat{J}_i = J_i$ and $\hat{Y}_i = Y_i$ and $\Psi = \frac{1}{2}\frac{d\sigma_S}{dt}$. Therefore in systems fulfilling the above-mentioned phenomenological assumptions, the entropy production σ_S reaches a minimum at steady state and can be considered as a Lyapunov function candidate. A system where the inlet flow is due to diffusion with a diffusion rate that is proportional to the difference of chemical potential between the inlet stream and the reactor is an example that fulfills the above-mentioned phenomenological assumptions.

The CSTR unfortunately does not belong to this class of systems. Indeed, from (3.6) and (3.13), the following fluxes and efforts can be deduced:

- fluxes: $J = \left[\mathcal{F}_X^{in}, rV, \dot{Q}\right]^t$
- driving forces:

$$Y = \left[\left(\left.\frac{\partial^t \tilde{S}}{\partial X}\right|_X - \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_{X_{in}}\right), \left.\frac{\partial^t S}{\partial n}\right|_X \mathbf{\Gamma}, \left(\left.\frac{\partial \tilde{S}}{\partial U}\right|_X - \frac{1}{T_w}\right)\right]^t$$

  with $\mathbf{\Gamma}$ the matrix of the stoichiometric coefficients.

If the Onsager relations were fulfilled, this would mean that the fluxes were linear functions of the driving forces, i.e. the molar inlet flow of A would be a proportional to the difference of chemical potential of A between the inlet and the inside of the reactor, of the affinity of the reaction and of the temperature difference between the reactor and the environment. This would be verified if the inlet flow rates were due to diffusion instead of convection. Therefore the entropy production would not be a priori a good Lyapunov candidate for the CSTR case, yet the above arguments might be a good source of information for deriving an appropriate alternative Lyapunov function candidate.

A first possible alternative is to consider the quantity Ψ defined by Glansdorff and Prigogine and stated in (3.12). If Ψ was the variation of some function of the state along the trajectories, then this function would be an appropriate Lyapunov candidate. It can be shown that for the CSTR the fluxes $\hat{J}_i$ and the corresponding forces $\hat{Y}_i$ are given by following expressions:

Flux $\hat{J}_i$	Force $\hat{Y}_i$
$q_l C_i^{in} h_i^{in} - \frac{q_l}{V} H + \kappa (T_w - T)$	$\frac{1}{T}$
$-\left(q_l C_i^{in} - \frac{q_l}{V} n_i\right)$	$\frac{\mu_i}{T}$
rV	$\frac{Aff}{T}$

For the CSTR the function Ψ is unfortunately not equal to the variation of some function of the state along the trajectories. This has motivated the work of Tarbell [92] who looked for a positive factor ϵ such that $\epsilon\Psi$ is the derivative of a function $\Phi(X)$ along the trajectories. But an appropriate factor ϵ is found only when the equilibrium point is close to the chemical equilibrium, i.e. for the highest conversion equilibrium point.

Let us now consider the work of Rouchon and Creff [88] on the stability analysis of the flash dynamics, for which the entropy production is a Lyapunov function although the flash dynamics do not fulfill the Onsager relations. Unlike the CSTR model, the flash dynamics has no multiple steady states. Furthermore numerical simulations show that the stable equilibria of the CSTR are not local minima of the entropy production. Let us therefore investigate the differences between the flash and the CSTR from the viewpoint of the entropy production variation.

The time derivative of σ_S can then be computed from (3.6) as follows:

$$\begin{aligned}\frac{d\sigma_S}{dt} &= \frac{\partial^t \sigma_S}{\partial X}\frac{dX}{dt} \\ &= \left(\frac{dX}{dt}\right)^t \frac{\partial^2 \tilde{S}}{\partial X^2}\left(\frac{dX}{dt} + \mathcal{F}_X^{out}\right) + \left(\left.\frac{\partial \tilde{S}}{\partial X}\right|_X - \frac{1}{T_w}\right)\frac{\partial^t \dot{Q}}{\partial X}\frac{dX}{dt} \\ &\quad + \frac{\partial^t \tilde{S}}{\partial X}\frac{\partial \sigma_n}{\partial X}\frac{dX}{dt}\end{aligned}$$

The Gibbs-Duhem equation (1.11) that links the degree one homogeneity of the thermodynamical potentials and the Gibbs' relation is written as follows :

$$0 = X^t \frac{d}{dt}\left(\frac{\partial \tilde{S}}{\partial X}\right) = X^t \left(\frac{\partial^2 \tilde{S}}{\partial X^2}\right)\frac{dX}{dt} \tag{3.15}$$

From (3.4) and (3.15) the time derivative of σ_S becomes:

$$\frac{d\sigma_S}{dt} = \left(\frac{dX}{dt}\right)^t \frac{\partial^2 \tilde{S}}{\partial X^2}\frac{dX}{dt} + \left(\left.\frac{\partial \tilde{S}}{\partial U}\right|_X - \frac{1}{T_w}\right)\frac{\partial^t \dot{Q}}{\partial X}\frac{dX}{dt} + \frac{\partial^t \tilde{S}}{\partial X}\frac{\partial \sigma_n}{\partial X}\frac{dX}{dt} \quad (3.16)$$

In the case of the flash, only the first term exists because there is no reaction and no heat exchange. The stability of the equilibrium derives from the concavity of the entropy function ($\frac{\partial^2 S}{\partial X^2} < 0$). For the CSTR, if this result obviously still holds, we also have to account for the other two terms of the right hand side of (3.16). Unfortunately it is not possible to deduce the sign of these two terms. In summary, we can say that the existence of the equilibrium point multiplicity and of the instability of one of them is related to the chemical reaction.

3.2.2 Energy-based stability analysis

The entropy does not provide substantial arguments at this point for a physically based Lyapunov stability analysis. Let us therefore concentrate on the internal energy and more precisely on the thermal energy, in line with the classical intuitive process engineering arguments on the stability/instability of the three equilibrium points of the CSTR model.

Indeed, the classical intuitive process engineering arguments are based on the function $\Delta^{eq}(T)$ that has been introduced in Chapter 2. The equilibrium temperatures $\bar{T}$ are the solutions of the following equation:

$$\Delta^{eq}\left(\bar{T}\right) = r^{eq}\left(\bar{T}\right) V\left(-\Delta_r H\right)\left(\bar{T}\right) - \left[\kappa\left(\bar{T} - T_w\right) + q_l \mathscr{C}_p^{in}\left(\bar{T} - T^{in}\right)\right] = 0$$

or by reorganizing the terms:

$$r\left(\bar{T}, \bar{n}_A, \bar{n}_B\right) V\left(-\Delta_r H\right)\left(\bar{T}\right) = \kappa\left(\bar{T} - T_w\right) + q_l \mathscr{C}_p^{in}\left(\bar{T} - T^{in}\right) \quad (3.17)$$

In the system, the internal energy can take two forms: "thermal" energy whose measure is the temperature, and the energy stored in the form of the chemical bonds. When a mole of A reacts to give B, an amount $(-\Delta_r H)$ of bond energy is transformed into thermal energy. Therefore the left-hand term of (3.17) represents the thermal energy that is produced per time unit by the chemical reaction at the equilibrium. The right-hand term of (3.17) represents the

thermal energy per time unit that is withdrawn from the reactor by diffusion and convection. Around the intermediate equilibrium, if the temperature is higher (resp. lower) than the equilibrium temperature, $\Delta^{eq}(T) > 0$ (resp. $\Delta^{eq}(T) < 0$). Following the intuitive approach, this means that the production rate of thermal energy by the reaction is greater (resp. smaller) than the power that is withdrawn, and thus the temperature will further increase (resp. decrease) (Figure 3.1). This argument explains that the equilibrium is unstable. The same arguments are used to explain that the extreme equilibria are stable. Nevertheless these arguments are only intuitive. Indeed, the difference between the production rate of thermal energy by the reaction and the power that is withdrawn does not depend only on temperature but also on the quantity of A and B in the reactor. The use of the function $\Delta^{eq}(T)$ in the above-mentioned arguments implies that we have considered that $n_A = n_A^{eq}(T)$ and $n_B = n_B^{eq}(T)$. A more rigorous approach should have considered any value of n_A and n_B.

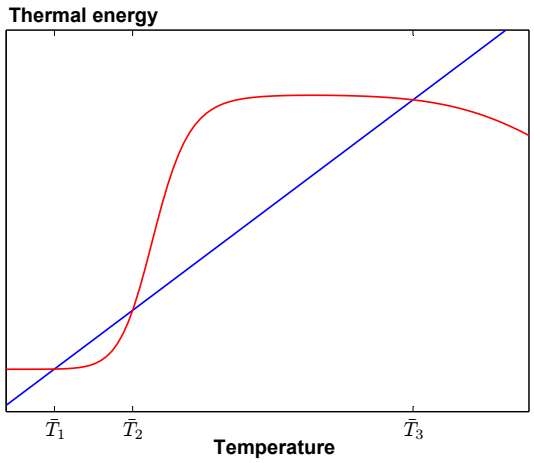


Figure 3.1: Representation of the intuitive approach (sigmoid curve: left-hand side of (3.17); straight line: right-hand side of (3.17))

We shall now use the intuitive arguments to derive a Lyapunov function candidate. An important feature of the function $\Delta^{eq}(T)$ is that it is equal

to zero for the three equilibrium values of T. Therefore $\left(\Delta^{eq}(T)\right)^2$, which is represented in Figure 3.2, has three local minima in $\bar{T}_1$, $\bar{T}_2$ and $\bar{T}_3$, the three equilibrium temperatures (with $\bar{T}_1 < \bar{T}_2 < \bar{T}_3$) .

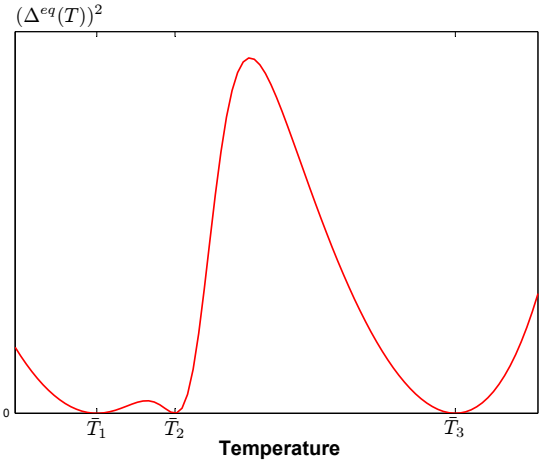


Figure 3.2: Graph of $\left(\Delta^{eq}(T)\right)^2$

The time derivative of $\left(\Delta^{eq}(T)\right)^2$ is equal to:

$$\frac{d\left(\Delta^{eq}\right)^2}{dt} = 2\Delta^{eq}(T)\frac{d\Delta^{eq}}{dT}\frac{dT}{dt}$$

The time evolution of the temperature is given by the following relation (see (2.27)):

$$\mathscr{C}_p(n_A, n_B)\, V\frac{dT}{dt} = r(T, n_A, n_B)\, V\left(-\Delta_r H\right)(T) - \left[\kappa(T - T_w) + q_l\mathscr{C}_p^{in}\left(T - T^{in}\right)\right]$$

One may note that the right-hand term is equal to $\Delta^{eq}(T)$ when setting $n_A = n_A^{eq}(T)$ and $n_B = n_B^{eq}(T)$.

Table 3.1 gives the sign of $\frac{d(\Delta^{eq})^2}{dt}$ with respect to the sign of the other terms. While the sign of $\Delta^{eq}(T)$ and $\frac{d\Delta^{eq}}{dT}$ are known since they only depend on T, the sign of $\frac{dT}{dt}$ depends both on T, n_A and n_B. Simulation runs confirm that depending on the initial value of n_A and n_B, different behaviours of $\left(\Delta^{eq}(T)\right)^2$

$\Delta^{eq}(T)$	$\frac{d\Delta^{eq}}{dT}$	$\frac{dT}{dt}$	$\frac{d(\Delta^{eq})^2}{dt}$
+	+	+	+
+	-	+	-
+	+	-	-
+	-	-	+
-	+	+	-
-	-	+	+
-	+	-	+
-	-	-	-

Table 3.1: Sign of $\frac{d(\Delta^{eq})^2}{dt}$

are observed, sometimes strictly decreasing, sometimes increasing before reaching a maximum and then decreasing (i.e. the temperature is moving away from the equilibrium value before going back to it). The function $(\Delta^{eq}(T))^2$ cannot therefore be considered as a global Lyapunov function but it might be worth looking to what happens if the initial conditions of the triple (T, n_A, n_B) are restricted to a limited set of the positive orthant. Let us first look to the subsets in which $(\Delta^{eq}(T))^2$ is decreasing and then analyze if these are invariant sets or if they contain such invariant sets (with the objective to possibly apply the La Salle theorem [63]).

First note that the reaction $r(T, n_A, n_B)$ is an increasing function of n_A and a decreasing function of n_B (Assumption 2.8). This implies that:

$$\mathscr{C}_p(n_A, n_B) V \frac{dT}{dt} < \Delta^{eq}(T) \quad \text{if} \quad n_A < n_A^{eq}(T) \quad \text{and} \quad n_B \geq n_B^{eq}(T) \tag{3.18a}$$

$$\mathscr{C}_p(n_A, n_B) V \frac{dT}{dt} > \Delta^{eq}(T) \quad \text{if} \quad n_A > n_A^{eq}(T) \quad \text{and} \quad n_B \leq n_B^{eq}(T) \tag{3.18b}$$

It is straightforward to see that $(\Delta^{eq}(T))^2$ is decreasing along the state trajec-

tories in the following domains:

$$\begin{aligned}
\mathscr{X}_1 &= \left\{ (T, n_A, n_B) | \, T < \bar{T}_1, n_A > n_A^{eq}(T), n_B \leq n_B^{eq}(T) \right\} \\
&\quad \cup \left\{ (T, n_A, n_B) | \, T_{max} < T < \bar{T}_3, n_A > n_A^{eq}(T), n_B \leq n_B^{eq}(T) \right\} \\
\mathscr{X}_2 &= \left\{ (T, n_A, n_B) | \, \bar{T}_1 < T < T_{min}, n_A < n_A^{eq}(T), n_B \geq n_B^{eq}(T) \right\} \\
&\quad \cup \left\{ (T, n_A, n_B) | \, T > \bar{T}_3, n_A < n_A^{eq}(T), n_B \geq n_B^{eq}(T) \right\}
\end{aligned}$$

where T_{min} and T_{max} denote the temperature corresponding to the local minimum and maximum of $\Delta^{eq}(T)$ ($\bar{T}_1 < T_{min} < \bar{T}_2 < T_{max} < \bar{T}_3$, see Figure 2.3).

The union of $\mathscr{X}_1$ and $\mathscr{X}_2$ are indeed two disconnected sets, one around the equilibrium $\left(\bar{T}_1, \bar{n}_{A_1}, \bar{n}_{B_1}\right)$ and the other around the equilibrium $\left(\bar{T}_3, \bar{n}_{A_3}, \bar{n}_{B_3}\right)$, i.e. around the two stable equilibria (see Figure 3.3). Let us denote by D_1 and D_3 each of these subsets.

It is worth noting that none of D_1 and D_3 are invariant sets. Indeed let us consider the following boundaries:

$$\begin{aligned}
\partial D_1 &= \left\{ (T, n_A, n_B) | \, T = \bar{T}_1, n_A < n_A^{eq}(T), n_B \geq n_B^{eq}(T) \right\} \\
\partial D_3 &= \left\{ (T, n_A, n_B) | \, T = \bar{T}_3, n_A < n_A^{eq}(T), n_B \geq n_B^{eq}(T) \right\}
\end{aligned}$$

From (3.18), we know that on these boundaries:

$$\mathscr{C}_p(n_A, n_B) V \frac{dT}{dt} < \Delta^{eq}(T) = 0$$

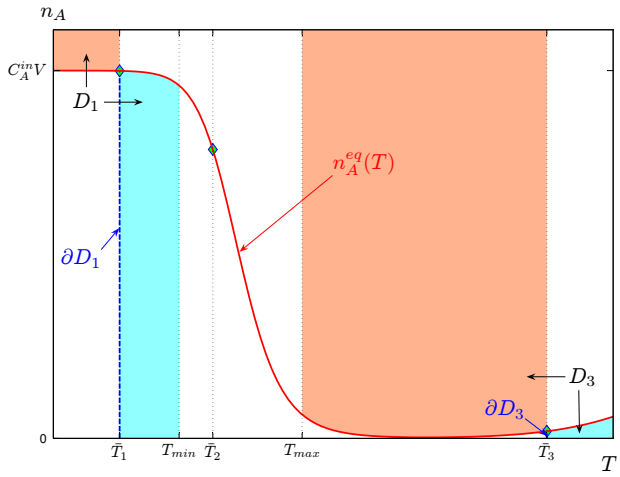
and the temperature time derivative points towards the exterior of the domain.

In order to find out invariant sets of the system or attraction domains for the equilibria, one could draw the phase plane of the system. More precisely, it is possible to split the space into subspaces delimited by the three surfaces given by

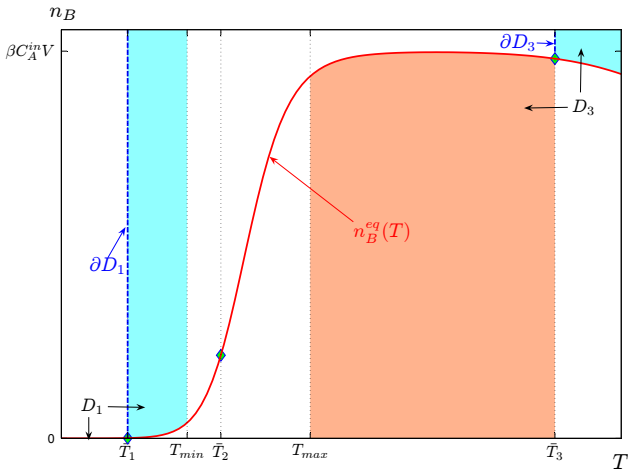
$$\mathscr{S}_i = \left\{ (T, n_A, n_B) \left| \frac{dx_i}{dt} = 0 \right. \right\}, \quad \text{with } i = 1, 2, 3 \text{ and } x = [T, n_A, n_B]^t$$

Hence in each of the delimited subspaces, the general orientation of the tangent vector can be found since the surface $\mathscr{S}_i$ divides $\mathbb{R}^3$ into two parts:

$$\left\{ (T, n_A, n_B) \left| \frac{dx_i}{dt} > 0 \right. \right\} \quad \text{and} \quad \left\{ (T, n_A, n_B) \left| \frac{dx_i}{dt} < 0 \right. \right\}$$



(a) (T, n_A)-plane



(b) (T, n_B)-plane

Figure 3.3: Domains of decreasing $(\Delta^{eq}(T))^2$ around both equilibrium points $\bar{T}_1$ and $\bar{T}_3$ (orange: $\mathscr{X}_1$, blue: $\mathscr{X}_2$)

$\mathscr{S}_i$ is the subset of the state space where the time variation of the i^{th} state variable is equal to zero and this surface divides the space into domains where the i^{th} state variable is increasing and domains where it is decreasing. The orientation of the tangent vector along these surfaces allows to find invariant sets delimited by parts of $\mathscr{S}_i$ $(i = 1, 2, 3)$.

The exercise can become rapidly tedious for systems of dimension larger than three, and even in dimension three the methodology is difficult to visualize. As a matter of illustration and in order to keep the approach simple enough, Example 3.1 presents a two-dimensional case, namely a CSTR with an irreversible reaction.

Example 3.1. *Let us consider a CSTR in which an irreversible reaction occurs. As mentioned at the end of Section 3.2.1 this case can be considered as a particular case of the reversible reaction. In this instance, the system dimension is equal to 2 since the dependence on n_B vanishes from the time derivative of n_A. The dynamical model is given as follows:*

$$\begin{cases} \mathscr{C}_p\left(n_A, n_B\right) V \dfrac{dT}{dt} = \kappa\left(T_w - T\right) + q_l \mathscr{C}_p^{in}\left(T^{in} - T\right) \\ \qquad\qquad\qquad\qquad + r\left(T, n_A, n_B\right) V \left(-\Delta_r H\right)(T) \\ \dfrac{dn_A}{dt} = \dfrac{q_l}{V}\left(C_A^{in} V - n_A\right) - r\left(T, n_A, n_B\right) V \end{cases}$$

In order to find out invariants sets of the system or attraction domains for the equilibria, let us draw the phase plane of the system. More precisely let us split the plane (T, n_A) into different zones in which the time variation of n_A and T are analyzed. The graph of the function $n_A^{eq}(T)$ corresponds to the set of points for which $\frac{dn_A}{dt} = 0$. By analogy, let us define $\hat{n}_A^{eq}(T)$ as the value of n_A for which the time derivative of T is equal to zero, i.e.:

$$r\left(T, \hat{n}_A^{eq}(T)\right) V \left(-\Delta_r H\right)(T) = \kappa\left(T - T_w\right) + q_l \mathscr{C}_p^{in}\left(T - T^{in}\right)$$

The curve representing $\hat{n}_A^{eq}(T)$ obviously crosses the curve representing $n_A^{eq}(T)$ at the three equilibrium points. The derivative of $\hat{n}_A^{eq}(T)$ with respect to the temperature is given by the following expression:

$$\frac{d\hat{n}_A^{eq}}{dT} = \frac{\kappa + q_l \mathscr{C}_p^{in} - \left(-\Delta_r H\right)(T) R_T - rV \frac{d(-\Delta_r H)(T)}{dT}}{\left(-\Delta_r H\right)(T) R_A}$$

As explained in Chapter 2, the term $rV\frac{d(-\Delta_r H)}{dT}$ *can be neglected. Moreover for low and high temperatures,* $R_T = \frac{\partial(rV)}{\partial T}$ *is small so that* $\hat{n}_A^{eq}(T)$ *is increasing for low and high temperatures, and decreasing for intermediate temperatures. Similarly to the fact that the curve* $n_A^{eq}(T)$ *is delimiting in the plane* (T, n_A) *the zones where the quantity of A is increasing or decreasing, the curve* $\hat{n}_A^{eq}(T)$ *is delimiting the zones of increasing or decreasing temperature. The decreasing temperature zones are under the curve* $\hat{n}_A^{eq}(T)$ *while the decreasing* n_A *zones are above* $n_A^{eq}(T)$*. This is schematically represented in Figure 3.4(a). In each zone an arrow indicates the general orientation of the tangent vector.*

Let us assume that the numerical values of the parameters are such that $\max(\hat{n}_A^{eq}(T)) > C_A^{in}V$*. From Figure 3.4(a), we can identify an invariant set around the low temperature stable equilibrium point. If we note by* $\hat{T}_{max}$ *the temperature corresponding to a local maximum of* $\hat{n}_A^{eq}(T)$*, the domain delimited by the following curves is an invariant:*

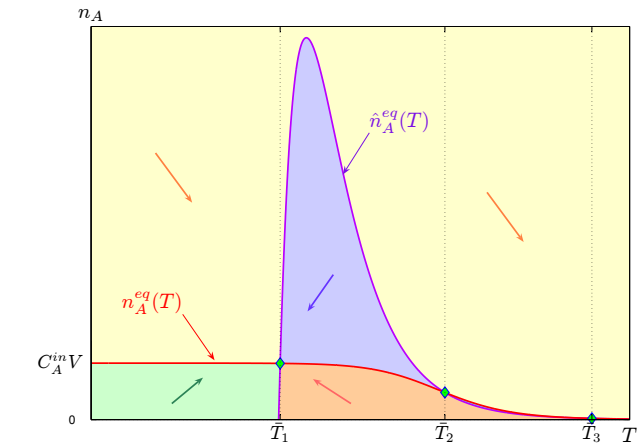
$$\mathscr{X}_3 = \left\{ \begin{array}{lll} T \leq \bar{T}_2 & & \\ n_A \leq \max(\hat{n}_A^{eq}(T)) & for & 0 < T \leq \hat{T}_{max} \\ n_A \leq \hat{n}_A^{eq}(T) & for & \hat{T}_{max} < T \leq \bar{T}_2 \end{array} \right\}$$

This invariant is shown in Figure 3.4(b).

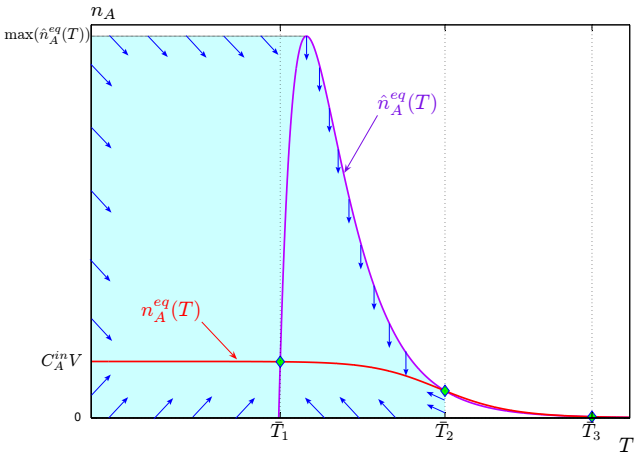
The above analysis has led us to a methodology for identifying invariant sets as illustrated in Example 3.1 for the two dimensional system case. It is obvious that such an approach is quite appealing and, with that respect, would deserve to be possibly further explored. However, although this analysis could lead to invariants sets for the stable equilibrium points of the CSTR, the link with the physics is unfortunately not obvious.

3.3 Conclusion

This chapter was dedicated to the stability analysis of a typical process example, the CSTR, by considering thermodynamics and energy considerations. Unlike for electrical and mechanical systems, the link between Lyapunov stability theory and energy of the system is not straightforward. Different Lyapunov



(a)



(b)

Figure 3.4: Trajectory directions in the CSTR with irreversible kinetics: (a) general orientation of the tangent vector (b) invariant $\mathscr{X}_3$

function candidates related to the thermodynamics, more specifically based on the entropy, the entropy production and the internal energy, have been considered. These provide new insight and physical interpretation in the stability/instability of the equilibrium points of the CSTR. In particular, the local stability analysis based on the first Lyapunov method has resulted in an extension of the results of [42] for less restrictive conditions on the system dynamics and thermodynamics (reversible reaction, total heat capacity of the mixture depending on the composition).

Besides invariants sets for the stable equilibrium points of the CSTR can be identified by considering an internal energy based Lyapunov function. Yet thermodynamic functions like the entropy and the entropy production as candidate Lyapunov functions exhibit their limitation in the case of open reaction systems. It has to be pointed out that the link between Lyapunov stability theory and the energy of reaction systems is not fully solved nor understood, and that there remain open questions that need to be addressed before obtaining a fully comprehensive thermodynamics based Lyapunov stability theory for reaction systems.

Finally let us mention that the results of this chapter (except those of Section 3.2.2) are valid for exothermic as well as for endothermic reactions. Indeed, neither the sign of $(-\Delta_r H)$ nor the number of equilibrium points has been used as an argument for the analysis. The analysis of Section 3.2.2 can also be extended to the endothermic case by adapting the signs of the inequalities.

Chapter 4

The power-shaping approach

In the previous chapters we have analyzed the stability of the open-loop CSTR equilibrium points using thermodynamic potentials such as the energy or the entropy, and also the irreversible entropy creation function. We have shown that these functions give only a partial answer to the physical interpretation of the open-loop stability and hence are difficult to use for the question of closed-loop stability.

Passivity is another concept of nonlinear system theory that can be linked to physical considerations. Indeed passivity considers some storage function which represents a quantity that is decreasing unless the system is restocked by the inputs. The most evident example of a storage function is the energy in an electro-mechanical system. Let us consider for instance a RLC circuit and the total energy that is stored in the inductor and in the capacities. The total energy is decreasing due to the presence of the resistances, and it is restocked by the power supplied by the sources. In passivity-based control the concept of passivity is used for the controller design. More recently an extension of passivity based control, namely power-shaping control, has been suggested for the control of nonlinear dynamical systems. The aim of this chapter is to apply

the power-shaping control methodology to the CSTR study case, and by this mean to find a more precise physical interpretation to its dynamical behaviour.

In passivity-based control, the controller reshapes the storage function so that the closed loop system has a stable equilibrium at some desired point. This concept has been applied to electro-mechanical systems [70][81][83] where the storage function is the total energy of the system. The controller provides to the system a finite amount of energy so as to drive the system to the desired state. That is why this technique is named energy-balancing passivity based control. Passivity-based control has also been applied to thermodynamic systems similarly to energy-balancing passivity based control, but the storage function is related to the entropy instead of the energy [4][84].

Nevertheless energy-balancing passivity-based control can only be applied to systems without pervasive dissipation, i.e. systems where the power provided by the controller is equal to zero at the desired equilibrium point. To overcome this difficulty the concept of power shaping control was introduced, firstly for the stabilization of nonlinear RLC circuits [80]. Contrary to energy-balancing passivity-based control, the storage function used for the control is related to the power and not to the energy. Power-shaping control has subsequently been applied to the control of mechanical and electro-mechanical systems [40].

Power-shaping control is based on a particular formulation of the system dynamics, namely a formulation that is derived from the Brayton-Moser equations for electrical circuits [15][16]. Although the first systems which have been described using this formalism are electrical circuits, it is shown in [40][55][56] that mechanical systems can also be expressed in this form. More recently it has been shown that the methodology of power-shaping control can be applied to any dynamical system, provided that it can be written in the Brayton-Moser formulation [40].

This chapter is dedicated to the analysis and control of the CSTR study case by the means of the power-shaping approach. First we shall introduce the concepts of the power-shaping approach in Section 4.1. Then in Section 4.2 we shall explain the general methodology for writing the Brayton-Moser form on the particluar case of a simplified CSTR with several reactions and reactants. This methodology shall be applied to obtain the Brayton-Moser formulation of

the dynamics of a CSTR with an irreversible reaction (Section 4.3). In Section 4.4, we shall design a control system for this CSTR using the power-shaping approach. The influence of the parameters on the controller performance shall be considered. The obtained controller shall also be analyzed with respect to modelling errors and measurement errors. Finally we shall present some preliminary results that aim at extendinging the power-shaping approach to CSTRs with multiple reactions (Section 4.5).

4.1 Power-shaping control

In this section, we briefly explain the principles of power-shaping control. In Section 4.1.1 we present how a dynamical system can be written in the suitable form for power-shaping control, i.e. the Brayton-Moser formulation. The controller design methodology is then set out in Section 4.1.2. The statements are given without any proof. For more details, the reader can refer to [40][55][56][80].

4.1.1 The Brayton-Moser equations

Let us consider a dynamical system of dimension d with m inputs. The state of the system is given by the vector $x \in \mathbb{R}^d$ and the input is given by vector $u_c \in \mathbb{R}^m$. The power-shaping control theory is based on the Brayton-Moser formulation of the system dynamics [15][16]. In this formulation the system dynamics are of the following form:

$$\boldsymbol{Q}(x)\frac{dx}{dt} = \nabla\mathscr{P}(x) + G(x)\,u_c \tag{4.1}$$

where $\boldsymbol{Q}(x) : \mathbb{R}^d \to \mathbb{R}^d \times \mathbb{R}^d$ is a non-singular square matrix, $\mathscr{P}(x) : \mathbb{R}^d \to \mathbb{R}$ is a scalar function of the state and $G(x) : \mathbb{R}^d \to \mathbb{R}^d \times \mathbb{R}^m$. Additionally, the symmetric part of the matrix $\boldsymbol{Q}(x)$ is negative semi-definite, i.e.:

$$\boldsymbol{Q}(x) + \boldsymbol{Q}^t(x) \preceq 0 \tag{4.2}$$

The function $\mathscr{P}(x)$ is called the *potential function*. In electrical and mechanical systems, the potential function has the units of power and is related to the

dissipated power in the system. For electrical systems it is related to the so-called content and co-content of the resistances [56][80] while it is related to the Rayleigh dissipation function for the mechanical systems [55].

Let us now assume the system dynamics is given by the following relation:

$$\frac{dx}{dt} = f(x) + g(x)\, u_c \tag{4.3}$$

where $f(x) : \mathbb{R}^d \rightarrow \mathbb{R}^d$ and $g(x) : \mathbb{R}^d \rightarrow \mathbb{R}^d \times \mathbb{R}^m$. The system (4.3) can be written in the form (4.1) if there exists a non-singular matrix $\boldsymbol{Q}(x)$ fulfilling (4.2) and that solves the following partial differential equation:

$$\nabla(\boldsymbol{Q}(x) f(x)) = \nabla^t(\boldsymbol{Q}(x) f(x)) \tag{4.4}$$

This condition is equivalent to the existence of the potential function $\mathscr{P}(x)$[1]. Once the matrix $\boldsymbol{Q}(x)$ has been determined, the expression of $\mathscr{P}(x)$ can be found by solving the following partial differential equation system:

$$\nabla \mathscr{P}(x) = \boldsymbol{Q}(x) f(x) \tag{4.5}$$

Condition (4.4) is in fact an integrability condition for (4.5).

The function $G(x)$ is given by the following relation:

$$G(x) = \boldsymbol{Q}(x)\, g(x)$$

4.1.2 Controller design

Let us assume that the system dynamics (4.3) can be expressed in the Brayton-Moser form presented before. The desired equilibrium state is denoted by x^*. The principle of power-shaping control is to choose the input $u_c(x)$ such that in closed loop the system dynamics are given by the following relation:

$$\boldsymbol{Q}(x) \frac{dx}{dt} = \nabla \mathscr{P}_d(x)$$

where $\mathscr{P}_d(x) : \mathbb{R}^d \rightarrow \mathbb{R}$ is the reshaped potential function. The desired equilibrium point x^* must be a local minimum of the potential function $\mathscr{P}_d(x)$ in order to be locally stable.

[1] Indeed it states that if $\mathscr{P}(x)$ exists, its Hessian matrix has to be symmetric.

The control input $u_c(x)$ reshapes the open-loop potential function by adding a term $\mathscr{P}_a(x)$ as follows:

$$\boldsymbol{Q}(x)\frac{dx}{dt} = \nabla\mathscr{P}(x) + \boldsymbol{Q}(x)\,g(x)\,u_c(x) = \nabla\mathscr{P}(x) + \nabla\mathscr{P}_a(x)$$

where

$$\nabla\mathscr{P}_a(x) = \boldsymbol{Q}(x)\,g(x)\,u_c(x) \tag{4.6}$$

A control law that fulfills (4.6) is given in the following proposition:

Proposition 4.1. *Assume there exists a real-valued scalar function $\mathscr{P}_a(x)$ such that the following relation is satisfied:*

$$g^{\perp}(x)\,\boldsymbol{Q}^{-1}(x)\,\nabla\mathscr{P}_a(x) = 0 \tag{4.7}$$

where $g^{\perp}(x) : \mathbb{R}^d \to \mathbb{R}^{d-m} \times \mathbb{R}^d$ is a full-rank left annihilator[1] of $g(x)$ and x^* is a local minimum of the following function:

$$\mathscr{P}_d(x) = \mathscr{P}(x) + \mathscr{P}_a(x)$$

Then the following control law:

$$u_c(x) = \left(g^t(x)\,\boldsymbol{Q}^t(x)\,\boldsymbol{Q}(x)\,g(x)\right)^{-1} g^t(x)\,\boldsymbol{Q}^t(x)\,\nabla\mathscr{P}_a(x) \tag{4.8}$$

ensures that x^* is a locally stable equilibrium with Lyapunov function $\mathscr{P}_d(x)$.

Remark 4.1. *Condition* (4.7) *states that the closed loop potential function $\mathscr{P}_d(x)$ cannot be chosen arbitrarily. Indeed the function $\mathscr{P}_a(x)$ must be chosen such that there exists a control input $u_c(x)$ that solves* (4.6)*. Given a function $\mathscr{P}_a(x)$, let us assume that $u_c(x)$ exists such that* (4.6) *is fulfilled. Then we obviously have:*

$$g^{\perp}(x)\,\boldsymbol{Q}^{-1}(x)\,\nabla\mathscr{P}_a(x) = g^{\perp}(x)\,\boldsymbol{Q}^{-1}(x)\,\boldsymbol{Q}(x)\,g(x) = 0$$

As a consequence (4.7) *is a necessary condition so as $u_c(x)$ to exist.*

[1] i.e. $g^{\perp}(x)\,g(x) = 0$ with $\operatorname{rank}\left(g^{\perp}(x)\right) = d - m$

Remark 4.2. *We have assumed that the dynamical system* (4.3) *is input affine. This assumption is in fact not necessary and Proposition 4.1 can still be applied, with some adaptations. Indeed let us consider some more general system dynamics as follows:*

$$\frac{dx}{dt} = f(x) + g(x, u_c)$$

The Brayton-Moser form is given as follows:

$$\boldsymbol{Q}(x) = \nabla \mathscr{P} + \boldsymbol{Q}(x)\, g(x, u_c)$$

As a consequence (4.6) *becomes as follows:*

$$\nabla \mathscr{P}_a(x) = \boldsymbol{Q}(x)\, g(x, u_c) \tag{4.9}$$

The condition (4.7) *for the choice of the function* $\mathscr{P}_a(x)$ *is not valid anymore. Instead, the function* $\mathscr{P}_a(x)$ *must be chosen such that there exists a function* $u_c(x)$ *that solves* (4.9)*. The stabilizing control law is then the solution of* (4.9) *for the given function* $\mathscr{P}_a(x)$*.*

Corollary 4.1. *In addition to the assumptions of Proposition 4.1, assume that* x^* *is an isolated minimum of* $\mathscr{P}_d(x)$ *and the largest invariant contained in the set:*

$$\left\{ x \in \Omega | \nabla^t \mathscr{P}_d(x) \left[\boldsymbol{Q}^{-1}(x) + \left(\boldsymbol{Q}^t(x) \right)^{-1} \right] \nabla \mathscr{P}_d(x) = 0 \right\}$$

equals $\{x^*\}$*, where* Ω *is a compact invariant set that contains only one local minimum of* $\mathscr{P}_d(x)$*, namely* x^**. Then* x^* *is a locally asymptotically stable equilibrium of the closed loop system with control input* (4.8)[1]*.*

4.2 The Brayton-Moser partial differential equation for a general simplified CSTR

4.2.1 The dynamical model

As explained in the previous section, the change from the usual form of the system dynamics (4.3) into its Brayton-Moser formulation (4.1) requires the

[1] This can be shown by using La Salle's theorem with $\mathscr{P}_d(x)$ as the Lyapunov function of the closed loop system.

solution of the partial differential equation system (4.4). The solution of such equations can turn out to be quite intricate. In order to keep the resolution as simple as possible we shall work with a simplified version of the CSTR model.

Let us consider a CSTR with N_r independent reactions. In order to simplify the model, we add the following assumptions to the previous Assumptions 2.1 to 2.10:

Assumption 4.1. The volumetric constant pressure heat capacity of the mixture $\mathscr{C}_p$ is independent of the composition.

Assumption 4.2. The reaction heats $(-\Delta_r H)$ of the reactions are independent of the temperature.

Assumption 4.3. The system is controlled by the cooling fluid flow rate which directly acts via the heat transfer coefficient κ. Therefore we shall consider in the sequel that the control input u_c is the quantity $\frac{\kappa}{\mathscr{C}_p V}$.

Under these assumptions, the general form of the dynamics of a non-isothermal CSTR can be derived from (2.29).

Since the volumetric constant pressure heat capacity of the mixture $\mathscr{C}_p$ is independent of the composition, it is only necessary to consider among all the chemical species in the mixture those that intervene in the kinetics of the reactions. Let N_c be the number of chemical species which intervene in the expression of the reaction kinetics. For each species i the time evolution is given as follows (with $i = 1, \ldots, N_c$):

$$\frac{dn_i}{dt} = \frac{q_l}{V}\left(C_i^{in} V - n_i\right) + \sum_{l=1}^{N_r} \Gamma_{il} r_l\left(T, n\right) \tag{4.10}$$

where Γ_{il} is the stoichiometric coefficient of species i in the reaction l. The temperature evolution equation becomes as follows:

$$\frac{dT}{dt} = \frac{q_l}{V}\left(T^{in} - T\right) + \sum_{l=1}^{N_r} \gamma_l r_l\left(T, n\right) + u_c\left(T_w - T\right)$$

where $\gamma_l = \frac{(-\Delta_r H)_l}{\mathscr{C}_p V}$ and $(-\Delta_r H)_l$ is the reaction heat of the reaction l. The time evolution equations of n_A and T have the same form and the dynamics of

the system can be written as follows:

$$\frac{dx}{dt} = \frac{q_l}{V}\left(x^{in} - x\right) + \mathbf{\Gamma} r\left(x\right) + u_c \begin{pmatrix} 0 \\ \vdots \\ 0 \\ T_w - T \end{pmatrix} \tag{4.11}$$

where $x = [n_A, \ldots, n_{N_c}, T]^t$. $\mathbf{\Gamma} \in \mathbb{R}^{N_c+1} \times \mathbb{R}^{N_r}$ is a matrix that contains the stoichiometric coefficient of species i in the reaction l in position (i, l) if $1 \leq i \leq N_c$ and that contains γ_l in the l^{th} column if $i = N_c + 1$. Applying the notations of Section 4.1 to (4.11), we have:

$$f\left(x\right) = \frac{q_l}{V}\left(x^{in} - x\right) + \mathbf{\Gamma} r\left(x\right) \quad \text{and} \quad g\left(x\right) = u_c \begin{pmatrix} 0 \\ \vdots \\ 0 \\ T_w - T \end{pmatrix} \tag{4.12}$$

4.2.2 Integrability condition: the Brayton-Moser partial differential equation

As explained in Section 4.1 the first step to find the Brayton-Moser form of the dynamics is the solution of a partial differential equation, i.e. find a matrix $\boldsymbol{Q}\left(x\right)$ that fulfills the conditions (4.2) and (4.4). By using (4.11), we can write the following relation (for $i = 1, \ldots, N_c + 1$):

$$\left(\boldsymbol{Q}\left(x\right) f\left(x\right)\right)_i = \sum_{k=1}^{N_c+1} q_{ik}\left(\frac{q_l}{V}\left(x_k^{in} - x_k\right) + \Gamma_{kl} r_l\left(x\right)\right)$$

By differentiating the above expression, the following relation is obtained (for $j = 1, \ldots, N_c + 1$):

$$\begin{aligned}\left(\nabla\left(\boldsymbol{Q}\left(x\right) f\left(x\right)\right)\right)_{ij} = -\frac{q_l}{V} q_{ij} + \sum_{k=1}^{N_c+1}\left[q_{ik}\sum_{l=1}^{N_r}\Gamma_{kl}\frac{\partial r_l}{\partial x_j}\right] \\ + \sum_{k=1}^{N_c+1}\frac{\partial q_{ik}}{\partial x_j}\left(\frac{q_l}{V}\left(x_k^{in} - x_k\right) + \Gamma_{kl} r_l\left(x\right)\right)\end{aligned}$$

where $q_{ij}(x) : \mathbb{R}^{N_c+1} \to \mathbb{R}$ for $i, j = 1, \ldots, N_c + 1$ is the entry in position (i, j) of the matrix $\boldsymbol{Q}(x)$. Consequently, condition (4.4) can be rewritten as follows:

$$\begin{aligned} &-\frac{q_l}{V} q_{ij} + \sum_{k=1}^{N_c+1} \left[q_{ik} \sum_{l=1}^{N_r} \Gamma_{kl} \frac{\partial r_l}{\partial x_j} \right] + \sum_{k=1}^{N_c+1} \frac{\partial q_{ik}}{\partial x_j} \left(\frac{q_l}{V} \left(x_k^{in} - x_k \right) + \Gamma_{kl} r_l(x) \right) \\ &= -\frac{q_l}{V} q_{ji} + \sum_{k=1}^{N_c+1} \left[q_{jk} \sum_{l=1}^{N_r} \Gamma_{kl} \frac{\partial r_l}{\partial x_i} \right] + \sum_{k=1}^{N_c+1} \frac{\partial q_{jk}}{\partial x_i} \left(\frac{q_l}{V} \left(x_k^{in} - x_k \right) + \Gamma_{kl} r_l(x) \right) \end{aligned} \tag{4.13}$$

for all $i, j = 1, \ldots, N_c + 1$.

This partial differential equation is difficult to solve in general. So we shall now restrict ourselves to a particular set of possible matrices $\boldsymbol{Q}(x)$ to find a solution for (4.4). This set is such that the partial differential equation system is transformed into an algebraic one. (4.13) is transformed into an algebraic equation by setting:

$$\forall i, j, k = 1, \ldots, N_c + 1, \; i \neq j : \quad \frac{\partial q_{ik}}{\partial x_j} = 0 \tag{4.14}$$

(4.13) becomes then as follows:

$$-\frac{q_l}{V} q_{ij} + \sum_{k=1}^{N_c+1} \left[q_{ik} \sum_{l=1}^{N_r} \Gamma_{kl} \frac{\partial r_l}{\partial x_j} \right] = -\frac{q_l}{V} q_{ji} + \sum_{k=1}^{N_c+1} \left[q_{jk} \sum_{l=1}^{N_r} \Gamma_{kl} \frac{\partial r_l}{\partial x_i} \right] \tag{4.15}$$

The above set of algebraic equations is still complex to solve due to the general form of the kinetics. Therefore, we shall add the following assumption:

Assumption 4.4. The kinetics of reaction l can be written as a product as follows:

$$r_l(x) = k_l(T) \prod_{m=1}^{N_c} \phi_m^{(l)}(n_m)$$

The functions $\phi_m^{(l)}(n_m)$ are smooth functions of their argument and $\phi_m^{(l)}(0) = 0$ if the species n_m intervenes in the kinetics of reaction l; otherwise $\phi_m^{(l)}(n_m) = 1$. $k_l(T)$ is the kinetic coefficient of the reaction l. $k_l(T)$ is such that the reaction rate $r_l(x)$ fulfills Assumption 2.9.

From Assumption 2.9, we have:

$$\begin{array}{cc} k_l(T) > 0 & \dfrac{dk_l}{dT} > 0 \\ \lim\limits_{T\to 0} k_l(T) = 0 & \lim\limits_{T\to 0} \dfrac{dk_l}{dT} = 0 \\ \lim\limits_{T\to \infty} k_l(T) = k_{l_\infty} > 0 & \lim\limits_{T\to \infty} \dfrac{dk_l}{dT} = 0 \end{array} \tag{4.16}$$

This assumption restricts the set of reaction kinetics that are considered since it excludes for example the Michaelis-Menten kinetics for enzymatic reactions. However the considered ones still cover a large number of practical cases, and among them the reactions with mass action law kinetics.

Under Assumption 4.4, (4.15) is written as follows (for $i, j = 1, \ldots, N_c + 1$ with $i \neq j$):

- for $i, j \neq N_c + 1$:

$$\begin{aligned} &-\frac{q_l}{V} q_{ij}(n_i) + \sum_{l=1}^{N_r} k_l(T)\, \phi_i^{(l)}(n_i)\, \frac{\partial \phi_j^{(l)}}{\partial n_j} \left(\sum_{k=1}^{N_c+1} q_{ik}(n_i)\, \Gamma_{kl} \right) \prod_{m\neq i,j}^{N_c} \phi_m^{(l)}(n_m) \\ &= -\frac{q_l}{V} q_{ji}(n_j) + \sum_{l=1}^{N_r} k_l(T)\, \phi_j^{(l)}(n_j)\, \frac{\partial \phi_i^{(l)}}{\partial n_i} \left(\sum_{k=1}^{N_c+1} q_{jk}(n_j)\, \Gamma_{kl} \right) \prod_{m\neq i,j}^{N_c} \phi_m^{(l)}(x_m) \end{aligned} \tag{4.17a}$$

- for $j = N_c + 1$:

$$\begin{aligned} &-\frac{q_l}{V} q_{ij}(n_i) + \sum_{l=1}^{N_r} \phi_i^{(l)}(n_i)\, \frac{dk_l}{dT} \left(\sum_{k=1}^{N_c+1} q_{ik}(n_i)\, \Gamma_{kl} \right) \prod_{m=1, m\neq i}^{N_c} \phi_m^{(l)}(n_m) \\ &= -\frac{q_l}{V} q_{ji}(T) + \sum_{l=1}^{N_r} k_l(T)\, \frac{\partial \phi_i^{(l)}}{\partial n_i} \left(\sum_{k=1}^{N_c+1} q_{jk}(T)\, \Gamma_{kl} \right) \prod_{m=1, m\neq i}^{N_c} \phi_m^{(l)}(n_m) \end{aligned} \tag{4.17b}$$

A general solution of (4.17a) and (4.17b) has not been found, yet. Despite of this, some characteristics of the solution (if it exists) can be derived. Indeed (4.17a) has to be satisfied for any (n, T) and in particular for T tending to 0. By taking the limit of (4.17a) for T tending to 0, we find that the following relation has to be fulfilled for $i, j \neq N_c + 1$ and $i \neq j$:

$$-\frac{q_l}{V} q_{ij}(n_i) = -\frac{q_l}{V} q_{ji}(n_j)$$

This means that $q_{ij} = q_{ji}$ and q_{ij} and q_{ji} have to be constants. Thus the only elements that can depend on the composition in the matrices $\boldsymbol{Q}(x)$ that solve (4.17a) and (4.17b) are the diagonal terms. All non-diagonal elements (except for the last line and the last column) are constant.

4.3 The Brayton-Moser formulation of the CSTR with an irreversible reaction

As already mentioned, a general solution of (4.17a) and (4.17b) has not been found, yet. Furthermore, to this stage we do not even know if a solution exists. Therefore we shall in a first instance work with the most simple case, namely the case of an irreversible reaction with one reactant. The extension of the following analysis to more complex reactions shall be considered in Section 4.5.

4.3.1 The dynamical model

In order to simplify the system dynamics to reduce its dimension as much as possible, we shall add the following assumptions to the previous ones:

Assumption 4.5. The reaction is irreversible.

Assumption 4.6. The reaction kinetics follow the mass action law.

Remark 4.3. *In this section we consider the case of an irreversible reaction whereas in Chapters 2 and 3 we have considered a reversible reaction. The reason for this choice is to reduce the number of variables of the system in order to simplify the calculations, and in particular the solution of the partial differential equation* (4.4)*. As mentioned in Section 3.2.1 irreversible reactions are a particular case of reversible reactions, and the assumptions of Chapters 2 and 3 do not exclude irreversible reactions. Therefore the analysis of the previous chapters is still valid for the particular case of the irreversible reaction considered in this chapter. Considerations about the extension of the power-shaping approach to CSTRs with more complex reaction kinetics shall be presented in Section 4.5.*

As a consequence from Assumptions 4.5 and 4.6, the reaction kinetics can be written as follows:

$$r\left(n_A, T\right) V = k\left(T\right) n_A$$

where $k\left(T\right)$ is the kinetic coefficient. From Assumption 4.4, $k\left(T\right)$ fulfills the conditions (4.16).

Under these assumptions, the dynamical behaviour of the CSTR can be represented by a two-dimensional system [7][93] as follows (see (2.29)):

$$\begin{cases} \dfrac{dn_A}{dt} = \dfrac{q_l}{V}\left(C_A^{in} V - n_A\right) - k\left(T\right) n_A \\ \dfrac{dT}{dt} = \dfrac{q_l}{V}\left(T^{in} - T\right) + \gamma k\left(T\right) n_A + u_c\left(T_w - T\right) \end{cases} \tag{4.18}$$

with $\gamma = \dfrac{(-\Delta_r H)}{\mathscr{C}_p V}$.

Using the notations of (4.3), we have:

$$f\left(x\right) = \begin{pmatrix} \frac{q_l}{V}\left(C_A^{in} V - n_A\right) - k\left(T\right) n_A \\ \frac{q_l}{V}\left(T^{in} - T\right) + \gamma k\left(T\right) n_A \end{pmatrix} \quad \text{and} \quad g\left(x\right) = \begin{pmatrix} 0 \\ T_w - T \end{pmatrix} \tag{4.19}$$

The assumptions of Chapter 2 are still fulfilled so that the dynamical behaviour described in that chapter still applies to the simplified model studied here.

4.3.2 The Brayton-Moser matrix $\boldsymbol{Q}\left(n_A, T\right)$ and the potential function $\mathscr{P}\left(n_A, T\right)$

The first step in order to apply the power-shaping approach consists in writing the dynamic system (4.18) in the Brayton-Moser form. The methodology has been described in Section 4.1.1. We shall in a first instance find a non-singular matrix $\boldsymbol{Q}\left(n_A, T\right) : \mathbb{R}^2 \rightarrow \mathbb{R}^2 \times \mathbb{R}^2$ that fulfills conditions (4.2) and (4.4) with $f\left(x\right)$ given in (4.19). The matrix $\boldsymbol{Q}\left(n_A, T\right)$ is the solution of the

partial differential equation (4.4) which in our case is given by (4.13) as follows:

$$\begin{aligned}
&- q_{11} n_A \frac{dk}{dT} - q_{12} \frac{q_l}{V} + q_{12} \gamma n_A \frac{dk}{dT} + \frac{\partial q_{11}}{\partial T} \left(\frac{q_l}{V} \left(C_A^{in} V - n_A \right) - k n_A \right) \\
&+ \frac{\partial q_{12}}{\partial T} \left(\frac{q_l}{V} \left(T_{in} - T \right) + \gamma k n_A \right) \\
&= - q_{21} \frac{q_l}{V} - q_{21} k + q_{22} \gamma k + \frac{\partial q_{21}}{\partial n_A} \left(\frac{q_l}{V} \left(C_A^{in} V - n_A \right) - k n_A \right) \\
&+ \frac{\partial q_{22}}{\partial n_A} \left(\frac{q_l}{V} \left(T_{in} - T \right) + \gamma k n_A \right)
\end{aligned} \tag{4.20}$$

where $q_{ij}\left(n_A, T\right) : \mathbb{R}^2 \to \mathbb{R}$ for $i, j = 1, 2$ is the entry in position (i, j) of the matrix $\boldsymbol{Q}\left(n_A, T\right)$. The following lemma gives a possible solution of (4.20).

Lemma 4.1. *The following matrix* $\boldsymbol{Q}\left(n_A, T\right)$ *allows to write the dynamical system* (4.18) *in the form* (4.1)*:*

$$\boldsymbol{Q}\left(n_A, T\right) = \begin{pmatrix} \gamma q_{12} & q_{12} \\ \frac{q_{22}(T)\gamma k(T) + q_{12}\frac{q_l}{V}}{\frac{q_l}{V} + k(T)} & q_{22}\left(T\right) \end{pmatrix}$$

where $q_{12} \neq 0$ *is a constant and* $q_{22}(T)$ *is a function that depends only on* T *and such that* $q_{12} \neq \gamma q_{22}\left(T\right)$*.*

Proof. (4.18) can be written in the form (4.1) if $\boldsymbol{Q}\left(n_A, T\right)$ is non-singular and if it fulfills condition (4.4).

The determinant of proposed matrix $\boldsymbol{Q}\left(n_A, T\right)$ is non-zero if $q_{12} \neq 0$ and if $q_{12} \neq \gamma q_{22}\left(T\right)$:

$$\det \boldsymbol{Q}\left(n_A, T\right) = q_{12} \frac{q_l}{V} \left(\frac{q_{22}\left(T\right)\gamma - q_{12}}{\frac{q_l}{V} + k\left(T\right)} \right)$$

As a consequence $\boldsymbol{Q}\left(n_A, T\right)$ is non-singular.

Condition (4.4) is fulfilled if $\boldsymbol{Q}\left(n_A, T\right)$ solves (4.20). Let us insert the proposed expression for $\boldsymbol{Q}\left(n_A, T\right)$ into (4.20). The right-hand term is given by the

following expression:

$$\begin{aligned}
&- q_{21}\frac{q_l}{V} - q_{21}k + q_{22}\gamma k + \frac{\partial q_{21}}{\partial n_A}\left(\frac{q_l}{V}\left(C_A^{in}V - n_A\right) - kn_A\right) \\
&\quad + \frac{\partial q_{22}}{\partial n_A}\left(\frac{q_l}{V}\left(T_{in} - T\right) + \gamma k n_A\right) \\
&= -\frac{q_{22}\left(T\right)\left(T\right)\gamma k\left(T\right) + q_{12}\frac{q_l}{V}}{\frac{q_l}{V} + k\left(T\right)}\frac{q_l}{V} - \frac{q_{22}\left(T\right)\gamma k\left(T\right) + q_{12}\frac{q_l}{V}}{\frac{q_l}{V} + k\left(T\right)}k + q_{22}\left(T\right)\gamma k \\
&= -q_{22}\left(T\right)\gamma k\left(T\right) - q_{12}\frac{q_l}{V} + q_{22}\left(T\right)\gamma k \\
&= -q_{12}\frac{q_l}{V}
\end{aligned} \tag{4.21a}$$

The left-hand term is given by the following relation:

$$\begin{aligned}
&- q_{11}n_A\frac{dk}{dT} - q_{12}\frac{q_l}{V} + q_{12}\gamma n_A\frac{dk}{dT} + \frac{\partial q_{11}}{\partial T}\left(\frac{q_l}{V}\left(C_A^{in}V - n_A\right) - kn_A\right) \\
&\quad + \frac{\partial q_{12}}{\partial T}\left(\frac{q_l}{V}\left(T_{in} - T\right) + \gamma k n_A\right) \\
&= -\gamma q_{12}n_A\frac{dk}{dT} - q_{12}\frac{q_l}{V} + q_{12}\gamma n_A\frac{dk}{dT} \\
&= -q_{12}\frac{q_l}{V}
\end{aligned} \tag{4.21b}$$

The right-hand term (4.21a) and the left-hand term (4.21b) of (4.20) are equal which completes the proof. □

Remark 4.4. *The form of matrix* $\boldsymbol{Q}\left(x\right)$ *proposed in the above lemma has been obtained by applying the methodology proposed in Section 4.2, and more precisely by applying* (4.14)*. Indeed it can be seen that the proposed form transforms the partial differential equation into an algebraic one in the second line of* (4.21a) *and* (4.21b) *where the terms containing the partial derivatives of* $q_{ij}\left(n_A, T\right)$ *have been canceled.*

In order to apply the power-shaping methodology, the matrix $\boldsymbol{Q}\left(n_A, T\right)$ must also fulfill the condition (4.2). The final form of the matrix $\boldsymbol{Q}\left(n_A, T\right)$ is stated in the following lemma.

Lemma 4.2. *The following non-singular matrix* $\boldsymbol{Q}(n_A, T)$ *fulfills both* (4.2) *and* (4.4)*:*

$$\boldsymbol{Q}(n_A, T) = \begin{pmatrix} \gamma & 1 \\ \frac{k+4\frac{q_l}{V}\alpha}{k} & \frac{k^2+4\alpha\frac{q_l}{V}\left(\frac{q_l}{V}+k\right)}{\gamma k^2} \end{pmatrix} q_{12} \tag{4.22}$$

where $0 < \alpha \leq 1$ *and* $q_{12} < 0$ *are two real coefficients.*

Proof. From Lemma 4.1, it follows directly that $\boldsymbol{Q}(n_A, T)$ is non-singular and that it fulfills (4.4).

Besides, the symmetric part of $\boldsymbol{Q}(n_A, T)$ is given by the following expression:

$$\boldsymbol{Q}(n_A, T) + \boldsymbol{Q}^t(n_A, T) = \begin{pmatrix} \gamma & \frac{k+2\frac{q_l}{V}\alpha}{k} \\ \frac{k+2\frac{q_l}{V}\alpha}{k} & \frac{k^2+4\alpha\frac{q_l}{V}\left(\frac{q_l}{V}+k\right)}{\gamma k^2} \end{pmatrix} 2q_{12}$$

The trace and the determinant of this matrix are as follows:

$$\begin{aligned} \operatorname{tr}\left(\boldsymbol{Q}+\boldsymbol{Q}^t\right) &= 2q_{12}\frac{k^2\left(\gamma^2+1\right)+4\alpha\frac{q_l}{V}\left(\frac{q_l}{V}+k\right)}{\gamma k^2} < 0 \\ \det\left(\boldsymbol{Q}+\boldsymbol{Q}^t\right) &= 16\frac{q_{12}^2}{k^2}\left(\frac{q_l}{V}\right)^2\alpha(1-\alpha) \geq 0 \end{aligned}$$

The sum of the eigenvalues is equal to the trace and their product is equal to the determinant. Consequently the eigenvalues of the symmetric part of $\boldsymbol{Q}(n_A, T)$ are negative and $\boldsymbol{Q}(n_A, T) + \boldsymbol{Q}^t(n_A, T)$ is negative semi-definite. Furthermore if $\alpha < 1$, $\boldsymbol{Q}(n_A, T) + \boldsymbol{Q}^t(n_A, T)$ is negative definite. □

Remark 4.5. *Lemma 4.2 does not give a unique solution to* (4.20)*, but a family of solutions. Indeed it gives the set of matrices that satisfy* (4.2) *and* (4.4) *and such that* (4.20) *is an algebraic equation.* (4.22) *is the general form of the matrices contained in this set, parametrized by the values of* q_{12} *and* α*.*

Once the expression of the matrix $\boldsymbol{Q}(n_A, T)$ is found, the potential function $\mathscr{P}(n_A, T)$ can be found by solving (4.5). The final Brayton-Moser formulation of (4.18) is given in the following proposition.

Proposition 4.2. *The dynamics of the CSTR* (4.18) *can be expressed in the Brayton-Moser form* (4.1) *with:*

$$\boldsymbol{Q}(n_A, T) = \begin{pmatrix} \gamma & 1 \\ \frac{k+4\frac{q_l}{V}\alpha}{k} & \frac{k^2+4\alpha\frac{q_l}{V}\left(\frac{q_l}{V}+k\right)}{\gamma k^2} \end{pmatrix} q_{12}$$

where $0 < \alpha \leq 1$ *and* $q_{12} < 0$ *are two real coefficients and*

$$\mathscr{P}(n_A, T) = |q_{12}| \Bigg[\frac{q_l}{V} \frac{1}{2\gamma} \left(\gamma \left(C_A^{in} V - n_A \right) + \left(T^{in} - T \right) \right)^2 - 4\alpha \left(\frac{q_l}{V} \right)^2 \int_{\Theta}^{T} \frac{\gamma C_A^{in} V k(\tau) + \left(\frac{q_l}{V} + k(\tau) \right) \left(T^{in} - \tau \right)}{\gamma k(\tau)^2} \mathrm{d}\tau \Bigg] \quad (4.23)$$

where Θ *is a reference temperature (*$\Theta > 0$*).*

Proof. From Lemma 4.2 it follows directly that $\boldsymbol{Q}(n_A, T)$ fulfills the necessary conditions for the Brayton-Moser formulation of the dynamics. It is then easy to check that (4.23) is a solution of (4.5) with the above expression for $\boldsymbol{Q}(n_A, T)$. □

The quadratic term of (4.23) is clearly linked to the convection phenomena in the CSTR whereas the integral term is related to the reaction kinetics.

Remark 4.6. *The choice of the reference temperature* Θ *only affects* $\mathscr{P}(n_A, T)$ *to an additive constant. It has therefore no influence on the shape of* $\mathscr{P}(n_A, T)$*.*

Remark 4.7. *As clarified in Remark 4.5, the above proposed matrix represents in reality a family of matrices. As a consequence Proposition 4.2 gives a family of Brayton-Moser formulations of the CSTR dynamics. This family of solutions is parametrized by the values of* q_{12} *and* α*. From the expression* (4.23) *of* $\mathscr{P}(n_A, T)$*, it can be seen that* q_{12} *is only a scaling factor, whereas* α *influences the shape of* $\mathscr{P}(n_A, T)$ *by acting on the weight of the kinetic term with respect to the convection term.*

4.3.3 Stability analysis using the Brayton-Moser formulation

Let us now use the Brayton-Moser formulation to analyze the dynamical behaviour of the CSTR. The equilibrium points $\left(\bar{n}_A, \bar{T}\right)$ of the open-loop system are the solutions of $f\left(\bar{n}_A, \bar{T}\right) = 0$. As a consequence, the following equation can be written:

$$\boldsymbol{Q}\left(\bar{n}_A, \bar{T}\right) f\left(\bar{n}_A, \bar{T}\right) = \nabla \mathscr{P}\left(\bar{n}_A, \bar{T}\right) = 0$$

The matrix $\boldsymbol{Q}\left(\bar{n}_A, \bar{T}\right)$ is non-singular and the equilibrium points of the system are consequently the critical points of $\mathscr{P}\left(n_A, T\right)$ and conversely.

Proposition 4.3. *The asymptotically stable equilibria are local minima of the function $\mathscr{P}\left(n_A, T\right)$ and the unstable equilibrium is a saddle point.*

Proof. First let us determine the nature of the critical points of $\mathscr{P}\left(n_A, T\right)$ by computing the eigenvalues of the Hessian matrix $\boldsymbol{\mathcal{H}}\left(\mathscr{P}\right)$ at these points:

$$\mathrm{tr}\left(\boldsymbol{\mathcal{H}}\left(\mathscr{P}\right)\right) = -\frac{q_{12}}{\gamma k\left(\bar{T}\right)^2}\frac{q_l}{V}\left[4\alpha\frac{q_l}{V}\left(k\left(\bar{T}\right)+\frac{q_l}{V}-\gamma\bar{n}_A\frac{dk}{dT}\right)+k\left(\bar{T}\right)^2\left(1+\gamma^2\right)\right]$$

$$\det\left(\boldsymbol{\mathcal{H}}\left(\mathscr{P}\right)\right) = 4\alpha\frac{q_{12}^2}{k\left(\bar{T}\right)^2}\left(\frac{q_l}{V}\right)^3\left(-\gamma\bar{n}_A\frac{dk}{dT}+k\left(\bar{T}\right)+\frac{q_l}{V}\right)$$

Besides, the eigenvalues of the linearized system around the equilibria λ_1 and λ_2 are as follows:

$$\begin{aligned}\lambda_1 &= -\frac{q_l}{V}\\ \lambda_2 &= \gamma\bar{n}_A\frac{dk}{dT}-k\left(\bar{T}\right)-\frac{q_l}{V}\end{aligned}$$

At the unstable equilibrium $\lambda_2 > 0$ whereas at the stable ones $\lambda_2 < 0$. Indeed by including Assumptions 4.1 to 4.6, (2.21) is written as follows:

$$0 > q_l\mathscr{C}_p\left(k\left(\bar{T}\right)+\frac{q_l}{V}\right)-\frac{q_l}{V}\left(-\Delta_r H\right)\frac{dk}{dT}\bar{n}_A$$

As a consequence, $\boldsymbol{\mathcal{H}}\left(\mathscr{P}\right)$ is positive definite at the stable equilibria, whereas it is indefinite at the unstable one. □

The shape of $\mathscr{P}\left(n_A, T\right)$ is shown in Figure 4.1 around the unstable and the high temperature equilibrium.

Lemma 4.3. *There exists a reference temperature Θ_0 such that for all $T > 0$:*

$$\int_{\Theta_0}^{T}\frac{\gamma C_A^{in}Vk\left(\tau\right)+\left(\frac{q_l}{V}+k\left(\tau\right)\right)\left(T^{in}-\tau\right)}{\gamma k\left(\tau\right)^2}\mathrm{d}\tau \leq 0$$

Moreover Θ_0 is equal to one of the two equilibrium temperatures corresponding to the stable equilibria.

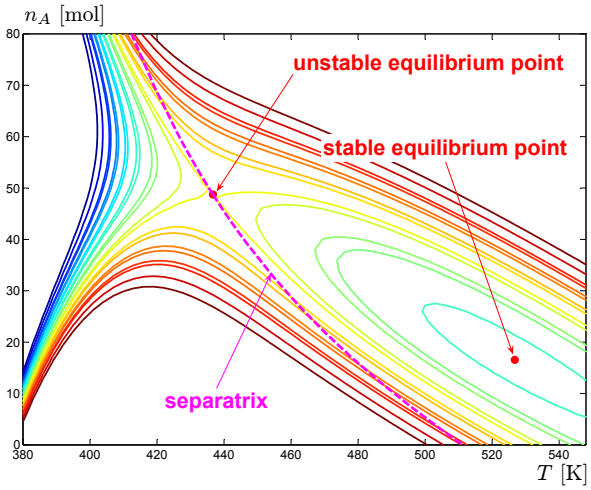


Figure 4.1: Level curves of $\mathscr{P}(n_A, T)$ (the low temperature equilibrium point lies outside of the figure frame)

Proof. Let us choose some positive value Θ and let us define the function $\rho(T)$ as follows:

$$\rho(T) = \int_{\Theta}^{T} \frac{\gamma C_A^{in} V k(\tau) + \left(\frac{q_l}{V} + k(\tau)\right)\left(T^{in} - \tau\right)}{\gamma k(\tau)^2} \mathrm{d}\tau$$

It is easy to see that:

$$\frac{d\rho}{dT} = \frac{\gamma C_A^{in} V k(T) + \left(\frac{q_l}{V} + k(T)\right)\left(T^{in} - T\right)}{\gamma k(T)^2}$$

with

$$\lim_{T\to 0} \frac{d\rho}{dT} = \infty \quad \text{and} \quad \lim_{T\to\infty} \frac{d\rho}{dT} = -\infty$$

so that

$$\lim_{T\to 0} \rho(T) = \lim_{T\to\infty} \rho(T) = -\infty$$

As a consequence the function $\rho(T)$ has a global maximum for some positive value Θ_0 of T:

$$\Theta_0 = \arg\max_{T>0} \rho(T) \quad \text{with} \quad \left.\frac{d\rho}{dT}\right|_{\Theta_0} = 0$$

We can now write the following relation:

$$\int_{\Theta_0}^{T} \frac{\gamma C_A^{in} V k(\tau) + \left(\frac{q_l}{V} + k(\tau)\right)\left(T^{in} - \tau\right)}{\gamma k(\tau)^2} \mathrm{d}\tau = -\rho(\Theta_0) + \rho(T)$$

Since $\rho(\Theta_0) \geq \rho(T)$, we obviously have the following inequality:

$$\int_{\Theta_0}^{T} \frac{\gamma C_A^{in} V k(\tau) + \left(\frac{q_l}{V} + k(\tau)\right)\left(T^{in} - \tau\right)}{\gamma k(\tau)^2} \mathrm{d}\tau \leq 0$$

Let us now assume that $\Theta_0 \neq \bar{T}$ where $\bar{T}$ is any of the three equilibrium temperatures of the CSTR. Since $\rho(\Theta_0)$ is the global maximum of $\rho(T)$, we have:

$$\left.\frac{d\rho}{dT}\right|_{\Theta_0} = \frac{\gamma C_A^{in} V k(\Theta_0) + \left(\frac{q_l}{V} + k(\Theta_0)\right)\left(T^{in} - \Theta_0\right)}{\gamma k(\Theta_0)^2} = 0$$

which implies that:

$$\gamma C_A^{in} V k(\Theta_0) + \left(\frac{q_l}{V} + k(\Theta_0)\right)\left(T^{in} - \Theta_0\right) = 0$$

Θ_0 is not an equilibrium temperature and hence (n_A, Θ_0) is not an equilibrium point for any value of n_A. In particular (n_{A_0}, Θ_0) with $n_{A_0} = \frac{\frac{q_l}{V} C_A^{in} V}{k(\Theta_0) + \frac{q_l}{V}}$ is not an equilibrium point. At this point the time variation of n_A and T are equal to:

$$\begin{aligned}
\frac{dn_A}{dt}(n_{A_0}, \Theta_0) &= \frac{q_l}{V}\left(C_A^{in} V - n_{A_0}\right) - k(\Theta_0) n_{A_0} = 0 \\
\frac{dT}{dt}(n_{A_0}, \Theta_0) &= \frac{q_l}{V}\left(T^{in} - \Theta_0\right) + \gamma k(\Theta_0) n_{A_0} \\
&= -\frac{q_l}{V} \frac{\gamma C_A^{in} V k(\Theta_0)}{\frac{q_l}{V} + k(\Theta_0)} + \gamma k(\Theta_0) \frac{\frac{q_l}{V} C_A^{in} V}{k(\Theta_0) + \frac{q_l}{V}} = 0
\end{aligned}$$

This implies that (n_{A_0}, Θ_0) is an equilibrium point of the CSTR, which in contradiction with our assumption. As a consequence Θ_0 is an equilibrium temperature.

Furthermore since Θ_0 is a maximum of $\rho(T)$, $\frac{d^2\rho}{dT^2}(\Theta_0) < 0$.

$$\frac{d^2\rho}{dT^2}(\Theta_0) = \frac{1}{\gamma k\left(\bar{T}\right)^2}\left(\gamma \bar{n}_A \frac{dk}{dT} - \left(k\left(\bar{T}\right) + \frac{q_l}{V}\right)\right)$$

As it has already been proved, this quantity is negative for the two stable equilibrium points whereas it is positive for the unstable one[1]. The maximum of $\rho(T)$ can therefore only be located at $\bar{T}_1$ or at $\bar{T}_3$. □

[1] see Proof of Proposition 4.3

Proposition 4.4. *Let us choose the reference temperature in expression* (4.23) Θ_0 *such that for all* $T > 0$*:*

$$\int_{\Theta_0}^{T} \frac{\gamma C_A^{in} V k(\tau) + \left(\frac{q_l}{V} + k(\tau)\right)\left(T^{in} - \tau\right)}{\gamma k(\tau)^2} \mathrm{d}\tau \leq 0 \tag{4.24}$$

With this choice of Θ_0*, the potential function* $\mathscr{P}(n_A, T)$ *in* (4.23) *is a Lyapunov function for the open-loop CSTR if* $\alpha \neq 1$*.*

Proof. In order to be a Lyapunov function, $\mathscr{P}(n_A, T)$ has to be positive, continuously differentiable and radially unbounded [63].

We know from Lemma 4.3 that there exists Θ_0 such that (4.24) is fulfilled. Moreover Θ_0 is a stable equilibrium temperature of the open-loop CSTR.

Let us denote by n_{A_0} the equilibrium value of n_A corresponding to the equilibrium temperature Θ_0. The quadratic term of $\mathscr{P}(n_A, T)$ is obviously non-negative. Furthermore it is equal to zero at the three equilibrium points. As a consequence $\mathscr{P}(n_A, T) \geq 0$ with $\mathscr{P}(n_{A_0}, \Theta_0) = 0$

It is easy to see that the assumptions on $k(T)$ imply that $\mathscr{P}(n_A, T)$ is continuously differentiable. The first term of $\mathscr{P}(n_A, T)$ is obviously radially unbounded. Let us take the limit of the other terms for T tending to infinity. Since

$$\lim_{T \to \infty} \frac{\gamma C_A^{in} V k(T) + \left(\frac{q_l}{V} + k(T)\right)\left(T^{in} - T\right)}{\gamma k(T)^2} = -\infty$$

we can conclude that $\mathscr{P}(n_A, T)$ is radially unbounded.

The time evolution of $\mathscr{P}(n_A, T)$ is given by the following relation:

$$\begin{aligned} \frac{d\mathscr{P}}{dt} &= \nabla^t \mathscr{P}(x) f(x) = \nabla^t \mathscr{P}(x) \boldsymbol{Q}(x) \nabla \mathscr{P}(x) \\ &= \frac{1}{2} \nabla^t \mathscr{P}(x) \left(\boldsymbol{Q}(x) + \boldsymbol{Q}^t(x)\right) \nabla \mathscr{P}(x) \qquad \leq 0 \end{aligned}$$

If $\alpha \neq 1$, the equality holds only for $\nabla \mathscr{P}(x) = 0$, i.e. for the equilibria. As a consequence $\mathscr{P}(n_A, T)$ is strictly decreasing along the system trajectories. □

4.4 Controller design via the power-shaping approach

4.4.1 Controller design

The aim is to design a control law $u_c = u_c(n_A, T)$ such that the closed loop system has an asymptotically stable equilibrium at the desired state (n_A^*, T^*). Let us apply the methodology described in Section 4.1.2. First let us determine the class of functions $\mathscr{P}_a(n_A, T)$ such that there exists a control input $u_c(n_A, T)$ that fulfills (4.6).

Lemma 4.4. *There exists a control input $u_c(n_A, T)$ that fulfills (4.6) only if the function $\mathscr{P}_a(n_A, T)$ is of the following form:*

$$\mathscr{P}_a(n_A, T) = f_a\underbrace{\left(n_A + \int_{T_0}^{T} v(\tau)\,\mathrm{d}\tau\right)}_{z} = f_a(z) \tag{4.25}$$

where $f_a(z)$ is any smooth real-valued function and

$$v(T) = \frac{k(T)^2 + 4\alpha\frac{q_l}{V}\left(\frac{q_l}{V} + k(T)\right)}{\gamma k(T)^2}$$

Proof. This lemma is a direct consequence of Remark 4.1. Indeed (4.7) is a necessary condition for the existence of a function $u_c(n_A, T)$ that fulfills (4.6). The full-rank left annihilators of $g(n_A, T)$ are given by $g^{\perp}(x) = [\varphi\ 0]$ with $\varphi \in \mathbb{R}^*$. (4.7) becomes as follows:

$$\frac{q_{12}\varphi}{\det(\boldsymbol{Q}(x))}\left(v(T)\frac{\partial \mathscr{P}_a}{\partial n_A} - \frac{\partial \mathscr{P}_a}{\partial T}\right) = 0$$

where

$$v(T) = \frac{k(T)^2 + 4\alpha\frac{q_l}{V}\left(\frac{q_l}{V} + k(T)\right)}{\gamma k(T)^2}$$

The solution of this partial differential equation is of the following form:

$$\mathscr{P}_a(n_A, T) = f_a\left(n_A + \int_{T_0}^{T} v(\tau)\,\mathrm{d}\tau\right)$$

where $f_a(z) : \mathbb{R} \to \mathbb{R}$ is a smooth real-valued function and T_0 is any positive temperature. □

The following lemma states the conditions so that the closed-loop potential function

$$\mathscr{P}_d\left(n_A, T\right) = \mathscr{P}_a\left(n_A, T\right) + \mathscr{P}\left(n_A, T\right)$$

has a local minimum at the desired equilibrium state (n_A^*, T^*). However to use it, we shall make the following assumption:

Assumption 4.7. No open-loop equilibrium temperature is equal to T_w.

Remark 4.8. *It is rather unlikely that one of the three equilibrium temperatures is exactly equal to T_w since there is no reason that the temperature of the cooling fluid is exactly equal to an equilibrium temperature of the open-loop CSTR. Furthermore, this case can be avoided in practice because the cooling fluid temperature is a parameter on which it usually easy to act, so that it is not equal to any of the three equilibrium temperatures.*

Lemma 4.5. *Let us consider the closed-loop potential function given as follows:*

$$\mathscr{P}_d\left(n_A, T\right) = \mathscr{P}\left(n_A, T\right) + \mathscr{P}_a\left(n_A, T\right)$$

where $\mathscr{P}\left(n_A, T\right)$ is the open-loop potential function given in (4.23) *and $\mathscr{P}_a\left(n_A, T\right)$ is a function of the form* (4.25)*. Assumption 4.7 is fulfilled.*

(n_A^*, T^*) is a critical point of the function $\mathscr{P}_d\left(n_A, T\right)$ if and only if the following conditions are fulfilled:

$$n_A^* = \frac{\frac{q_l}{V} C_A^{in} V}{\frac{q_l}{V} + k\left(T^*\right)}, \quad T^* \neq T_w \tag{4.26}$$

and

$$\left.\frac{df_a}{dz}\right|_{z^*} = -\left|q_{12}\right| u_c^*\left(T_w - T^*\right) \tag{4.27}$$

where

$$u_c^*\left(T_w - T^*\right) = -\frac{q_l}{V}\left(T^{in} - T^*\right) - \gamma k\left(T^*\right) n_A^* \tag{4.28}$$

Proof. (n_A^*, T^*) is a critical point of the function $\mathscr{P}_d\left(n_A, T\right)$ if and only if $\nabla \mathscr{P}_d\left(n_A^*, T^*\right) = 0$, i.e. if $\nabla \mathscr{P}_a\left(x^*\right) = -\nabla \mathscr{P}\left(x^*\right)$. By replacing the terms by

their respective expressions, the following relation is obtained:

$$\frac{1}{|q_{12}|}\begin{pmatrix}1\\ v\left(T^*\right)\end{pmatrix}\left.\frac{df_a}{dz}\right|_{z^*} = \begin{pmatrix}\gamma\frac{q_l}{V}\left(C_A^{in}V-n_A^*\right)+\frac{q_l}{V}\left(T^{in}-T^*\right)\\ \frac{q_l}{V}\left(C_A^{in}V-n_A^*\right)+\frac{4\alpha\left(\frac{q_l}{V}\right)^2}{k^*}C_A^{in}V+v\left(T^*\right)\left(T^{in}-T^*\right)\end{pmatrix} \tag{4.29}$$

where $z^* = n_A^* + \int_{T_0}^{T^*} v\left(\tau\right)\mathrm{d}\tau$ and $k^* = k\left(T^*\right)$. By combining the two lines of the above equation, it can be seen that (4.29) has a solution if and only if n_A^* and T^* are related by the following expression:

$$n_A^* = \frac{\frac{q_l}{V}C_A^{in}V}{\frac{q_l}{V}+k\left(T^*\right)}$$

The matrix $\boldsymbol{Q}\left(n_A,T\right)$ is non-singular. Consequently $\left(n_A^*,T^*\right)$ is a minimum of $\mathscr{P}_d\left(n_A,T\right)$ if and only if:

$$f\left(n_A^*,T^*\right)+g\left(n_A^*,T^*\right)u_c\left(n_A^*,T^*\right)=\boldsymbol{Q}^{-1}\left(n_A^*,T^*\right)\nabla\mathscr{P}_d\left(n_A^*,T^*\right)=0$$

which can be developed as follows:

$$\begin{cases}0=\frac{q_l}{V}\left(C_A^{in}V-n_A^*\right)-k\left(T^*\right)n_A^*\\ 0=\frac{q_l}{V}\left(T^{in}-T^*\right)+\gamma k\left(T^*\right)n_A^*+u_c\left(n_A^*,T^*\right)\left(T_w-T^*\right)\end{cases} \tag{4.30}$$

Assume now that there exists a control input $u_c\left(n_A,T\right)$ such that T_w is the temperature at a critical point of $\mathscr{P}_d\left(n_A,T\right)$. From the second equation of (4.30), we then have the following relation:

$$0=\frac{q_l}{V}\left(T^{in}-T_w\right)+\gamma k\left(T_w\right)\frac{\frac{q_l}{V}C_A^{in}V}{\frac{q_l}{V}+k\left(T_w\right)}$$

This relation implies that T_w is also an equilibrium point of the open-loop system. But this case has been eliminated by assumption. As a consequence there is no critical point of $\mathscr{P}_d\left(n_A,T\right)$ such that $T^*=T_w$. This proves (4.26).

Now (4.29) reduces to the following relation:

$$\frac{1}{|q_{12}|}\left.\frac{df_a}{dz}\right|_{z^*}=\gamma k\left(T^*\right)n_A^*+\frac{q_l}{V}\left(T^{in}-T^*\right)=u_c^*\left(T_w-T^*\right)$$

where $u_c^*\left(T_w-T^*\right)=-\frac{q_l}{V}\left(T^{in}-T^*\right)-\gamma k\left(T^*\right)n_A^*$. □

Remark 4.9. *The control input u_c does not intervene in the differential equation for the time evolution of n_A in* (4.18)*. As a consequence* (4.26) *could also have been deduced directly from* (4.18)*, as it can be seen in the first equation of* (4.30)*.*

Remark 4.10. $u_c^*\left(T_w - T^*\right) = -\frac{q_l}{V}\left(T^{in} - T^*\right) - \gamma k\left(T^*\right) n_A^*$ *is the equilibrium value of the input.*

As stated in Proposition 4.1, (n_A^*, T^*) should be a local minimum of the function $\mathscr{P}_d\left(n_A, T\right)$, i.e. the Hessian matrix $\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)$ of the function $\mathscr{P}_d\left(n_A, T\right)$ must be positive definite at (n_A^*, T^*). The Hessian matrix $\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)$ of the function $\mathscr{P}_d\left(n_A, T\right)$ is given by the following expression:

$$\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*, T^*\right) = \begin{pmatrix} -\gamma\frac{q_l}{V} - \omega & -\frac{q_l}{V} - \omega v\left(T^*\right) \\ -\frac{q_l}{V} - \omega v\left(T^*\right) & -\frac{1}{\gamma {k^*}^2}\frac{q_l}{V}\left({k^*}^2 - 4\alpha\frac{q_l}{V}\Psi^*\right) - \omega v\left(T^*\right)^2 \end{pmatrix} q_{12}$$

where

$$\omega = \frac{1}{|q_{12}|}\left.\frac{d^2 f_a}{dz^2}\right|_{z^*}$$

and

$$\Psi^* = -\left(k^* + \frac{q_l}{V}\right) + \left.\frac{dk}{dT}\right|_{T^*} \gamma n_A^*$$

Lemma 4.6. *Let us consider the closed-loop potential function given as follows:*

$$\mathscr{P}_d\left(n_A, T\right) = \mathscr{P}\left(n_A, T\right) + \mathscr{P}_a\left(n_A, T\right)$$

where $\mathscr{P}\left(n_A, T\right)$ is the open-loop potential function given in (4.23) *and $\mathscr{P}_a\left(n_A, T\right)$ is a function of the form given in* (4.25)*.*

There exists no ω such that $\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*, T^*\right)$ is positive definite if:

$$4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - {k^*}^2\Psi^* \leq 0$$

In the other cases, i.e. if:

$$1 \geq \alpha > \frac{{k^*}^2\Psi^*}{4\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2} \tag{4.31}$$

	$4\alpha\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2-k^{*^2}\Psi^*>0$	$4\alpha\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2-k^{*^2}\Psi^*<0$
$\Psi^*>0$	Case 1	Case 2
$\Psi^*<0$	Case 3	Case 4

Table 4.1: Determination of the sign of $\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*,T^*\right)$

the Hessian matrix $\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*,T^*\right)$ *is positive definite if:*

$$\omega>\frac{k^{*^2}\gamma\frac{q_l}{V}\Psi^*}{4\alpha\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2-k^{*^2}\Psi^*} \tag{4.32}$$

Proof. $\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*,T^*\right)$ is positive definite if and only if its trace and its determinant fulfill the following inequalities, respectively:

$$\begin{aligned}&\operatorname{tr}\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*,T^*\right)\\&=|q_{12}|\left[\omega\left(1+v\left(T^*\right)^2\right)+\frac{1}{\gamma k^{*^2}}\frac{q_l}{V}\left(k^{*^2}\left(\gamma^2+1\right)-4\alpha\frac{q_l}{V}\Psi^*\right)\right]<0\end{aligned} \tag{4.33a}$$

$$\begin{aligned}&\det\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*,T^*\right)\\&=\frac{4\alpha q_{12}}{\gamma k^{*^4}}\left(\frac{q_l}{V}\right)^2\left[-q_{12}k^{*^2}\gamma\frac{q_l}{V}\Psi^*+\omega q_{12}\left(4\alpha\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2-k^{*^2}\Psi^*\right)\right]>0\end{aligned} \tag{4.33b}$$

First let us consider the case where $4\alpha\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2-k^{*^2}\Psi^*=0$. Then $\det\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*,T^*\right)$ becomes as follows:

$$\det\boldsymbol{\mathcal{H}}\left(\mathscr{P}_d\right)\left(n_A^*,T^*\right)=-\frac{16\alpha^2q_{12}^2}{k^{*^4}}\left(\frac{q_l}{V}\right)^4\left(k^*+\frac{q_l}{V}\right)^2<0$$

and (4.33b) is not fulfilled.

The other different possible cases are summarized in Table 4.1.

In **cases 1 and 3**, we have $4\alpha\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2-k^{*^2}\Psi^*>0$. This implies that the following inequality is fulfilled for any value of Ψ^*:

$$\frac{\frac{q_l}{V}k^{*^2}\gamma\Psi^*}{4\alpha\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2-k^{*^2}\Psi^*}>-\frac{q_l}{V}\frac{1}{1+v\left(T^*\right)^2}\left(\frac{k^{*^2}\left(\gamma^2+1\right)-4\alpha\frac{q_l}{V}\Psi^{*^2}}{k^{*^2}\gamma}\right) \tag{4.34}$$

Indeed the reorganization the terms of (4.34) leads to the following inequality:

$$\Psi^{*^2} + 2\left(\frac{q_l}{V} + k^*\right)\Psi^* + \left(1+\gamma^2\right)\left(k^* + \frac{q_l}{V}\right)^2 > 0 \tag{4.35}$$

The discriminant of this equation is equal to $-4\gamma^2\left(k^* + \frac{q_l}{V}\right)^2$ which is obviously negative. As a consequence (4.35) is always satisfied and so is also (4.34).

In these two cases, (4.33a) and (4.33b) can be rewritten as follows, respectively:

$$\omega > -\frac{q_l}{V}\frac{1}{1+v\left(T^*\right)^2}\left(\frac{k^{*^2}\left(\gamma^2+1\right) - 4\alpha\frac{q_l}{V}\Psi^{*^2}}{k^{*^2}\gamma}\right) \tag{4.36a}$$

and

$$\omega > \frac{\frac{q_l}{V}k^{*^2}\gamma\Psi^*}{4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - k^{*^2}\Psi^*} \tag{4.36b}$$

By taking (4.34) into account, it is obvious that (4.36b) implies (4.36a). As a consequence, it is sufficient that the following inequality is satisfied:

$$\omega > \frac{\frac{q_l}{V}k^{*^2}\gamma\Psi^*}{4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - k^{*^2}\Psi^*}$$

In **case 2**, we have $4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - k^{*^2}\Psi^* < 0$. By a similar development as in cases 1 and 3, the following inequality is fulfilled for any value of Ψ^*:

$$\frac{\frac{q_l}{V}k^{*^2}\gamma\Psi^*}{4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - k^{*^2}\Psi^*} < -\frac{q_l}{V}\frac{1}{1+v\left(T^*\right)^2}\left(\frac{k^{*^2}\left(\gamma^2+1\right) - 4\alpha\frac{q_l}{V}\Psi^{*^2}}{k^{*^2}\gamma}\right) \tag{4.37}$$

In this case, (4.33a) and (4.33b) can be rewritten as follows, respectively:

$$\omega > -\frac{q_l}{V}\frac{1}{1+v\left(T^*\right)^2}\left(\frac{k^{*^2}\left(\gamma^2+1\right) - 4\alpha\frac{q_l}{V}\Psi^{*^2}}{k^{*^2}\gamma}\right) \tag{4.38a}$$

and

$$\omega < \frac{\frac{q_l}{V}k^{*^2}\gamma\Psi^*}{4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - k^{*^2}\Psi^*} \tag{4.38b}$$

By taking (4.37) into account, it is obvious that (4.38a) and (4.38b) cannot be fulfilled by the same value of ω. As a consequence, in case 2 there is no value for ω such that (4.33a) and (4.33b) are fulfilled.

Case 4 cannot be encountered. Indeed if $\Psi^* < 0$, then trivially:

$$4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - {k^*}^2\Psi^* > 0$$

and

$$ {k^*}^2\left(\gamma^2 + 1\right) - 4\alpha\frac{q_l}{V}\Psi^* > 0 \qquad \square$$

The control action can be found by applying Proposition 4.1 with the above considerations. This is stated in the following proposition.

Proposition 4.5. *If* (4.31) *and* (4.32) *are fulfilled, then the following control law:*

$$u_c\left(n_A, T\right)\left(T_w - T\right) = \omega\left(n_A^* - n_A - \int_{T^*}^{T} v\left(\tau\right) d\tau\right) + u_c^*\left(T_w - T^*\right) \tag{4.39}$$

stabilizes the desired equilibrium point (n_A^*, T^*).

Proof. Let us choose following function $\mathscr{P}_a\left(n_a, T\right)$:

$$\mathscr{P}_a\left(n_A, T\right) = f_a\left(z\right) = -q_{12}\left[\frac{1}{2}\omega\left(z - z^*\right)^2 + u_c^*\left(T_w - T^*\right)\left(z - z^*\right)\right] \tag{4.40}$$

with $z = n_A + \int_{T_0}^{T} v\left(\tau\right) \mathrm{d}\tau$.

From Lemmas 4.4 and 4.6 the assumptions of Proposition 4.1 are fulfilled. Replacing the elements of (4.8) by their expressions in the case of the CSTR leads to the following control law which ensures that (n_A^*, T^*) is a locally stable closed-loop equilibrium:

$$u_c\left(n_A, T\right)\left(T_w - T\right) = \omega\left(n_A^* - n_A - \int_{T^*}^{T} v\left(\tau\right) d\tau\right) + u_c^*\left(T_w - T^*\right) \qquad \square$$

Remark 4.11. $u_c\left(n_A, T\right)$ *is not defined if* $T = T_w$. *However it can be seen on* (4.18) *that in this case the control action* u_c *does not influence the closed loop system dynamics. It can therefore be chosen arbitrary, for example by setting* $u_c\left(n_A, T_w\right) = 0$.

The controller has several parameters that can be chosen for tuning the control action. The final control law is fixed by the choice of $\boldsymbol{Q}(n_A, T)$ and of $\mathscr{P}_a(n_A, T)$ and it is therefore obvious that this choice also influences the control action and hence the closed-loop behaviour. The parameter α of the matrix $\boldsymbol{Q}(n_A, T)$ appears in the expression of the function $v(T)$ and hence in the expression of $\mathscr{P}_a(n_A, T)$. (4.31) gives a condition on the choice of α so that a stabilizing control action can be found.

The function $f_a(z)$ influences the closed-loop behaviour since it fixes the function $\mathscr{P}_a(n_A, T)$. The unique limitations in the choice of $f_a(z)$ are the conditions on its first and second derivative at the set point given in Lemma 4.5 and in Proposition 4.6, i.e. respectively:

$$\frac{1}{|q_{12}|}\left.\frac{df_a}{dz}\right|_{z^*} = \gamma k(T^*) n_A^* + \frac{q_l}{V}\left(T^{in} - T^*\right) = -u_c^*(T_w - T^*)$$

and

$$\frac{1}{|q_{12}|}\frac{d^2 f_a}{dz^2} = \omega > \frac{{k^*}^2 \gamma \frac{q_l}{V} \Psi^*}{4\alpha \frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - k^{*2}\Psi^*}$$

In this thesis we have chosen a particular form for $f_a(z)$, as it can be seen in the proof of Proposition 4.5, namely a second order polynomial because of its simplicity (see (4.40)). Other functions can be chosen provided that the above conditions are fulfilled. In the sequel, we shall work with the expression of $f_a(z)$ given in (4.40).

q_{12} is a scaling factor and hence it vanishes when calculating the control action. As a consequence, with our choice of $f_a(z)$, the control action has two tuning parameters, α and ω. Their possible values are restricted by the Lemma 4.6 in order to ensure the local convergence towards the desired set-point.

Corollary 4.2. *If, in addition to the assumptions of Proposition 4.5, $\alpha < 1$, then the desired equilibrium point (n_A^*, T^*) is asymptotically stable.*

Proof. (n_A^*, T^*) is an isolated minimum[1] of $\mathscr{P}_d(n_A, T)$. If $\alpha < 1$, then the symmetric part of $\boldsymbol{Q}(n_A, T)$ is negative definite: $\boldsymbol{Q}(n_A, T) + \boldsymbol{Q}^t(n_A, T) \prec 0$.

[1]This fact is stated here without proof. Nevertheless it will ensue directly from the analysis of Section 4.4.2 (see Remark 4.14)

The following equation:

$$\nabla^t \mathscr{P}_d\left(n_A, T\right)\left[\boldsymbol{Q}\left(n_A, T\right) + \boldsymbol{Q}^t\left(n_A, T\right)\right]^{-1} \nabla \mathscr{P}_d\left(n_A, T\right) = 0$$

implies $\nabla \mathscr{P}_d\left(n_A, T\right) = 0$. Let us consider the following set:

$$\Omega = \left\{\left(n_A, T\right) | \mathscr{P}_d\left(n_A, T\right) \leq c\right\}$$

where $c \in \mathbb{R}$ is such that Ω contains only one local minimum of $\mathscr{P}_d\left(n_A, T\right)$ and such that the curve $\mathscr{P}_d\left(n_A, T\right) = c$ is closed. Ω is hence compact and invariant. From Corollary 4.1, (n_A^*, T^*) is asymptotically stable. □

Remark 4.12. *The control action $u_c\left(n_A, T\right)$ acts in* (4.18) *via the following term:*

$$g\left(n_A, T\right) u_c\left(n_A, T\right) = \begin{pmatrix} 0 \\ \omega\left(n_A^* - n_A - \int_{T^*}^{T} v\left(\tau\right) d\tau\right) + u_c^*\left(T_w - T^*\right) \end{pmatrix}$$

This term does not depend on the difference $(T_w - T)$ anymore. This means that the actual control input is the transferred heat.

4.4.2 Global convergence of the closed-loop system

The controller designed in the previous section only guarantees a local convergence to the desired equilibrium point, i.e. the system will converge to desired point if and only if the initial conditions are close enough to it. Global convergence is ensured if and only if the shaped potential function $\mathscr{P}_d\left(n_A, T\right)$ does not have other local minima, i.e. if and only if (n_A^*, T^*) is a global minimum of the function $\mathscr{P}_d\left(n_A, T\right)$.

Let us consider the following function:

$$\begin{aligned}\Delta\left(T\right) = \gamma \frac{q_l}{V}\left(C_A^{in} V - n_A^{eq}\left(T\right)\right) + \frac{q_l}{V}\left(T_{in} - T\right) \\ + u_c^*\left(T_w - T^*\right) - \omega \underbrace{\left(n_A^{eq}\left(T\right) - n_A^* + \int_{T^*}^{T} v\left(\tau\right) \mathrm{d}\tau\right)}_{z\left(n_A^{eq}(T), T\right) - z^*}\end{aligned} \tag{4.41}$$

where the function $n_A^{eq}(T)$ has been defined in (2.11a). In the simplified case of the CSTR which is considered in this chapter, $n_A^{eq}(T)$ is given by the following relationship:

$$n_A^{eq}(T) = \frac{\frac{q_l}{V} C_A^{in} V}{k(T) + \frac{q_l}{V}}$$

Remark 4.13. *The function $\Delta(T)$ defined in (4.41) is directly related to the function $\Delta^{eq}(T)$ defined in (2.14):*

$$\Delta(T) = \frac{\Delta^{eq}(T)}{\mathscr{C}_p V}$$

with

$$\kappa(T_w - T) = \mathscr{C}_p V \left[u_c^* (T_w - T^*) - \omega \left(n_A^{eq}(T) - n_A^* + \int_{T^*}^{T} v(\tau)\, \mathrm{d}\tau \right) \right]$$

Lemma 4.7. *A state $\left(n_A^{\#}, T^{\#}\right)$ is an equilibrium state of the closed loop system if and only if it is contained in the following set:*

$$\Omega = \left\{ \Delta\left(T^{\#}\right) = 0,\ n_A^{\#} = n_A^{eq}\left(T^{\#}\right) \right\}$$

Proof. Let $\left(n_A^{\#}, T^{\#}\right)$ be an equilibrium state of the closed loop system. Hence we have:

$$\begin{cases} \dfrac{dn_A}{dt} = 0 = \dfrac{q_l}{V}\left(C_A^{in} V - n_A^{\#}\right) - k\left(T^{\#}\right) n_A^{\#} \\ \dfrac{dT}{dt} = 0 = \dfrac{q_l}{V}\left(T^{in} - T^{\#}\right) + \gamma k\left(T^{\#}\right) n_A^{\#} \\ \qquad\qquad + \omega \left(n_A^* - n_A^{\#}\left(T^{\#}\right) - \displaystyle\int_{T^*}^{T^{\#}} v(\tau)\, \mathrm{d}\tau \right) + u_c^* (T_w - T^*) \end{cases} \tag{4.42}$$

The first equation can be rewritten as follows:

$$n_A^{\#} = \frac{\frac{q_l}{V} C_A^{in} V}{k\left(T^{\#}\right) + \frac{q_l}{V}} = n_A^{eq}\left(T^{\#}\right)$$

When replacing this expression into the second equation of (4.42), the right-hand term is equal to $\Delta\left(T^{\#}\right)$.

To prove the "only-if" part, let us consider a state $\left(n_A^{\#}, T^{\#}\right)$ that is contained in Ω. By replacing n_A by the expression of $n_A^{eq}\left(T^{\#}\right)$ in (4.18), it is

obvious that $\frac{dn_A}{dt} = 0$ if $\left(n_A^{\#}, T^{\#}\right) \in \Omega$. Let us now consider the temperature dynamics:

$$\begin{aligned}\frac{dT}{dt} &= \frac{q_l}{V}\left(T^{in} - T^{\#}\right) + \gamma k\left(T^{\#}\right) n_A^{\#} + u_c\left(n_A^{\#}, T^{\#}\right)\left(T_w - T^{\#}\right) \\ &= \frac{q_l}{V}\left(T^{in} - T^{\#}\right) + \gamma k\left(T^{\#}\right) n_A^{eq}\left(T^{\#}\right) + u_c^*\left(T_w - T^*\right) \\ &\quad + \omega\left(n_A^* - n_A^{eq}\left(T^{\#}\right) - \int_{T^*}^{T^{\#}} v\left(\tau\right) d\tau\right)\end{aligned}$$

The right-hand term is equal to $\Delta\left(T^{\#}\right)$ and consequently, we have $\frac{dT}{dt} = 0$. □

Remark 4.14. *The critical points of $\mathscr{P}_d\left(n_A, T\right)$ are also the equilibrium points of the closed-loop system. Hence all the critical points of $\mathscr{P}_d\left(n_A, T\right)$ are contained in the set*

$$\Omega = \left\{\Delta\left(T^{\#}\right) = 0,\ n_A^{\#} = n_A^{eq}\left(T^{\#}\right)\right\}$$

The shape of $\Delta\left(T\right)$ and of $n_A^{eq}\left(T\right)$ imply that the minima of $\mathscr{P}_d\left(n_A, T\right)$ are obviously isolated minima, as it has been assumed in the proof of Corollary 4.2.

The function $\Delta\left(T\right)$ is linear in the parameter ω. Therefore it can be written as follows:

$$\Delta\left(T\right) = \Delta_0\left(T\right) + \omega\Delta_\omega\left(T\right)$$

Following Remark 4.13, we have:

$$\Delta_0\left(T\right) = \left(\frac{\Delta^{eq}\left(T\right)}{\mathscr{C}_p V}\right)\Bigg|_{\kappa=0} + u_c^*\left(T_w - T^*\right)$$

As a consequence $\Delta_0\left(T\right)$ has the same shape as $\Delta^{eq}\left(T\right)$. The existence of the three open-loop equilibria implies that $\Delta^{eq}\left(T\right)$ and consequently $\Delta_0\left(T\right)$ are decreasing for low and high temperatures, but increasing on one determined interval. As a consequence, $\Delta\left(T\right)$ can have several zeros, depending on the term $\omega\Delta_\omega\left(T\right)$.

Proposition 4.6. *If the parameter α fulfills the following condition:*

$$\forall T \in \mathbb{R}^+ :\ 1 \geq \alpha > \frac{\Psi\left(T\right) k^2\left(T\right)}{4\frac{q_l}{V}\left(k\left(T\right) + \frac{q_l}{V}\right)^2} \tag{4.43}$$

where

$$\Psi(T) = -\left(k(T) + \frac{q_l}{V}\right) + \frac{dk}{dT}\gamma n_A^{eq}(T) \tag{4.44}$$

then there exists a lower bound on ω *such that* $\Delta(T)$ *has only one zero.*

Proof. The parameter ω reshapes the function $\Delta_0(T)$ into the function $\Delta(T)$ as follows:

$$\frac{d\Delta}{d\omega} = \Delta_\omega(T) = -\int_{T^*}^{T} \frac{-k^2(\tau)\Psi(\tau) + 4\alpha\frac{q_l}{V}\left(k(\tau) + \frac{q_l}{V}\right)^2}{\gamma k^2(\tau)\left(\frac{q_l}{V} + k(\tau)\right)} \mathrm{d}\tau$$

If the numerator is positive, i.e. if

$$\forall T \in \mathbb{R}^+ : \ 1 \geq \alpha > \frac{\Psi(T)\, k^2(T)}{4\frac{q_l}{V}\left(k(T) + \frac{q_l}{V}\right)^2}$$

then $\Delta_\omega(T)$ is of the sign of $-(T - T^*)$. As a consequence for $\omega > 0$, we have:

$$\begin{aligned} &\Delta(T) > \Delta_0(T) && \text{for } T < T^* \\ &\Delta(T) < \Delta_0(T) && \text{for } T > T^* \\ &\Delta(T) = \Delta_0(T) && \text{for } T = T^* \end{aligned}$$

Figure 4.2 presents all the possible configurations for $\Delta_0(T)$. It is obvious that if the value of ω is sufficiently high, then $\Delta(T)$ has only one zero: the desired closed-loop equilibrium. In the cases (a), (b) and (c), the lower bound on ω is negative and consequently any positive value of ω ensures the global convergence. □

Remark 4.15. *Figure 4.2(a) is the particular case where there is only one equilibrium in the open-loop CSTR.*

Proposition 4.6 is illustrated in Figure 4.3.

Proposition 4.7. *If* (4.43) *is fulfilled and*

$$\forall T \in \mathbb{R}^+ : \ \omega > \frac{\frac{q_l}{V}\Psi(T)\gamma k^2}{-k^2\Psi(T) + 4\alpha\frac{q_l}{V}\left(k + \frac{q_l}{V}\right)} \tag{4.45}$$

then the controller (4.39) *achieves global stability of the desired equilibrium point.*

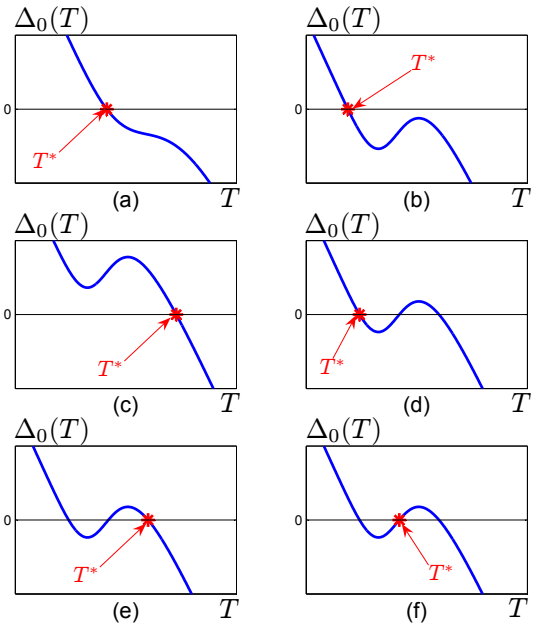


Figure 4.2: Possible configurations for $\Delta_0(T)$

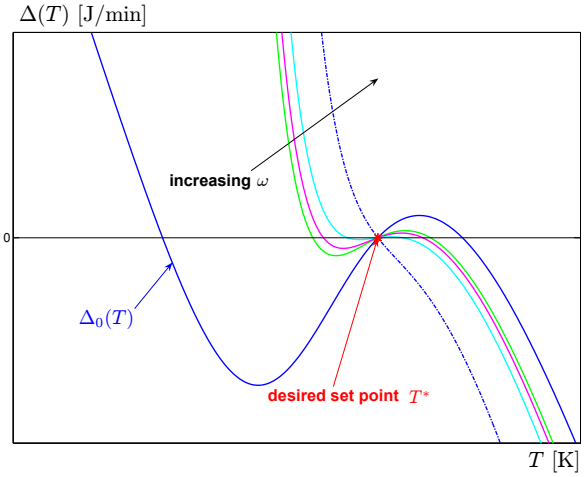


Figure 4.3: Influence of ω on $\Delta(T)$

Proof. (4.43) and (4.45) imply (4.31) and (4.32), respectively. Using Proposition 4.5, the desired equilibrium is locally stable.

Moreover, the derivative of $\Delta(T)$ is given as follows:

$$\frac{d\Delta}{dT} = \frac{\frac{q_l}{V}\Psi(T)\gamma k(T)^2 - \omega\left(-k(T)^2\Psi(T) + 4\alpha\frac{q_l}{V}\left(k + \frac{q_l}{V}\right)\right)}{\gamma k(T)^2\left(k(T) + \frac{q_l}{V}\right)}$$

Conditions (4.43) and (4.45) imply that $\frac{d\Delta}{dT} < 0$ for all $T > 0$. $\Delta(T)$ is monotonically increasing and hence has a unique zero, namely the desired closed-loop equilibrium. □

Remark 4.16. *The above proposition gives a sufficient condition, but not a necessary one. If α and ω are such that local stability is ensured and such that the shape of $\Delta(T)$ is similar to the shape in Figure 4.2 (b) or (c), there is only one closed-loop equilibrium even if the assumptions of Proposition 4.6 are not fulfilled.*

Remark 4.17. *The conditions for the global convergence* (4.43) *and* (4.45) *are very similar to the ones for the local convergence* (4.31) *and* (4.32)*, respectively, but instead of being satisfied only at the desired set point temperature T^*, they have to be satisfied at any T.*

The shape of the function $\mathscr{P}_d(n_A, T)$ is shown in Figures 4.4 and 4.5. In the first case, the parameters α and ω were chosen such that local convergence is achieved (i.e. (4.32) is fulfilled, but not (4.45)). The function $\mathscr{P}_d(n_A, T)$ has two local minima and consequently the convergence to the desired state is only local. In the second case the parameters α and ω were chosen such that global convergence is achieved (i.e. (4.45) is fulfilled). The function $\mathscr{P}_d(n_A, T)$ has a single minimum and the convergence to the desired state is global.

Remark 4.18. *Even if the conditions of Proposition 4.7 are satisfied, global convergence can be lost if the input is bounded. Local convergence will however be kept. It would be interesting to discuss the size of the attraction region with the proposed controller in case of input constraints compared to other controller proposed in the literature (e.g. in [99][100]).*

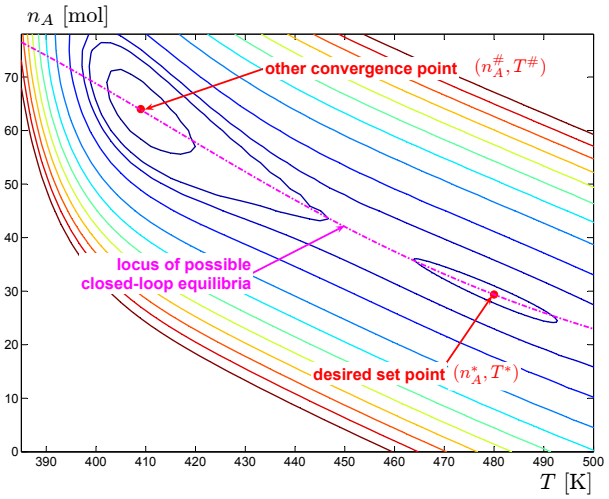


Figure 4.4: Level curves of $\mathscr{P}_d(n_A, T)$ (local convergence)

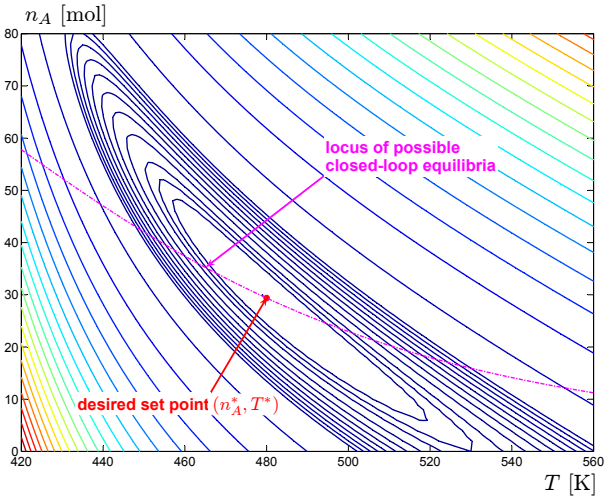


Figure 4.5: Level curves of $\mathscr{P}_d(n_A, T)$ (global convergence)

Example 4.1. *A negative value of the input u_c corresponds to a negative heat coefficient κ. This is of course not physical. Let us assume that the cooling fluid is sufficiently cold, so that we always have $T > T_w$. In fact a negative input then means that the term $u_c\,(T_w - T)$ has to be positive, i.e. we have a to heat the system. Indeed assume that the initial state of the reactor is on the left-hand side of the open loop system separatrix whereas the desired set point is on the right-hand-side. Intuitively, if $T < T^*$, the controller will try to heat the system. But this is not possible by acting on the cooling fluid flow rate since this would mean $\kappa < 0$, and the controller will saturate at $u_c = 0$ which corresponds to the open-loop case. Since the initial state is on the left-hand side of the open-loop separatrix, the trajectories will converge to the open-loop low-temperature equilibrium and will not cross the separatrix. Figure 4.6 shows the temperature evolution when the input is lower and upper-bounded. The lower bound is $u_c = 0$.*

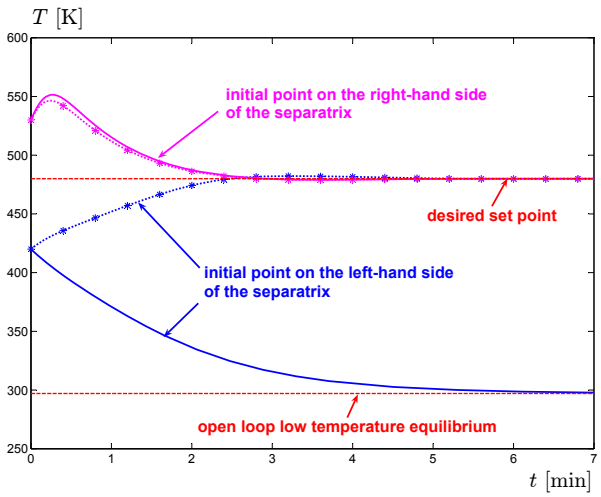


Figure 4.6: Temperature evolution with bounded input (continuous line: with bounded input, dotted line: non-bounded input)

4.4.3 Analysis of the convergence rate

Let us now analyze the influence of the controller parameters on the convergence rate. Therefore we shall linearize the closed-loop system around the desired equilibrium point. Indeed the rate of convergence is linked to the value of the eigenvalues of the matrix of the linearized system.

The matrix of the linearized closed-loop system is given as follows:

$$\mathbf{\Lambda}^{(cl)} = \begin{pmatrix} -\left(\frac{q_l}{V} + k^*\right) & -n_A^* \left.\frac{dk}{dT}\right|_{T^*} \\ \gamma k^* - \omega & -\frac{q_l}{V} + \gamma n_A^* \left.\frac{dk}{dT}\right|_{T^*} - \omega v\left(T^*\right) \end{pmatrix}$$

The sum Σ and the product Π of the eigenvalues $\lambda_1^{(cl)}$ and $\lambda_2^{(cl)}$ of $\mathbf{\Lambda}^{(cl)}$ are given as follows, respectively:

$$\begin{aligned} \Sigma = \lambda_1^{(cl)} + \lambda_2^{(cl)} = \operatorname{tr}\left(\mathbf{\Lambda}^{(cl)}\right) &= -2\frac{q_l}{V} - k^* + \gamma n_A^* \left.\frac{dk}{dT}\right|_{T^*} - \omega v\left(T^*\right) \\ &= -\frac{q_l}{V} + \Psi^* - \omega v\left(T^*\right) \end{aligned} \tag{4.46}$$

$$\begin{aligned} \Pi = \lambda_1^{(cl)}\lambda_2^{(cl)} &= \det\left(\mathbf{\Lambda}^{(cl)}\right) \\ &= -\frac{q_l}{V}\Psi^* + \frac{\omega}{\gamma k^{*2}}\left(4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)^2 - k^{*2}\Psi^*\right) \end{aligned} \tag{4.47}$$

Remark 4.19. *Condition* (4.33b) *is the same as* $\Pi > 0$*. With a similar argument than in the proof of Proposition 4.6, it is possible to show that* $\Pi > 0$ *implies* $\Sigma < 0$*.*

The eigenvalues and the corresponding time constants $\theta^{(cl)}$ are given by the following relations ($|\lambda_1^{(cl)}| < |\lambda_2^{(cl)}|$):

$$\lambda_1^{(cl)} = \frac{\Sigma + \sqrt{\Sigma^2 - 4\Pi}}{2} \qquad \theta_1^{(cl)} = \frac{2}{-\Sigma - \sqrt{\Sigma^2 - 4\Pi}}$$
$$\lambda_2^{(cl)} = \frac{\Sigma - \sqrt{\Sigma^2 - 4\Pi}}{2} \qquad \theta_2^{(cl)} = \frac{2}{-\Sigma + \sqrt{\Sigma^2 - 4\Pi}}$$

The dominant time constant is $\theta_1^{(cl)}$.

Influence of ω We have:

$$\frac{d\theta_1^{(cl)}}{d\omega} = \frac{d\Sigma}{d\omega}\left[\frac{2}{\left(\Sigma+\sqrt{\Sigma^2-4\Pi}\right)^2}\left(1+\frac{2}{2\sqrt{\Sigma^2-4\Pi}}\right)\right] + \frac{d\Pi}{d\omega}\left[\frac{-2}{\left(\Sigma+\sqrt{\Sigma^2-4\Pi}\right)^2}\left(\frac{4}{2\sqrt{\Sigma^2-4\Pi}}\right)\right]$$

with $\frac{d\Sigma}{d\omega} = -v\left(T^*\right) < 0$ and $\frac{d\Pi}{d\omega} = \frac{1}{\gamma k^{*2}}\left(4\alpha\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2 - k^{*2}\Psi^*\right) > 0$. As a consequence, $\frac{d\theta_1^{(cl)}}{d\omega} < 0$. The convergence rate is increasing with increasing values of ω (Figure 4.7).

Influence of α We have:

$$\frac{d\theta_1^{(cl)}}{d\alpha} = \frac{d\Sigma}{d\alpha}\left[\frac{2}{\left(\Sigma+\sqrt{\Sigma^2-4\Pi}\right)^2}\left(1+\frac{2}{2\sqrt{\Sigma^2-4\Pi}}\right)\right] + \frac{d\Pi}{d\alpha}\left[\frac{-2}{\left(\Sigma+\sqrt{\Sigma^2-4\Pi}\right)^2}\left(\frac{4}{2\sqrt{\Sigma^2-4\Pi}}\right)\right]$$

with

$$\frac{d\Sigma}{d\alpha} = -4\frac{q_l}{V}\omega\frac{k^*+\frac{q_l}{V}}{\gamma k^{*2}} < 0$$

and

$$\frac{d\Pi}{d\alpha} = \frac{4\frac{q_l}{V}\left(k^*+\frac{q_l}{V}\right)^2}{\gamma k^{*2}}\omega > 0$$

As a consequence, $\frac{d\theta_1^{(cl)}}{d\omega} < 0$. The convergence rate is increasing with increasing values of α (see Figure 4.8).

4.4.4 Robustness analysis

The control law given in Proposition 4.5 requires the knowledge of the temperature dependence of the kinetic coefficient $k\left(T\right)$ and of the complete state, i.e. also the on-line concentration. In most practical applications, the kinetic coefficient is determined experimentally and the on-line measurement of the concentration is not always achievable or there may be measurement errors. In

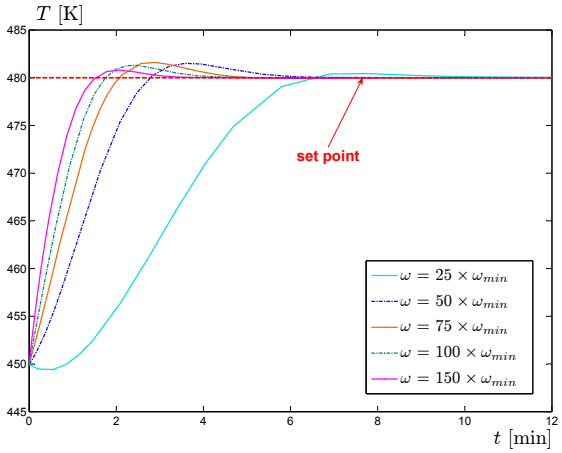


Figure 4.7: Influence of ω on the convergence rate (ω_{min}: lower bound on ω to ensure local convergence)

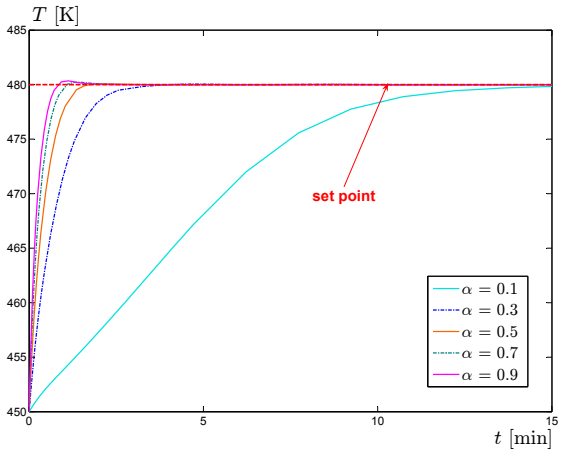


Figure 4.8: Influence of α on the convergence rate

this section we shall analyze the effect on the closed-loop convergence and stability of modelling errors in the kinetic coefficient $k(T)$. We shall also study the influence of error measurements on the stability of the closed-loop equilibrium.

Modelling errors on $k(T)$

Assume there is a modelling error on the kinetic coefficient. The aim is to stabilize the state (n_A^*, T^*). The controller is designed using the estimated function $\hat{k}(T)$ instead of the real kinetic coefficient $k(T)$:

$$\hat{k}(T) = (1 + \xi(T))\, k(T) \tag{4.48}$$

with $\xi(T) > -1$.

Assumption 4.8. Despite the error on $k(T)$, the equilibrium value of n_A is known:

$$n_A^* = n_A^{eq}(T^*) = \frac{q_l}{V} \frac{C_A^{in} V}{\frac{q_l}{V} + k(T^*)} \neq \frac{q_l}{V} \frac{C_A^{in} V}{\frac{q_l}{V} + \hat{k}(T^*)}$$

Assumption 4.9. Despite the error on $k(T)$, the equilibrium value of the control input u_c^* is known:

$$u_c^* = -\frac{q_l}{V}(T_{in} - T^*) - \gamma k(T^*)\, n_A^* \neq -\frac{q_l}{V}(T_{in} - T^*) - \gamma \hat{k}(T^*)\, n_A^*$$

Assumption 4.10. The control input has been designed such that, based on the estimated value of the kinetic coefficient, the desired equilibrium is asymptotically stable, i.e.:

$$\omega > \frac{\hat{k}^{*^2} \gamma \frac{q_l}{V} \hat{\Psi}^*}{4\alpha \frac{q_l}{V} \left(\hat{k}^* + \frac{q_l}{V}\right)^2 - \hat{k}^{*^2} \hat{\Psi}^*}$$

and

$$1 > \alpha > \frac{\hat{k}^{*^2} \hat{\Psi}^*}{4 \frac{q_l}{V} \left(\hat{k}^* + \frac{q_l}{V}\right)^2}$$

with

$$\hat{\Psi}^* = -\left(\hat{k}^* + \frac{q_l}{V}\right) + \left.\frac{d\hat{k}}{dT}\right|_{T^*} \gamma n_A^*$$

From Proposition 4.5, the control input applied to the system is given as follows:

$$u_c\left(T_w - T\right) = \omega\left(n_A^* - n_A - \int_{T^*}^{T} \hat{v}\left(\tau\right) d\tau\right) + u_c^*\left(T_w - T^*\right)$$

with

$$\hat{v}\left(T\right) = \frac{\hat{k}^2\left(T\right) + 4\alpha\frac{q_l}{V}\left(\hat{k}\left(T\right) + \delta\right)}{\gamma\hat{k}^2\left(T\right)}$$

Assumptions 4.8 and 4.9 imply that (n_A^*, T^*) is still an equilibrium of the closed-loop system.

The matrix of the linearized system around (n_A^*, T^*) is given as follows:

$$\mathbf{\Lambda}^{(cl)} = \begin{pmatrix} -\left(\frac{q_l}{V} + k^*\right) & -n_A^* \left.\frac{dk}{dT}\right|_{T^*} \\ \gamma k^* - \omega & -\frac{q_l}{V} + \gamma n_A^* \left.\frac{dk}{dT}\right|_{T^*} - \omega\hat{v}\left(T^*\right) \end{pmatrix}$$

The trace and the determinant of $\mathbf{\Lambda}^{(cl)}$ are given by the following relations:

$$\begin{aligned} \operatorname{tr}\mathbf{\Lambda}^{(cl)} &= \Psi^* - \frac{q_l}{V} - \omega\hat{v}\left(T^*\right) \\ \det\mathbf{\Lambda}^{(cl)} &= -\frac{q_l}{V}\Psi^* + \omega\frac{-\hat{k}^{*2}\Psi^* + 4\alpha\frac{q_l}{V}\left(k^* + \frac{q_l}{V}\right)\left(\hat{k}^* + \frac{q_l}{V}\right)}{\gamma\hat{k}^{*2}} \end{aligned}$$

Using (4.48), we can write the following equation:

$$\begin{aligned} \hat{\Psi}^* &= \gamma n_A^* \left.\frac{d\hat{k}}{dT}\right|_{T^*} - \left(\hat{k}^* + \frac{q_l}{V}\right) \\ &= \left(\gamma n_A^* \left.\frac{dk}{dT}\right|_{T^*} - \left(k^* + \frac{q_l}{V}\right)\right)\left(1 + \xi\left(T^*\right)\right) + \frac{q_l}{V}\xi\left(T^*\right) \\ &\quad + \gamma n_A^* k^*\left(1 + \xi\left(T^*\right)\right) \left.\frac{dk}{dT}\right|_{T^*} \\ &= \Psi^*\left(1 + \xi^*\right) + \gamma n_A^* k^* \left.\frac{d\xi}{dT}\right|_{T^*} + \frac{q_l}{V}\xi^* \end{aligned}$$

where $\xi^* = \xi\left(T^*\right)$. As a consequence the trace and the determinant of $\mathbf{\Lambda}^{(cl)}$ can be rewritten as follows:

$$\left(1 + \xi^*\right)\operatorname{tr}\mathbf{\Lambda}^{(cl)} = \hat{\Psi}^* - \frac{q_l}{V} - \omega\hat{v}\left(T^*\right) - \left[\left.\frac{d\xi}{dT}\right|_{T^*} \gamma k^* n_A^* + 2\xi^*\frac{q_l}{V} + \omega\xi^*\hat{v}\left(T^*\right)\right]$$

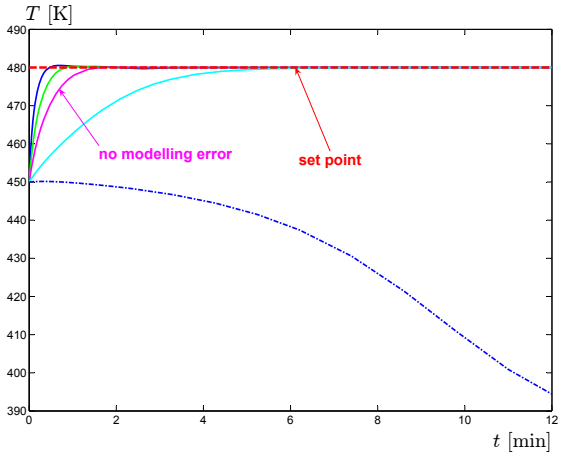


Figure 4.9: Influence of the modelling error on $k(T)$ (with different values of the modelling error)

and

$$(1+\xi^*)\det \mathbf{\Lambda}^{(cl)} = -\frac{q_l}{V}\hat{\Psi}^* + \omega\left(4\alpha\frac{q_l}{V}\left(\hat{k}^* + \frac{q_l}{V}\right)^2 - \hat{k}^{*2}\hat{\Psi}^*\right)$$
$$+ k^* n_A^* \left.\frac{d\xi}{dT}\right|_{T^*}\left(\frac{q_l}{V}\gamma + \omega\right) + \frac{q_l}{V}\xi^* \frac{\frac{q_l}{V}\gamma\hat{k}^{*2} + \omega\left(\hat{k}^{*2} + 4\alpha\frac{q_l}{V}\left(\hat{k}^* + \frac{q_l}{V}\right)\right)}{\gamma\hat{k}^{*2}}$$

The closed-loop equilibrium is asymptotically stable if and only if the trace is strictly negative and the determinant is strictly positive. Using the inequalities of Assumption 4.10, this means that if $\xi^* > 0$ and $\left.\frac{d\xi}{dT}\right|_{T^*} \geq 0$, the closed-loop equilibrium is asymptotically stable. But if these two conditions are not fulfilled, then the closed-loop equilibrium can become unstable. This can be seen in Figure 4.9.

Measurement errors on n_A

The aim is to stabilize the set point (n_A^*, T^*). Let us assume that there is a measurement error on the concentration. Instead of the real value n_A, the sensor measures the value $\hat{n}_A$ which is used to compute the control input. The

measurement error is given as follows:

$$\hat{n}_A = (1 + \xi(t))\, n_A$$

with $\xi(t) > -1$.

Assumption 4.11. The parameters of the control input have been chosen such that without measurement error the desired set point is exponentially asymptotically stable.

Assumption 4.12. The relative measurement error is bounded, i.e. for all $t > 0$, $|\xi(t)| < \hat{\xi}$.

Using Assumption 4.11 the control input is given by the following expression:

$$u_c(T_w - T) = u_c^*(T_w - T^*) - \omega\left(\hat{n}_A - n_A^* + \int_{T^*}^{T} v(\tau)\,\mathrm{d}\tau\right)$$

The closed-loop dynamics of the system are given by the following differential equations:

$$\begin{cases} \dfrac{dn_A}{dt} = \dfrac{q_l}{V}\left(C_A^{in}V - n_A\right) - k(T)\, n_A \\ \dfrac{dT}{dt} = \dfrac{q_l}{V}\left(T^{in} - T\right) + \gamma k(T)\, n_A + u_c^*(T_w - T^*) \\ \qquad\qquad - \omega\left(\hat{n}_A - n_A^* + \displaystyle\int_{T^*}^{T} v(\tau)\,\mathrm{d}\tau\right) \end{cases} \tag{4.49}$$

The measurement error adds a non-vanishing perturbation term to the expected closed-loop dynamics. The dynamics of the perturbed system can be written in a more compact form as follows:

$$\frac{d}{dt}\begin{pmatrix} n_A \\ T \end{pmatrix} = f^{(cl)}(n_A, T) + \tilde{f}(n_A, t) \tag{4.50}$$

with the following unperturbed closed-loop dynamics:

$$f^{(cl)}(n_A, T) = \begin{pmatrix} \frac{q_l}{V}\left(C_A^{in}V - n_A\right) - k(T)\, n_A \\ \frac{q_l}{V}(T_{in} - T) + \gamma k(T)\, n_A + u^*(T_w - T^*) - \omega\left(n_A - n_A^* + \int_{T^*}^{T} v(\tau)\,\mathrm{d}\tau\right) \end{pmatrix}$$

and the perturbation term:

$$\tilde{f}\left(n_A, t\right) = \begin{pmatrix} 0 \\ -\omega n_A \xi\left(t\right) \end{pmatrix}$$

Proposition 4.8. *There exists an upper bound on $\hat{\xi}$ and positive constants ρ_0, ε, a and b, such that the trajectories of the perturbed system* (4.49) *satisfy the following relations for all $\|x\left(t_0\right) - x^*\| < \rho_0$:*

$$\begin{aligned} &\|x\left(t\right) - x^*\| < a \left\|x\left(t_0\right) - x^*\right\| e^{-b\left(t - t_0\right)} && \forall t:\ 0 \leq t_0 \leq t < \theta + t_0 \\ &\|x\left(t\right) - x^*\| \leq \varepsilon, && \forall t:\ t \geq t_0 + \theta \end{aligned}$$

with $x = \left(n_A, T\right)$ and $x^* = \left(n_A^*, T^*\right)$ for some finite θ.

Proof. First let us consider the system without any perturbation:

$$\frac{d}{dt}\begin{pmatrix} n_A \\ T \end{pmatrix} = f^{(cl)}\left(n_A, T\right) \tag{4.51}$$

From Assumption 4.11, this system has an exponentially asymptotically stable equilibrium point at $\left(n_A^*, T^*\right)$. Let $0 < \rho$ be a real value such that the disc:

$$\Omega_\rho = \left\{\left(n_A, T\right) \mid \|\left(n_A, T\right) - \left(n_A^*, T^*\right)\| < \rho\right\}$$

is contained in the domain of the system (i.e. $n_A \geq 0$ and $T > 0$). ρ is obviously finite. Hence the Jacobian matrix

$$\begin{pmatrix} \frac{\partial f_1^{(cl)}}{\partial n_A} & \frac{\partial f_1^{(cl)}}{\partial T} \\ \frac{\partial f_2^{(cl)}}{\partial n_A} & \frac{\partial f_2^{(cl)}}{\partial T} \end{pmatrix} = \begin{pmatrix} -\left(k\left(T\right) + \frac{q_l}{V}\right) & -n_A \frac{dk}{dT} \\ \gamma k\left(T\right) - \omega & -\frac{q_l}{V} + \gamma n_A \frac{dk}{dT} - \omega v\left(T\right) \end{pmatrix}$$

is bounded on Ω_ρ. $\left(n_A^*, T^*\right)$ is an exponentially asymptotically stable equilibrium of (4.51). As a consequence, there exist positive constants $\rho_0 < \rho$, a_1 and b_1 such that for all $\|x\left(t_0\right) - x^*\| < \rho_0$ the following relation is satisfied:

$$\|x\left(t\right) - x^*\| < a_1 \left\|x\left(t_0\right) - x^*\right\| e^{-b_1\left(t - t_0\right)} \quad \forall t > t_0 > 0$$

From Lyapunov's converse theorem[1], there exists a Lyapunov function $\mathscr{V}\left(n_A, T\right) : \Omega_{\rho_0} \to \mathbb{R}$ that fulfills the following conditions:

$$c_1 \left\|x\left(t\right) - x^*\right\|^2 \leq \mathscr{V}\left(n_A, T\right) \leq c_2 \left\|x\left(t\right) - x^*\right\|^2$$

[1] see [63]: Theorem 4.14, p.162

$$\frac{\partial \mathscr{V}}{\partial x} f^{(cl)}\left(n_A, T\right) \leq -c_3 \left\|x\left(t\right) - x^*\right\|^2$$
$$\left\| \frac{\partial \mathscr{V}}{\partial x} \right\| \leq c_4 \left\|x\left(t\right) - x^*\right\|$$

for some positive constants c_1, c_2, c_3 and c_4.

Now let us consider the perturbed system (4.50). The perturbation term $\tilde{f}\left(n_A, t\right)$ is bounded on Ω_{ρ_0}. Indeed:

$$\left\| \begin{pmatrix} 0 \\ -\omega n_A \xi\left(t\right) \end{pmatrix} \right\| < |\omega|(n_A^* + \rho_0)\,\hat{\xi} = \delta, \quad \forall t < 0,\ \forall \left(n_A, T\right) \in \Omega_{\rho_0}$$

where Ω_{ρ_0} is the disc of radius ρ_0 centred at (n_A^*, T^*). Let us assume that the measurement error is sufficiently small such that:

$$\frac{c_4}{c_3}\sqrt{\frac{c_2}{c_1}}|\omega|\frac{(n_A^* + \rho_0)}{\rho_0}\hat{\xi} < 1 \tag{4.52}$$

and let us consider a real value ζ as follows:

$$\frac{c_4}{c_3}\sqrt{\frac{c_2}{c_1}}|\omega|\frac{(n_A^* + \rho_0)}{\rho_0}\hat{\xi} < \zeta < 1$$

Let us apply Lyapunov's theorem for perturbed systems[1]. For all initial conditions such that $\left\|x\left(t_0\right) - x^*\right\| < \sqrt{\frac{c_1}{c_2}}\rho_0$, the trajectories of the perturbed system satisfy:

$$\left\|x\left(t\right) - x^*\right\| < a_2 \left\|x\left(t_0\right) - x^*\right\| e^{-b_2(t - t_0)} \quad \forall 0 \leq t_0 \leq t < \theta + t_0$$

and $\left\|x\left(t\right) - x^*\right\| \leq \varepsilon$, $\forall t \geq t_0 + \theta$ for some finite θ, with:

$$a_2 = \sqrt{\frac{c_2}{c_1}},\ b_2 = \frac{c_4}{c_3}\sqrt{\frac{c_2}{c_1}}\frac{\delta}{\zeta},\ \varepsilon = \frac{(1 - \zeta)\,c_3}{2c_2}$$

The upper bound on $\hat{\xi}$ is given by relation (4.52). □

Proposition 4.8 implies that if the measurement error is sufficiently small and the initial condition is sufficiently near to the desired set point, then the trajectories of the system will converge to a disc centered at the desired set point. This can be seen in Figure 4.10.

[1] see [63]: Theorem 9.2, p.347

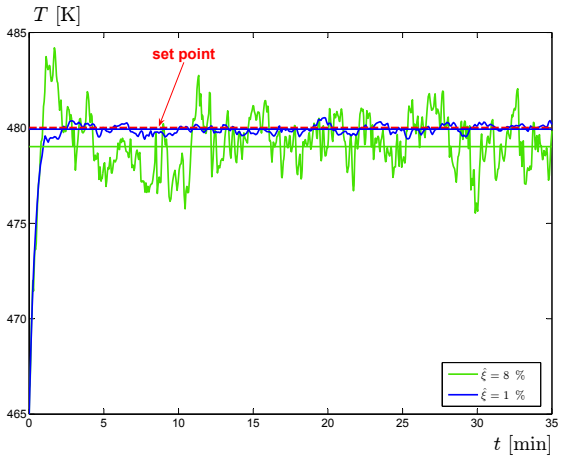


Figure 4.10: Influence of the measurement error on the closed-loop trajectories (horizontal line: mean temperature from 15 min to 60 min)

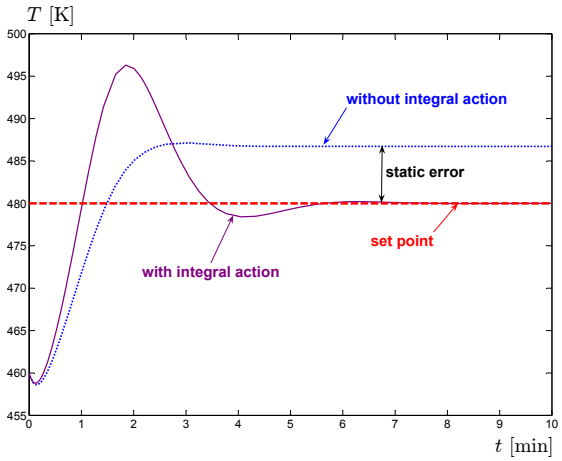


Figure 4.11: Cancellation of the static error due to an erroneous estimation of n_A^* and u_c^*

Cancellation of the static error

The form of the controller proposed in Proposition 4.5 is very similar to a proportional controller and in particular it does not contain an integral term. This means that static errors could appear. For instance up to now, we have always considered that the values of n_A^* and u_c^* corresponding to the desired temperature T^* are exactly known. But in practice these values are determined either experimentally or by using the expressions (4.26) and (4.28) which contain terms that are also determined experimentally.

Let us assume that erroneous values $\hat{n}_A^*$ and $\hat{u}_c^*$ are used in the control law (4.39). The closed-loop dynamics are then given as follows:

$$\begin{cases} \dfrac{dn_A}{dt} = \dfrac{q_l}{V}\left(C_A^{in}V - n_A\right) - k\left(T\right)n_A \\ \dfrac{dT}{dt} = \dfrac{q_l}{V}\left(T^{in} - T\right) + \gamma k\left(T\right)n_A + \hat{u}_c\left(T_w - T\right) \end{cases} \tag{4.53}$$

with

$$\hat{u}_c\left(n_A, T\right)\left(T_w - T\right) = \omega\left(\hat{n}_A^* - n_A - \int_{T^*}^{T} v\left(\tau\right)d\tau\right) + \hat{u}_c^*\left(T_w - T^*\right)$$

The equilibrium points of the above system are given by the set $\left\{\left(\bar{n}_A, \bar{T}\right) \middle| \bar{n}_A = n_A^{eq}\left(\bar{T}\right), \hat{\Delta}\left(\bar{T}\right) = 0\right\}$ where $\hat{\Delta}\left(T\right)$ is defined as follows:

$$\hat{\Delta}\left(T\right) = \frac{q_l}{V}\left(T^{in} - T\right) + \gamma k\left(T\right)n_A^{eq}\left(T\right) + \hat{u}_c\left(T_w - T\right)$$

By comparing with (4.41), it is easy to see that:

$$\hat{\Delta}\left(T\right) = \Delta\left(T\right) + \left(\hat{u}_c^* - u_c^*\right)\left(T_w - T^*\right) + \omega\left(\hat{n}_A^* - n_A^*\right)$$

Since the equilibrium points of (4.53) are the zeros of $\hat{\Delta}\left(T\right)$, we obviously will have a static error (see Figure 4.11).

In order to cancel this static error, we shall add an integral action to the controller. (4.53) is then rewritten as follows:

$$\begin{cases} \dfrac{dn_A}{dt} = \dfrac{q_l}{V}\left(C_A^{in}V - n_A\right) - k\left(T\right)n_A \\ \dfrac{dT}{dt} = \dfrac{q_l}{V}\left(T^{in} - T\right) + \gamma k\left(T\right)n_A + \hat{u}_c\left(T_w - T\right) + \dfrac{\omega}{\tau_I}e\left(t\right) \\ \dfrac{de}{dt} = T^* - T \end{cases}$$

It is easy to see that the unique equilibrium point is now $(n_A^* = n_A^{eq}(T), T^*)$ as desired. Around this equilibrium point the characteristic polynomial of the linearized dynamics is given by the following expression:

$$-\lambda^3 + \Sigma\lambda^2 + \left(\frac{\omega}{\tau_I} - \Pi\right)\frac{\omega}{\tau_I} - \left(\frac{q_l}{V} + k^*\right)$$

Using the Routh-Herwitz criterion, the equilibrium is locally asymptotically stable if and only if the following conditions are fulfilled:

$$\Sigma < 0 \quad \text{and} \quad \frac{\omega}{\tau_I} < 0 \quad \text{and} \quad \frac{\omega}{\tau_I}\left(\Sigma + \frac{q_l}{V} + k^*\right) < \Sigma\Pi$$

Remark 4.20. *It is not necessary any more that ω and α are such that $\Pi > 0$. It is sufficient that $\Pi - \frac{\omega}{\tau_I} > 0$.*

As a conclusion, the addition of an integral action with an adequately chosen gain cancels a static error. This is illustrated in Figure 4.11.

4.5 Extension to more complex systems

The power-shaping approach has given interesting results on the case study of a CSTR with an irreversible reaction. It is therefore of major interest to see if this approach can be extended to more complex systems, and more particularly to systems with more than one reacting chemical species and/or with multiple reactions.

We shall now look at some particular cases of more complex reactions to get a first intuition of the existence of non-singular and negative semi-definite solutions of (4.17a) and (4.17b). The detailed solution of (4.17a) and (4.17b) for three particular cases (namely parallel reactions, reactions with two reactants and consecutive reactions) is shown in Appendix D. In the three cases it has been assumed that the kinetic functions $\phi_m^{(l)}(n_m)$ can be expressed as powers of n_m, i.e.:

$$\phi_m^{(l)}(n_m) = (n_m)^{\zeta_m^{(l)}}$$

Parallel reactions and reactions with two reactants For the case of parallel reactions, a solution to (4.17a) and (4.17b) has been found only if

the kinetics of the two reactions have a particular form (kinetics of the same order or at least one first-order reaction). In the case of one reaction with two reactants, a solution to (4.17a) and (4.17b) has been found in the general case. However in both cases, the obtained matrix may have a non-negative symmetric part. Therefore the corresponding potential functions cannot be used in general as a Lyapunov functions for the open-loop system because they may be non-decreasing along the system trajectories.

In the case of parallel reactions with more general kinetics, (4.17a) and (4.17b) have no non-singular solution. This does not mean that the dynamics cannot be put into the Brayton-Moser form. But if the Brayton-Moser form exists, then the relation (4.14) is not fulfilled and the partial differential equation (4.13) has to be solved.

As shown in [40], given a matrix $\boldsymbol{Q}(x)$ that fulfills (4.4), other solutions to (4.4) can be built departing from the first one. Applying this methodology on the matrices that have been found could lead to another matrix $\boldsymbol{Q}(x)$ that would be negative-definite and hence give a Lyapunov function for the open-loop system.

Remark 4.21. *In the particular case of parallel reactions with first order kinetics, an additional solution for the matrix* $\boldsymbol{Q}(x)$ *has been found, which does not exist for higher order kinetics. This particular solution has a very similar form to the form of the matrix proposed in Lemma 4.1. This seems to indicate that the matrix* $\boldsymbol{Q}(n_A, T)$ *that has been used in the previous sections is a particular solution of* (4.20) *that exists only in the case of first-order kinetics.*

Consecutive reactions In this case (4.17a) and (4.17b) have no non-singular solution. This does not mean that the dynamics cannot be put into the Brayton-Moser form. But if the Brayton-Moser form exists, then the relation (4.14) is not fulfilled and the partial differential equation (4.13) has to be solved.

4.6 Conclusion

A description of the power-shaping control approach of the simplified CSTR has been presented in this chapter. The main results that have been obtained by this approach have been presented and illustrated by some simulation results. Contrary to previous works and approaches, a global Lyapunov function for the exothermic CSTR has been found using the power-shaping approach. This Lyapunov function could then be used to design a controller for stabilizing the reactor at a desired temperature. Some results about the local and global convergence of the controller have also been shown.

The Lyapunov function that has been found is the potential function of the Brayton-Moser formulation of the CSTR dynamics. It contains a quadratic term that is linked to the convection phenomena and a more complex term that is linked to the reaction kinetics. The obtained controller also clearly shows that the real manipulated variable is the heat flow, as we can expect it from physical considerations. As a consequence the same controller can be implemented practically by acting on the temperature of the cooling fluid instead of the heat transfer coefficient as it has been assumed in the above study. Although the potential function has a physical meaning for the Brayton-Moser formulation of electrical or mechanical systems, the physical interpretation of the potential function of the CSTR has still to be found. This interpretation could possibly give more insight about the multiple open loop equilibria, and also on the action of the controller.

We have analyzed the influence of the controller parameters on the closed-loop system performance. The controller obtained by the power-shaping control approach depends on the knowledge of the reaction kinetics and of the on-line measurements of the concentration. Both quantities are usually not exactly known and therefore we have performed a robustness study. We have shown that the controller is robust against modelling errors on the kinetics, and we have shown how the choice of the controller parameters influences the robustness. The obtained controller is also robust against concentration measurement errors.

Finally we studied the possibility of extending the previous work to more

complex systems, and more precisely CSTRs with multiple reactions and/or multiple reactants. The extension seems to be rather complex, even for simple cases such as two parallel reactions or two consecutive reactions with mass action law kinetics. Indeed, in the simple CSTR case with a single first-order kinetics reaction, the solution of the partial differential equation needed to write the system dynamics in the Brayton-Moser form has been found by transforming it into an algebraic one. For the three considered particular cases the corresponding algebraic equation system has either no non-singular solution (consecutive reactions, parallel reactions) or a solution that may have a non-negative symmetric part (parallel reactions with reactions of the same order or with at least one first-order reaction, reaction with two reactants). The study presented here is only embryonic and it does not imply that the power-shaping control approach cannot be applied. But the Brayton-Moser form of the dynamics (if it exists) actually needs the solution of the partial differential equation, and not of its simplified version which is the algebraic equation. Nevertheless in the cases where an indefinite matrix $\boldsymbol{Q}(x)$ has been found, the work presented in [40] offers the possibility of finding an alternative negative semi-definite matrix without having to solve the partial differential equation. Also in this study we have only considered a particular form of the kinetics, namely we have assumed that the kinetics can be written as a product of powers of the concentration (i.e. a more general form of the mass action law) and a kinetic term. This is only a restricted class of the possible kinetic laws. Indeed it could also be interesting to apply the power-shaping control to other forms of kinetics such as the Monod kinetics (biological systems) or the Michaelis-Menten kinetics (enzymatic reactions), for instance.

The Brayton-Moser formulation of the dynamics is very similar to a port-Hamiltonian system. A port-Hamiltonian formulation of the dynamics can be obtained directly using the Brayton-Moser potential function $\mathscr{P}(n_A, T)$ as the Hamiltonian function, and the symmetric (resp. skew-symmetric part) of $\boldsymbol{Q}^{-1}(n_A, T)$ as the dissipative (resp. interconnection) matrix. The power-shaping approach seems quite similar to the interconnection and damping assignment method that has been presented for instance in [54] and [87]. But contrary to this approach, in power-shaping control the interconnection and

dissipative matrices of the system are not modified by the control action. Let us also mention that the output in the Brayton-Moser formulation can be any function of the state whereas in the port-Hamiltonian expression of the dynamics, the outputs are conjugated to the inputs. A port-Hamiltonian representation of some simple CSTRs has been given in [87] where the system inputs are the dilution rate $\frac{q_l}{V}$ and the exchanged heat $u_c\,(T_w - T)$. Like in the present study, the port-Hamiltonian approach presented in [87] has only been applied for some particular cases, and no generalization to more complex systems has been found, yet. A possible way for extending the present approach to more complex systems could therefore be to take advantage from the similarity of the two formulations, for example by first obtaining a port-Hamiltonian expression of the dynamics and then applying the power-shaping approach to the corresponding Brayton-Moser form, as it has been shown in [40] for an electrostatic micro-actuator.

Chapter 5

Conclusion

In this part of the thesis we have analyzed the dynamical behaviour of an exothermic CSTR by starting from physical considerations on the system. The CSTR case study has been chosen because of its simple model and at the same time its complex dynamical behaviour.

First we have modelled the CSTR departing from the basic principles of thermodynamics, namely the mass and energy conservation. The model has been established using as less tight modelling assumptions as possible, and when modelling assumptions were necessary we have clearly stated them. The obtained dynamical model for the CSTR differs from the usual model which is often encountered in system theory. Indeed the model usually used in system theory is a simplified model of the more exact thermodynamic model that has been established here. We have also shown the underlying simplifying assumptions which allow the transition from the more exact thermodynamic model to the simplified model. The most important difference between the two models is that here we have considered the extensive quantities as the state variables (i.e. the quantity of matter of each species and the internal energy) and not the temperature. This is fully justified from a thermodynamic point of view: the dynamical behaviour of the CSTR is due to the flows (matter flow, heat flow) that it exchanges with the environment, and to the chemical reaction. These phenomena act on the extensive quantities which leads to model

the system dynamics by the means of balance equations. The time evolution of the intensive variables is obtained from the balance equations via a change of variables. This change of variables requires the knowledge of the relation between the extensive variables and the intensive ones, and thus we needed the quasi-staticity assumption. We have analyzed the dynamical behaviour using our more general model. We have re-obtained the well-known results that were obtained on the simplified model, but with less tight assumptions (for instance, the reaction heat depends on the temperature, the heat capacity of the mixture depends on the composition). Consequently we have shown that the results are valid in a more general case.

Then we have performed a stability analysis of the dynamical behaviour of the CSTR from a thermodynamic point of view. In the same way as it has already been done for electro-mechanical systems, we tried to relate the Lyapunov theory to physical considerations on the system. Different physical quantities of the system (and more specifically quantities related to the entropy, the entropy production and the internal energy) have been considered as Lyapunov function candidates. Contrary to electro-mechanical systems, the link between the physical quantities and the mathematical tools is not obvious. Nevertheless this stability analysis provides a new insight in the dynamical behaviour of the CSTR. Even if the entropy or the entropy production can seem to be a priori good Lyapunov function candidates, they show their limitations in the case of open systems. However these quantities can be used as Lyapunov function candidates for isolated systems such as for instance adiabatic batch reactors. The internal energy related Lyapunov function candidate has led to define invariant sets.

Finally we considered another approach to analyze the dynamical behaviour of the CSTR. We have applied the power-shaping control approach on the simplified CSTR model. This approach requires to write the dynamical model equations in a particular form, namely the Brayton-Moser equations. The Brayton-Moser equations have been developed for the modelling of electrical circuits and then have been extended to mechanical systems. For these two classes of systems, they provide a potential function that is related to the dissipated power. We have managed to write also the dynamical model of the CSTR

in form of the Brayton-Moser equations. This formulation provided directly a Lyapunov function for the open-loop CSTR defined on the whole state space. A first rough physical interpretation of this Lyapunov function has also been given, but a precise one has still to be found. An alternative Brayton-Moser formulation could provide another potential function with a better physical interpretation. The work presented in [40] may be a way for obtaining this alternative form. The Brayton-Moser formulation of the CSTR dynamics have then been used to design a control system that stabilizes any desired temperature. The closed-loop dynamics are also written in the Brayton-Moser formulation, which consequently provides a Lyapunov function for the closed-loop dynamics. The obtained controller is robust against modelling errors on the kinetics and against concentration measurement errors. Finally we have shown that CSTRs with more complex kinetics (parallel reactions, two reactants) can also be modelled in the Brayton-Moser formulation. But the associated potential cannot be used as a Lyapunov function, since it is not decreasing along the systems trajectories. Again the work presented in [40] may be a way for obtaining another potential which is decreasing along the trajectories.

The approach that has been followed in this part of the thesis provides advances in the understanding of the dynamical behaviour of the CSTR, and of chemical processes in general. First elements that could be used for a thermodynamics-based control approach have been emphasized. However a more formal framework could be helpful for formalizing these results. Therefore in the sequel of this work, we shall formalize the thermodynamics in a mathematical framework and express the dynamical behaviour of thermodynamic systems in this framework.

Part II

Differential geometric approach

The approach that has been adopted in Part I is based on physical considerations on the system. Indeed we tried to interpret physical properties in terms of mathematical objects from nonlinear dynamical system theory. For instance the entropy and the entropy production have been considered as Lyapunov function candidates. Although a precise interpretation has not been found yet, some advances in the understanding of the dynamical behaviour have been achieved. In this part, we shall now consider the issue from another angle: we shall start from the mathematics and express the dynamical behaviour of thermodynamic systems by using mathematical tools. This more formal framework should be helpful for formalizing the previous results and extending them.

A similar approach has already led to significant advances in the control of electro-mechanical systems. Classical mechanics is based on the Newtonian equation and on constraints. These can be translated into an elegant mathematical theory using tools from the differential geometry, namely the symplectic manifolds. Classical electrodynamics based on the Maxwell equations and the Kirchhoff's laws can also nicely be expressed in this framework. In other words the physical notions can be defined in a formal mathematical framework. Once the correspondence between the physical quantities and the mathematical objects has been established, classical control theory can be applied on the mathematical objects and then be physically interpreted.

Significant results have been achieved using this approach on Hamiltonian systems. Hamiltonian systems are defined by their geometric structure (symplectic structure) that takes into account the interactions inside the system (e.g. circuits or mechanisms), and a scalar function, the Hamiltonian function, that represents the energy of the system. They are well suited for the formulation of physical systems in which reversible phenomena take place. Using the concepts of control theory, Hamiltonian systems have been extended in order to include interaction with the environment [17][95]. When dissipative phenomena take place in the system (e.g. friction or resistors), Hamiltonian systems have been extended by considering tensor fields which are no more skew-symmetric. The Hamiltonian function is no more conserved and obeys a dissipation equality with a non-zero dissipation rate [104]. Indeed the Hamiltonian function represents the electro-mechanical energy (i.e. energy stored in the inductors and

capacities, the kinetic energy and the potential energy) but does not represent the internal energy which takes into account thermal effects. Irreversible phenomena result in a transformation of the stored energy into internal energy by heat effects for example. In other words, the dissipation is treated as *external* to the system and the temperature effects are not modelled. But in chemical processes, and more generally in thermodynamic systems, the heat effects and the chemical reaction (which are typical examples of irreversible phenomena) are of the utmost importance. Therefore an alternative formalism that manages to represent the internal energy has to be introduced.

There is no clear mathematical structure that arises from the classical way of introducing thermodynamics in thermodynamics textbooks. The physical notions are intuitive ones and do not have an exact mathematical definition. This is probably what led the Russian mathematician V.I. Arnold to claim the following about thermodynamics [9]: "*Every mathematician knows it is impossible to understand an elementary course in thermodynamics.*" Indeed consider for example the Gibbs' equation that has been presented in Chapter 1. There we introduced the Gibbs' equation from the first law of thermodynamics, without considering some phenomenological laws nor any time evolution equation. But in several textbooks, the Gibbs' equation is introduced by considering the time evolution of the internal energy [91]. By doing this, different concepts are actually mixed together. Indeed the Gibbs' relation expresses the properties of matter (via the fundamental relation), i.e. the thermodynamic equilibrium states. There is no link with any process that the system undergoes. The quasi-staticity assumption concerns the time evolution of the state and is not necessary to use Gibbs' relation. It is only necessary if we want to use the Gibbs' relation to express the time evolution, i.e. if we assume that all intermediate states of a process are thermodynamic equilibrium states. We need to clearly separate the properties of matter (i.e. the thermodynamic equilibrium states) on one side, and the process that undergoes the system (i.e. the interactions with the environment through the fluxes) on the other side.

Recently a formalism has been developed that at the same time accounts for the energy and the entropy balance equations, and generalizes the previously mentioned Hamiltonian approach. This approach is in line with Gibbs'

work [43]. It considers objects from the differential geometry, and more precisely the contact structures, for the representation of thermodynamic systems. Hence the contact formalism relates the thermodynamic properties, laws, quantities etc. to geometric objects. The thermodynamic properties and the time evolution of the state are represented by distinct objects. Indeed, as it shall be explained in Chapter 6, the thermodynamic properties of matter are described by the use of Pfaffian equations whereas the time evolution of the state is described by a particular vector field [10][20][73][75]. The contact geometry has been used to formulate reversible transformations [74] and also to generalize port-Hamiltonian systems to port contact systems representing open irreversible systems [26][27][28][29][31][32].

In this part of the thesis we shall present the contact formalism for the representation of open thermodynamic systems that undergo reversible and irreversible phenomena. In Chapter 6 we shall first present the formalism and how the Gibbs' relation leads to a geometric formulation of the thermodynamics. We shall give the basic features of this formalism, and then we shall show how to model a complex thermodynamic system using this formalism. Chapter 7 focuses on the relation between the dynamical properties of the systems (equilibrium points, asymptotic stability), and the mathematical properties of the geometric objects used to model the system. Finally in Chapter 8 we shall discuss the proposed formalism with respect to two other formalisms for the representation of thermodynamic systems, namely the GENERIC formalism (General Equation for the Non-Equilibrium Reversible-Irreversible Coupling), proposed by Öttinger, Grmela and coworkers [46][47] and the Matrix formalism, proposed by Jongschaap and coworkers [60][61].

Chapter 6

A geometric approach of the thermodynamics

The fundamental principles of thermodynamics have been described in Chapter 1 via an approach based on the physical understanding of the system. We started from familiar concepts (e.g. the temperature of a system) and then went over to more theoretical concepts (e.g. the fundamental relation or the Gibbs' relation).

We have already touched upon some geometric interpretation of the thermodynamics with the fundamental relation. Indeed, the thermodynamics are endowed with a geometric structure as it shall be shown in this chapter. This geometric structure allows to translate the fundamental principles of thermodynamics into mathematical terms, and more precisely by using concepts of differential geometry. Chapter 1 follows the standard approach for introducing Gibbs' relation that it is used in most of classical thermodynamic textbooks (e.g. [91][103]), i.e. Gibbs' relation is presented as a consequence of the first principle. Actually Gibbs' relation expresses the relations between the thermodynamic equilibrium states of the system, independently of its dynamical behaviour. The formalism that is presented in this chapter clearly distinguishes between the thermodynamic model (that is linked to Gibbs' relation) and the

dynamical behaviour of the system (that is linked to the fluxes and hence to the phenomenological laws).

The origin of the structured mathematical representation of thermodynamics are the work of Carathéodory [20], Gibbs [43] and Herman [50]. The structure of thermodynamics corresponds to a particular type of differential geometric structure, namely a contact structure [10][75]. The contact formalism might be used to describe reversible thermodynamic transformations [74] as well as irreversible thermodynamic processes [31]. It may be used for open thermodynamic systems that are not in equilibrium with their environment [27][30][31][35].

As it shall be explained in Section 6.1, the contact formalism uses Pfaffian equations in order to describe the thermodynamic properties of matter. The contact structure that endows the thermodynamic phase space is associated to Gibbs' relation. In Section 6.2 we shall show that the dynamics of open physical systems undergoing irreversible physical phenomena may be described by contact vector fields generated by contact Hamiltonian functions leaving invariant some Legendre submanifold. Finally in Section 6.3 we shall describe a method for modelling open thermodynamic systems in the contact formalism starting from the balance equations. A short summary of differential geometry in Appendix E recalls the concepts that are used in this chapter.

6.1 The thermodynamic model[1]

First let us consider an odd-dimensional, connected, differentiable manifold[2] denoted by $\mathscr{M}$. Assume there exists a 1-form θ fulfilling the following condition:

[1]The text of this section has been extracted from [37] (except Examples 6.1, 6.2 and 6.3). © 2009 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

[2]The definition of a differentiable manifold, and also of the other elements of differential geometry that are used in this part (1-form, cotangent bundle etc.), can be found in Appendix E.

$$\theta \wedge (\mathrm{d}\theta)^{d_M} \neq 0 \tag{6.1}$$

where $(2d_M + 1)$ is the dimension of $\mathscr{M}$ and $\wedge$ denotes the exterior product (see Definition E.20 in Appendix E). Then θ is called a *contact form* and the manifold $(\mathscr{M}, \theta)$ endowed with the contact form θ is called a *contact manifold*. According to Darboux's theorem, condition (6.1) implies that there exists a local set of coordinates $(x_0, x_1, \ldots, x_{d_M}, p_1, \ldots, p_{d_M})$ such that θ can be expressed in the following way in a neighbourhood $\mathscr{V}$ of every point of $\mathscr{M}$:

$$\theta|_{\mathscr{V}} = \mathrm{d}x_0 - p^t \mathrm{d}x \tag{6.2}$$

where $x = [x_1, \ldots, x_{d_M}]^t$, $p = [p_1, \ldots, p_{d_M}]^t$ and $|_{\mathscr{V}}$ indicates the restriction to $\mathscr{V}$.

The d_M-dimensional integral manifolds $\mathscr{L} \subset \mathscr{M}$ of the Pfaffian equation $\theta = 0$ are called *Legendre submanifolds* of $(\mathscr{M}, \theta)$. In the set of local coordinates, each Legendre submanifold can be generated by a differentiable function $F(x_I, p_J)$ of d_M variables where $I \cup J = \{1, \ldots, d_M\}$ is a disjoint partition of the set of indices. The coordinates of each point of the Legendre submanifold $\mathscr{L}$ fulfill then the following relations:

$$x_0 \overset{\mathscr{L}}{=} F(x_I, p_J) - p_J^t \frac{\partial F}{\partial p_J}, \quad x_J \overset{\mathscr{L}}{=} -\frac{\partial F}{\partial p_J}, \quad p_I \overset{\mathscr{L}}{=} \frac{\partial F}{\partial x_I} \tag{6.3}$$

Conversely, given a set of coordinates and any disjoint partition $I \cup J$ of the set of indices $\{1, ..., d_M\}$ and a differentiable function $F(x_I, p_J)$ of d_M variables, the relations (6.3) define a Legendre submanifold.

Gibbs' theory [43] for thermodynamic systems can be translated directly into these tools of differential geometry. Let us now consider a simple thermodynamic system with d_F degrees of freedom. The state of the system is situated in the thermodynamic phase space $\mathcal{T}$ defined as follows:

Definition 6.1 (Thermodynamic phase space)**.** The thermodynamic phase space $\mathcal{T}$ of a thermodynamic system is given by:

$$\mathcal{T} = \mathbb{R} \times \mathrm{T}^* \mathscr{N}$$

where $\mathrm{T}^*\mathcal{N}$ is the cotangent bundle[1] of the manifold $\mathcal{N}$ of the extensive variables (excluding the entropy).

Remark 6.1. *For the sake of simplicity we shall restrict to a presentation in some coordinates and hence identify the thermodynamic phase space with the real vector space* $\mathcal{T} = \mathbb{R}^{2d_F+1}$.

Example 6.1. *The thermodynamic phase space of a simple thermodynamic system with* N_c *components is the space spanned by coordinate axes that correspond to the parameters* U, S, V, $n_1,\ldots,n_{N_c}$, T, P, $\mu_1,\ldots$ *and* μ_{N_c} *of the system, i.e. the thermodynamic configuration space (see Definition 1.4) completed with the intensive variables.*

The thermodynamic phase space is a $(2d_F+1)$-dimensional manifold. Let us consider the Gibbs' relation given by (1.7). It can be rewritten in the following way:

$$\mathrm{d}S - \frac{1}{T}\mathrm{d}U - \frac{P}{T}\mathrm{d}V + \frac{\mu^t}{T}\mathrm{d}n = 0 \tag{6.4}$$

By comparing this relation with (6.2), we can interpret the Gibbs' relation as a contact form on the thermodynamic phase space $\mathcal{T}$. Using the notations of (6.2), let us consider the following 1-form:

$$\theta_S = \mathrm{d}x_0 - p^t\mathrm{d}x$$

where x_0 is associated to S, x is associated to $(U,V,n_1,\ldots,n_{N_c})^t$ and p is associated to $\left(\frac{1}{T},\frac{P}{T},-\frac{\mu_1}{T},\ldots,-\frac{\mu_1}{T}\right)^t$. It can be shown that θ_S fulfills (6.1) [11].

(6.4) is then equivalent to the definition of a Legendre submanifold $\mathscr{L}$ of $(\mathcal{T},\theta_S)$. The thermodynamic system describing the properties of a system is one solution of (6.4) and thus it corresponds to one Legendre submanifold. However each solution of (6.4), i.e. each possible Legendre submanifold does not give a model with any physical meaning.

Remark 6.2. *A thermodynamic system is associated to one particular Legendre submanifold* $\mathscr{L}$ *of the* $(\mathcal{T},\theta_S)$*, i.e. the only points of* $\mathcal{T}$ *that correspond to physically meaningful states of the system are those situated on* $\mathscr{L}$*. The notations* U, V, n, T, P *and* μ *refer to physical quantities and therefore we shall*

[1] see Definition E.18 in Appendix E.

use it only for points of $\mathscr{L}$. On the rest of the thermodynamic phase space $\mathcal{T}$, we shall use the notations x_0, x and p:

$$\left\{\begin{array}{lcl} x_0 & \overset{\mathscr{L}}{=} & S \\ x & \overset{\mathscr{L}}{=} & [U, V, n_1, \ldots, n_{N_c}]^t \\ p & \overset{\mathscr{L}}{=} & \left[\frac{1}{T}, \frac{P}{T}, -\frac{\mu_1}{T}, \ldots, -\frac{\mu_{N_c}}{T}\right]^t \end{array}\right. \tag{6.5}$$

Let us recall that the intensive and extensive quantities of a thermodynamic system are related by the fundamental relation (see Section 1.3.3). Let us consider the fundamental relation associated to the entropy form of the Gibbs' relation, i.e. the entropy function $\tilde{S}(U, V, n_1, \ldots, n_{N_c})$. From (1.10), we have the following equalities:

$$\frac{1}{T} = \left(\frac{\partial \tilde{S}}{\partial U}\right)_{V,n}, \quad \frac{P}{T} = \left(\frac{\partial \tilde{S}}{\partial V}\right)_{U,n}, \quad -\frac{\mu_i}{T} = \left(\frac{\partial \tilde{S}}{\partial n_i}\right)_{U,V,n_{j\neq i}}$$

These relations can be compared to the relations given in (6.3): one can then observe that the fundamental relation is in fact a generating function of the Legendre submanifold $\mathscr{L}$ associated to the thermodynamic model of the system with the following partition of the indices:

$$I = \{1, ..., d_F\} \quad \text{and} \quad J = \emptyset$$

For thermodynamic systems the generating function are the so-called thermodynamic potentials but they might be generalized to mechanical and electrical systems as well [30][31].

The relation between the more physical approach and the formal approach presented in this chapter is shown in Figure 6.1. The left-hand figure is equivalent to Figure 1.2 where the two axes corresponding to U and $V, n_1, n_2, \ldots$ have been gathered in one single axis.

Example 6.2. *Let us consider an ideal gas. The entropy function is a fundamental relation that characterizes the thermodynamic model. For an ideal gas, the entropy function is given as follows*[1]*:*

$$\tilde{S}(U, V, n) = n\left(s_0 + C_v \ln\left(\frac{U - n(u_0 - C_v T_0)}{nC_v T_0}\right) - R \ln\left(\frac{nRT_0}{P_0 V}\right)\right)$$

[1] A similar comment as in Remark 3.1 can be done about this expression that also breaks the third principle of thermodynamics.

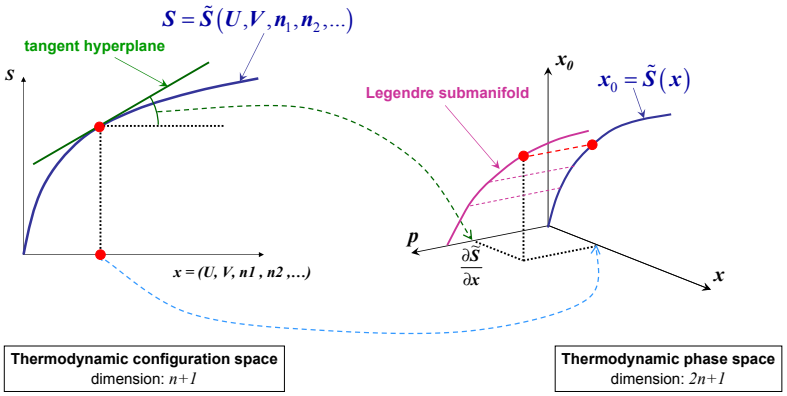


Figure 6.1: Intuitive construction of the Legendre submanifold starting from the thermodynamic configuration space (for partition $I = \{1, ..., d_F\}$ and $J = \emptyset$)

where s_0 and u_0 are the molar entropy and the molar internal energy at the reference temperature T_0 and at the reference pressure P_0 and C_v is the molar constant volume heat capacity. A possible generating function for the Legendre submanifold associated to the ideal gas is given by the following expression (with the partition of indexes $I = \{1, 2, 3\}$ and $J = \emptyset$):

$$\begin{aligned} F(x) &= \tilde{S}(U, V, n \,|U = x_U,\ V = x_V,\ n = x_n) \\ &= x_n \left(s_0 + C_v \ln \left(\frac{x_U - x_n (u_0 - C_v T_0)}{x_n C_v T_0} \right) - R \ln \left(\frac{x_n R T_0}{P_0 x_V} \right) \right) \end{aligned} \tag{6.6}$$

Indeed let us take a particular point (x_0, x, p) of the manifold generated by $F(x)$ via (6.3). Since $(x_0, x, p) \in \mathscr{L}$, we have:

$$p_U = \frac{\partial F}{\partial x_U} = \frac{x_n C_v}{x_U - x_n (u_0 - C_v T_0)} \tag{6.7a}$$

$$p_V = \frac{\partial F}{\partial x_V} = \frac{R}{x_V} x_n \tag{6.7b}$$

From (6.5) we have the following correspondence relations if we restrict on the Legendre submanifold $\mathscr{L}$ representing the ideal gas:

$$\left\{ \begin{array}{rcccl} x & = & [x_U, x_V, x_n]^t & \overset{\mathscr{L}}{=} & [U, V, n]^t \\ p & = & [p_U, p_V, p_n]^t & \overset{\mathscr{L}}{=} & \left[\frac{1}{T}, \frac{P}{T}, -\frac{\mu}{T}\right]^t \end{array} \right.$$

As a consequence (6.7a) *and* (6.7b) *can be rewritten as follows:*

$$\begin{aligned}\frac{1}{T} &= \frac{nC_v}{U - n\left(u_0 - C_v T_0\right)} \\ \frac{P}{T} &= n\frac{R}{V}\end{aligned}$$

By rearranging the terms, it is easy to see that these two relations correspond indeed to the relations of an ideal gas.

However the Legendre submanifold may be defined with respect to another set of coordinates, i.e. with another partition. The corresponding generating function is obtained by performing a Legendre transform on the entropy function $\tilde{S}\left(U, V, n_1, \ldots, n_{N_c}\right)$. The obtained generating functions are called Massieu-Planck functions and can be related to other thermodynamic potentials such as for instance the Helmholtz free energy or the Gibbs' free energy.

Example 6.3. *Let us consider the partition of the indexes* $I = \{3, \ldots, d_F\}$ *and* $J = \{1, 2\}$*, and the corresponding generating function* $F\left(x_I, p_J\right)$*. On the Legendre submanifold we have from* (6.3)*:*

$$\begin{aligned}x_0 &\overset{\mathscr{L}}{=} F\left(x_I, p_J\right) - p_1\frac{\partial F}{\partial p_1} - p_2\frac{\partial F}{\partial p_2} \\ x_1 &\overset{\mathscr{L}}{=} -\frac{\partial F}{\partial p_1} \\ x_2 &\overset{\mathscr{L}}{=} -\frac{\partial F}{\partial p_2}\end{aligned}$$

As a consequence:

$$x_0 - p_1 x_1 - p_2 x_2 \overset{\mathscr{L}}{=} F\left(x_I, p_J\right) = S - \frac{U}{T} - \frac{PV}{T}$$

Besides the Gibbs' free energy is given by the following expression:

$$G = U + PV - TS$$

and therefore:

$$F\left(x_I, p_J\right) = -\frac{1}{T}\tilde{G}\left(T, P, n\right)$$

The function $F\left(x_I, p_J\right)$ *is related to the Gibbs' free energy function* $\tilde{G}\left(T, P, n\right)$*.*

6.2 The system dynamics[1]

The dynamics of a physical system undergoing some reversible and irreversible phenomena may be expressed by the means of a so-called contact vector field. Contact vector fields are the analogue of Hamiltonian vector fields on symplectic manifolds. In the sequel we shall only give a brief description of contact vector fields and their expression in canonical coordinates[2].

Let us consider the contact manifold $(\mathcal{T}, \theta_S)$. A unique vector field $\mathcal{X}_f$ can be associated to every scalar function $f \in \mathcal{C}^\infty(\mathcal{T})$ defined on $\mathcal{T}$ [10][27][69]. These particular vector fields define transformations that preserve the contact structure and are called *contact vector fields* [75]. The contact vector field $\mathcal{X}_f$ is said to be generated by $f(x_0, x, p)$ and it is expressed in the local canonical coordinates as follows:

$$\mathcal{X}_f(x_0, x, p) = \begin{pmatrix} f \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & -p^t \\ 0 & 0 & -\boldsymbol{I}_{d_F} \\ p & \boldsymbol{I}_{d_F} & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial f}{\partial x_0} \\ \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial p} \end{pmatrix} \tag{6.8}$$

where $\boldsymbol{I}_{d_F}$ is the identity matrix of dimension d_F. The function $f(x_0, x, p)$ is called the *contact Hamiltonian function* by analogy with the Hamiltonian vector field on symplectic manifolds. Note that there is a bijection between the contact vector fields and the smooth functions.

A particular subclass of contact vector fields shall be of great importance in the sequel, namely the contact vector fields that are tangent to a given Legendre submanifold. The characteristic of such contact vector fields is stated in the following proposition.

Proposition 6.1. *A contact vector field $\mathcal{X}_f$ is tangent to a given Legendre submanifold $\mathscr{L}$ if and only if its contact Hamiltonian function is equal to zero on $\mathscr{L}$, i.e. if and only if:*

$$f(x_0, x, p | (x_0, x, p) \in \mathscr{L}) = 0$$

[1] The text of this section has been extracted from [37]. © 2009 IEEE: see copyright information in the footnote on page 150.

[2] For more details, the reader can refer to [10][69].

or equivalently:

$$\mathscr{L} \subset f^{-1}(0)$$

Proof. For a proof of this proposition see e.g. [75]. □

The image of the Legendre submanifold $\mathscr{L}$ by the transformation defined by the contact vector field $\mathcal{X}_f$ is then $\mathscr{L}$ itself.

Let us now consider the dynamical behaviour of some thermodynamic system. As explained in the previous section, the physically admissible states are situated on some Legendre submanifold $\mathscr{L}$ of the thermodynamic phase space $\mathcal{T}$ endowed with a contact structure by Gibbs' relation. Under the assumption of a quasi-static process (Assumption 1.1), at each time, the current state variables fulfill the fundamental relation of the thermodynamic model. In other words, the trajectory of the system remains on the Legendre submanifold $\mathscr{L}$ which is consequently an invariant of the system dynamics. Therefore the dynamical evolution of the system can be represented by a contact vector field. Since the trajectory has to remain on the Legendre submanifold, the contact vector field must be tangent to it. As a consequence the contact Hamiltonian function that generates the contact vector field has to be equal to zero on the Legendre submanifold $\mathscr{L}$ associated to the thermodynamic model.

Contact vector fields have been defined for thermodynamic systems undergoing reversible [74] and irreversible transformations [49]. They have been extended to open systems which are not in equilibrium with their environment [27][30][31][35] by considering contact Hamiltonian functions which depend also on some external (input) variable and have then been called control contact systems.

In summary, the system dynamics of a quasi-static thermodynamic process can be represented by the following relation:

$$\begin{cases} \dfrac{dx_0}{dt} = f(x_0, x, p, \xi_{ext}) - p^t \dfrac{\partial f}{\partial p} \\ \dfrac{dx}{dt} = -\dfrac{\partial f}{\partial p} \\ \dfrac{dp}{dt} = p\dfrac{\partial f}{\partial x_0} + \dfrac{\partial f}{\partial x} \end{cases} \tag{6.9}$$

where $f(x_0, x, p, \xi_{ext})$ is the contact Hamiltonian function such that $f(x_0, x, p, \xi_{ext}) = 0$ on the Legendre submanifold representing the thermodynamic model. ξ_{ext} are the external input variables.

The following example illustrates that the dynamics of a thermodynamic system can indeed be represented by contact Hamiltonian functions. First we establish the dynamical model of the system by physical considerations. Then we propose a contact Hamiltonian function that manages to represent the dynamics in the contact formulation.

Example 6.4. *Let us consider a cell containing a gas. The cell is heated by the environment. The heat transfer rate is proportional to the difference between the environment temperature T_{env} and the cell temperature T. The heat transfer coefficient is denoted by κ. If the gas is an ideal gas, a possible generating function of the Legendre submanifold of an ideal gas has been given in Example 6.2.*

The internal energy balance is obtained by considering the inlet and outlet energy flows. The walls of the cell are assumed to be rigid so that the volume is constant. The following relations are then obtained:

$$\begin{cases} \dfrac{dU}{dt} = \kappa (T_{env} - T) \\ \dfrac{dV}{dt} = 0 \\ \dfrac{dn}{dt} = 0 \end{cases} \tag{6.10}$$

Let us consider the following contact Hamiltonian function candidate:

$$f(x_0, x, p) = \left(\frac{\partial F}{\partial x_U} - p_U \right) \kappa \left(T_{env} - \frac{1}{p_U} \right) \tag{6.11}$$

where $F(x)$ is given in (6.6) in the case of an ideal gas. Since $\frac{\partial F}{\partial x_U} = p_U$ on $\mathscr{L}$, it is obvious that $\mathscr{L} \subset f^{-1}(0)$. By introducing (6.11) into (6.9) and then restricting to the Legendre submanifold, one obtains :

$$\begin{aligned} \left. \frac{dU}{dt} = \frac{dx_U}{dt} \right|_{\mathscr{L}} &= - \left. \frac{\partial f}{\partial p_U} \right|_{\mathscr{L}} \\ &= - \left. \left(-\kappa \left(T_{env} - \frac{1}{p_U} \right) + \left(\frac{\partial F}{\partial x_U} - p_U \right) \kappa \frac{1}{p_U^2} \right) \right|_{\mathscr{L}} \\ &= \kappa (T_{env} - T) \end{aligned}$$

This is exactly the same expression as in (6.10) *that has been derived previously from physical considerations. This means that* (6.11) *can indeed represent the dynamical behaviour of the system.*

6.3 The contact model of thermodynamic systems[1]

As it has been shown in the previous section, the contact formalism allows to express the dynamical behaviour of some thermodynamic system. The two main tools are the generating function of the Legendre submanifold associated to the thermodynamic properties of the system, and the contact Hamiltonian function. We have already shown how to deduce the generating function of the Legendre submanifold from the fundamental relation of the system, i.e. from physical considerations. But we have not shown how to deduce the expression of the contact Hamiltonian function from the balance equations.

In this section we suggest to consider a class of contact Hamiltonian functions which are derived from the phenomenological laws giving rise to the dynamics. We also show how the choice of the entropy contact form enables to derive the total entropy balance and hence the entropy production from the contact Hamiltonian function. We shall first consider open simple thermodynamic systems, and then we shall apply the obtained results in a network approach to derive the contact model of complex thermodynamic systems.

6.3.1 Simple thermodynamic systems

First we shall start with simple thermodynamic systems which are the smallest possible entities to be taken within a complete thermodynamic system (see Definition 1.2).

[1]The content of this section has been published in [35] (© 2007 EUCA).

Expression of the contact Hamiltonian function

The state of the simple thermodynamic system is changing with time due to exchanges with the environment or due to chemical reactions. The exchanges with the environment depend on some external variables ξ_{ext}. These external variables can be either extensive (e.g. an external volume flow) or intensive (e.g. the external temperature).

Models of phenomenological laws [14] and reaction kinetics [67] in chemical engineering give the expressions of the energy balance $\mathcal{Q}_U$, the volume variation $\mathcal{Q}_V$ and the matter balance $\mathcal{Q}_n$ in terms of the state variables and the external variables ξ_{ext}. As explained in Chapter 1, they result from physical phenomena: conduction, convection, chemical reaction etc. For instance, the material balance equation is given by (1.13):

$$\mathcal{Q}_{n_i}\left(S,U,V,n,P,V,T,\xi_{ext}\right)=\sum_{j=1}^{N_F}\left(\mathcal{F}_{n_i}^{j}\right)+\sigma_{n_i}$$

where $\mathcal{F}_{n_i}^{j}$ is the molar inlet flow rate of i in flow j and σ_{n_i} is the production rate of i due to chemical reactions. The dynamical model is then written as the system of the energy, volume and mass balance equations as follows:

$$\begin{cases}\dfrac{dU}{dt}=\mathcal{Q}_U\left(S,U,V,n,P,T,\mu,\xi_{ext}\right)\\ \dfrac{dV}{dt}=\mathcal{Q}_V\left(S,U,V,n,P,T,\mu,\xi_{ext}\right)\\ \dfrac{dn}{dt}=\mathcal{Q}_n\left(S,U,V,n,P,T,\mu,\xi_{ext}\right)\end{cases}\tag{6.12}$$

Note that $\mathcal{Q}_n$ is a vector of dimension N_c with one element for each component of the system whereas $\mathcal{Q}_U$ and $\mathcal{Q}_V$ are scalars.

In order to define a dynamical contact system which leaves the thermodynamic properties invariant and represents the balance equations given by (6.12) we shall suggest a contact Hamiltonian function $f\left(x_0,x,p,\xi_{ext}\right)$. Contrary to the case of isolated systems, the contact Hamiltonian function depends on the external variables. As already explained, this function must fulfill the following properties:

- the invariance property: $f\left(x_0,x,p,\xi_{ext}\,|(x_0,x,p)\in\mathscr{L}\right)=0$ where $\mathscr{L}$ is

the Legendre submanifold associated to the thermodynamic model of the system.

- the vector field generated by (6.8) and restricted to $\mathscr{L}$ must be equivalent to the balance equations given by (6.12):

$$\mathcal{X}_f|_{\mathscr{L}} = \begin{pmatrix} \mathcal{Q}_U\left(S,U,V,n,P,T,\mu,\xi_{ext}\right) \\ \mathcal{Q}_V\left(S,U,V,n,P,T,\mu,\xi_{ext}\right) \\ \mathcal{Q}_n\left(S,U,V,n,P,T,\mu,\xi_{ext}\right) \end{pmatrix}$$

The following proposition gives a possible expression for a contact Hamiltonian function that fulfills the above conditions.

Proposition 6.2. *Let us consider a thermodynamic system. The dynamics of the thermodynamic system is represented by the balance equations given in* (6.12)*. Let us assume that the generating function $F(x)$ of the Legendre submanifold is given for the partition $I = \{1,\dots,d_F\}$ and $J = \emptyset$ where d_F is the number of degrees of freedom of the system. An admissible contact Hamiltonian that can express the dynamics of the thermodynamic system is given by the following expression:*

$$f(x,p) = \left(\frac{\partial F}{\partial x} - p\right)^t \mathcal{Q}\left(x,p,\xi_{ext}\right) \tag{6.13}$$

where $\mathcal{Q}(x,p,\xi_{ext}) = [\mathcal{Q}_U, \mathcal{Q}_V, \mathcal{Q}_n]$. The dependence in x and p is obtained by replacing U, V and n by x_U, x_V and x_n; T, P and μ by $\frac{1}{p_U}$, $\frac{p_V}{p_U}$ and $-\frac{p_n}{p_U}$; S by $F(x)$.

Proof. The condition that $f(x_0,x,p,\xi_{ext})$ vanishes on the Legendre submanifold is obviously satisfied through the factor $\left(\frac{\partial F}{\partial x} - p\right)$. Now let us calculate the vector field generated by this function using (6.8):

$$\frac{dx}{dt} = -\frac{\partial f}{\partial p} = \mathcal{Q} - \frac{\partial \mathcal{Q}}{\partial p}\left(\frac{\partial F}{\partial x} - p\right) \tag{6.14}$$

On the Legendre submanifold, $\left(\frac{\partial F}{\partial x} - p\right) = 0$ and $x = [U,V,n]^t$, $p = \left[\frac{1}{T}, \frac{P}{T}, \frac{-\mu}{T}\right]^t$ and $F(x) = x_0 = S$. So we find:

$$\left.\frac{dx}{dt}\right|_{\mathscr{L}} = \frac{d}{dt}\begin{pmatrix} U \\ V \\ n \end{pmatrix} = \begin{pmatrix} \mathcal{Q}_U\left(U,S,V,n,P,T,\mu,\xi_{ext}\right) \\ \mathcal{Q}_V\left(U,S,V,n,P,T,\mu,\xi_{ext}\right) \\ \mathcal{Q}_n\left(U,S,V,n,P,T,\mu,\xi_{ext}\right) \end{pmatrix} \qquad \square$$

Remark 6.3. *Instead of replacing S by $F(x)$ in the expression of $\mathcal{Q}$ to obtain expression* (6.13)*, we could have replaced S simply by x_0. This would have given another expression for the contact Hamiltonian that would also correspond to the dynamics given by the physics of the system. This can be seen in* (6.14)*: because we restrict to the Legendre submanifold $\mathscr{L}$, the second term vanishes and the first term does not change if we choose either to replace S by x_0 or $F(x)$. The advantage of removing the dependence of the contact Hamiltonian function in x_0 is to allow to extend the result from simple systems to the interconnection of simple systems. Moreover the usual flows considered in the modelling of real chemical systems do not depend on the entropy.*

This shows also that given a physical model there is no unique contact Hamiltonian that can represent the system dynamics. This point shall be further discussed in Chapter 7.

Example 6.5. *The contact Hamiltonian candidate* (6.11) *of Example 6.4 has been found using Proposition 6.2.*

Finally the dynamics of the intensive variables can be deduced using the expression of the vector field given in (6.8):

$$\begin{aligned}\frac{dp}{dt} &= \frac{\partial f}{\partial x} - p\frac{\partial f}{\partial x_0} \\ &= \frac{\partial^2 F}{\partial x^2}\mathcal{Q}(x,p,\xi_{ext}) + \frac{\partial \mathcal{Q}}{\partial x}\left(\frac{\partial F}{\partial x} - p\right)\end{aligned}$$

By restricting to the Legendre submanifold, we find the following expression for the dynamics of the intensive variables:

$$\left.\frac{dp}{dt}\right|_{\mathscr{L}} = \frac{d}{dt}\begin{pmatrix} T^{-1} \\ \frac{P}{T} \\ -\frac{\mu}{T}\end{pmatrix} = \frac{\partial^2 F}{\partial x^2}\begin{pmatrix} \mathcal{Q}_U(U,S,V,n,P,T,\mu,\xi_{ext}) \\ \mathcal{Q}_V(U,S,V,n,P,T,\mu,\xi_{ext}) \\ \mathcal{Q}_n(U,S,V,n,P,T,\mu,\xi_{ext})\end{pmatrix}$$

The entropy production rate

An interesting property of the contact Hamiltonian function is that it has the dimension of an entropy rate. It is the consequence of the choice of the entropy contact form given by (6.4) and the associated canonical coordinates given

by (6.5) for the thermodynamic phase space. This may be compared to the alternative formulation where the energy contact form has been used as the contact form and the contact Hamiltonian for simple thermodynamic systems has power units [27][31][32].

An interesting feature of the formulation of the dynamics using the entropy contact form is that it embeds the entropy balance equation as the first component of the vector field given in (6.8).

Restricting the first component of $\mathcal{X}_f$ to the Legendre submanifold $\mathscr{L}$, one obtains the balance equation of the entropy:

$$\frac{dS}{dt} = \left.\frac{dx_0}{dt}\right|_{\mathscr{L}}$$

Using (6.8), we find:

$$\frac{dx_0}{dt} = f\left(x, p, \xi_{ext}\right) - p^t \frac{\partial f}{\partial p} \tag{6.15}$$

Let us consider the expression of the contact Hamiltonian function given in Proposition 6.2 and restrict ourselves to the Legendre submanifold. Then (6.15) becomes:

$$\left.\frac{dx_0}{dt}\right|_{\mathscr{L}} = p^t \mathcal{Q}\left(U, S, V, n, P, T, \mu, \xi_{ext}\right) \tag{6.16}$$

The entropy production rate σ_S can be found by subtracting the net incoming entropy flow $\mathcal{F}_S$ from (6.16). Finally we have:

$$\sigma_S = \left[p^t \mathcal{Q}\left(U, S, V, n, P, T, \mu, \xi_{ext}\right) - \mathcal{F}_S\left(U, S, V, n, P, T, \mu, \xi_{ext}\right)\right]\big|_{\mathscr{L}} \geq 0$$

6.3.2 Interconnected thermodynamic systems

In this section we consider thermodynamic systems that are an interconnection of simple systems that exchange matter, energy and volume between them and with the external environment. We shall deduce the contact Hamiltonian function for the complete interconnection from the contact Hamiltonian function of the individual compartments.

Contact model of the compartments

We assume that the connected system is composed of m interconnected simple systems called compartments. Compartment j has $d_F^{(j)}$ degrees of freedom with $j = 1, \ldots, m$. If compartment j contains $N_c^{(j)}$ different chemical species, then $d_F^{(j)} = N_c^{(j)} + 2$. According to Section 6.1, a $\left(2d_F^{(j)} + 1\right)$-dimensional thermodynamic phase space $\mathcal{T}^{(j)}$ can be associated to each compartment j. $\mathcal{T}^{(j)}$ is endowed with the entropy contact form:

$$\theta_S^{(j)} = \mathrm{d}x_0^{(j)} - \left(p^{(j)}\right)^t \mathrm{d}x^{(j)}$$

defined in the canonical coordinates: the entropy-coordinate $x_0^{(j)}$, the coordinate-vector of the conservative quantities $x^{(j)}$ and coordinate-vector of the intensive quantities $p^{(j)}$ with $j = 1, \ldots, m$. The behaviour of each compartment can be described by contact structures. For compartment j:

- there exists a generating function $F^{(j)}\left(x^{(j)}\right)$ of the Legendre submanifold $\mathscr{L}^{(j)}$ such that:

$$\begin{aligned} x_0^{(j)} &\overset{\mathscr{L}^{(j)}}{=} F\left(x_{I_j}^{(j)}, p_{J_j}^{(j)}\right) - \left(p_{J_j}^{(j)}\right)^t \frac{\partial F^{(j)}}{\partial p_{J_j}^{(j)}} \\ x_{J_j}^{(j)} &\overset{\mathscr{L}^{(j)}}{=} -\frac{\partial F^{(j)}}{\partial p_{J_j}^{(j)}} \\ p_{I_j}^{(j)} &\overset{\mathscr{L}^{(j)}}{=} \frac{\partial F^{(j)}}{\partial x_{I_j}^{(j)}} \end{aligned}$$

  where $I_j \cup J_j = \left\{1, \ldots, d_F^{(j)}\right\}$ is a disjoint partition of the indices.

- the dynamics of the compartment are given by a contact Hamiltonian function $f^{(j)}\left(x, p, \xi_{ext}\right)$ where

$$x = \left[x^{(1)}, \ldots, x^{(m)}\right]^t \quad \text{and} \quad p = \left[p^{(1)}, \ldots, p^{(m)}\right]^t$$

  Indeed the contact Hamiltonian function $f^{(j)}\left(x, p, \xi_{ext}\right)$ does not depend only on $\left(x^{(j)}, p^{(j)}\right)$ but on (x, p) since the fluxes may depend on the state of the other compartments. The variables contained in ξ_{ext} represent quantities external to the interconnected system and that influence the

flows between the compartments inside the interconnection and between the interconnection and the environment.

Compartment j receives incoming flows from the external environment $\mathcal{Q}^{0j}$ and from the other compartments $\mathcal{Q}^{ij}$ with $i = 1, \ldots, m$. We obviously have

$$\mathcal{Q}^{ij} = -\mathcal{Q}^{ji}$$

Since the time variation of the quantity of matter $n^{(j)}$ of each compartment contains a term that is not linked to any flow between compartments, we define:

$$\mathcal{Q}_n^{jj} = \sigma_n^j$$

with $\sigma_n^{(j)} = \left[\sigma_{n_1}^{(j)}, \ldots, \sigma_{n_{N_c^{(j)}}}^{(j)}\right]^t$ the vector of the production/consumption rate of the components of compartment j. The fluxes $\mathcal{Q}^{ij}$ depend on the state $\left(x^{(j)}, p^{(j)}\right)$ of the current compartment, but also on the state $\left(x^{(i)}, p^{(i)}\right)$ of the compartment i. An example of an interconnection variable is the force exerted on a wall which is function of the pressure in the neighbour compartment.

Using Proposition 6.2, we can choose the following expression for the contact Hamiltonian of compartment j:

$$\begin{aligned} & f^{(j)}\left(x, p, \xi_{ext}\right) \\ &= \left(\frac{\partial F^{(j)}}{\partial x^{(j)}} - p^{(j)}\right)^t \left(\mathcal{Q}^{0j}\left(x^{(j)}, p^{(j)}, \xi_{ext}\right) + \sum_{i=1}^{m} \mathcal{Q}^{ij}\left(x^{(i)}, p^{(i)}, x^{(j)}, p^{(j)}, \xi_{ext}\right)\right) \end{aligned}$$

Contact model of the complete system

The behaviour of the total system is determined by the individual behaviour of each compartment and the way that they are interacting together.

In a first step let us construct the thermodynamic phase space of the complex system. A state for the entire system is physically possible if it is possible for each compartment. This means that we must have:

$$\theta_S^{(j)} = \mathrm{d}x_0^{(j)} - \left(p^{(j)}\right)^t \mathrm{d}x^{(j)} = 0 \qquad \forall j = 1, \ldots, m \tag{6.17}$$

Using the fact that the entropy is an extensive quantity, we may define the

total entropy of the system as follows:

$$x_0^{tot} = \sum_{j=1}^{m} x_0^{(j)} \tag{6.18}$$

Finally, by using (6.17) and (6.18), we find that all thermodynamically possible states fulfill the following equality:

$$\mathrm{d}x_0^{tot} = \sum_{j=1}^{m} \mathrm{d}x_0^{(j)} = \sum_{j=1}^{m} \left(p^{(j)}\right)^t \mathrm{d}x^{(j)} = p^t \mathrm{d}x$$

Therefore we shall define the thermodynamical phase space of the complex system by the $\left(1 + 2\sum_{j=1}^{m} d_F^{(j)}\right)$-dimensional real vector space endowed with the entropy contact form:

$$\theta_S = \mathrm{d}x_0^{tot} - \sum_{j=1}^{m} \left(p^{(j)}\right)^t \mathrm{d}x^{(j)} = \mathrm{d}x_0^{tot} - p^t \mathrm{d}x \tag{6.19}$$

with canonical coordinates:

$$x_0^{tot} = \sum_{j=1}^{m} x_0^{(j)}, \quad x = \left[x^{(1)}, \ldots, x^{(m)}\right]^t, \quad p = \left[p^{(1)}, \ldots, p^{(m)}\right]^t$$

The thermodynamically possible states for the complex system are located on a submanifold $\mathscr{L}$ of dimension $\sum_{j=1}^{m} d_F^{(j)}$ such that for all $(x_0^{tot}, x, p) \in \mathscr{L}$ and $\forall j =\in \{1, \ldots, m\}$, $\exists x_0^{(j)} \in \mathbb{R}$ such that:

$$\left(x_0^{(j)}, x^{(j)}, p^{(j)}\right) \in \mathscr{L}^{(j)} \quad \text{and} \quad \sum_{j=1}^{m} x_0^{(j)} = x_0^{tot} \tag{6.20}$$

This submanifold is again a Legendre submanifold with respect to the contact form given by (6.19) as it is stated in the following proposition.

Proposition 6.3. *The generating function of the Legendre submanifold $\mathscr{L}$ representing the properties of the complex system according to* (6.20) *is generated by the generating function $F(x_I, p_J)$, sum of the generating functions of the Legendre submanifolds $\mathscr{L}^{(j)}$ of each compartment using following relation:*

$$F(x_I, p_J) = \sum_{j=1}^{m} F^{(j)}\left(x_{I_j}^{(j)}, p_{J_j}^{(j)}\right)$$

where

$$x_I = \left[x_{I_1}^{(1)}, \ldots, x_{I_m}^{(m)}\right] \quad \textit{and} \quad p_J = \left[p_{J_1}^{(1)}, \ldots, p_{J_m}^{(m)}\right]$$

Proof. First let us prove that $I \cup J$ is indeed a disjoint partition of the indexes:

$$I \cup J \;=\; \left(\bigcup_{j=1}^{m} I_j\right) \cup \left(\bigcup_{j=1}^{m} J_j\right) = \bigcup_{j=1}^{m} (I_j \cup J_j) = \bigcup_{j=1}^{m} \left\{1, \ldots, d_F^{(j)}\right\}$$

It is now sufficient to prove that x_0^{tot}, x_J and p_I can be calculated by using (6.3). From (6.20), we have:

$$x_0^{tot} \;=\; \sum_{j=1}^{m} x_0^{(j)}$$

Since $\left(x_0^{(j)}, x^{(j)}, p^{(j)}\right) \in \mathscr{L}^{(j)}$, we have:

$$x_0^{(j)} = F\left(x_{I_j}^{(j)}, p_{J_j}^{(j)}\right) - \left(p_{J_j}^{(j)}\right)^t \frac{\partial F^{(j)}}{\partial p_{J_j}^{(j)}}$$

Consequently:

$$\begin{aligned} x_0^{tot} &= \sum_{j=1}^{m} \left[F\left(x_{I_j}^{(j)}, p_{J_j}^{(j)}\right) - \left(p_{J_j}^{(j)}\right)^t \frac{\partial F^{(j)}}{\partial p_{J_j}^{(j)}}\right] \\ &= F\left(x_I, p_J\right) - \sum_{j=1}^{m} \left(p_{J_j}^{(j)}\right)^t \frac{\partial F^{(j)}}{\partial p_{J_j}^{(j)}} \\ &= F\left(x_I, p_J\right) - \sum_{j=1}^{m} \left(p_{J_j}^{(j)}\right)^t \frac{\partial F}{\partial p_{J_j}^{(j)}} \\ &= F\left(x_I, p_J\right) - \left(p_J\right)^t \frac{\partial F}{\partial p_J} \end{aligned}$$

and

$$\begin{aligned} x_J = \left[x_{J_1}^{(1)}, \ldots, x_{J_m}^{(m)}\right]^t &= \left[-\frac{\partial F^{(1)}}{\partial p_{J_1}^{(1)}}, \ldots, -\frac{\partial F^{(m)}}{\partial p_{J_m}^{(m)}}\right]^t \\ &= \left[-\frac{\partial F}{\partial p_{J_1}^{(1)}}, \ldots, -\frac{\partial F}{\partial p_{J_m}^{(m)}}\right]^t = -\frac{\partial^t F}{\partial p_J} \end{aligned}$$

$$p_I = \left[p^{(1)}_{I_1}, \dots, p^{(m)}_{I_m}\right]^t = \left[\frac{\partial F^{(1)}}{\partial x^{(1)}_{I_1}}, \dots, \frac{\partial F^{(m)}}{\partial x^{(m)}_{I_m}}\right]^t$$
$$= \left[\frac{\partial F}{\partial x^{(1)}_{I_1}}, \dots, \frac{\partial F}{\partial x^{(m)}_{I_m}}\right]^t = \frac{\partial^t F}{\partial x_I} \qquad \square$$

Remark 6.4. *In Proposition 6.3 the partitions of the indices for each compartment may be different, i.e.* $I_1 \neq \ldots \neq I_m$. *This is not an issue from a strict theoretical point of view. However this has not very much sense from a thermodynamic point of view. Indeed depending on the partition, the generating function corresponds to some physical quantity as it has been mentioned in Section 6.1 and illustrated in Example 6.3. Choosing different partitions for each of the compartments implies that the generating functions* $F^{(j)}\left(x^{(j)}_{I_j}, p^{(j)}_{J_j}\right)$ *do not represent the same physical quantity. Consequently the* x_0*-coordinate cannot be interpreted as the total entropy of the system any more. As an example, let us consider a system with two compartments with the same number of components, i.e.* $d^{(1)}_F = d^{(2)}_F = d_F$. *Let us take for the first compartment* $I_1 = \{1, ..., d_F\}$ *and* $J_1 = \emptyset$, *and for the second compartment* $I_2 = \{3, ..., d_F\}$ *and* $J_2 = \{1, 2\}$. *As already explained, the generating function* $F^{(1)}\left(x^{(1)}_{I_1}, p^{(1)}_{J_1}\right)$ *of the first compartment can be interpreted as its entropy function* $\tilde{S}^{(1)}$ *whereas the generating function* $F^{(2)}\left(x^{(2)}_{I_2}, p^{(2)}_{J_2}\right)$ *of the second compartment can be interpreted as the Gibbs' free energy function divided by the temperature* $\frac{\tilde{G}^{(2)}}{T^{(2)}}$. *Although these two quantities have the same units and can be added as suggested in Proposition 6.3, their sum has no physical interpretation any more. If instead we choose* $I_2 = I_1 = \{1, \dots, d_F\}$ *and* $J_1 = J_2 = \emptyset$, *then* $F^{(1)}\left(x^{(1)}_{I_1}, p^{(1)}_{J_1}\right)$ *and* $F^{(2)}\left(x^{(2)}_{I_2}, p^{(2)}_{J_2}\right)$ *may be interpreted as the entropy functions of the first and the second compartment, respectively. As a consequence the generating function of the total system* $F(x_I, p_J) = F^{(1)}\left(x^{(1)}_{I_1}, p^{(1)}_{J_1}\right) + F^{(2)}\left(x^{(2)}_{I_2}, p^{(2)}_{J_2}\right)$ *is associated to the total entropy function of the system.*

In the same way, the Legendre transform of the generating function of the Legendre submanifold of the complete system can be done with respect to any of the variables of the individual compartments. But in the general case, the obtained Legendre transform of the generating function cannot be interpreted

as a classical thermodynamic potential anymore.

Let us now look for a contact Hamiltonian function that allows to describe the dynamics of the global system. This function $f\left(x_0^{tot}, x, p, \xi_{ext}\right)$ has to meet the following conditions:

- $f\left(x_0^{tot}, x, p, \xi_{ext}\right) = 0$ for $\left(x_0^{tot}, x, p\right) \in \mathscr{L}$
- $\left.\frac{dx^{(j)}}{dt}\right|_{\mathscr{L}^{(j)}} = -\left.\frac{\partial f}{\partial p^{(j)}}\right|_{\mathscr{L}}$ and $\left.\frac{dp^{(j)}}{dt}\right|_{\mathscr{L}^{(j)}} = \left.\frac{\partial f}{\partial x^{(j)}}\right|_{\mathscr{L}}$ for $j = 1, ..., m$

Proposition 6.4. *Let us consider a thermodynamic system that is an interconnection of m simple thermodynamic systems. The contact Hamiltonian function describing the dynamics of compartment j is given by $f^{(j)}\left(x, p, \xi_{ext}\right)$ that are not depending on the $x_0^{(j)}$-coordinate. If $f^{(j)}\left(x, p, \xi_{ext}\right)$ is of the following form:*

$$f^{(j)}\left(x, p, \xi_{ext}\right) = f_0^{(j)}\left(x^{(j)}, p^{(j)}, \xi_{ext}\right) \tilde{f}^{(j)}\left(x, p, \xi_{ext}\right) \tag{6.21}$$

where $f_0^{(j)}\left(x^{(j)}, p^{(j)}, \xi_{ext}\right)$ and $\tilde{f}^{(j)}\left(x, p, \xi_{ext}\right)$ are smooth functions defined on the thermodynamic phase space such that

$$f_0^{(j)}\left(x^{(j)}, p^{(j)}, \xi_{ext}\right)|_{\mathscr{L}^{(j)}} = 0$$

then a contact Hamiltonian function that can describe the dynamics of the global system is given by the following expression:

$$\begin{aligned} & f\left(x, p, \xi_{ext}\right) \\ & \quad = \sum_{j=1}^{m} f^{(j)}\left(x^{(j)}, p^{(j)}, \mathcal{Q}^{0j}\left(x^{(j)}, p^{(j)}, \xi_{ext}\right), \mathcal{Q}^{ij}\left(x^{(i)}, p^{(i)}, x^{(j)}, p^{(j)} \xi_{ext}\right)\right) \\ & \quad = \sum_{j=1}^{m} f^{(j)}\left(x, p, \xi_{ext}\right) \end{aligned} \tag{6.22}$$

Proof. The first condition is obviously satisfied. Indeed if $\left(x_0^{tot}, x, p\right) \in \mathscr{L}$, then there exists $x_0^{(j)}$ such that for all $j = 1, \ldots, m$, $\left(x_0^{(j)}, x^{(j)}, p^{(j)}\right) \in \mathscr{L}^{(j)}$. Since $f^{(j)}\left(x, p, \xi_{ext}\right)$ describes the dynamics of compartment j, we have:

$$\left.f^{(j)}\left(x, p, \xi_{ext}\right)\right|_{\mathscr{L}} = 0$$

Consequently $f\left(x,p,\xi_{ext}\right)$ given in (6.22) is equal to zero on $\mathscr{L}$. For the second condition, let us compute $\frac{\partial f}{\partial p^{(j)}}$:

$$\frac{\partial f}{\partial p^{(j)}} = \sum_{k=1}^{m}\frac{\partial f^{(k)}}{\partial p^{(j)}} = \frac{\partial f^{(j)}}{\partial p^{(j)}} + \sum_{\substack{k=1\\k\neq j}}^{m}\frac{\partial f^{(k)}}{\partial p^{(j)}} \tag{6.23}$$

Nothing can be said about $\frac{\partial f^{(k)}}{\partial p^{(j)}}$ in general. Let us now restrict (6.23) to $\mathscr{L}$:

$$\left.\frac{\partial f}{\partial p^{(j)}}\right|_{\mathscr{L}} = \left.\frac{\partial f^{(j)}}{\partial p^{(j)}}\right|_{\mathscr{L}} + \sum_{\substack{k=1\\k\neq j}}^{m}\left.\frac{\partial f^{(k)}}{\partial p^{(j)}}\right|_{\mathscr{L}}$$

From the condition (6.21) on the form of $f^{(j)}\left(x,p,\xi_{ext}\right)$, we have:

$$\left.\frac{\partial f^{(k)}}{\partial p^{(j)}}\right|_{\mathscr{L}} = \tilde{f}^{(k)}\left.\frac{\partial f_0^{(k)}}{\partial p^{(j)}}\right|_{\mathscr{L}} + f_0^{(k)}\left.\frac{\partial \tilde{f}^{(k)}}{\partial p^{(j)}}\right|_{\mathscr{L}} = 0$$

Consequently we have the following equality:

$$\left.\frac{\partial f}{\partial p^{(j)}}\right|_{\mathscr{L}} = \left.\frac{\partial f^{(j)}}{\partial p^{(j)}}\right|_{\mathscr{L}} = \left.\frac{\partial f^{(j)}}{\partial p^{(j)}}\right|_{\mathscr{L}^{(j)}}$$

Finally:

$$\left.\frac{dx^{(j)}}{dt}\right|_{\mathscr{L}} = -\left.\frac{\partial f^{(j)}}{\partial p^{(j)}}\right|_{\mathscr{L}^{(j)}} = -\left.\frac{\partial f^{(j)}}{\partial p^{(j)}}\right|_{\mathscr{L}^{(j)}}$$

Since $f\left(x_0^{tot},x,p,\xi_{ext}\right) = 0$ on $\mathscr{L}$, this manifold is an invariant set for the system dynamics. So the dynamics for p and x_0^{tot} are satisfied. □

The advantage of removing the dependence on $x_0^{(j)}$ in the contact Hamiltonian function $f^{(j)}\left(x_0^{(j)},x^{(j)},p^{(j)},\xi_{ext}\right)$ clearly appears now. Indeed, if we had kept the dependence in $x_0^{(j)}$, by adding the contact Hamiltonian function of each compartment like it is done in (6.22), we would have obtained a function depending on $x_0^{(j)}$ with $j = 1,\ldots,m$ while we are looking for a function depending on x_0^{tot}, x and p.

Remark 6.5. *We have defined the interconnections between the compartments in a general way. In particular, we include feedback interconnections, which can be very useful either for modelling a compartment that would be a controller or a recycle stream.*

The contact Hamiltonian function of the global system allows to deduce directly the overall entropy production, knowing the incoming and outgoing entropy flows:

$$\begin{aligned} \frac{dS^{tot}}{dt} &= \left.\frac{dx_0^{tot}}{dt}\right|_{\mathscr{L}} = f\left(x,p\right)|_{\mathscr{L}} - \left.\left(p^T\frac{\partial f}{\partial p}\right)\right|_{\mathscr{L}} \\ \sigma_S &= \frac{dS^{tot}}{dt} - \mathcal{F}_S = \left.\left(p^T\frac{\partial f}{\partial p}\right)\right|_{\mathscr{L}} - \mathcal{F}_S \end{aligned} \tag{6.24}$$

Example 6.6. *Let us consider an isolated cell divided into two parts by a membrane that is only permeable to heat. The volume of each side is assumed to be constant and no chemical reaction takes place. This corresponds to an interconnected system with two compartments (one for each side of the cell) where the only flow is:*

$$\mathcal{Q}_U^{12} = \kappa\left(T^{(1)} - T^{(2)}\right)$$

where $T^{(1)}$ *and* $T^{(2)}$ *are the temperatures in each compartment of the cell and* κ *is the heat transfer coefficient. There is no interaction with the environment, so* $\xi_{ext} = \emptyset$.

According to Proposition 6.2, the contact Hamiltonian function of both compartments are equal to:

$$f^{(1)}\left(x^{(1)},p^{(1)},\mathcal{Q}_U^{21}\left(x^{(1)},p^{(1)},x^{(2)},p^{(2)}\right)\right) = \kappa\left(\frac{\partial F^{(1)}}{\partial x_U^{(1)}} - p_U^{(1)}\right)\left(\frac{1}{p_U^{(2)}} - \frac{1}{p_U^{(1)}}\right)$$

and

$$f^{(2)}\left(x^{(2)},p^{(2)},\mathcal{Q}_U^{12}\left(x^{(2)},p^{(2)},x^{(1)},p^{(1)}\right)\right) = \kappa\left(\frac{\partial F^{(2)}}{\partial x_U^{(2)}} - p_U^{(2)}\right)\left(\frac{1}{p_U^{(1)}} - \frac{1}{p_U^{(2)}}\right)$$

where $F^{(1)}\left(x^{(1)}\right)$ *and* $F^{(2)}\left(x^{(2)}\right)$ *are the generating functions of the Legendre manifolds of each of the compartments (with partition of the indices:* $I_1 = I_2 = \{1\}$ *and* $J_1 = J_2 = \emptyset$*). The contact Hamiltonian functions are indeed of the form required in condition* (6.21)*. So the contact Hamiltonian function for the whole system is written as follows:*

$$\begin{aligned} f\left(x,p\right) &= f^{(1)}\left(x,p\right) + f^{(2)}\left(x,p\right) \\ &= -\kappa\left(-\frac{\partial F^{(1)}}{\partial x_U^{(1)}} + p_U^{(1)} + \frac{\partial F^{(2)}}{\partial x_U^{(2)}} - p_U^{(2)}\right)\left(\frac{1}{p_U^{(2)}} - \frac{1}{p_U^{(1)}}\right) \end{aligned} \tag{6.25}$$

It can be easily checked that this contact Hamiltonian function allows to correctly describe the systems dynamics of the complete system. As an example let us show that this expression allows to go back to the initial balance equations. Let us compute the time variation of $x_U^{(1)}$ *and* $x_U^{(2)}$ *generated by* (6.25) *using* (6.9)*:*

$$\begin{aligned}
\frac{dx_U^{(1)}}{dt} &= -\frac{\partial f}{\partial p_U^{(1)}} \\
&= \kappa\left(\frac{1}{p_U^{(2)}} - \frac{1}{p_U^{(1)}}\right) - \kappa\left(-\frac{\partial F^{(1)}}{\partial x_U^{(1)}} + p_U^{(1)} + \frac{\partial F^{(2)}}{\partial x_U^{(2)}} - p_U^{(2)}\right)\left(\frac{1}{p_U^{(1)}}\right)^2 \\
\frac{dx_U^{(2)}}{dt} &= -\frac{\partial f}{\partial p_U^{(2)}} \\
&= -\kappa\left(\frac{1}{p_U^{(2)}} - \frac{1}{p_U^{(1)}}\right) + \kappa\left(-\frac{\partial F^{(1)}}{\partial x_U^{(1)}} + p_U^{(1)} + \frac{\partial F^{(2)}}{\partial x_U^{(2)}} - p_U^{(2)}\right)\left(\frac{1}{p_U^{(2)}}\right)^2
\end{aligned}$$

Let us now restrict to the Legendre submanifold of the total system $\mathscr{L}$*. On* $\mathscr{L}$ *we have:*

$$\begin{aligned}
p_U^{(1)} &= \frac{\partial F}{\partial x_U^{(1)}} = \frac{\partial F^{(1)}}{\partial x_U^{(1)}} \\
p_U^{(2)} &= \frac{\partial F}{\partial x_U^{(2)}} = \frac{\partial F^{(2)}}{\partial x_U^{(2)}}
\end{aligned}$$

where $F\left(x^{(1)}, x^{(2)}\right) = F^{(1)}\left(x^{(1)}\right) + F^{(2)}\left(x^{(2)}\right)$ *is the generating function of the Legendre submanifold of the total system. As a consequence:*

$$\begin{aligned}
\frac{dU^{(1)}}{dt} = \left.\frac{dx_U^{(1)}}{dt}\right|_{\mathscr{L}} &= \kappa\left(\frac{1}{p_U^{(2)}} - \frac{1}{p_U^{(1)}}\right) = \kappa\left(T^{(2)} - T^{(1)}\right) \\
\frac{dU^{(2)}}{dt} = \left.\frac{dx_U^{(2)}}{dt}\right|_{\mathscr{L}} &= -\kappa\left(\frac{1}{p_U^{(2)}} - \frac{1}{p_U^{(1)}}\right) = \kappa\left(T^{(1)} - T^{(2)}\right)
\end{aligned}$$

These are the internal energy balance equations on each of the compartments.

In order to find the total entropy production of this system, we use the

contact Hamiltonian function (6.25) *and apply it to* (6.24)*:*

$$\begin{aligned}
&\frac{dx_0^{tot}}{dt} - p^t \frac{\partial f}{\partial p} + f\left(x,p\right) \\
&= f\left(x,p\right) + \kappa \left(\frac{1}{p_U^{(2)}} - \frac{1}{p_U^{(1)}} \right) \left(p_U^{(1)} - p_U^{(2)} \right) \\
&\quad - \kappa \left(-\frac{\partial F^{(1)}}{\partial x_U^{(1)}} + p_U^{(1)} + \frac{\partial F^{(2)}}{\partial x_U^{(2)}} - p_U^{(2)} \right) \left(\left(\frac{1}{p_U^{(1)}} \right)^2 - \left(\frac{1}{p_U^{(2)}} \right)^2 \right)
\end{aligned}$$

By restricting to the Legendre submanifold, we obtain:

$$\begin{aligned}
\frac{dS^{tot}}{dt} = \left. \frac{dx_0^{tot}}{dt} \right|_{\mathscr{L}} &= \kappa \left(\frac{1}{p_U^{(2)}} - \frac{1}{p_U^{(1)}} \right) \left(p_U^{(1)} - p_U^{(2)} \right) \\
&= \kappa \frac{\left(T^{(2)} - T^{(1)} \right)^2}{T^{(1)} T^{(2)}}
\end{aligned}$$

Since the cell is isolated, there is no external entropy flow, i.e. $\mathcal{F}_S = 0$*. So the expression of* $\frac{dS^{tot}}{dt}$ *is also equal to the total entropy production rate. It is easy to check that this quantity is indeed positive.*

6.4 Conclusion

In this chapter we have presented a more abstract point of view of the thermodynamics. We have shown that the usual concepts of thermodynamics that have been presented in Chapter 1 can be expressed in a mathematical framework using differential geometry.

The dynamics of a network of simple thermodynamic systems has been formulated in terms of contact systems. It is an extension of the formulation using contact structures and Legendre submanifolds of the thermodynamic phase space for reversible transformations [10][21][50][73][74][75] to open irreversible thermodynamical systems. It is also a departure from the work in [26], [27] and [32] since we have used an entropy 1-form instead of the energy 1-form as the contact form of the thermodynamic phase space. We have shown that this structure is well-adapted to the formulation of the dynamics of irreversible thermodynamic systems as the contact Hamiltonian function may be derived

from the balance equations on the energy, the volume and the matter. A striking feature of this formulation is that the total entropy balance may be derived directly from the contact Hamiltonian function.

First we have considered simple systems and then we have extended it to more complex systems that can be modelled via a set of compartments that exchange energy, volume and matter. This can be useful for the modelling of chemical processes because these are typically networks of unit operations. The dynamical behaviour of the whole system is contained in one unique function, the contact Hamiltonian function. Hence adding, withdrawing or changing a compartment or changing the interconnection affects directly the contact Hamiltonian function of the whole system. Therefore, the analysis of the contact Hamiltonian function allows to see how one compartment influences the dynamical behaviour of the whole system.

In this chapter we have always used the coordinate representation of the objects. Therefore at first sight it could seem that the contact formalisms amounts to replacing the classical notations of thermodynamics (S, U, n etc.) by other ones (x_0, x_U, x_n, etc.). One of the major characteristics of differential geometry is to get rid of using coordinate representations and to allow to work directly with the considered objects. Up to now we have not used this property at all.

We have chosen to present the approach using coordinates instead of working simply with the objects because it is the coordinate representation that allows us to make the link with physics. In this way we introduce the formalism by using elements which are familiar to people who are more used to thermodynamics than to differential geometry. Let us also mention that other choices of local coordinates also allow to make the link with the physics. An example is the choice by Eberard and coworkers who worked with the energy contact form [27][31][32]. As already said, the advantage of our choice is that the contact Hamiltonian function is deduced from the balances on the conserved extensive quantities whose flows are usually known. But other choices could be better if for example one of the intensive variables is constrained (e.g. constant pressure maintained by an exhaust valve) and the flow of an extensive variable is then not directly known.

However we could work in an abstract way considering only the differential geometric objects, and turning to the coordinate representation only when a physical interpretation is needed. This is in fact one of the reasons for introducing the contact formalism into thermodynamics. Indeed in this way we are now allowed to use the whole differential geometric machinery on thermodynamic systems. The long-term view is now to use this powerful machinery to derive new results in the domain of the control of thermodynamic systems, in the same way that the use of symplectic geometry has led to results for mechanical and electro-mechanical systems [10][69].

Chapter 7

Some properties of conservative port contact systems[1]

In the previous chapter, the dynamics of open irreversible thermodynamic systems has been formulated as contact vector fields with generating functions depending on some external variable and called conservative port contact systems. Nevertheless in order to use the contact formalism for process control considerations, it is important to know how the dynamical properties of the system are expressed in this formalism. The aim of this chapter is to present how equilibrium points and Lyapunov's first stability theorem are expressed in terms of the contact formalism. Since this formalism is closely related to the geometric structure of thermodynamics, this analysis can then be used to physically interpret the existence and/or the stability conditions of the steady states.

[1]The text of this chapter has been extracted from [37]. © 2009 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

We shall present the expression of the dynamical properties in Section 7.1. Some possible physical interpretation of these results are then provided in Section 7.2.

7.1 Expression of the dynamical properties

7.1.1 Equivalent contact Hamiltonian functions

For systems describing mass and heat transport phenomena coupled with chemical reactions, as they arise in process systems, a family of contact Hamiltonian functions has been suggested in Chapter 6[1]. They have been derived starting from the expression of the fluxes in the balance equations of the internal energy, the volume and the quantity of each component. As it has been emphazised in Remark 6.3, there can be several contact Hamiltonian functions to describe the same thermodynamic system in the sense that they generate contact vector fields that are equal on the Legendre submanifold characterizing the thermodynamic properties of the system. This comes from the fact that the contact vector field is obtained by lifting a vector field defined only on the Legendre submanifold (in this case, the balance equations on the extensive variables) to a contact vector field on the whole thermodynamic phase space [31] and that such a lift may be not uniquely defined. In this section we shall characterize the set of the contact Hamiltonian functions that give rise to the same dynamical behaviour on a given Legendre submanifold.

Definition 7.1. Consider a Legendre submanifold $\mathscr{L}$ of the contact manifold $(\mathcal{T}, \theta)$. Let f_1 and f_2 be two contact Hamiltonian functions that are equal to zero on $\mathscr{L}$. f_1 and f_2 are said to be *equivalent on* $\mathscr{L}$ if the generated contact vector fields $\mathcal{X}_{f_1}$ and $\mathcal{X}_{f_2}$ are equal on $\mathscr{L}$, i.e. $\mathcal{X}_{f_1}|_{\mathscr{L}} = \mathcal{X}_{f_2}|_{\mathscr{L}}$.

The two following propositions show how to construct some families of contact Hamiltonian functions that are equivalent on $\mathscr{L}$.

Proposition 7.1. *Let us consider a Legendre submanifold $\mathscr{L}$ generated by the function $F(x_I, p_J)$ in the canonical coordinates as stated in relation* (6.3),

[1] see also [35].

where $I \cup J$ is a disjoint partition of the set of indices. Let $f_1(x_0, x, p)$ be a contact Hamiltonian function that is equal to zero on $\mathscr{L}$. There always exist at least one smooth real-valued function $f_0(x_0, x, p)$ and one smooth real-valued function $\tilde{f}_1(x_0, x, p)$ such that $f_1(x_0, x, p)$ can be decomposed as follows:

$$f_1(x_0, x, p) = f_0(x_0, x, p)\, \tilde{f}_1(x_0, x, p)$$

where $f_0(x_0, x, p) = 0$ on $\mathscr{L}$ and $\tilde{f}_1(x_0, x, p) \not\equiv 0$.

Consider the two following alternative contact Hamiltonian functions:

$$f_2(x_0, x, p) = f_0\,(x_0, x, p)\ \underbrace{\tilde{f}_1\left(x_0, x, p |\, x_K = -\frac{\partial F}{\partial p_K}, p_L = \frac{\partial F}{\partial x_L}\right)}_{\tilde{f}_2(x_0, x_I, x_{J\setminus K}, p_J, p_{I\setminus L})}$$

$$f_3(x_0, x, p) = f_0\,(x_0, x, p)\ \underbrace{\tilde{f}_1\left(x_0, x, p |\, x_0 = F(x_I, p_J) - p_J^t \frac{\partial F}{\partial p_J}\right)}_{\tilde{f}_3(x,p)}$$

where K and L are subsets of J and I, respectively.

The restriction of the contact vector fields generated by the functions $f_1\,(x_0, x, p)$, $f_2\,(x_0, x, p)$ and $f_3(x_0, x, p)$ to the Legendre submanifold $\mathscr{L}$ are the same, i.e. $f_1(x_0, x, p)$, $f_2(x_0, x, p)$ and $f_3(x_0, x, p)$ are equivalent contact Hamiltonian functions on $\mathscr{L}$.

Proof. Since $f_0(x_0, x, p) = 0$ on $\mathscr{L}$, it is straightforward to see that $f_2(x_0, x, p)$ and $f_3(x_0, x, p)$ are equal to zero on $\mathscr{L}$. Consequently the vector fields generated by $f_2(x_0, x, p)$ and $f_3(x_0, x, p)$ leave the Legendre submanifold $\mathscr{L}$ invariant. Moreover, by using (6.3), it can be observed that:

$$\tilde{f}_1(x_0, x, p)\Big|_{\mathscr{L}} = \tilde{f}_2(x_0, x, p)\Big|_{\mathscr{L}} = \tilde{f}_3(x_0, x, p)\Big|_{\mathscr{L}} \tag{7.1}$$

Let us now write in canonical coordinates the expression of the generated vector

fields by using (6.8):

$$\begin{aligned}\mathcal{X}_{f_i} &= \begin{pmatrix} f_i \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & -p^t \\ 0 & 0 & -\boldsymbol{I}_{d_F} \\ p & \boldsymbol{I}_{d_F} & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial f_0}{\partial x_0}\tilde{f}_i + f_0\frac{\partial \tilde{f}_i}{\partial x_0} \\ \frac{\partial f_0}{\partial x}\tilde{f}_i + f_0\frac{\partial \tilde{f}_i}{\partial x} \\ \frac{\partial f_0}{\partial p}\tilde{f}_i + f_0\frac{\partial \tilde{f}_i}{\partial p} \end{pmatrix} \\ &\overset{\mathscr{L}}{=} \begin{pmatrix} 0 & 0 & -p^t \\ 0 & 0 & -\boldsymbol{I}_{d_F} \\ p & \boldsymbol{I}_{d_F} & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial f_0}{\partial x_0} \\ \frac{\partial f_0}{\partial x} \\ \frac{\partial f_0}{\partial p} \end{pmatrix} \tilde{f}_i\Big|_{\mathscr{L}}\end{aligned}$$

where $i = 1, 2, 3$. By using (7.1), one immediately obtains:

$$\mathcal{X}_{f_1}|_{\mathscr{L}} = \mathcal{X}_{f_2}|_{\mathscr{L}} = \mathcal{X}_{f_3}|_{\mathscr{L}} \qquad \square$$

Another interesting property of equivalent contact Hamiltonian functions is that they can be combined to find another equivalent contact Hamiltonian function. This is stated in the following proposition.

Proposition 7.2. *Let $\mathscr{L}$ be a Legendre submanifold of the contact manifold $(\mathcal{T}, \theta)$. Let $f_1, f_2, ..., f_k$ be k equivalent contact Hamiltonian functions on $\mathscr{L}$ with:*

$$f_1|_{\mathscr{L}} = f_2|_{\mathscr{L}} = ... = f_k|_{\mathscr{L}} = 0$$

Let $\alpha_1, \alpha_2, ..., \alpha_k$ be k scalar numbers with $\sum_{i=1}^{k} \alpha_i = 1$. Then the following contact Hamiltonian function:

$$f = \sum_{i=1}^{k} \alpha_i f_i$$

is also an equivalent contact Hamiltonian function to $f_1, f_2, ..., f_k$ on $\mathscr{L}$ with $f|_{\mathscr{L}} = 0$.

Proof. It is straightforward that $f|_{\mathscr{L}} = 0$ since we have the following equality:

$$f_1|_{\mathscr{L}} = f_2|_{\mathscr{L}} = \ldots = f_k|_{\mathscr{L}} = 0$$

Let us now express the contact vector field generated by the function f ex-

pressed in the canonical coordinates using relation (6.8):

$$\begin{aligned}
\mathcal{X}_f &= \begin{pmatrix} f \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & -p^t \\ 0 & 0 & -\boldsymbol{I}_{d_F} \\ p & \boldsymbol{I}_{d_F} & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial f}{\partial x_0} \\ \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial p} \end{pmatrix} \\
&= \sum_{i=1}^{k} \alpha_i \begin{pmatrix} f_i \\ 0 \\ 0 \end{pmatrix} + \sum_{i=1}^{k} \alpha_i \begin{pmatrix} 0 & 0 & -p^t \\ 0 & 0 & -\boldsymbol{I}_{d_F} \\ p & \boldsymbol{I}_{d_F} & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial f_i}{\partial x_0} \\ \frac{\partial f_i}{\partial x} \\ \frac{\partial f_i}{\partial p} \end{pmatrix} \\
&= \sum_{i=1}^{k} \alpha_i \mathcal{X}_{f_i}
\end{aligned}$$

Now let us restrict $\mathcal{X}_f$ to the Legendre submanifold. By using the fact that:

$$\mathcal{X}_{f_1}|_{\mathscr{L}} = \mathcal{X}_{f_2}|_{\mathscr{L}} = ... = \mathcal{X}_{f_k}|_{\mathscr{L}}$$

one obtains the following relation:

$$\mathcal{X}_f|_{\mathscr{L}} = \sum_{i=1}^{k} \alpha_i \, \mathcal{X}_{f_i}|_{\mathscr{L}} = \sum_{i=1}^{k} \alpha_i \, \mathcal{X}_{f_1}|_{\mathscr{L}} = \mathcal{X}_{f_1}|_{\mathscr{L}}$$

Consequently, following Definition 7.1, $f = \sum_{i=1}^{k} \alpha_i f_i$ is an equivalent contact Hamiltonian function to $f_1, f_2, ..., f_k$ on $\mathscr{L}$. □

Definition 7.1 and Proposition 7.1 are illustrated by the following example.

Example 7.1. *Let us consider again the system presented in Example 6.4, namely a cell containing a gas heated by the environment. The heat transfer rate is proportional to the difference between the environment T_{env} and the cell temperature T. The heat transfer coefficient is denoted by κ. In Chapter 6, we have shown that the following contact Hamiltonian function can represent the system dynamics (see* (6.11)*):*

$$f_1(x_0, x, p) = \left(\frac{\partial F}{\partial x_U} - p_U \right) \kappa \left(T_{env} - \frac{1}{p_U} \right)$$

Now let us choose the functions $f_0(x_0, x, p)$ and $\tilde{f}_1(x_0, x, p)$ as follows:

$$f_0(x_0, x, p) = \left(\frac{\partial F}{\partial x_U} - p_U \right), \; \tilde{f}_1(x_0, x, p) = \kappa \left(T_{env} - \frac{1}{p_U} \right)$$

It is straightforward to see that $f_0(x_0, x, p) = 0$ *on* $\mathscr{L}$ *and* $\tilde{f}_1(x_0, x, p) \neq 0$ *for:*

$$(x_0, x, p) \in \mathscr{L} \backslash \left\{ \left(x_0, x, p_U = \frac{1}{T_{env}} \right) \right\}$$

Therefore, from Proposition 7.1 the following contact Hamiltonian function $f_2(x_0, x, p)$ *is equivalent on* $\mathscr{L}$ *to* $f_1(x_0, x, p)$*:*

$$\begin{aligned} f_2(x_0, x, p) &= f_0(x_0, x, p)\, \tilde{f}_1\left(x_0, x, \frac{\partial F}{\partial x} \right) \\ &= \left(\frac{\partial F}{\partial x_U} - p_U \right) \kappa \left(T_{env} - \left(\frac{\partial F}{\partial x_U} \right)^{-1} \right) \end{aligned}$$

It can be easily checked out that the contact vector field generated by $f_2(x_0, x, p)$ *can also represent the dynamics of the system by redoing Example 6.4 with* $f_2(x_0, x, p)$ *instead of* $f_1(x_0, x, p)$*.*

7.1.2 Equilibrium points

Let us now derive the equilibrium points of the dynamical system and express them as particular points of the contact Hamiltonian function.

Proposition 7.3. *Consider a contact manifold* $(\mathcal{T}, \theta)$ *and a contact vector field* $\mathcal{X}_f$*.* $\mathcal{X}_f$ *is generated by the contact Hamiltonian function* $f(x_0, x, p)$ *given in the canonical coordinates* (x_0, x, p)*. Let us consider a state* $(\bar{x}_0, \bar{x}, \bar{p}) \in (\mathcal{T}, \theta)$*. Then* $(\bar{x}_0, \bar{x}, \bar{p}) \in \{(x_0, x, p) \,|\mathcal{X}_f(x_0, x, p) = 0\}$ *if and only if the following conditions are fulfilled:*

$$\left. \frac{\partial f}{\partial p} \right|_{(\bar{x}_0, \bar{x}, \bar{p})} = 0 \tag{7.2a}$$

$$f(\bar{x}_0, \bar{x}, \bar{p}) = 0 \tag{7.2b}$$

$$\left. \frac{\partial f}{\partial x} \right|_{(\bar{x}_0, \bar{x}, \bar{p})} = -\bar{p} \left. \frac{\partial f}{\partial x_0} \right|_{(\bar{x}_0, \bar{x}, \bar{p})} \tag{7.2c}$$

Proof. Let us consider a point $(\bar{x}_0, \bar{x}, \bar{p}) \in (\mathcal{T}, \theta)$. $\mathcal{X}_f(\bar{x}_0, \bar{x}, \bar{p}) = 0$ implies the following equality:

$$\mathcal{X}_f(\bar{x}_0, \bar{x}, \bar{p}) = \begin{pmatrix} f(\bar{x}_0, \bar{x}, \bar{p}) \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & -\bar{p}^t \\ 0 & 0 & -\boldsymbol{I}_{d_F} \\ \bar{p} & \boldsymbol{I}_{d_F} & 0 \end{pmatrix} \begin{pmatrix} \left. \frac{\partial f}{\partial x_0} \right|_{(\bar{x}_0, \bar{x}, \bar{p})} \\ \left. \frac{\partial f}{\partial x} \right|_{(\bar{x}_0, \bar{x}, \bar{p})} \\ \left. \frac{\partial f}{\partial p} \right|_{(\bar{x}_0, \bar{x}, \bar{p})} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

By developing the above expression, one obtains the following relations:

$$\begin{aligned} 0 &= f(\bar{x}_0, \bar{x}, \bar{p}) - \bar{p}^t \left.\frac{\partial f}{\partial p}\right|_{(\bar{x}_0,\bar{x},\bar{p})} \\ 0 &= -\left.\frac{\partial f}{\partial p}\right|_{(\bar{x}_0,\bar{x},\bar{p})} \\ 0 &= \bar{p} \left.\frac{\partial f}{\partial x_0}\right|_{(\bar{x}_0,\bar{x},\bar{p})} + \left.\frac{\partial f}{\partial x}\right|_{(\bar{x}_0,\bar{x},\bar{p})} \end{aligned}$$

The second and third equations directly lead to the conditions (7.2a) and (7.2c), respectively. By introducing condition (7.2a) into the first equation, one obtains the condition (7.2b).

To prove the "only if" part, one only needs to check that if $(\bar{x}_0, \bar{x}, \bar{p})$ fulfills the conditions (7.2a) to (7.2c), then $\mathcal{X}_f(\bar{x}_0, \bar{x}, \bar{p}) = 0$ by considering the expression of $\mathcal{X}_f$ in canonical coordinates given by (6.8). □

Corollary 7.1. *Consider a contact manifold $(\mathcal{T}, \theta)$ and a contact vector field $\mathcal{X}_f$ generated by the contact Hamiltonian function $f(x_0, x, p)$ given in the canonical coordinates (x_0, x, p). Assume that $f(x_0, x, p)$ does not depend on x_0. Let us consider a state $(\bar{x}_0, \bar{x}, \bar{p}) \in (\mathcal{T}, \theta)$. Then $\mathcal{X}_f(\bar{x}_0, \bar{x}, \bar{p}) = 0$ if and only if $(\bar{x}_0, \bar{x}, \bar{p})$ is a critical point and a zero of $f(x_0, x, p)$.*

Proof. It is obvious to check that if $f(x_0, x, p)$ does not depend on x_0, the conditions (7.2a) and (7.2c) become $\nabla f(\bar{x}_0, \bar{x}, \bar{p}) = 0$, which is equivalent to say that $(\bar{x}_0, \bar{x}, \bar{p})$ is a critical point of $f(x_0, x, p)$. Condition (7.2b) is equivalent to the fact that $(\bar{x}_0, \bar{x}, \bar{p})$ is a zero of $f(x_0, x, p)$. □

Proposition 7.3 and Corollary 7.1 can be applied to find the equilibrium points of some physical process. Let us consider a system whose dynamical behaviour is expressed by a contact Hamiltonian function $f(x_0, x, p)$ using relation (6.9) where $f(x_0, x, p) = 0$ on some Legendre submanifold $\mathscr{L}$ of the thermodynamic phase space. $\mathscr{L}$ represents the thermodynamic model of the system. The equilibria of the physical system are the points that fulfill the conditions (7.2a) to (7.2c) which are also located on the Legendre submanifold associated to the thermodynamic model. Moreover if $f(x_0, x, p)$ does not

depend on x_0, then from Corollary 7.1, the equilibrium points of the physical system are all the critical points of $f(x_0, x, p)$ that are situated on $\mathscr{L}$.

Nevertheless an equilibrium point on the Legendre submanifold can never be an isolated local extremum of the contact Hamiltonian function. Indeed there exist points in the neighbourhood of the critical points for which the contact Hamiltonian function takes the same value as at the critical point (namely zero), since the value of the contact Hamiltonian function is constant on the Legendre submanifold.

Example 7.1 (continued)**.** *Let us consider again Example 7.1 with the following contact Hamiltonian function:*

$$f_1(x_0, x, p) = \kappa \left(\frac{\partial F}{\partial x_U} - p_U \right) \left(T_{env} - \frac{1}{p_U} \right)$$

where $F(x)$ is the generating function in canonical coordinates of the Legendre submanifold representing the ideal gas for the following partition of the indices: $I = \{1, 2, 3\}$ and $J = \emptyset$. $f_1(x_0, x, p)$ does not depend on x_0. Therefore the equilibrium points $(\bar{x}, \bar{p})$ are the points for which the gradient of the contact Hamiltonian function is equal to zero:

$$\nabla f_1(\bar{x}, \bar{p}) = \begin{pmatrix} \frac{\partial f_1}{\partial x}\Big|_{(\bar{x},\bar{p})} \\ \frac{\partial f_1}{\partial p}\Big|_{(\bar{x},\bar{p})} \end{pmatrix} = \begin{pmatrix} \kappa \, \frac{\partial^2 F}{\partial x_U^2}\Big|_{(\bar{x},\bar{p})} \left(T_{env} - \frac{1}{\bar{p}_U} \right) \\ \kappa(\frac{1}{\bar{p}_U} - T_{env}) + \kappa(\, \frac{\partial F}{\partial x_U}\Big|_{(\bar{x},\bar{p})} - \bar{p}_U)(\frac{1}{\bar{p}_U^2}) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{7.3}$$

The set Ω of critical points $(\bar{x}_0, \bar{x}, \bar{p})$ is therefore:

$$\Omega = \left\{ (\bar{x}_0, \bar{x}, \bar{p}) \,\middle|\, \bar{p}_U = \frac{1}{T_{env}}, \bar{p}_U = \left. \frac{\partial F}{\partial x_U} \right|_{\bar{x}} \right\}$$

We are only interested in equilibrium points located in $\mathscr{L}$, i.e. the set $\Omega \cap \mathscr{L}$:

$$\Omega \cap \mathscr{L} = \left\{ (\bar{x}_0, \bar{x}, \bar{p}) \,\middle|\, \bar{p_U} = \frac{1}{T_{env}}, \bar{p}_U = \left. \frac{\partial F}{\partial x_U} \right|_{\bar{x}}, \bar{x}_0 = F(\bar{x}) \right\}$$

Since on the Legendre submanifold, the variable p_U is associated to the inverse of the temperature, the equilibrium points are all the states for which the temperature inside the cell is equal to the temperature outside. The result is presented graphically in Figure 7.1 where it can be seen that the equilibrium is a saddle point of the contact Hamiltonian function.

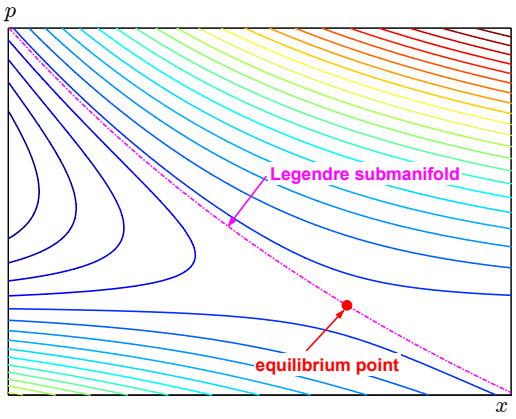


Figure 7.1: Contour plot of the contact Hamiltonian function for Example 7.1

7.1.3 Sufficient stability condition

Let us now develop a sufficient condition for the asymptotic stability of an equilibrium point, on the generating function of the Legendre submanifold and the contact Hamiltonian function. Indeed we shall express Lyapunov's first theorem in terms of these two functions.

Lyapunov's first theorem is based on the fact that for hyperbolic equilibrium points, the trajectories of the linearized system (around the equilibrium point) are topologically equivalent to those of the system. We shall first linearize the system dynamics when expressed in the contact structure formalism. Then we shall apply Lyapunov's first method in order to derive a sufficient stability criterion for a given equilibrium point. The result is stated in the following proposition.

Proposition 7.4. *Let $\mathscr{L}$ be a Legendre submanifold of the contact manifold $(\mathcal{T}, \theta)$. The generating function of $\mathscr{L}$ is $F(x_I, p_J)$ in the canonical coordinates, with $I \cup J$ a disjoint partition of the indexes. Consider a system whose dynamical behaviour on $\mathscr{L}$ is given by the contact Hamiltonian function $f(x_0, x, p)$ with $f(x_0, x, p)|_{\mathscr{L}} = 0$. Let us assume that $(\bar{x}_0, \bar{x}, \bar{p}) \in \mathscr{L}$ is an equilibrium of the system. Let us define the matrix $\mathbf{\Lambda}(x_0, x, p)$ given by*

following expression:

$$\begin{aligned}
&\mathbf{\Lambda}\left(x_0,x,p\right)\\
&=\left[\begin{pmatrix} -\frac{\partial^2 f}{\partial p_I^2} & (\frac{\partial^2 f}{\partial x_J \partial p_I})^t \\ \frac{\partial^2 f}{\partial x_J \partial p_I} & -\frac{\partial^2 f}{\partial x_J^2} \end{pmatrix} + \begin{pmatrix} 0 & (\frac{\partial^2 f}{\partial x_0 \partial p_I})^t p_J^t \\ p_J \frac{\partial^2 f}{\partial x_0 \partial p_I} & \Psi\left(x_0,x,p\right) \end{pmatrix}\right] \partial^2 F\\
&+\begin{pmatrix} -(\frac{\partial^2 f}{\partial x_0 \partial p_I})^t \frac{\partial^t F}{\partial x_I} & 0 \\ \Phi\left(x_0,x,p\right) & \frac{\partial f}{\partial x_0}\boldsymbol{I} + p_J \frac{\partial^2 f}{\partial x_0 \partial p_J} \end{pmatrix}\\
&+\begin{pmatrix} -\left(\frac{\partial^2 f}{\partial x_I \partial p_I}\right)^t & -\frac{\partial^2 f}{\partial p_I \partial p_J} \\ \left(\frac{\partial^2 f}{\partial x_I \partial x_J}\right)^t & \frac{\partial^2 f}{\partial x_J \partial p_J} \end{pmatrix}
\end{aligned} \tag{7.4}$$

where

$$\partial^2 F = \begin{pmatrix} \frac{\partial^2 F}{\partial x_I^2} & \frac{\partial^2 F}{\partial x_I \partial p_J} \\ \left(\frac{\partial^2 F}{\partial x_I \partial p_J}\right)^t & \frac{\partial^2 F}{\partial p_J^2} \end{pmatrix}$$

and $\boldsymbol{I}$ *is the identity matrix of adequate size.* $\Psi\left(x_0,x,p\right)$ *and* $\Phi\left(x_0,x,p\right)$ *are defined as follows:*

$$\begin{aligned}
\Psi\left(x_0,x,p\right) &= -\frac{\partial^2 f}{\partial x_0^2} p_J p_J^t - \frac{\partial^2 f}{\partial x_0 \partial x_J} p_J^t - p_J \frac{\partial^2 f}{\partial x_0 \partial p_J}\\
\Phi\left(x_0,x,p\right) &= \frac{\partial^2 f}{\partial x_0^2} p_J \frac{\partial^t F}{\partial x_I} + \frac{\partial^2 f}{\partial x_0 \partial x_J} \frac{\partial^t F}{\partial x_I} + p_J \frac{\partial^2 f}{\partial x_0 \partial x_I}
\end{aligned}$$

Then $(\bar{x}_0,\bar{x},\bar{p})$ *is a locally asymptotically stable equilibrium of the dynamics restricted to* $\mathscr{L}$ *if the matrix* $\mathbf{\Lambda}\left(\bar{x}_0,\bar{x},\bar{p}\right)$ *has eigenvalues with strictly negative real parts. If* $\mathbf{\Lambda}(\bar{x}_0,\bar{x},\bar{p})$ *has one or more eigenvalues with strictly positive real part, then* $(\bar{x}_0,\bar{x},\bar{p})$ *is an unstable equilibrium point of the dynamics reduced to* $\mathscr{L}$*.*

Proof. First let us linearize the system dynamics around the equilibrium point $(\bar{x}_0,\bar{x},\bar{p})$. We are interested only in the dynamics restricted to $\mathscr{L}$. The time variation of the variables x_0, x_J and p_I are linked to the time variation of x_I and p_J since the trajectories remain on the Legendre submanifold $\mathscr{L}$. Therefore it is sufficient to linearize the following reduced dynamical system

consisting in the time evolution of x_I and p_J:

$$\begin{cases} \dfrac{dx_I}{dt} = -\dfrac{\partial f}{\partial p_I} = z_x(x_0, x, p) \overset{\mathscr{L}}{=} \mathcal{Z}_x(x_I, p_J) \\ \dfrac{dp_J}{dt} = p_J \dfrac{\partial f}{\partial x_0} + \dfrac{\partial f}{\partial x_J} = z_p(x_0, x, p) \overset{\mathscr{L}}{=} \mathcal{Z}_p(x_I, p_J) \end{cases} \tag{7.5}$$

The linearized dynamics of x_I is given by following expression:

$$\begin{aligned} \frac{d\tilde{x}_I}{dt} &= \left(\frac{\partial^t \mathcal{Z}_x}{\partial x_I}\right)_{(\bar{x}_0,\bar{x},\bar{p})} \tilde{x}_I + \left(\frac{\partial^t \mathcal{Z}_p}{\partial x_I}\right)_{(\bar{x}_0,\bar{x},\bar{p})} \tilde{p}_J \\ &= \left[\frac{\partial^t z_x}{\partial x_0}\frac{\partial^t F}{\partial x_I} - \frac{\partial^t z_x}{\partial x_0} p_J^t \left(\frac{\partial^2 F}{\partial x_I \partial p_J}\right)^t \right. \\ &\qquad \left. - \frac{\partial^t z_x}{\partial x_J}\left(\frac{\partial^2 F}{\partial x_I \partial p_J}\right)^t + \frac{\partial^t z_x}{\partial x_I} + \frac{\partial^t z_x}{\partial p_I}\frac{\partial^2 F}{\partial x_I^2}\right]_{(\bar{x}_0,\bar{x},\bar{p})} \tilde{x}_I \\ &\quad + \left[-\frac{\partial^t z_x}{\partial x_0} p_J^t \left(\frac{\partial^2 F}{\partial x_I \partial p_J}\right)^t - \frac{\partial^t z_x}{\partial x_J}\left(\frac{\partial^2 F}{\partial p_J^2}\right)^t \right. \\ &\qquad \left. + \frac{\partial^t z_x}{\partial p_J} + \frac{\partial^t z_x}{\partial p_I}\frac{\partial^2 F}{\partial x_I \partial p_J}\right]_{(\bar{x}_0,\bar{x},\bar{p})} \tilde{p}_J \end{aligned}$$

where $\tilde{x}_I = x_I - \bar{x}_I$ and $\tilde{p}_J = p_J - \bar{p}_J$. This result has been obtained by using the relations between the variables on $\mathscr{L}$ given by (6.3). The linearized dynamics of p_J is given by the same relation when replacing $z_x(x_0, x, p)$ by $z_p(x_0, x, p)$. $z_x(x_0, x, p)$ and $z_p(x_0, x, p)$ can now be replaced by their expression in terms of $f(x_0, x, p)$. For the sake of brevity and clarity, the calculation details are not given here. The result is the following expression for the linearized system:

$$\begin{pmatrix} \dfrac{d\tilde{x}_I}{dt} \\ \dfrac{d\tilde{p}_J}{dt} \end{pmatrix} = \mathbf{\Lambda}(\bar{x}_0, \bar{x}, \bar{p}) \begin{pmatrix} \tilde{x}_I \\ \tilde{p}_J \end{pmatrix} \tag{7.6}$$

where the expression for $\mathbf{\Lambda}(x_0, x, p)$ is given in Proposition 7.4.

Following Lyapunov's first method, the dynamical system (7.5) has a locally asymptotically stable equilibrium at $(\bar{x}_0, \bar{x}, \bar{p})$ if the linearized system (7.6) has an asymptotically stable equilibrium at $(\bar{x}_0, \bar{x}, \bar{p})$, i.e. if $\mathbf{\Lambda}(\bar{x}_0, \bar{x}, \bar{p})$ has eigenvalues with strictly negative real parts. If the linearized system (7.6) is unstable, i.e. if $\mathbf{\Lambda}(\bar{x}_0, \bar{x}, \bar{p})$ has one or more eigenvalues with strictly positive real

part, then $(\bar{x}_0, \bar{x}, \bar{p})$ is an unstable equilibrium point of the dynamical system (7.5). □

Corollary 7.2. *In addition to the assumptions of Proposition 7.4, let us assume that $f(x_0, x, p)$ does not depend on x_0. Then $(\bar{x}_0, \bar{x}, \bar{p})$ is a locally asymptotically stable equilibrium of the dynamics restricted to $\mathscr{L}$ if the matrix $\mathbf{\Lambda}(x, p)$ has eigenvalues with strictly negative real parts at $(\bar{x}_0, \bar{x}, \bar{p})$ where $\mathbf{\Lambda}(x, p)$ is given by the following expression:*

$$\mathbf{\Lambda}\left(x,p\right) = \begin{pmatrix} -\frac{\partial^2 f}{\partial p_I^2} & (\frac{\partial^2 f}{\partial x_J \partial p_I})^t \\ \frac{\partial^2 f}{\partial x_J \partial p_I} & -\frac{\partial^2 f}{\partial x_J^2} \end{pmatrix} \partial^2 F + \begin{pmatrix} -\left(\frac{\partial^2 f}{\partial x_I \partial p_I}\right)^t & -\frac{\partial^2 f}{\partial p_I \partial p_J} \\ \left(\frac{\partial^2 f}{\partial x_I \partial x_J}\right)^t & \frac{\partial^2 f}{\partial x_J \partial p_J} \end{pmatrix} \tag{7.7}$$

If $\mathbf{\Lambda}(\bar{x}, \bar{p})$ has one or more eigenvalues with strictly positive real part, then $(\bar{x}_0, \bar{x}, \bar{p})$ is an unstable equilibrium point of the dynamics reduced to $\mathscr{L}$.

Proof. The proof is straightforward by including the fact that $f(x_0, x, p)$ does not depend on x_0 in the expression of the matrix $\mathbf{\Lambda}\left(x_0, x, p\right)$ in Proposition 7.4. □

Example 7.1 (continued)**.** *Let us consider again Example 7.1 with the contact Hamiltonian function:*

$$f_1\left(x_0, x, p\right) = \kappa \left(\frac{\partial F}{\partial x_U} - p_U\right)\left(T_{env} - \frac{1}{p_U}\right)$$

where $F(x)$ is the generating function in canonical coordinates of the Legendre submanifold representing the ideal gas for following partition of the indices: $I = \{1, 2, 3\}$ and $J = \emptyset$. $f_1\left(x_0, x, p\right)$ does not depend on x_0. The matrix $\mathbf{\Lambda}$ of Proposition 7.4 is given by relation (7.7):

$$\begin{aligned} \mathbf{\Lambda}(x,p) &= -\frac{\partial^2 f_1}{\partial p_U^2}\frac{\partial^2 F}{\partial x_U^2} - \frac{\partial^2 f_1}{\partial x_U \partial p_U} \\ &= \kappa \frac{\partial^2 F}{\partial x_U^2}\frac{1}{p_U^2} + \kappa \frac{\partial^2 F}{\partial x_U^2}\left(\frac{\partial F}{\partial x_U} - p_U\right)\frac{2}{p_U^3} \end{aligned}$$

The equilibrium point of the system is given by (see (7.3)):

$$\bar{p}_U = \frac{1}{T_{env}} \quad \textit{and} \quad \bar{p}_U = \left.\frac{\partial F}{\partial x_U}\right|_{\bar{x}}$$

Therefore at the equilibrium, the matrix $\mathbf{\Lambda}$ *becomes:*

$$\mathbf{\Lambda}(\bar{x},\bar{p}) = \kappa T_{env}^2 \left.\frac{\partial^2 F}{\partial x_U^2}\right|_{\bar{x}} \tag{7.8}$$

The equilibrium is asymptotically stable if $F(x)$ *is concave and unstable if* $F(x)$ *is convex.*

Our choice of partition of the indexes for the generating function is such that $F(x)$ *represents the entropy as a function of the extensive variables. Hence,* (7.8) *can be written as follows:*

$$\mathbf{\Lambda}(\bar{x},\bar{p}) = \kappa T_{env}^2 \left.\frac{\partial^2 F}{\partial x_U^2}\right|_{\bar{x}} = \kappa T_{env}^2 \left.\frac{\partial^2 \tilde{S}}{\partial U^2}\right|_{(\bar{U},\bar{V},\bar{n})}$$

A direct consequence of the second principle of thermodynamics is the concavity of the entropy function, i.e. $\frac{\partial^2 \tilde{S}}{\partial U^2}$ *is negative definite [19]. Indeed we have:*

$$\frac{\partial^2 \tilde{S}}{\partial U^2} = \frac{\partial}{\partial U}\left(\frac{1}{T}\right) = -\left(C_v T^2\right)^{-1} < 0$$

As a consequence, the concavity of the entropy implies the stability of the equilibrium.

Remark 7.1. *The previous proposition and its corollary fail if one of the eigenvalues has a zero real part. A theorem exists that can be applied if the linearization fails, namely the Centre Manifold Theorem [63][77]. To apply this theorem, a change of variables has to be done such that the dynamical system is written as follows in the new variables:*

$$\frac{d}{dt}\begin{pmatrix} y_1 \\ y_2 \end{pmatrix} = \begin{pmatrix} \mathbf{\Lambda}_0 & 0 \\ 0 & \mathbf{\Lambda}_- \end{pmatrix}\begin{pmatrix} y_1 \\ y_2 \end{pmatrix} + \begin{pmatrix} g_0(y_1,y_2) \\ g_-(y_1,y_2) \end{pmatrix} \tag{7.9}$$

where the size of y_1 *is equal to the number of pure imaginary eigenvalues of* $\mathbf{\Lambda}$*,* $\mathbf{\Lambda}_0$ *has pure imaginary eigenvalues and the eigenvalues of* $\mathbf{\Lambda}_-$ *have strictly negative real part. If* $g_0(y_1,y_2)$ *and* $g_-(y_1,y_2)$ *are twice differentiable with* $g_0(0,0) = g_-(0,0) = 0$ *and* $\nabla g_0(0,0) = \nabla g_-(0,0) = 0$*, then there exists* $\delta > 0$ *and a differentiable function* $\varphi(y_1)$ *such that the manifold* $y_2 = \varphi(y_1)$ *(the centre manifold) defined for* $\|y_1\| < \delta$ *is invariant for* (7.9) *with* $\varphi(0) = 0$

and $\left.\frac{d\varphi}{dy_1}\right|_{y_1=0} = 0$. *The function* $\varphi(y_1)$ *is the solution of the following partial differential equation:*

$$0 = \mathbf{\Lambda}_- \varphi(y_1) + g_-(y_1, \varphi(y_1)) - \frac{\partial \varphi}{\partial y_1}\left[\mathbf{\Lambda}_0 y_1 + g_0(y_1, \varphi(y_1))\right] \tag{7.10}$$

On this manifold, the system dynamics are given as follows:

$$\frac{dy_1}{dt} = \mathbf{\Lambda}_0 y_1 + g_0(y_1, h(y_1))$$

The stability of the equilibrium $y_1 = 0$ *of the above reduced dynamical system is then same as the stability of the equilibrium* $(y_1, y_2) = (0, 0)$ *of the total system.*

Assume the change of variables that allows to transform the dynamics (7.5) *into the form* (7.9) *is given by the matrix* $\mathbf{\Pi}$ *as follows:*

$$\begin{pmatrix} y_1 \\ y_2 \end{pmatrix} = \begin{pmatrix} \mathbf{\Pi}_{II} & \mathbf{\Pi}_{IJ} \\ \mathbf{\Pi}_{JI} & \mathbf{\Pi}_{JJ} \end{pmatrix} \begin{pmatrix} x_I - \bar{x}_I \\ p_J - \bar{p}_J \end{pmatrix}$$

Then the centre manifold $\varphi(y_1)$ *is the solution of* (7.10) *with:*

$$g_0(y_1, y_2) = -\boldsymbol{P}_{II}\frac{\partial f}{\partial p_I} + \boldsymbol{P}_{IJ}\left[p_J \frac{\partial f}{\partial x_0} + \frac{\partial f}{\partial x_J} - \mathbf{\Lambda}_0 y_1\right]$$
$$g_-(y_1, y_2) = -\boldsymbol{P}_{JI}\frac{\partial f}{\partial p_I} + \boldsymbol{P}_{JJ}\left[p_J \frac{\partial f}{\partial x_0} + \frac{\partial f}{\partial x_J} - \mathbf{\Lambda}_- y_2\right]$$

A general solution has not been found, yet. However this does not mean that in concrete cases an analytical solution can not been found.

7.2 Physical interpretation of the stability condition

In the above example, the stability condition of Proposition 7.4 has been related to the concavity of the entropy function. This suggests that the stability condition can possibly be related to the thermodynamic laws and therefore may be given a physical interpretation. Let us now give some physical insight into the mathematical aspects developed in the previous section. In other words we

shall here link in a general way the sufficient stability condition to the usual thermodynamic considerations on the system.

Let us consider the dynamical behaviour of some thermodynamic system whose state is given by $2d_F + 1$ thermodynamic state variables. The thermodynamic model is represented by the Legendre submanifold $\mathscr{L}$ of the contact manifold $(\mathcal{T}, \theta)$ where $\mathcal{T}$ is the thermodynamic phase space and θ is the Gibbs' relation. Without any loss of generality, we shall consider here the case where θ is the Gibbs' relation in its entropy form (6.4). The following considerations remain true for other forms of the Gibbs' relation by adapting the correspondence relations between the canonical coordinates and the thermodynamic state variables as they are given by (6.5) for the entropy form. In addition let us make the following assumptions:

Assumption 7.1. The generating function of the Legendre submanifold is given for the partition of the indexes $I = \{1, ..., d_F\}$ and $J = \emptyset$ where d_F is the dimension of the Legendre submanifold (i.e. the number of degrees of freedom of the system).

In other words, the generating function of the Legendre submanifold is the entropy as a function of the extensive quantities, as it has been explained in Section 6.1. Consequently the coordinates of the points of $\mathscr{L}$ fulfill the following relations:

$$x_0 = \tilde{S}(x), \quad p = \frac{\partial \tilde{S}}{\partial x} \tag{7.11}$$

where

$$\tilde{S}(x) = \tilde{S}\left(x | x = [U, V, n]^t\right)$$

is the fundamental relation of the thermodynamic model. As it has been mentioned in Section 6.1, it is always possible to find generating function of the Legendre submanifold for the partition of the indexes $I = \{1, ..., d_F\}$ and $J = \emptyset$ (i.e. $\tilde{S}(x)$) from other generating functions given for other partitions. Indeed these generating functions are related by Legendre transforms.

Assumption 7.2. The system dynamics are given by the balance equations on the extensive quantities related to the x-coordinates (i.e. the internal energy,

the volume and the quantity of each species when θ is the entropy form of Gibbs' relation).

Assumption 7.3. The net flow rates of the extensive quantities related to the x-coordinates do not depend on the quantity related to the x_0-coordinate (i.e. the entropy when θ is the entropy form of Gibbs' relation).

Assumption 7.3 can always be fulfilled by using Proposition 7.1.

Assumptions 7.2 and 7.3 imply that the dynamical behaviour of the system can be modelled on $\mathscr{L}$ as follows:

$$\left.\frac{dx}{dt}\right|_{\mathscr{L}} = [\mathcal{Q}(x,p)]_{\mathscr{L}} \tag{7.12}$$

where the i^{th} element of the vector $\mathcal{Q}$ is the net flow rate of the extensive quantity corresponding to the x_i-coordinate.

As it has been shown in Section 6.3.1 in Proposition 6.2 these assumptions imply that:

$$f(x,p) = \left(\frac{\partial^t \tilde{S}}{\partial x} - p^t\right)\mathcal{Q}(x,p) \tag{7.13}$$

is a possible contact Hamiltonian function $f(x,p)$ for the representation of the system dynamics. The expression (7.13) can be inserted into Corollary 7.1 to obtain the equilibrium points of the system. The following relation is obtained:

$$\left.\begin{pmatrix} \frac{\partial^2 \tilde{S}}{\partial x^2}\mathcal{Q}(x,p) - \frac{\partial \mathcal{Q}}{\partial x}(\frac{\partial \tilde{S}}{\partial x} - p) \\ -\mathcal{Q}(x,p) + \frac{\partial \mathcal{Q}}{\partial p}(\frac{\partial \tilde{S}}{\partial x} - p) \end{pmatrix}\right|_{(\bar{x}_0,\bar{x},\bar{p})} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

All the equilibrium points with physical meaning are situated on $\mathscr{L}$, i.e.:

$$\left(\left.\frac{\partial \tilde{S}}{\partial x}\right|_{(\bar{x}_0,\bar{x},\bar{p})} - \bar{p}\right) = 0$$

As a consequence, the equilibrium condition reduces to $\mathcal{Q}(\bar{x},\bar{p}) = 0$. In other words, the net flow rates of the extensive quantities are equal to zero at equilibrium, which is in accordance with the physical intuition.

Let us now check the sufficient stability condition given by Corollary 7.2 for the contact Hamiltonian function (7.13). A simple calculus gives the following expressions for the partial derivatives of f:

$$\begin{aligned}
\left(\frac{\partial^2 f}{\partial p^2}\right)_{i,j} &= \sum_{k=1}^{d_F}\left(\left(\frac{\partial \tilde{S}}{\partial x_k} - p_k\right)\frac{\partial^2 \mathcal{Q}_k}{\partial p_i \partial p_j}\right) - \frac{\partial \mathcal{Q}_i}{\partial p_j} - \frac{\partial \mathcal{Q}_j}{\partial p_i} \\
\left(\frac{\partial^2 f}{\partial x \partial p}\right)_{i,j} &= \sum_{k=1}^{d_F}\left(\frac{\partial^2 \tilde{S}}{\partial x_i \partial x_k}\frac{\partial \mathcal{Q}_k}{\partial p_j}\right) - \frac{\partial \mathcal{Q}_j}{\partial x_i} + \sum_{k=1}^{d_F}\left(\left(\frac{\partial \tilde{S}}{\partial x_k} - p_k\right)\frac{\partial^2 \mathcal{Q}_k}{\partial p_j \partial x_i}\right)
\end{aligned}$$

From (7.11), the restriction of the above expressions to $\mathscr{L}$ is given as follows:

$$\begin{aligned}
\left(\frac{\partial^2 f}{\partial p^2}\right)\Big|_{\mathscr{L}} &= -\left(\frac{\partial \mathcal{Q}}{\partial p} + \frac{\partial^t \mathcal{Q}}{\partial p}\right) \\
\left(\frac{\partial^2 f}{\partial x \partial p}\right)\Big|_{\mathscr{L}} &= \frac{\partial^2 \tilde{S}}{\partial x^2}\left.\frac{\partial \mathcal{Q}}{\partial p}\right|_{(\bar{x}_0,\bar{x},\bar{p})} - \left.\frac{\partial^t \mathcal{Q}}{\partial x}\right|_{(\bar{x}_0,\bar{x},\bar{p})}
\end{aligned}$$

Since the equilibrium points of physical interest lie on $\mathscr{L}$, the expression of the matrix $\mathbf{\Lambda}(\bar{x},\bar{p})$ given by (7.7) can be rewritten as follows:

$$\mathbf{\Lambda}(\bar{x},\bar{p}) = \left.\frac{\partial \mathcal{Q}}{\partial p}\right|_{(\bar{x}_0,\bar{x},\bar{p})}\left.\frac{\partial^2 \tilde{S}}{\partial x^2}\right|_{(\bar{x}_0,\bar{x},\bar{p})} + \left.\frac{\partial \mathcal{Q}}{\partial x}\right|_{(\bar{x}_0,\bar{x},\bar{p})} \tag{7.14}$$

Example 7.1 (continued)**.** *Assumptions 7.1 to 7.3 are fulfilled by the system of Example 7.1 with* $\mathcal{Q}(x,p) = \kappa\left(T_{env} - p_U^{-1}\right)$*. It is easy to check that applying* (7.14) *gives the same result as in* (7.8) *.*

The matrix $\mathbf{\Lambda}(\bar{x},\bar{p})$ as given in equation (7.14) is composed of two parts. The first term is linked to the dependence of the flow rates on the intensive quantities while the second term is linked to the dependence of the flow rates on the extensive quantities. In the first term one may also note the presence of the Hessian of the entropy function $\tilde{S}(x)$. As we have considered the entropy form of Gibbs' relation, this is equivalent to the Hessian of the entropy function $\tilde{S}(x)$, which is a symmetric definite negative matrix, according to the second principle of thermodynamics [19]. Although nothing can be said in the general case about the spectrum of $\mathbf{\Lambda}(\bar{x},\bar{p})$, let us now consider some particular cases of phenomena that result in a dynamical behaviour of the system, namely the conduction, the convection and the chemical reaction.

- Conduction is a phenomenon due to a spatial gradient in the intensive variables of the system. There is no dependence on the extensive variables. Therefore the flow rates due to conduction solely intervene in the first term of the matrix $\mathbf{\Lambda}(\bar{x},\bar{p})$. If the two matrices of the first term are symmetric and if their product commutes, then the eigenvalues of $\mathbf{\Lambda}(\bar{x},\bar{p})$ are strictly negative if $\left.\frac{\partial \mathcal{Q}}{\partial p}\right|_{(\bar{x}_0,\bar{x},\bar{p})}$ has strictly positive eigenvalues [65]. Let us consider the simple case where the conduction flow rate is proportional to the difference of the intensive variable of the system with the environment: $\mathcal{Q}^{conv}(p) = \boldsymbol{L}(p)(p - p_{env})$. $\boldsymbol{L}(p)$ is a symmetric matrix of adequate size and p_{env} refers to the environment. If $\boldsymbol{L}(p)$ has constant coefficients, the matrix $\mathbf{\Lambda}(\bar{x},\bar{p})$ becomes:

$$\mathbf{\Lambda}(\bar{x},\bar{p}) = \boldsymbol{L}\left.\frac{\partial^2 \tilde{S}}{\partial x^2}\right|_{(\bar{x}_0,\bar{x},\bar{p})}$$

  $\boldsymbol{L}$ and $\frac{\partial^2 \tilde{S}}{\partial x^2}$ are symmetric operators and $\frac{\partial^2 \tilde{S}}{\partial x^2}$ is negative definite. If in addition the product of these two matrices commutes, then $\mathbf{\Lambda}(\bar{x},\bar{p})$ has eigenvalues with negative real part if $\boldsymbol{L}$ is positive definite and the equilibrium point is asymptotically stable. This is for example the case when $\boldsymbol{L}$ is diagonal, i.e. a spatial gradient in an intensive variable p_i induces a variation only for its conjugated extensive variable x_i. The heat conduction following Fourier's law is an example where $\boldsymbol{L}$ is diagonal whereas the Soret effect or the Dufour effect (matter flows due to temperature gradients and conversely) imply non-diagonal terms[1] in $\boldsymbol{L}$ [25] .

- The convection is due to a motion of matter. In the case of forced convection, the net flow rate usually depends on the extensive variables. Therefore the flow rates due to convection solely intervene in the second term of the matrix $\mathbf{\Lambda}(\bar{x},\bar{p})$.

- The chemical reaction rate depends as well on the extensive variables as on the intensive quantities. Therefore the chemical reaction intervenes in both terms of the matrix $\mathbf{\Lambda}(\bar{x},\bar{p})$.

[1] Still these effects are most often considered as marginal in practical chemical engineering applications.

The vector of flow rates $\mathcal{Q}$ can be written as a sum of several vectors $\mathcal{Q}^{(j)}$ of the same length and each representing a different phenomenon (e.g. convection, conduction, chemical reaction):

$$\mathcal{Q}(x,p) = \sum_j \mathcal{Q}^{(j)}(x,p)$$

The matrix $\mathbf{\Lambda}(\bar{x},\bar{p})$ can then be written as follows:

$$\begin{aligned}\mathbf{\Lambda}(\bar{x},\bar{p}) &= \sum_j \left[\left.\frac{\partial \mathcal{Q}^{(j)}}{\partial p}\right|_{(\bar{x}_0,\bar{x},\bar{p})} \left.\frac{\partial^2 \tilde{S}}{\partial x^2}\right|_{(\bar{x}_0,\bar{x},\bar{p})} + \left.\frac{\partial \mathcal{Q}^{(j)}}{\partial x}\right|_{(\bar{x}_0,\bar{x},\bar{p})} \right] \\ &= \sum_j \mathbf{\Lambda}^{(j)}(\bar{x},\bar{p})\end{aligned}$$

with a matrix $\mathbf{\Lambda}^{(j)}(\bar{x},\bar{p})$ for each vector $\mathcal{Q}^{(j)}$. It is therefore possible to analyze each phenomenon that generates a flow rate and to determine how it contributes to the stability of the system equilibrium.

7.3 Conclusion

The dynamical behaviour of thermodynamic systems can be modelled using the contact structure formalism. More precisely it may be expressed in terms of contact geometry as a contact vector field which leaves invariant a particular Legendre submanifold, representing the thermodynamic properties of the system, and generated by a contact Hamiltonian function representing the phenomena giving rise to the dynamics. From its very beginning, this geometric theory is also strongly related to the thermodynamic principles. The aim of this chapter was to express the properties of the dynamical behaviour of the system in terms of the elements of the contact structure formalism.

In a first instance, we have discussed the definition of the contact Hamiltonian functions and we have given a family of equivalent contact Hamiltonian functions in the sense that they generate vector fields whose restriction on the Legendre submanifold are identical. In terms of physical modelling they are undistinguishable. In a second instance, we have studied the equilibrium points of the system in terms of the contact Hamiltonian function. Furthermore we

have shown that for a particular class of contact Hamiltonian functions corresponding to the most common modelling assumptions, these points are their critical points. Using then Lyapunov's first stability theorem, we have established a criterion for the asymptotic stability of the equilibrium points. This criterion depends on the thermodynamic model of the system and the contact Hamiltonian function. Finally we have related this stability criterion to the underlying physical phenomena and in particular to the concavity of the entropy function. The stability criterion that we have established can be used to determine wether a flow of some extensive quantity entering or leaving the system tends to stabilize or to destabilize an equilibrium. Indeed we have written this stability criterion in terms of the derivative of the flows with respect to the intensive and extensive quantities. The sign of the eigenvalues of these matrices indicates the influence of the considered flow on the stability.

In this chapter we did not consider controlled systems in the sense that the external variables defining the thermodynamic state of the environment of the system have been taken to be constant. However one may also consider controlled contact systems by expressing the contact Hamiltonian function as functions of some external time-varying variable [27][31][32][35]. Such systems encompass port-Hamiltonian systems, hence one may hope to extend the interconnection and damping assignment passivity-based control (IDA-PBC) methods [82][83] to controlled contact systems. A possible option might be to use this property for the stabilization of unstable equilibrium points by shaping the flow rates of the extensive quantities in order to compensate the fluxes that tend to destabilize the desired equilibrium point.

Chapter 8

Alternative formal approaches of the thermodynamics

In the previous chapters of this thesis, we have proposed a formulation of the dynamical behaviour of complex open physical systems using its contact structure derived from the Gibbs' relation. The dynamical system is defined in terms of a contact vector field which is obtained by lifting the balance equations on the extensive variables on the thermodynamic phase space. The aim of this chapter is to discuss the use of contact structures for the description of thermodynamic systems with respect to two formalisms used for describing coupled sets of reversible and irreversible processes, namely the GENERIC (General Equation for the Non-Equilibrium Reversible-Irreversible Coupling) formulation and the Matrix formulation. The results are illustrated on the elementary example of a coupled mechanical and thermodynamic system.

The GENERIC formalism was first developed by Grmela and Öttinger with the aim to model the hydrodynamics of complex fluids like polymers and to embed systems with both reversible and irreversible phenomena in a single framework [46][47][85]. It has been first developed for isolated thermodynamic

systems, but Muschik and Jongschaap have proposed two different approaches to extend it to open systems [61][76]. The Matrix Model was developed by Jongschaap to describe the thermodynamics of complex fluids [33][60][61]. In the Matrix formalism, there is a clear distinction between two kinds of variables: on one side the internal variables characterizing the state of the subsystems, and on the other side the external variables referring to the environment of the subsystems. The GENERIC formalism expresses the dynamics as a sum of a gradient system and of a Hamiltonian system whereas the Matrix formalism expresses the dynamics as a semi-linear mapping between thermodynamic forces and flows. Like in the representation of the dynamics of port-Hamiltonian systems, in these two formalisms a symmetric and a skew-symmetric matrix are used to represent the reversible and the irreversible phenomena, respectively..

As already mentioned, in this chapter we shall analyze two formalisms for the description of thermodynamic systems, namely the GENERIC formalism (Section 8.1) and the Matrix formalism (Section 8.2). In both sections, we shall first briefly present the considered formalism, and then we shall show how these formulations can be included in the contact formalism. We shall recall the definition and the interpretation of the matrices that aim at representing the reversible and irreversible phenomena. Section 8.3 illustrates the contact formalism in comparison with the GENERIC and Matrix ones by considering the simple example of a gas-piston system also treated in [61]. Finally we shall critically discuss the two alternative formalisms with respect to the contact formalism for the representation of thermodynamic systems (Section 8.4).

8.1 The GENERIC formalism

The GENERIC formalism (General Equation for the Non-Equilibrium Reversible-Irreversible Coupling) consists in the sum of a Hamiltonian and of a dissipative dynamical system, generated by two different generating functions, namely the entropy and the energy [46][47][49]. In this section we shall recall the definition of the GENERIC formalism for isolated systems defined on the extensive variables and subject to conservation laws. Then we shall show how to extend it to open systems in Section 8.1.2.

8.1.1 Representation of isolated systems

In the GENERIC formalism, the time evolution of the d_F independent variables required for the description of the system, denoted by $Z \in \mathbb{R}^{d_F}$, is expressed as the sum of a Hamiltonian system and a dissipative system. The Hamiltonian system [69] is defined with respect to a Poisson bracket (with structure matrix denoted by $\boldsymbol{L}(Z)$) and generated by the total energy $E^{tot}(Z)$ of the system as the Hamiltonian function. The dissipative system is defined with respect to the Riemannian metric with the positive symmetric structure matrix $\boldsymbol{M}(Z)$ and generated by the total entropy, denoted by $S^{tot}(Z)$, as the potential function. These two contributions are the reversible and the irreversible contributions, respectively.

Definition 8.1. A GENERIC system on the vector space $\mathbb{R}^{d_F} \ni Z$ is defined by a Poisson bracket denoted by $\{\,,\,\}$ with structure matrix $\boldsymbol{L}(Z)$ and a pseudo-Riemannian metric denoted by $[\,,\,]$, with semi-definite positive structure matrix $\boldsymbol{M}(Z)$. The GENERIC system is generated by two functions $E^{tot}(Z)$ and $S^{tot}(Z)$ fulfilling the following conditions:

$$\forall g(Z) \in \mathcal{C}^\infty\left(\mathbb{R}^{d_F}\right): \quad \left[g(Z),\, E^{tot}(Z)\right] = 0, \quad \text{i.e.} \quad \boldsymbol{M}(Z)\,\frac{\partial E^{tot}}{\partial Z} = 0 \tag{8.1a}$$

$$\forall g(Z) \in \mathcal{C}^\infty\left(\mathbb{R}^{d_F}\right): \quad \left\{g(Z),\, S^{tot}(Z)\right\} = 0, \quad \text{i.e.} \quad \boldsymbol{L}(Z)\,\frac{\partial S^{tot}}{\partial Z} = 0 \tag{8.1b}$$

The system dynamics are then given by the following differential equation:

$$\frac{dZ}{dt} = \{Z,\, E_{tot}\} + [Z,\, S_{tot}]\,, \text{ i.e. } \frac{dZ}{dt} = \boldsymbol{L}(Z)\,\frac{\partial E^{tot}}{\partial Z} + \boldsymbol{M}(Z)\,\frac{\partial S^{tot}}{\partial Z} \tag{8.2}$$

Remark 8.1. *The bracket $[\,,\,]$ is called the Ginzburg-Landau dissipative bracket [46]. The Ginzburg-Landau dissipative bracket is symmetric (i.e. for all $A, B \in \mathcal{C}^\infty(Z)$, $[A(Z), B(Z)] = [B(Z), A(Z)]$) and satisfies the positivity condition $[A(Z), A(Z)] \geq 0$ for all $A \in \mathcal{C}^\infty\left(\mathbb{R}^{d_F}\right)$.*

This definition is physically justified in models where the generating function is chosen to be the total entropy function $S^{tot}(Z)$ and the total energy function $E^{tot}(Z)$ of some complex thermodynamic system [46][47][48][49]. Condition (8.1a) implies that the energy function is a Casimir function of the

(Ginzburg-Landau) dissipative bracket. As a consequence, using also the skew-symmetry of the Poisson bracket, the total energy is conserved:

$$\frac{dE^{tot}}{dt} = \left\{E^{tot},\, E^{tot}\right\} + \left[E^{tot},\, S^{tot}\right] = 0$$

Condition (8.1b) implies that the entropy function is a Casimir function of the Poisson bracket. Hence, using the positivity of the pseudo-Riemannian metric, the entropy balance equation becomes as follows:

$$\frac{dS^{tot}}{dt} = \left\{S^{tot},\, E^{tot}\right\} + \left[S^{tot},\, S^{tot}\right] = \left[S^{tot},\, S^{tot}\right] \geq 0$$

Therefore by using two different generating functions satisfying the conditions (8.1a) and (8.1b), one may express simultaneously the energy conservation and the irreversible entropy production.

Remark 8.2. *It could seem that the two potentials are chosen independently. However when considering quasi-static processes for the subsystems (as it is the case in this work, see Assumption 1.1) they both are the sum of entropy and energy functions characterizing the thermodynamic equilibrium states of the subsystems. Therefore they are linked by the fundamental relation* (1.2) *of each of the subsystems.*

Remark 8.3. *The Hamiltonian part of dynamics (i.e. the Poisson bracket) in* (8.2) *refers to reversible phenomena, whereas the dissipative part (i.e. the dissipative bracket) refers to irreversible phenomena. This can be seen in the expression for the entropy production since the Poisson bracket does not appear in it:*

$$\sigma_S = \frac{dS^{tot}}{dt} = \frac{\partial^t S^{tot}}{\partial Z}\boldsymbol{M}\left(Z\right)\frac{\partial S^{tot}}{\partial Z}$$

Defining the thermodynamic forces by $Y_k = \dfrac{\partial S^{tot}}{\partial Z_k}$ with $k = 1, 2, ..., d_F$ and defining the flux variable J_k by the law of fluxes as $J_k = \displaystyle\sum_{l=1}^{d_F} M_{kl}(Z)\frac{\partial S^{tot}}{\partial Z_l}$, the entropy production σ_S can be written as a bilinear product of the thermody-

namic forces and the conjugated fluxes [25][1]:

$$\sigma_S = \sum_{k=1}^{d_F} J_k Y_k = Y^t J$$

If the selected pairs (Y_k, J_k) are such that they follow the Onsager reciprocal relations, then the matrix $\boldsymbol{M}(Z)$ is a matrix in which the entries are equal to the parameters appearing in the phenomenological laws.

Remark 8.4. *It is also interesting to note that the system* (8.2) *with the conditions* (8.1a) *and* (8.1b) *may also be expressed as a dissipative Hamiltonian system [79] with a bracket that is the sum of the Poisson and Riemannian brackets as follows:*

$$\langle g_1, g_2 \rangle = \{g_1, g_2\} + [g_1, g_2]$$

The dynamics (8.2) *can then be expressed by the following relation:*

$$\frac{dZ}{dt} = \langle Z, E_{tot} + S_{tot} \rangle$$

8.1.2 Extension to open systems

In order to apply the GENERIC formulation to open systems, two approaches can be found in the literature [61][76]. The first approach consists in extending the open system to a combined system composed of the open system and the environment endowed with some thermodynamic properties. In this case the total system is the universe, which is isolated by definition. Usually the thermodynamic model of the environment is very simple as for instance a thermostat for which the entropy function is linear in the internal energy [31]. The second approach, developed in [61], represents open systems in an intrinsic way by introducing interface or external variables representing the fluxes and intensive variables at the boundary of the open system and is better suited for the composition of subsystems into complex systems. This approach is similar to approaches for controlling open physical systems in the sense that it uses pairs of conjugated variables to describe the interaction of the open system with its

[1] see also (3.13)

environment as they appear for dissipative control systems [18][96][104], input-output Hamiltonian systems [17][95] and port-Hamiltonian systems [97][98]. In the GENERIC formalism, two pairs of conjugated external variables are defined. First we shall define a pair of variables $(\dot{X}_{ham},\, F_{ham}) \in \mathbb{R}^{m_1} \times \mathbb{R}^{m_1}$, associated with the formulation of an open Hamiltonian system, actually a port-Hamiltonian system with port variables $(\dot{X}_{ham},\, F_{ham})$ and secondly a pair of variables $(\dot{X}_{diss},\, F_{diss}) \in \mathbb{R}^{m_2} \times \mathbb{R}^{m_2}$, associated with an open dissipative system. The GENERIC representation of open systems is then defined as the sum of a port-Hamiltonian [97] and a dissipative system [22] as follows.

Definition 8.2. An *open GENERIC system* on the vector space $\mathbb{R}^{d_F}$ of extensive variables with the two pairs of external variables, denoted by $(\dot{X}_{ham},\, F_{ham}) \in \mathbb{R}^{m_1} \times \mathbb{R}^{m_1}$ and $(\dot{X}_{diss},\, F_{diss}) \in \mathbb{R}^{m_2} \times \mathbb{R}^{m_2}$ is defined by a skew-symmetric tensor with the following structure matrix:

$$\tilde{\boldsymbol{L}}\,(Z) = \begin{pmatrix} 0 & 0 & \boldsymbol{\Gamma}(Z) \\ 0 & 0 & 0 \\ -\boldsymbol{\Gamma}^t(Z) & 0 & \boldsymbol{L}\,(Z) \end{pmatrix}$$

and a symmetric tensor with the following positive structure matrix:

$$\tilde{\boldsymbol{M}}(Z) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \boldsymbol{\Pi}(Z) \\ 0 & \boldsymbol{\Pi}^t(Z) & \boldsymbol{M}\,(Z) \end{pmatrix}$$

with $\boldsymbol{\Gamma}(Z) \in \mathbb{R}^{m_1} \times \mathbb{R}^{d_F}$ and $\boldsymbol{\Pi}(Z) \in \mathbb{R}^{m_2} \times \mathbb{R}^{d_F}$. The dynamics is generated by two functions $E^{tot}\,(Z)$ and $S^{tot}\,(Z)$ satisfying the conditions (8.1a) and (8.1b) and the system of algebro-differential equations:

$$\begin{pmatrix} -\dot{X}_{ham} \\ \dot{X}_{diss} \\ \frac{dZ}{dt} \end{pmatrix} = \tilde{\boldsymbol{L}}\,(Z) \begin{pmatrix} F_{ham} \\ 0 \\ \frac{\partial E^{tot}}{\partial Z} \end{pmatrix} + \tilde{\boldsymbol{M}}(Z) \begin{pmatrix} 0 \\ F_{diss} \\ \frac{\partial S^{tot}}{\partial Z} \end{pmatrix} \tag{8.3}$$

Remark 8.5. *Let us note that both extended skew-symmetric and symmetric tensors have a row of zeros that decouples the terms in the balance equations due to the symmetric and skew-symmetric parts.*

Let us now consider the balance equations of the total energy and the total entropy. The energy balance equation is obtained by computing the product $\frac{\partial^t E^{tot}}{\partial Z}\frac{dZ}{dt}$:

$$\frac{dE^{tot}}{dt} = F_{ham}^t \dot{X}_{ham} + \frac{\partial^t E^{tot}}{\partial Z}\mathbf{\Pi}\left(Z\right) F_{diss}$$

The two terms on the right hand side may be interpreted as the power entering the system through its boundaries, the first one being the supply rate of the port-Hamiltonian system and the second one energy flow due to the coupling with the dissipative system. The pair of external variables ($\dot{X}_{ham}$, F_{ham}) is conjugated with respect to the power (rate of energy) as their product has the dimension of power (it is a term of the energy balance equation). The entropy balance equation is obtained by computing the product $\frac{\partial^t S^{tot}}{\partial Z}\frac{dZ}{dt}$:

$$\frac{dS^{tot}}{dt} = \frac{\partial^t S^{tot}}{\partial Z}\boldsymbol{M}\left(Z\right)\frac{\partial S^{tot}}{\partial Z} + \dot{X}_{diss}^t F_{diss} - \frac{\partial^t S^{tot}}{\partial Z}\mathbf{\Gamma}^t\left(Z\right) F_{ham}$$

This is the entropy balance for isolated systems augmented with two terms. These two terms may be interpreted as the flow of entropy entering the system through its boundaries, the first one being the supply rate of the dissipative system with respect to the entropy storage function and the second one being the entropy flow due to the coupling with the port-Hamiltonian system. The pair of external variables ($\dot{X}_{diss}$, F_{diss}) is conjugated with respect to entropy flow (rate of entropy) as their product is a term of the entropy balance equation.

Remark 8.6. *The extension of Remark 8.3 to the case of open systems implies that* $(F_{ham}, \dot{X}_{ham})$ *refers to reversible exchanges with the environment, whereas* $(F_{diss}, \dot{X}_{diss})$ *refers to irreversible exchanges with the environment. As a consequence the matrix* $\tilde{\boldsymbol{L}}$ *fulfills* (8.1b)*, i.e. the following condition should be fulfilled:*

$$\mathbf{\Gamma}\left(Z\right)\frac{\partial S^{tot}}{\partial Z} = 0$$

The entropy balance can finally be written as follows:

$$\frac{dS^{tot}}{dt} = \frac{\partial^t S^{tot}}{\partial Z}\boldsymbol{M}\left(Z\right)\frac{\partial S^{tot}}{\partial Z} + \dot{X}_{diss}^t F_{diss}$$

Yet $\tilde{\boldsymbol{M}}$ *does not fulfill* (8.1a)*. Indeed irreversible phenomena may result in an energy flow and consequently* $\frac{\partial^t E^{tot}}{\partial Z}\mathbf{\Pi}\left(Z\right) F_{diss} \neq 0$.

Example 8.1. *Consider the example of a simple closed and isochore thermodynamic system exchanging heat with the environment through a heat conduction wall which has already been considered in Example 6.4. Let us choose the independent extensive variables $Z = U \in \mathbb{R}$. Then the total entropy function is simply the entropy function $\tilde{S}(U)$ defining the thermodynamical model $S^{tot}(Z) = \tilde{S}(U)$ and the total energy function is $E^{tot}(Z) = U$. The process is quasi-static and according to the Gibbs' relation, the gradient of the total entropy is given by the following relation:*

$$\frac{\partial S^{tot}}{\partial Z} = \frac{\partial \tilde{S}}{\partial U} = \frac{1}{T}$$

where T is the temperature of the system. It is also obvious that $\frac{\partial E^{tot}}{\partial Z} = 1$.

There is no reversible exchange with the environment, so that there is no need to keep the corresponding external variables. Let us define the external force variables $(F_{diss}, \dot{X}_{diss})$ by choosing for instance the external force variable for the dissipative system as $F_{diss} = (T_{env} - T)$, i.e. the temperature difference between the system and its environment. It is straightforward to check that the GENERIC representation of the isolated system is obtained by choosing $\boldsymbol{L} = 0$ and $\boldsymbol{M} = 0$. As a consequence, the GENERIC representation of the open system is written as follows:

$$\begin{pmatrix} \dot{X}_{grad} \\ \frac{dU}{dt} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ \frac{\partial E^{tot}}{\partial U} \end{pmatrix} + \begin{pmatrix} 0 & \boldsymbol{\Pi}(U) \\ \boldsymbol{\Pi}^t(U) & 0 \end{pmatrix} \begin{pmatrix} T_{env} - T \\ \frac{1}{T} \end{pmatrix}$$

where $\boldsymbol{\Pi} \in \mathbb{R}$. The value of $\boldsymbol{\Pi}$ is obtained by considering the internal energy balance equation of the open system and by equating it to the dynamics given in the above relation:

$$\frac{dU}{dt} = \dot{Q} = \kappa(T_{env} - T) = \boldsymbol{\Pi}^t(U)(T_{env} - T)$$

It is straightforward that $\boldsymbol{\Pi}(U) = \kappa$. This implies that the conjugated flow variable to F_{diss} is $\dot{X}_{diss} = \frac{\boldsymbol{\Pi}(U)}{T} = \frac{\kappa}{T}$. One may check that the product $F_{diss}\dot{X}_{diss} = \frac{\kappa(T_{env}-T)}{T}$ has the dimensions of an entropy flow. In this case this product is also equal to the total entropy variation which is equal to $\frac{\dot{Q}}{T}$, as it should be for a heat exchange.

8.1.3 Contact formulation of the GENERIC model

Actually one may formulate the conservative contact system associated with the GENERIC system by a lift on the complete thermodynamic phase space $\mathbb{R}^{2d_F+1} \ni (x_0,\, Z,\, p_Z)$ using a procedure which is very similar to the lift of dissipative Hamiltonian and port-Hamiltonian systems, recalled in Section 6.3 for systems of conservation laws. Indeed the contact formulation has already been suggested in [46][48][49] for dissipative Hamiltonian and GENERIC models of closed systems. More precisely, using the definition of contact vector fields, it is easy to check that the lift of the GENERIC system of Definition 8.1 is a conservative contact system with Legendre submanifold generated by the total entropy function S^{tot} and the following contact Hamiltonian function:

$$f_0\,(Z,\, p_Z) = -p_Z^t\, \boldsymbol{L}(Z)\, \frac{\partial E^{tot}}{\partial Z}(Z) - \left(p_Z - \frac{\partial S^{tot}}{\partial Z}(Z)\right)^t\, \boldsymbol{M}(Z)\, \frac{\partial S^{tot}}{\partial Z}(Z) \quad (8.4)$$

Now consider the differential equation of an open GENERIC system (8.3). Its lift to the thermodynamic phase space is again easily seen to be a control contact system with Legendre submanifold generated by the total entropy function $S^{tot}(Z)$ and the contact Hamiltonian, sum of the internal contact Hamiltonian function (8.4) and an interaction contact Hamiltonian function f_{int}:

$$f_{int}\,(Z,\, p_Z,\, F_{ham},\, F_{diss}) = -\left(p_Z - \frac{\partial S^{tot}}{\partial Z}\right)^t\, \left(-\boldsymbol{\Gamma}^t\,(Z)\; F_{ham} + \boldsymbol{\Pi}^t\,(Z)\; F_{diss}\right) \quad (8.5)$$

Finally it should be noted that in this framework, there is no obvious choice of flow variables conjugated to the force variables F_{ham} and F_{diss}. In the case of control contact systems with contact Hamiltonian function affine in the input variables, conjugated port variables have been defined [31][32].

8.2 The Matrix formalism

As already mentioned, the Matrix model has been developed to describe the thermodynamics of complex fluids [33][60][61]. Contrary to the GENERIC formalism, the Matrix model has been developed for driven systems, i.e. systems which interact with their environment. Hence in the Matrix formalism, there

is a clear distinction between two kinds of variables: on one hand the internal variables characterizing the state of the subsystems, and on the other hand the external variables referring to the environment of the subsystems.

8.2.1 Definition

The states of the subsystems are characterized by a set of extensive internal variables and a fundamental equation such that the rate of change of the energy due to the changes of non-thermal extensive state variable X is given by the following equation:

$$\mathcal{P}_{int} = F_{th}^t \frac{dX}{dt}$$

where $F_{th} = \frac{\partial \tilde{U}}{\partial X}$ is the set of conjugated thermodynamic forces and $U = \tilde{U}(S, X)$ is the fundamental equation.

Besides the action of the environment the subsystems is characterized by some controllable external forces F_e and some external rate variables $\dot{X}_e$ such that the mechanical power supplied to the system is given by the following relation:

$$\mathcal{P}_{ext} = F_e^t \dot{X}_e$$

As a consequence the time variation of the internal energy is given in terms of the internal variables and in terms of the external variables by these two following equations:

$$\frac{dU}{dt} = F_{th}^t \frac{dX}{dt} + T\frac{dS}{dt} \tag{8.6a}$$

$$\frac{dU}{dt} = F_e^t \dot{X}_e + \dot{Q} \tag{8.6b}$$

where $\dot{Q}$ is the heat provided to the system. Using the Principle of Macroscopic Time Reversal [60], the dynamics can finally be expressed as the sum of a non-dissipative and a dissipative coupling as follows:

$$\begin{pmatrix} F_e \\ \frac{dX}{dt} \end{pmatrix} = \begin{pmatrix} 0 & -\boldsymbol{\Upsilon}^t \\ \boldsymbol{\Upsilon} & 0 \end{pmatrix} \begin{pmatrix} \dot{X}_e \\ -F_{th} \end{pmatrix} + \begin{pmatrix} \boldsymbol{\eta} & 0 \\ 0 & \boldsymbol{\beta} \end{pmatrix} \begin{pmatrix} \dot{X}_e \\ -F_{th} \end{pmatrix} \tag{8.7}$$

where $\boldsymbol{\Upsilon}$ is skew-symmetric matrix linked to the reversible phenomena and $\boldsymbol{\beta}$ and $\boldsymbol{\eta}$ are positive matrices linked to the irreversible phenomena. It is worth

noting that the skew-symmetry of the part due to the reversible phenomena is due to the Principle of Macroscopic Time Reversal and is the counterpart of condition (8.1b) of the GENERIC formalism. This matrix is not associated to the operator $\boldsymbol{L}$ of the GENERIC formalism, whose skew-symmetry was inherited from the Poisson structure of classical mechanics.

The dissipation Δ_{diss} is obviously the difference between the mechanical power supplied by the environment and the internal rate of energy (without considering the rate of change of the thermal state variables), i.e.:

$$\Delta_{diss} = F_e^t \dot{X}_e - F_{th}^t \frac{dX}{dt} = \left(\dot{X}_e\right)^t \boldsymbol{\eta} \dot{X}_e + F_{th}^t \boldsymbol{\beta} F_{th} \tag{8.8}$$

8.2.2 Contact formulation of the Matrix model

The contact formulation of the Matrix system (8.7) may be obtained by lifting the system on the extended space $\mathbb{R}^{2(d_F-1)+1} \approx \mathbb{R} \times \mathrm{T}\mathbb{R}^{(d_F-1)}$ of dimension $2d_F - 1$. However this space would not be the real thermodynamic space associated with Gibbs' equation (8.6a) which includes the entropy and energy variables. We shall define the thermodynamic phase space $\mathbb{R}^{2d_F+1} \ni (x_0, x, p)^t$ with the following identification:

$$\left\{ \begin{array}{rcc} x_0 & = & S \\ x & = & [U, X]^t \\ p & = & [p_U, p_X]^t \end{array} \right. \tag{8.9}$$

The thermodynamic properties of the system are defined by the generating function given by the fundamental relation (1.2) expressed in the entropy form. On the Legendre submanifold $\mathscr{L}$, generated by $\tilde{S}(U, X)$, one has the following relations: $p_U|_{\mathscr{L}} = \frac{\partial \tilde{S}}{\partial U} = \frac{1}{T}$ and $p_X|_{\mathscr{L}} = \frac{\partial \tilde{S}}{\partial X} = -\frac{F_{th}}{T}$. Applying Proposition 6.2 to the balance equations (8.6b) and (8.7) allows to define the following internal contact Hamiltonian function:

$$f_0 = -\left(\frac{\partial \tilde{S}}{\partial X} - p_X\right)^t \boldsymbol{\beta} F_{th}$$

and the following control Hamiltonian function:

$$\begin{aligned} f_{int} &= \left(\frac{\partial \tilde{S}}{\partial X} - p_X\right)^t \boldsymbol{\Upsilon} \dot{X}_e + \left(\frac{\partial \tilde{S}}{\partial U} - p_U\right) \left[\left(\dot{X}_e\right)^t \boldsymbol{\eta} \dot{X}_e + \dot{Q} + F_{th} \boldsymbol{\Upsilon} \dot{X}_e\right] \\ &= -\left(p_X + p_U F_{th}\right)^t \boldsymbol{\Upsilon} \dot{X}_e + \left(\frac{\partial \tilde{S}}{\partial U} - p_U\right) \left[\left(\dot{X}_e\right)^t \boldsymbol{\eta} \dot{X}_e + \dot{Q}\right] \end{aligned}$$

It should be noted again that the contact Hamiltonian functions are tensor products, defined by the matrix $\boldsymbol{\beta}$ for the internal contact Hamiltonian function and by the matrix $\boldsymbol{\Upsilon}$ for the control contact Hamiltonian function, both with the dimension of an entropy flow. The term containing $\boldsymbol{\Upsilon}$ is linear in the intensive variables and cancels out when calculating the entropy production using the expression of the x_0-component of the contact vector field (6.8).

$$\begin{aligned} \frac{dS}{dt} = \left.\frac{dx_0}{dt}\right|_{\mathscr{L}} &= -p_U \left.\frac{\partial\left(f_0 + f_{int}\right)}{\partial p_U}\right|_{\mathscr{L}} - p_X \left.\frac{\partial\left(f_0 + f_{int}\right)}{\partial p_X}\right|_{\mathscr{L}} \\ &= \frac{1}{T}\left[\left(\dot{X}_e\right)^t \boldsymbol{\eta}^t \dot{X}_e + \dot{Q} + F_{th}^t \boldsymbol{\beta} F_{th}\right] \end{aligned}$$

As expected, the entropy variation is due to the dissipative effects (via the terms containing $\boldsymbol{\beta}$ and $\boldsymbol{\eta}$) and to the heat exchange. By comparison with (8.8), the dissipation Δ_{diss} represents the entropy variation that is not due to heat transfer.

8.3 Case study : the adiabatic piston

In this section, we shall illustrate the contact formalism by considering the example of a gas in a cylinder under a piston, an example which has been used in order to illustrate the GENERIC and Matrix formalism and to emphasize some relations with dissipative port-Hamiltonian systems in [54]. The chosen example is a gas in an adiabatic isolated cylinder closed by a piston (Figure 8.1). When the piston moves, friction effects cause the transformation of mechanical energy into heat. The system cannot exchange heat with the environment, but a heat transfer between the gas and the piston can take place.

The piston is considered as a solid and its volume is considered to be constant. Furthermore its mass is constant as it is subject to no mass exchange.

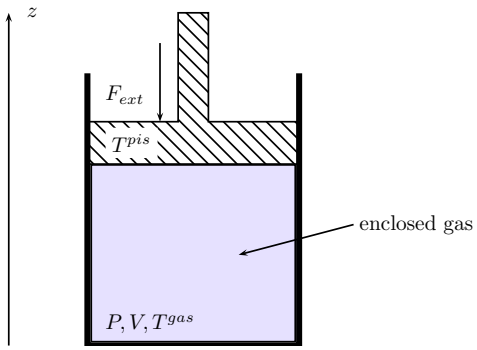


Figure 8.1: Case study: the adiabatic piston

Finally we assume that the temperature distribution in the piston is uniform. Hence it will be described as a simple thermodynamic system in motion, closed and undergoing isochore transformations. The displacements of the piston are assumed to be small enough so that the center of mass of the gas does not undergo significant motion. We shall also consider the additional assumption that there is no mass exchange with the environment.

As a consequence of the above assumptions, the state of the system can be described by $d_F = 5$ variables (2 degrees of freedom for the gas, 3 degrees of freedom for the piston). For instance, the following set of variables can define the state of the system:

- for the piston: the internal energy U^{pis}, the momentum q and the position z
- for the gas: the internal energy U^{gas} and the volume V

Remark 8.7. *For the sake of clarity in the notations, the superscripts "gas" and "pis" are not used when it is obvious to which system the quantity applies. For example we are not considering the motion of the center of mass of the gas, and thus the only momentum we have to consider is the one of the piston. Consequently we shall use the notation q instead of q^{gas}.*

8.3.1 Contact formulation

Description of the gas

For the sake of simplicity we can consider only the vector of extensive variables $x^{gas} = (U^{gas}, V)^t$ with the internal energy U^{gas} and its volume V. We note $(x_0^{gas}, x^{gas}, p^{gas})^t$ the state of the piston in the thermodynamic phase space $\mathbb{R}^5$ with intensive variable of the gas $p^{gas} = (p_U^{gas}, p_V^{gas})^t$. Then the thermodynamic properties of the system are described as the Legendre submanifold generated by the entropy function of the gas: $\tilde{S}^{gas}(U^{gas}, V)$.

The internal energy balance equation is composed of two terms, the heat flow coming from the piston and the mechanical power due to the displacement of the piston:

$$\frac{dU^{gas}}{dt} = \dot{Q}_{p\to g} - Av_{wall}P \tag{8.10a}$$

where v_{wall} denotes the displacement of the surface in contact with the piston and A its area. $P = \frac{\partial \tilde{S}^{gas}}{\partial V}(U^{gas}, V)$ is the gas pressure the gas.

The "balance" equation on the volume is equal to:

$$\frac{dV}{dt} = Av_{wall} \tag{8.10b}$$

The lift of these balance equations on the whole thermodynamic phase space is then again given in accordance with Section 6.3 (see Proposition 6.2) as the control contact system generated by the following contact Hamiltonian function:

$$\begin{aligned} &f^{gas}(x,p) \\ &= \left(\frac{\partial \tilde{S}^{gas}}{\partial V} - p_V^{gas}\right)(Av_{wall}) + \left(\frac{\partial \tilde{S}^{gas}}{\partial U^{gas}} - p_U^{gas}\right)\left(\dot{Q}_{p\to g} - v_{wall}AP\right) \end{aligned} \tag{8.11}$$

where the interconnection variables $\dot{Q}_{p\to g}\left(x^{gas}, p^{gas}, x^{pis}, p^{pis}\right)$ and the displacement of the wall $v_{wall}\left(x^{gas}, p^{gas}, x^{pis}, p^{pis}\right)$ depend on (x^{gas}, p^{gas}) and on the state of the piston $\left(x^{pis}, p^{pis}\right)$.

Description of the piston

The contact formulation of thermodynamic systems has been derived based on the Gibbs' equation. This relation has been explained in Chapter 1 for

systems at rest. But the piston is in motion. Consequently if applying directly the formalism as it has been presented in Chapter 6, the resulting contact Hamiltonian function and hence the related vector field would not model the motion of the piston.

Nevertheless this apparent issue can easily be solved by adapting the Gibbs' relation to include the variables representing the motion. The Gibbs' relation is still valid for the piston, i.e.:

$$\mathrm{d}S^{pis} = \frac{1}{T^{pis}}\mathrm{d}U^{pis} \tag{8.12}$$

since for the piston $\mathrm{d}V^{pis} = 0$ and $\mathrm{d}n^{pis} = 0$. Besides the total energy E^{pis} of the piston is given by the sum of the internal energy U^{pis}, the kinetic energy E^{kin} and the potential energy E^{pot} as follows:

$$E^{pis} = U^{pis} + E^{kin} + E^{pot}$$

The kinetic energy depends on the kinetic momentum q of the piston as follows:

$$E^{kin} = \tilde{E}^{kin}(q) = \frac{q^2}{2m}$$

where m is the mass of the piston. The potential energy is due to the gravity and is a function of the position z of the piston:

$$E^{pot} = \tilde{E}^{pot}(z) = mgz$$

By computing the derivatives of the functions $\tilde{E}^{kin}(q)$ and $\tilde{E}^{pot}(z)$ with respect to their argument, the following relations are obtained:

$$\frac{d\tilde{E}^{kin}}{dq} = \frac{q}{m} = v \quad \text{and} \quad \frac{d\tilde{E}^{pot}}{dz} = -F_{pot}$$

where v is the velocity of the piston and $F_{pot} = -mg$ is the potential force. As a consequence the total energy of the piston is given by the following expression:

$$\tilde{E}^{pis}\left(U^{pis}, q, z\right) = U^{pis} + \tilde{E}^{kin}(q) + \tilde{E}^{pot}(z)$$

which can be differentiated as follows:

$$\mathrm{d}E^{pis} = \mathrm{d}U^{pis} + v\mathrm{d}q - F_{pot}\mathrm{d}z$$

By inserting (8.12) into this relation, we finally obtain an extended form of the Gibbs' relation:

$$\mathrm{d}S^{pis} = \frac{1}{T}\mathrm{d}E^{pis} - \frac{v}{T}\mathrm{d}q + \frac{F_{pot}}{T}\mathrm{d}z \tag{8.13}$$

Following Chapter 1 the fundamental relation of the piston is given by its entropy function $\tilde{S}_0^{pis}\left(U^{pis}\right)$. As a consequence we can rewrite this fundamental relation as follows:

$$\tilde{S}\left(E^{pis}, q, z\right) = \tilde{S}_0^{pis}\left(E^{pis} - \frac{q^2}{m} - mgz\right) \tag{8.14}$$

It can be easily checked that the following relations are fulfilled:

$$\frac{\partial \tilde{S}}{\partial E^{pis}} = \frac{1}{T}, \qquad \frac{\partial \tilde{S}}{\partial q} = -\frac{v}{T}, \qquad \frac{\partial \tilde{S}}{\partial z} = \frac{F_{pot}}{T}$$

The contact formalism can now be applied directly by using (8.13) as the 1-form for endowing the thermodynamic phase space with a contact structure and (8.14) as the generating function of the Legendre manifold $\mathscr{L}^{pis}$. In the case of the piston the thermodynamic phase space can be taken as $\mathbb{R}^7$ with the local coordinates $\left(x_0^{pis}, x^{pis}, p^{pis}\right)$. The correspondence relations on the Legendre submanifold are given as follows:

$$\left\{\begin{array}{lcll} x_0^{pis} & & \overset{\mathscr{L}^{pis}}{=} & S^{pis} \\ x^{pis} & = & \left[x_E^{pis}, x_q^{pis}, x_z^{pis}\right]^t & \overset{\mathscr{L}^{pis}}{=} \quad \left[E^{pis}, q, z\right]^t \\ p^{pis} & = & \left[p_E^{pis}, p_q^{pis}, p_z^{pis}\right]^t & \overset{\mathscr{L}^{pis}}{=} \quad \left[\frac{1}{T^{pis}}, -\frac{v}{T^{pis}}, \frac{F_{pot}}{T^{pis}}\right]^t \end{array}\right.$$

The time variation of E^{pis}, q and z can be found from the total energy balance and the Newton equation as follows:

$$\frac{dE^{pis}}{dt} = \dot{Q}_{g\to p} + \left(F_{gas} - F_{ext}\right) v \tag{8.15a}$$

$$\begin{aligned} \frac{dq}{dt} &= F_{gas} - F_{ext} - F_{fric} - F_{pot} \\ &= F_{gas} - F_{ext} - F_{pot} - \alpha v \end{aligned} \tag{8.15b}$$

$$\frac{dz}{dt} = v \tag{8.15c}$$

where $\dot{Q}_{g\to p}$ is the heat transfer rate from the gas to the piston, F_{gas} is the force exerted by the gas on the piston, F_{ext} is the force exerted by the environment

on the piston and $F_{fric} = \alpha v$ is the force due to friction with α the friction coefficient.

The lift of the balance equation on the whole thermodynamic phase space is given in accordance with Section 6.3.1. Applying Proposition 6.2, the following contact Hamiltonian function is obtained:

$$\begin{aligned} f^{pis}\left(x, p, F_{ext}\right) = & \left(\frac{\partial \tilde{S}^{pis}}{\partial E^{pis}} - p_E^{pis}\right)\left(\dot{Q}_{g\to p} - \left(F_{gas} - F_{ext}\right)\frac{p_q^{pis}}{p_E^{pis}}\right) \\ & + \left(\frac{\partial \tilde{S}^{pis}}{\partial q} - p_q^{pis}\right)\left(F_{gas} - F_{ext} - \frac{p_z^{pis}}{p_E^{pis}} + \alpha\frac{p_q^{pis}}{p_E^{pis}}\right) \\ & - \left(\frac{\partial \tilde{S}^{pis}}{\partial z} - p_z^{pis}\right)\frac{p_q^{pis}}{p_E^{pis}} \end{aligned} \tag{8.16}$$

where the interconnection variables $\dot{Q}_{g\to p}$ and F_{gas} depend on $\left(x^{pis}, p^{pis}\right)$ and on the state of the gas (x^{gas}, p^{gas}).

The gas-piston system

The thermodynamic properties of the composed system are obtained according to Section 6.3 by considering the independent extensive variables $x = (x^{pis}, x^{gas})^t \in \mathbb{R}^5$ with associated intensive variables $p = (p^{pis}, p^{gas})^t$ and the composed thermodynamic phase space $\mathbb{R}^{11} \ni (x_0, x^t, p^t)$. The properties of the composed system are then simply defined by the Legendre submanifold with generating function being the sum of the generating functions:

$$F(x) = \tilde{S}^{pis}(x^{pis}) + \tilde{S}^{gas}(x^{gas})$$

The interconnection relations define the variables are defined as follows:

- the heat exchange due to conduction:

$$\dot{Q}_{p\to g} = -\dot{Q}_{g\to p} = \kappa\left(\frac{1}{p_E^{pis}} - \frac{1}{p_E^{gas}}\right) \tag{8.17}$$

- the kinematic relation relating the velocity of the piston with the velocity of displacement of the moving wall:

$$v_{wall} = v = -\frac{p_q^{pis}}{p_E^{pis}} \tag{8.18}$$

- the static equilibrium:

$$F^{gas} = AP = Ap_V^{gas} \tag{8.19}$$

As stated in Proposition 6.4 the contact system for the composed system is then simply generated by the sum of the contact Hamiltonian functions (8.11) and (8.16) with the interconnection relations (8.17) to (8.19):

$$f(x, p, \xi_{ext}) = f^{pis}(x, p, \xi_{ext}) + f^{gas}(x, p, \xi_{ext}) \tag{8.20}$$

The contact Hamiltonian function computed above can be used for instance in order to obtain an expression for the total entropy production. In our case, the system is isolated. Therefore, there is no external entropy flux, and the variation of the total entropy of the system is equal to the entropy production. The variation of the total entropy is obtained by computing the x_0-component of the vector field generated by the contact Hamiltonian function (8.20) and then restricting it to the Legendre submanifold generated by $F(x)$. We obtain the following expression for the entropy production σ_S:

$$\sigma_S = \left.\frac{dx_0^{tot}}{dt}\right|_{\mathscr{L}} = \left(\frac{\partial \tilde{S}^{gas}}{\partial U^{gas}} - \frac{\partial \tilde{S}^{pis}}{\partial E^{pis}}\right)\dot{Q}_{g\to p} + \left(\frac{\partial \tilde{S}^{pis}}{\partial q}\right)^2 \left(\frac{\partial \tilde{S}^{pis}}{\partial E^{pis}}\right)^{-1} \alpha$$

In terms of the usual thermodynamic quantities, this is equal to following relation:

$$\sigma_S = \left(\frac{1}{T^{gas}} - \frac{1}{T^{pis}}\right)\dot{Q}_{g\to p} + \alpha\frac{v^2}{T^{pis}} \tag{8.21}$$

We can clearly recover the two sources of irreversibility, namely the heat transfer and the viscous dissipation.

8.3.2 The GENERIC model

In this section we shall show how the complete piston-gas system would be modelled using the GENERIC formulation. As it is an open system subject to the external mechanical force F_{ext}, the system will be defined according to Section 8.1.2.

The state space of independent extensive variables may be chosen to be the following one:

$$Z = [U^{pis}, z, q, U^{gas}, V]$$

The total energy function of the system is the sum of the total energy of the piston and the gas:

$$E^{tot}(Z) = \frac{1}{2m}q^2 + mgz + U^{pis} + U^{gas}$$

The total entropy function of the system is equal to the entropy functions of the piston and of the gas:

$$S^{tot}(Z) = \tilde{S}_0^{pis}\left(U^{pis}\right) + \tilde{S}^{gas}\left(U^{gas}, V\right)$$

The gradient of these potentials define the two vectors of generating forces: $\frac{\partial E^{tot}}{\partial Z}$ for the reversible phenomena and $\frac{\partial S^{tot}}{\partial Z}$ for the irreversible phenomena in the system. For the piston-gas system, they are given in terms of the different energy functions and of the co-energy variables as follows:

$$\frac{\partial E^{tot}}{\partial Z} = \left(1, \frac{\partial E^{pot}}{\partial z}, \frac{\partial E^{kin}}{\partial q}, 1, 0\right)^t = \left(1, -F_{pot}, v, 1, 0\right)^t \tag{8.22a}$$

$$\frac{\partial S^{tot}}{\partial Z} = \left(\frac{\partial \tilde{S}^{pis}}{\partial U^{pis}}, 0, 0, \frac{\partial \tilde{S}^{gas}}{\partial U^{gas}}, \frac{\partial \tilde{S}^{gas}}{\partial V}\right)^t = \left(\frac{1}{T^{pis}}, 0, 0, \frac{1}{T^{gas}}, \frac{P}{T^{gas}}\right)^t \tag{8.22b}$$

Remark 8.8. *Note that the vector $\frac{\partial E^{tot}}{\partial Z}$ contains only the mechanical co-energy variables as independent variables, and the vector $\frac{\partial S^{tot}}{\partial Z}$ only the thermodynamic intensive variables as independent variables. The non-independence of the two potentials $E^{tot}(Z)$ and $S^{tot}(Z)$ is translated in the two coefficients of $\frac{\partial E^{tot}}{\partial Z}$ equal to* 1.

Let us first find the GENERIC model of the isolated system obtained by choosing $F_{ext} = 0$. The first step consists in splitting the left-hand side of the balance equations (8.10) and (8.15) into two vector fields; the first one, denoted by $\mathcal{X}_{ham}$, corresponding to a Hamiltonian vector field, and the second one, denoted by $\mathcal{X}_{diss}$, to the dissipative vector field in (8.2). The suggested choice corresponds to split it into a vector field corresponding to the reversible

phenomena and another one to the irreversible phenomena as follows:

$$\begin{pmatrix} \frac{dU^{pis}}{dt} \\ \frac{dz}{dt} \\ \frac{dq}{dt} \\ \frac{dU^{gas}}{dt} \\ \frac{dV}{dt} \end{pmatrix} = \underbrace{\begin{pmatrix} 0 \\ v \\ F^{gas} + F_{pot} \\ -PAv \\ Av \end{pmatrix}}_{\mathcal{X}_{ham}} + \underbrace{\begin{pmatrix} \dot{Q}_{g\to p} + \alpha v^2 \\ 0 \\ -\alpha v \\ -\dot{Q}_{g\to p} \\ 0 \end{pmatrix}}_{\mathcal{X}_{diss}} \tag{8.23}$$

For the Hamiltonian vector field, it appears that there exists a unique skew-symmetric matrix $\boldsymbol{L}$ that corresponds to the Poisson bracket such that the total energy $E^{tot}(Z)$ generates the Hamiltonian vector field $\mathcal{X}_{ham}$ and such that the total entropy is a Casimir function:

$$\boldsymbol{L} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & -1 & 0 & AP & -A \\ 0 & 0 & -AP & 0 & 0 \\ 0 & 0 & A & 0 & 0 \end{pmatrix} \tag{8.24}$$

where $P = \frac{\partial \tilde{S}^{gas}}{\partial V}(U^{gas}, V)$.

Remark 8.9. *It is easy to check directly that the structure matrix $\boldsymbol{L}$ satisfies the Jacobi identities. Note first that as the pressure satisfies $P > 0$ for any state, the rank of $\boldsymbol{L}(Z)$ is 2. Secondly there are three obvious independent Casimir functions, namely the internal energy of the piston $C_1(Z) = U^{pis}$, the entropy function of the gas $C_2(Z) = \tilde{S}^{gas}(U^{gas}, V)$, and the third one being the geometric relation (modulo some constant) between the volume and the position of the piston $C_3(Z) = V - Az$. The three Casimir functions have the immediate physical interpretation that the Hamiltonian vector field leaves invariant the internal energy of the piston, the entropy of the gas and the kinematic relation relating the moving wall of the gas with the piston. Finally it may be observed that $S^{tot}(Z) = \tilde{S}^{pis}(C_1(Z)) + C_2(Z)$ and is indeed generated by the chosen set of independent Casimir functions. The Hamiltonian vector field corresponds to isentropic transformations of both the gas subsystem and the total gas-piston system.*

For the dissipative vector field there is no unique solution for the matrix $\boldsymbol{M}(Z)$ as it has been noted e.g. in [76]. One possible semi-definite positive symmetric matrix $\boldsymbol{M}(Z)$ that generates the vector field $\mathcal{X}_{diss}$ and admits the total energy $E^{tot}(Z)$ as Casimir function is the following one:

$$\boldsymbol{M} = \begin{pmatrix} \kappa T^{gas}T^{pis} + T^{pis}\alpha v^2 & 0 & -\alpha T^{pis} v & -\kappa T^{gas}T^{pis} & 0 \\ 0 & 0 & 0 & 0 & 0 \\ -\alpha T^{pis} v & 0 & \alpha T^{pis} & 0 & 0 \\ -\kappa T^{gas}T^{pis} & 0 & 0 & \kappa T^{gas}T^{pis} & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{8.25}$$

with

$$T^{pis} = \left(\frac{\partial \tilde{S}^{pis}}{\partial U^{pis}}\right)^{-1}(U^{pis});\ T^{gas} = \left(\frac{\partial \tilde{S}^{gas}}{\partial U^{gas}}\right)^{-1}(U^{gas}, V);\ v = \frac{\partial E^{kin}}{\partial q}(q)$$

Remark 8.10. *Note that the matrix $\boldsymbol{M}$ is symmetric and positive semi-definite as the friction and conduction coefficients α and κ are positive as well as the temperatures, but it is not definite. Actually it has rank 2 and admits three Casimir functions: $D_1(Z) = z$ and $D_2(Z) = V$ and, by construction, the total energy $E^{tot}(Z)$. The first two Casimir functions implies that the dissipative vector field corresponds to isochore transformations.*

Let us now extend the model in order to account for the exchanges with the environment. The only exchange with the environment is due to the external force F_{ext}. As this interaction with the environment does not imply any irreversible phenomenon, it is sufficient to augment the Hamiltonian vector field. The GENERIC formulation of the open system can then be written as follows:

$$\begin{pmatrix} -\dot{X}_{ham} \\ \frac{dZ_{open}}{dt} \end{pmatrix} = \begin{pmatrix} 0 & \boldsymbol{\Gamma}(Z) \\ -\boldsymbol{\Gamma}^t(Z) & \boldsymbol{L}(Z) \end{pmatrix} \begin{pmatrix} F_{ext} \\ \frac{\partial E^{tot}}{\partial Z} \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & \boldsymbol{M}(Z) \end{pmatrix} \begin{pmatrix} 0 \\ \frac{\partial S^{tot}}{\partial Z} \end{pmatrix}$$

The second row can be developed and the following expression is obtained:

$$\frac{dZ}{dt} = -\boldsymbol{\Gamma}^t(Z)\, F_{ext} + \boldsymbol{L}(Z)\frac{\partial E^{tot}}{\partial Z} + \boldsymbol{M}(Z)\frac{\partial S^{tot}}{\partial Z} \tag{8.26}$$

Actually the external force solely appears in the momentum balance (8.15b), hence it is easy to define the interaction matrix $\mathbf{\Gamma}$:

$$\mathbf{\Gamma}(Z) = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

The conjugated port variable $\dot{X}_{ham}$ associated to F_{ext} is consequently equal to the velocity of the piston:

$$-\dot{X}_{ham} = \mathbf{\Gamma}\frac{\partial E^{tot}}{\partial Z} = v$$

8.3.3 The Matrix model

We have recalled in Section 8.2 that the Matrix model only represents the balance equations on the extensive thermodynamic variable at the exclusion of the entropy balance equation. Gibbs' equation in the energy form may be generalized to encompass the thermodynamic states of the piston and the gas:

$$\mathrm{d}U^{tot} = T^{pis}\mathrm{d}S^{pis} + T^{gas}\mathrm{d}S^{gas} - P\mathrm{d}V$$

with respect to the fundamental equation:

$$\tilde{U}^{tot}(S^{pis}, S^{gas}, V) = \tilde{U}^{pis}(S^{pis}) + \tilde{U}^{gas}(S^{gas}, V)$$

For the gas-piston system the conjugated pair of extensive variable and intensive variable of the Matrix model is reduced to $(X, F_{th}) = (V, -P)$. The external flux and effort variables F_e, $\dot{X}_e$ are deduced from the balance equation of the total internal energy balance:

$$\frac{dU^{tot}}{dt} = \frac{dU^{pis}}{dt} + \frac{dU^{gas}}{dt}$$

The internal energy balance of the piston is obtained from the energy balance (8.15a) as follows:

$$\begin{aligned}
\frac{dU^{pis}}{dt} &= \frac{dE^{pis}}{dt} - \frac{dE^{kin}}{dt} - \frac{dE^{pot}}{dt} \\
&= \dot{Q}_{g\to p} + (F_{gas} - F_{ext})\, v - \frac{\partial \tilde{E}^{pot}}{\partial z} v \\
&\quad - \frac{\partial \tilde{E}^{kin}}{\partial q}\left(F_{gas} - F_{ext} - F_{pot} - \alpha v\right) \\
&= \dot{Q}_{g\to p} + \alpha v^2
\end{aligned}$$

By combining with (8.10a) we obtain finally:

$$\frac{dU^{tot}}{dt} = \frac{dU^{pis}}{dt} + \frac{dU^{gas}}{dt} = (\alpha v - AP)\, v$$

which, according to (8.6b), leads to define:

$$F_e = \alpha v - AP \quad \text{and} \quad \dot{X}_e = v$$

The balance equation on the volume and the definition of the Matrix model in (8.7) lead to the Matrix model of the piston-gas system:

$$\begin{pmatrix} \alpha v - AP \\ \frac{dV}{dt} \end{pmatrix} = \begin{pmatrix} \alpha & -A \\ A & 0 \end{pmatrix} \begin{pmatrix} v \\ P \end{pmatrix} \tag{8.27}$$

Note that (8.27) reduces to a single balance equation on the volume corresponding the conservation of space. This result is indeed analogous to that presented in [61].

Note also that the final formulation of the Matrix model (8.27) does not include explicitly the energy balance.

The total dissipation can now be calculated using (8.8):

$$\Delta_{diss} = \dot{X}_e \boldsymbol{\eta} \dot{X}_e = \alpha v^2 \tag{8.28}$$

As shown in Section 8.2, the dissipation is related to the entropy variation which is not due to heat effects. Indeed by comparing with (8.21), we have:

$$\sigma_S = \left(\frac{1}{T^{gas}} - \frac{1}{T^{pis}} \right) \dot{Q}_{g \to p} + \frac{\Delta_{diss}}{T^{pis}}$$

8.4 Conclusion

In this chapter we have been considering the differential-geometric structure of the dynamical thermodynamic systems such as the GENERIC, the Matrix or the control contact system formulations.

All the considered formulations may be formulated in terms of contact systems as the lift of the balance equations on the extensive variables to the whole thermodynamic phase space and the expressions of the contact Hamiltonian

generating the contact vector field may be compared. The GENERIC and the Matrix formulations lead to a contact Hamiltonian function which is a tensor product of the thermodynamic forces whereas the control contact system admits more general expressions which allows for a more general expression of fluxes.

For the GENERIC formalism, we have discussed in details the structure matrices of the Hamiltonian and the dissipative vector fields and their respective Casimir functions with respect to their physical interpretation. In our example, there is a unique solution for the Poisson structure matrix but a non-unique solution for the Riemannian metric matrix. Note that for higher dimensional systems, the solution for the Poisson structure matrix is not unique anymore [76]. Both structure matrices depend on some intensive thermodynamic variables. These variables define the structure matrices as functions of the extensive variables by using the equations of state. Hence the structure matrices contain both the information about the phenomenological laws and about the thermodynamic model whereas in the contact formalism the thermodynamic model and the phenomenological laws are contained in two distinct objects.

The contact formalism is well suited for extending the formulation to open systems or control systems. In this case the contact Hamiltonian is additively augmented with a contact Hamiltonian function depending on the state variable of the environment. This feature has been used in order to define the contact formulation of a complex system composed of simple thermodynamic systems (possibly in motion) interconnected through a graph representing the exchange of fluxes between the subsystems. The GENERIC formulation does not include interconnections of subsystems and is less adapted to open systems. Hence the contact formalism is better adapted for control purposes.

The contact formulation opens the road for the analysis and control of open thermodynamic systems or coupled to mechanical or electromagnetic systems. A consequence of this formulation is to use the contact formulation and the expression of the entropy balance equation in order to analyze the stability of equilibria and extend the passivity-based methods for deriving stabilizing controller based on energy shaping to entropy shaping.

Chapter 9

Conclusion

This part of the thesis was dedicated to the study of a formal mathematical framework for the expression of the dynamical behaviour of thermodynamic systems. We have chosen the contact structure formalism that has been developed recently. This formalism is in line with Gibbs' work and associates objects from classical thermodynamics to objects from differential geometry. More precisely, the Gibbs' relation is associated to a 1-form and the fundamental relation is associated to a scalar function which is the generating function from a Legendre submanifold. The dynamical behaviour is encompassed in another scalar function, called the contact Hamiltonian function, that is equal to zero on the previously cited Legendre submanifold. This formalism accounts at the same time for the reversible and irreversible phenomena and generalizes the well-known Hamiltonian approach of reversible systems.

Previously to this thesis, the contact formalism had already been applied to open systems undergoing irreversible phenomena. But the link between the physical model of the system and its representation in the contact formalism was not obvious. Therefore we have studied a different form of the contact formalism than the one presented in the work of Eberard and coworkers [31]. Indeed Eberard and coworkers used the energy-form of the Gibbs' relation as the contact form for the representation of the thermodynamic systems. In our work we have used the entropy-form of the Gibbs' relation as the contact form.

We have shown that this approach is better suited to model thermodynamic systems, and more particularly chemical process, since the contact model of the system can be deduced directly from the energy and mass balances and does not require the prior knowledge of the entropy balance. We have shown how a possible contact Hamiltonian function can be deduced directly from the mass and energy balances, first for simple thermodynamic systems and then for complex systems which are an interconnection of simple thermodynamic systems. This can be very useful for the representation of chemical processes which are typically an interconnection of unit operations.

The contact Hamiltonian function contains the information about the dynamical behaviour of the system. We have linked the characteristics of the contact Hamiltonian function to the dynamical properties of the system. In this framework, we have shown that for a particular class of contact Hamiltonian functions the equilibrium points are their critical points. This particular class of contact Hamiltonian functions corresponds to the most common modelling assumptions. We have also established a necessary condition on the contact Hamiltonian function for an equilibrium point to be stable. This criterion has been derived from the Lyapunov's first method and depends both on the thermodynamic model (via the generating function of the Legendre submanifold) and on the contact Hamiltonian function. This criterion has been related to physical considerations on the system, and more particularly to the concavity of the entropy function. Using this stability criterion it is possible to determine whether a flow entering or leaving the system tends to stabilize or to destabilize an equilibrium.

Besides, two alternative formalisms for the representation of open thermodynamic systems have also been discussed in this part of the thesis, namely the GENERIC and the Matrix formalisms. In the case of interconnections of simple thermodynamic systems that are at thermodynamic equilibrium, these two formalisms are included in the contact formalism. As we have shown on a simple case study, the contact formalism is also better adapted for the representation of open systems and hence for being used for control purposes. Indeed the contact formalism allows to consider the system as interconnected blocks which can be treated individually, before considering their interconnection. This is

not the case for the GENERIC and Matrix formalisms where the system has to be considered as a whole. The GENERIC and Matrix formalisms can also be applied to distributed parameter systems. The case of distributed systems has not been considered in this thesis, but the extension of the contact formalism to such systems should not be an issue, if assuming that the thermodynamic equilibrium is reached locally. Indeed then local forms of the Gibbs' relation and of the thermodynamic flows can then be used.

As a conclusion the contact formalism appears to be a powerful tool for the analysis and control of the dynamical behaviour of open thermodynamic systems. It encompasses an interconnection based approach of thermodynamic systems which is of great interest when considering chemical processes. The elements of the contact representation of a thermodynamic system are closely related to thermodynamic properties and at the same time they are well defined objects of a formal mathematical theory. Hence the contact formalism gives a formal structure to the thermodynamics which allows us to link the dynamical behaviour of the system to its thermodynamic properties and to the underlying physical phenomena.

General conclusion

The aim of this thesis was to introduce physical insight into system theory results about the dynamical behaviour of chemical processes. The chosen approach has been to link the fundamentals of thermodynamics with tools from system theory. More precisely we have divided this study into two parts. In the first part we have started from classical chemical engineering considerations on the physics of the process and we have tried to relate these considerations to tools from system theory, such as the Lyapunov theory. In the second part we have developed and applied a mathematical formalism that encompasses the thermodynamic fundamental laws. This formalism has then be used to interpret physically the dynamical behaviour of thermodynamic systems.

The first part has been conducted on a classical case study of chemical engineering, namely the non-isothermal CSTR. This system is both easy to model and has a complex thermodynamic behaviour. The dynamical behaviour of this system has already been studied for a long time as it can be seen in the work of Aris, Amundsen and coworkers [7] or of Uppal and coworkers [93][94]. Several control methods have also been applied on this system (see e.g. [8][53][99]). Nevertheless most of the time these studies rest on a simplified version of the CSTR model. For instance, contrary to the logical approach for an open thermodynamic system, this simplified version does not use the internal energy balance, but the temperature evolution equation as one of the differential equations for representing the dynamical behaviour. The use of a simplified version of the dynamics breeds the risk of a loss of physical interpretation. Therefore in this thesis we have worked with a more exact form of the dynamics. Indeed we have used the dynamical model that is directly obtained from the energy and mass balance on the system. We have shown that the classical results on the simplified case are in fact valid in a more general case. Then we have used thermodynamic considerations on the system to derive physics based Lyapunov functions, similarly to what had already been done for electromechanical systems. More precisely we have used entropy and energy related quantities as Lyapunov function candidates. We have shown that these quantities exhibit limitations in the case of open reaction systems. Finally we have applied the power-shaping control approach to the CSTR case study. This approach has already been used for physics based control of electromechanical systems [40][56][80]. In our case this

approach has led to a global Lyapunov function for the uncontrolled exothermic CSTR. This Lyapunov function has been partially interpreted in terms of the physical phenomena that are taking place, namely the convection and the reaction. A controller for the CSTR has then be derived for the stabilization of the CSTR. In fact, this controller reshapes the previously obtained open loop Lyapunov function. Then we have shown that the obtained control action is robust with respect to modelling errors or to measurement errors. Finally some embryonic results for the extension of this approach to more complex systems have been presented.

In this thesis, we have shown that the transcription of the energy-based control approach that is used for electro-mechanical systems to chemical processes is not as obvious as it could seem in a first sight. Indeed in electro-mechanical systems the energy is used as the storage function or as a Lyapunov function. This is only possible because for those systems, the heat effects and the temperature are not taken into account. As a consequence, the above mentioned energy function is decreasing whenever dissipative effects (e.g. friction, damping, electrical resistor) are present. But of course the energy does not really decrease: the dissipative effects transform the mechanical, potential or electrical energy into heat. Contrary to electro-mechanical systems, in chemical processes the heat effects have to be considered in the energy function because the temperature is a major concern in such systems. Therefore we loose the nice property that the energy is decreasing and the transcription of the energy-based control approach needs another quantity to replace the energy function.

The second part of this thesis has been dedicated to a geometric approach of the thermodynamics. We introduced a mathematical formalism for the expression of the dynamical behaviour of thermodynamic systems, namely the contact structure formalism. Contrary to most of the previous studies, we used an expression for the contact structure of a thermodynamic system that is based on the entropy form of the Gibbs' relation instead of its energy form [28][31]. We have shown that this approach is better adapted for the modelling of processes in the contact formalism. A general methodology for deriving the expression of the contact structure elements (i.e. the Legendre submanifold generating function and the contact Hamiltonian function) from the fundamental relation

of a thermodynamic system and from its balance equations has been developed. This methodology also allows to derive the contact structure of interconnected systems, departing from the contact structures of the simple systems which are making up the complete system. The contact structure formalism has then been studied from the point of view of the dynamical behaviour. We have related some features of the dynamical behaviour of a system with properties of its contact structure elements. For instance, an equilibrium point of the system is expressed by a critical point of the contact Hamiltonian function. Lyapunov's first stability theorem has also been related to characteristics of the contact Hamiltonian function and of the Legendre submanifold generating function. This has allowed to state a sufficient stability criterion in terms of the contact structure of a system. This stability criterion has then been interpreted using physical considerations. It can be used to determine if a flow that system exchanges with its environment tends to stabilize or to destabilize a given equilibrium. Finally we have discussed the proposed mathematical formalization of thermodynamic systems with respect to two other existing formalisms, namely the GENERIC formalism (General Equation for the Non-Equilibrium Reversible-Irreversible Coupling) [46] and the Matrix formalism [60]. As it has been shown in the present thesis, these formalisms are both encompassed in the contact structure formalism in the case of interconnections of simple thermodynamic systems (i.e. without any space dependence of the thermodynamic state variables). The three formalisms have been applied to a case study of an open thermodynamic system in which reversible and irreversible phenomena take place. This case study has been used to illustrate the characteristics of the three formalisms from the point of view of open interconnected systems. The contact structure formalism seems to be well adapted for control purposes because it allows to handle open interconnected systems, which is more tedious with the two other formalisms.

This study aims at linking the dynamical behaviour of a thermodynamic system with the physical phenomena that give raise to this behaviour. This thesis gathers together results form irreversible thermodynamic theory, chemical engineering, system theory, differential geometry... and presents several new results that are obtained by the combination of these scientific areas. The title

of this thesis is "Thermodynamics and process control" because it is the long term objective of this study. This thesis is only the first step in this direction and sets the foundations and opens the door for further investigations in the domain of physics based control of chemical processes.

The link between the two parts of this thesis may not seem obvious. However actually these parts are two different approaches for achieving the same above mentioned objective. Further work should emphasize the links between the two approaches for example by integrating the results of Part I into the contact formalism. For example the physical interpretation of the stability criterion on the contact Hamiltonian function could help to improve the approach of Chapter 3.

The power-shaping approach seems to offer promising possibilities in this direction, as well as the contact structure approach. In [87] Ortega and coworkers give a port-Hamiltonian representation of simple CSTRs. A possible way for extending the power-shaping approach to more complex systems could therefore be to take advantage from the similarity of the port-Hamiltonian and the Brayton-Moser formulations. This approach could be used to extend the power-shaping approach to more complex systems and to find a precise physical interpretation of the potential function. The contact formalism also seems to open promising ways. The elements of the contact representation of a thermodynamic system are closely related to thermodynamic properties and at the same time they are well defined objects of a formal mathematical theory. Hence the contact formalism gives a formal structure to the thermodynamics which allows us to link the dynamical behaviour of the system to its thermodynamic properties and to the underlying physical phenomena. Furthermore as we have shown one of its great strengths is to allow an easy handling of interconnected systems. This is of utmost importance from two point of views: first, chemical processes are interconnections of unit operations and the contact model should facilitate the modelling and the analysis of such systems; second, implementing a control system can be seen as the addition of a subsystem in an interconnection. A link between the power-shaping approach and the contact structure formalism would therefore be of great interest in this framework, because it would allow to gather together these two results. Some embryonic results that

relate the Brayton-Moser formulation of RLC circuits and their contact formulation have already been established in [26][30]. The extension of this study to the contact formulation of thermodynamic systems could provide several leads for the generalization of the power-shaping approach to more complex systems or to interconnected systems. Finally for chemical engineering purposes, this study should be generalized to heterogeneous thermodynamic systems such as for example distillation columns or plug flow type reactors.

Bibliography

[1] P. Absil, R. Mahony and R. Sepulchre, *Optimization Algorithms on Matrix Manifolds*, Princeton University Press, Princeton, 2008.

[2] A. A. Alonso, J. R. Banga and I. Sanchez, *Passive control design for distributed process systems: Theory and applications*, AIChE Journal **46**, 2000, pp. 1593–1606.

[3] A. A. Alonso and B. E. Ydstie, *Stabilization of distributed systems using irreversible thermodynamics*, Automatica **37**, 2001, pp. 1739–1755.

[4] A. A. Alonso, B. E. Ydstie and J. R. Banga, *From irreversible thermodynamics to a robust control theory for distributed process systems*, Journal of Process Control **12**, 2002, pp. 507–517.

[5] L. T. Antelo, I. Otero-Muras, J. R. Banga and A. A. Alonso, *A systematic approach to plant-wide control based on thermodynamics*, Computers & Chemical Engineering **31**(5-6), 2007, pp. 677–691.

[6] R. Aris, *Elementary Chemical Reactor Analysis*, Dover Publications, Toronto, 1989.

[7] R. Aris and N. R. Amundson, *An analysis of chemical reactor stability and control–I : The possibility of local control, with perfect or imperfect control mechanisms*, Chemical Engineering Science **7**(3), 1958, pp. 121–131.

[8] R. Aris and N. R. Amundson, *An analysis of chemical reactor stability and control–II : The evolution of proportional control*, Chemical Engineering Science **7**(3), 1958, pp. 132–147.

[9] V. I. Arnold, *Contact geometry: the geometrical method of Gibbs's thermodynamics*, Proc. of the Gibbs Symposium, Yale University (USA), May 1989, pp. 163–180.

[10] V. I. Arnold, *Mathematical Methods of Classical Mechanics (translated by K. Vogtmann)*, 2^{nd} ed., Graduate texts in mathematics, vol. 60, Springer, New York, 1989.

[11] L. Benayoun, *Méthodes géométriques pour l'étude des systèmes thermodynamiques et la génération d'équations d'état*, Ph.D. thesis, Institut Polytechnique de Grenoble, 1999.

[12] J. S. Berger and D. D. Perlmutter, *Chemical reactor stability by Liapunov's direct method*, AIChE Journal **10**, 1964, pp. 233–238.

[13] O. Bilous and N. R. Amundson, *Chemical reactor stability and sensitivity*, AIChE Journal **1**, 1955, pp. 513–521.

[14] R. Bird, W. Stewart and E. Lightfoot, *Transport phenomena*, 2^{nd} ed., John Wiley and Sons, New York, 2002.

[15] R. Brayton and J. Moser, *A theory of nonlinear networks I*, Quaterly of Applied Mathematics **22**, 1964, pp. 1–33.

[16] R. Brayton and J. Moser, *A theory of nonlinear networks II*, Quaterly of Applied Mathematics **22**, 1964, pp. 81–104.

[17] R. Brockett, *Geometric Control Theory*, Lie groups: History, Frontiers and Applications, vol. 7, ch. Control theory and analytical mechanics, pp. 1–46, Math Sci Press, Brookline, 1977.

[18] B. Brogliato, R. Lozano, B. Maschke and O. Egeland, *Dissipative Systems Analysis and Control*, 2^{nd} ed., Communications and Control Engineering Series, Springer, London, 2007.

[19] H. Callen, *Thermodynamics and an Introduction to Thermostatics*, 2^{nd} ed., John Wiley & Sons, New York, 1985.

[20] C. Carathéodory, *Untersuchungen über die Grundlagen der Thermodynamik*, Mathematische Annalen **67**, 1909, pp. 355–386.

[21] M. Chen, *On the geometric structure of thermodynamics*, Journal of Mathematical Physics **40**(2), 1999, pp. 830–837.

[22] J. Cortés, A. van der Schaft and P. E. Crouch, *Characterization of gradient control systems*, SIAM Journal on Control and Optimization **44**(4), 2005, pp. 1192–1214.

[23] F. Couenne, C. Jallut, B. Maschke, P. Breedveld and M. Tayakout, *Bond graph modelling for chemical reactors*, Mathematical and Computer Modelling of Dynamical Systems **12**, 2006, pp. 159–174.

[24] W. R. Dammers and M. Tels, *Thermodynamic stability and entropy production in adiabatic stirred flow reactors*, Chemical Engineering Science **29**(1), 1974, pp. 83–90.

[25] S. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, Dover publications, New York, 1984.

[26] D. Eberard, *Extension des systèmes hamiltoniens à ports aux systèmes irréversibles: une approche par la géométrie de contact*, Ph.D. thesis, Université Claude Bernard, Lyon 1, 2006.

[27] D. Eberard, B. Maschke and A. van der Schaft, *Conservative systems with ports on contact manifolds*, Proc. 16^{th} IFAC World Congress, Prague (Czech Republic), July 2005.

[28] D. Eberard, B. Maschke and A. van der Schaft, *Port contact systems for irreversible thermodynamical systems*, Proc. 44^{th} IEEE Conference on Decision and Control and European Control Conference, Sevilla (Spain), December 2005, pp. 5977–5983.

[29] D. Eberard, B. Maschke and A. van der Schaft, *Systems theory of interconnected port contact systems*, Proc. International Symposium on Non-Linear Theory and its Applications, Bruges (Belgium), October 2005.

[30] D. Eberard, B. Maschke and A. van der Schaft, *Energy-conserving formulation of RLC-circuits with linear resistors*, Proc. 17^{th} International Symposium on Mathematical Theory of Networks and Systems, Kyoto (Japan), July 2006, pp. 71–76.

[31] D. Eberard, B. Maschke and A. van der Schaft, *An extension of pseudo-Hamiltonian systems to the thermodynamic space: towards a geometry of non-equilibrium thermodynamics*, Reports on Mathematical Physics **60**(2), 2007, pp. 175–198.

[32] D. Eberard, B. Maschke and A. van der Schaft, *On the interconnection structures of open physical systems*, Proc. 3^{rd} IFAC Workshop on Lagrangian and Hamiltonian methods for nonlinear control, Nagoya (Japan), July 2006, pp. 209–218.

[33] B. Edwards, H. Öttinger and R. Jongschaap, *On the relationships between thermodynamic formalisms for complex fluids*, Journal of non-equilibrium thermodynamics **22**, 1997, pp. 356–373.

[34] C. A. Farschman, K. P. Viswanath and B. E. Ydstie, *Process systems and inventory control*, AIChE Journal **44**(8), 1998, pp. 1841–1857.

[35] A. Favache, B. Maschke and D. Dochain, *Contact structures: application to interconnected thermodynamical systems*, Proc. European Control Conference 2007, Kos (Greece), July 2007, pp. 4095–4102.

[36] A. Favache and D. Dochain, *Thermodynamics and chemical systems stability: The CSTR case study revisited*, Journal of Process Control **19**(3), 2009, pp. 371–379.

[37] A. Favache, V. S. Dos Santos Martins, D. Dochain and B. Maschke, *Some properties of conservative port contact systems*, accepted for publication in IEEE Transactions on Automatic Control, 2009.

[38] M. Feinberg, *Lectures on Chemical Reaction Networks*, University of Wisconsin-Madison, Mathematics Research Center, 1979.

[39] M. Fjeld, O. Asbjornsen and K. Astrom, *Reaction invariants and their importance in the analysis of eigenvectors, state observability and controllability of the continuous stirred tank reactors*, Chemical Engineering Science **29**, 1974, pp. 1917–1926.

[40] E. Garcia-Canseco, D. Jeltsema, J. Scherpen and R. Ortega, *Power-based control of physical systems: two case studies*, Proc. 17^{th} IFAC World Congress, Seoul (Korea), 2008.

[41] G. Gavalas, *Nonlinear Differential Equations of Chemically Reacting Systems*, Springer, Berlin, 1968.

[42] C. Georgakis, *On the use of extensive variables in process dynamics and control*, Chemical Engineering Science **41**(6), 1986, pp. 1471–1484.

[43] J. Gibbs, *The Collected Works of J. Willard Gibbs*, Longman's, Green and Co., New York, 1931.

[44] P. Glansdorff and I. Prigogine, *On a general evolution criterion in macroscopic physics*, Physica **30**, 1964, pp. 351–374.

[45] C. Godbillon, *Géométrie différentielle et mécanique analytique*, Hermann, Paris, 1969.

[46] M. Grmela and H. Öttinger, *Dynamics and thermodynamics of complex fluids. I. Development of a general formalism*, Physical Review E **56**(6), 1997, pp. 6620–6632.

[47] M. Grmela and H. Öttinger, *Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism*, Physical Review E **56**(6), 1997, pp. 6633–6655.

[48] M. Grmela, *Lagrange hydrodynamics as extended Euler hydrodynamics: Hamiltonian and GENERIC structures*, Physics Letters A **296**(2-3), 2002, pp. 97–104.

[49] M. Grmela, *Reciprocity relations in thermodynamics*, Physica A: Statistical Mechanics and its Applications **309**(3-4), 2002, pp. 304–328.

[50] R. Herman, *Geometry, Physics and Systems*, Marcel Dekker, 1973.

[51] H. Hoang, F. Couenne, C. Jallut and Y. Le Gorrec, *Lyapunov based control for non isothermal continuous stirred tank reactor*, Proc. 17^{th} IFAC World Congress, Seoul (Korea), 2008.

[52] A. Isidori, *Nonlinear control systems*, 3^{rd} ed., Springer, London, 1995.

[53] F. Jadot, G. Bastin and F. Viel, *Robust global stabilisation of stirred tank reactors by saturated output feedback*, European Journal of Control **5**, 1999, pp. 361–371.

[54] D. Jeltsema, R. Ortega and J. M. Scherpen, *An energy-balancing perspective of interconnection and damping assignment control of nonlinear systems*, Automatica **40**(9), 2004, pp. 1643–1646.

[55] D. Jeltsema and J. M. Scherpen, *On mechanical mixed potential, content and co-content*, Proc. European Control Conference, Cambridge (United Kingdom), September 2003, pp. 73–78.

[56] D. Jeltsema and J. M. Scherpen, *A power-based description of standard mechanical systems*, Systems & Control Letters **56**(5), 2007, pp. 349–356.

[57] K. R. Jillson and B. E. Ydstie, *Complex process networks: passivity and optimality*, Proc. IFAC World Congress, Prague (Czech Republic), July 2005.

[58] K. R. Jillson and B. E. Ydstie, *Process networks with decentralized inventory and flow control*, Journal of Process Control **17**(5), 2007, pp. 399–413.

[59] E. Johannessen and S. Kjelstrup, *Minimum entropy production rate in plug flow reactors: An optimal control problem solved for SO_2 oxidation*, Energy **29**, 2004, pp. 2403–2423.

[60] R. Jongschaap, *The Matrix model, a driven state variables approach to non-equilibrium thermodynamics*, Journal of non-Newtonian fluid mechanics **96**, 2001, pp. 63–76.

[61] R. Jongschaap and H. Öttinger, *The mathematical representation of driven thermodynamic systems*, Journal of non-Newtonian fluid mechanics **120**, 2004, pp. 3–9.

[62] D. Jou, J. Casas-Vazquez and G. Lebon, *Extended Irreversible Thermodynamics*, Springer, Heidelberg, 2001.

[63] H. Khalil, *Nonlinear Systems*, 3^{rd} ed., Prentice Hall, Upper Saddle River, 2002.

[64] E. Kreyszig, *Introduction to Differential Geometry and Riemannian Geometry*, Mathematical Expositions, no. 16, University of Toronto Press, Toronto, 1968.

[65] E. Kreyszig, *Introductory Functional Analysis with Applications*, John Wiley & Sons, New York, 1989.

[66] J. Lafontaine, *Introduction aux variétés différentielles*, Collection Grenoble Sciences, Presses universitaires de Grenoble, 1996.

[67] O. Levenspiel, *Chemical Reaction Engineering*, 3^{rd} ed., John Wiley & Sons, New York, 1999.

[68] G. Lewis and M. Randall, *Thermodynamics*, 2^{nd} ed., Mc Graw Hill, New York, 1961.

[69] P. Libermann and C.-M. Marle, *Symplectic Geometry and Analytical Mechanics*, D. Reidel Publishing Company, Dordrecht, 1987.

[70] B. Maschke, R. Ortega and A. van der Schaft, *Energy-based Lyapunov functions for forced Hamiltonian systems with dissipation*, IEEE Transactions on Automatic Control **45**(8), 2000, pp. 1498–1502.

[71] Y. Matsushima, *Differentiable Manifolds (translated by E.T. Kobayashi)*, Marcel Dekker, New York, 1972.

[72] R. Mortimer, *Physical Chemistry*, The Benjamin/Cummings Publishing company, Redwood City, 1993.

[73] R. Mrugała, *Geometrical formulation of equilibrium phenomenological thermodynamics*, Reports on Mathematical Physics **14**(3), 1978, pp. 419–427.

[74] R. Mrugała, *On a special family of thermodynamic processes and their invariants*, Reports on Mathematical Physics **46**(3), 2000, pp. 461–468.

[75] R. Mrugała, J. Nulton, J. Schön and P. Salamon, *Contact structure in thermodynamic theory*, Reports on Mathematical Physics **29**(1), 1991, pp. 109–121.

[76] W. Muschik, S. Gümbel, M. Kröger and H. Öttinger, *A simple example for comparing GENERIC with rational non-equilibrium thermodynamics*, Physica A **285**, 2000, pp. 448–466.

[77] H. Nijmeijer and A. van der Schaft, *Nonlinear Dynamical Control Systems*, Springer, New York, 1990.

[78] L. Nummedal, S. Kjelstrup and M. Costea, *Minimizing the entropy production rate of an exothermic reactor with a constant heat-transfer coefficient: The ammonia reaction*, Industrial & Engineering Chemistry Research **42**, 2003, pp. 1044–1056.

[79] J.-P. Ortega and V. Planas-Bielsa, *Dynamics on Leibniz manifolds*, Journal of Geometry and Physics **52**, 2004, pp. 1–27.

[80] R. Ortega, D. Jeltsema and J. Scherpen, *Power shaping: A new paradigm for stabilization of nonlinear RLC-circuits*, IEEE Transactions on Automatic Control **48**(10), 2003, pp. 1762–1767.

[81] R. Ortega, A. van der Schaft, B. Maschke and G. Escobar, *Energy-shaping of port-controlled Hamiltonian systems by interconnection*, Proc. 38^{th} IEEE Conference on Decision and Control, Phoenix (USA), December 1999, pp. 1646–1651.

[82] R. Ortega, A. van der Schaft, I. Mareels and B. Maschke, *Putting energy back in control*, IEEE Control Systems Magazine **21**(2), 2001, pp. 18–33.

[83] R. Ortega, A. van der Schaft, B. Maschke and G. Escobar, *Interconnection and damping assignment: passivity-based control of port-controlled Hamiltonian systems*, Automatica **38**, 2002, pp. 585–596.

[84] I. Otero-Muras, G. Szederkényi, A. Alonso and K. Hangos, *Dynamic analysis and control of chemical and biochemical reaction networks*, Proc. International Symposium on Advanced Control of Chemical Processes, Gramado (Brazil), April 2006, pp. 165–170.

[85] H. Öttinger, *Non-equilibrium thermodynamics - a tool for applied rheologists*, Applied Rheology **9**, 1999, pp. 17–26.

[86] R. H. Perry and D. W. Green, *Perry's Chemical Engineers' Handbook*, 7^{th} ed., McGraw-Hill, New York, 1997.

[87] H. Ramírez, D. Sbarbaro and R. Ortega, *On the control of non-linear processes: an IDA-PBC approach*, Journal of Process Control **19**, 2009, pp. 405–414.

[88] P. Rouchon and Y. Creff, *Geometry of the flash dynamics*, Chemical Engineering Science **48**(18), 1993, pp. 3141–3147.

[89] M. Ruszkowski, V. Garcia-Osorio and B. Ydstie, *Passivity based control of transport reaction systems*, AIChE Journal **51**(12), 2005, pp. 3147–3165.

[90] D. S. Sabo and J. S. Dranoff, *On the stability of a continuous flow stirred-tank reactor*, AIChE Journal **12**(6), 1966, pp. 1547–5905.

[91] S. I. Sandler, *Chemical and Engineering Thermodynamics*, 3^{rd} ed., John Wiley & Sons, New York, 1999.

[92] J. M. Tarbell, *A thermodynamic Liapunov function for the near equilibrium CSTR*, Chemical Engineering Science **32**(12), 1977, pp. 1471–1476.

[93] A. Uppal, W. H. Ray and A. B. Poore, *On the dynamic behavior of continuous stirred tank reactors*, Chemical Engineering Science **29**(4), 1974, pp. 967–985.

[94] A. Uppal, W. H. Ray and A. B. Poore, *The classification of the dynamic behavior of continuous stirred tank reactors–influence of reactor residence time*, Chemical Engineering Science **31**(3), 1976, pp. 205–214.

[95] A. van der Schaft, *Three decades of mathematical system theory*, Lecture Notes in Control and Information Sciences, vol. 135, ch. System Theory and Mechanics, pp. 426–452, Springer, Berlin, 1989.

[96] A. van der Schaft, *L_2-Gain and Passivity Techniques in Nonlinear Control*, Lecture Notes in Control and Information Science, vol. 218, Springer, New York, 1996.

[97] A. van der Schaft and B. Maschke, *The Hamiltonian formulation of energy conserving physical systems with external ports*, Archiv für Elektronik und Übertragungstechnik **49**(5/6), 1995, pp. 362–371.

[98] A. van der Schaft and B. Maschke, *Modelling and control of mechanical systems*, ch. Interconnected Mechanical systems. Part 1: Geometry of interconnection and implicit Hamiltonian systems, pp. 1–16, Imperial College Press, London, 1997.

[99] F. Viel, F. Jadot and G. Bastin, *Global stabilization of exothermic chemical reactors under input constraints*, Automatica **33**, 1997, pp. 1437–1448.

[100] F. Viel, F. Jadot and G. Bastin, *Robust feedback stabilization of chemical reactors*, IEEE Transactions on Automatic Control **42**(4), 1997, pp. 473–481.

[101] R. B. Warden, R. Aris and N. R. Amundson, *An analysis of chemical reactor stability and control–IX : Further investigations into the direct method of Lyapunov*, Chemical Engineering Science **19**(3), 1964, pp. 173–190.

[102] R. B. Warden, R. Aris and N. R. Amundson, *An analysis of chemical reactor stability and control–VIII : The direct method of Lyapunov. Introduction and applications to simple reactions in stirred vessels*, Chemical Engineering Science **19**(3), 1964, pp. 149–172.

[103] K. Wark, Jr. and D. E. Richards, *Thermodynamics*, 6^{th} ed., Mc Graw-Hill, Boston, 1999.

[104] J. C. Willems, *Dissipative dynamical systems, part I: General theory*, Archiv of Rational Mechanics and Analysis **45**, 1972, pp. 321–351.

[105] J. L. Willems, *Stability Theory of Dynamical Systems*, Nelson, New York, 1970.

[106] B. E. Ydstie, *Passivity based control via the second law*, Computers & Chemical Engineering **26**(7-8), 2002, pp. 1037–1048.

[107] B. E. Ydstie and A. Alonso, *Process systems and passivity via the Clausius-Planck inequality*, Systems & Control letters **30**, 1997, pp. 253–264.

Appendix A

List of publications

The symbol "" marks the preprints that have not been accepted for publication yet.*

On the thesis's first part

Journal articles

A. Favache and D. Dochain, *Thermodynamics and chemical systems stability: The CSTR case study revisited*, Journal of Process Control **19**(3), 2009, pp. 371-379.

Proceedings of peer-reviewed conferences

A. Favache, D. Dochain and B. Maschke, *Dynamic behaviour of the CSTR: a thermodynamic point of view*, Proc. European Symposium on Computer-Aided Process Engineering 2008, Lyon (France), June 2008.

A. Favache and D. Dochain, *Power-shaping control of an exothermic continuous stirred tank reactor (CSTR)*, Proc. International Symposium on Advanced Control of Chemical Processes 2009, Koç (Turkey), July 2009, pp. 101-110

A. Favache and D.Dochain, *Analysis and control of the exothermic continu-*

ous stirred tank reactor: the power-shaping approach, accepted for the 48^{th} IEEE Conference on Decision and Control 2009, Shanghai (China), December 2009.

On the thesis's second part

Journal articles

A. Favache, V. S. Dos Santos Martins, D. Dochain and B. Maschke, *Some properties of conservative port contact systems*, accepted for publication in IEEE Transactions on Automatic Control, 2009.

*A. Favache, D. Dochain and B. Maschke, *An entropy-based formulation of irreversible processes based on contact structures*, submitted to Journal of Chemical Engineering Science, 2009.

Proceedings of peer-reviewed conferences

A. Favache, B. Maschke and D. Dochain, *Contact structures: application to interconnected thermodynamical systems*, Proc. European Control Conference 2007, Kos (Greece), July 2007, pp. 4095-4102.

A. Favache, V. S. Dos Santos Martins, D. Dochain and B. Maschke, *Stability Properties of Contact Structure Dynamical Systems*, Proc. European Control Conference 2009, Budapest (Hungary), August 2009.

A. Favache, D. Dochain and B. Maschke, *A geometric perspective to open irreversible thermodynamic systems: GENERIC, Matrix and port-contact systems*, accepted for the 48^{th} IEEE Conference on Decision and Control 2009, Shanghai (China), December 2009.

Appendix B

Calculation details for (3.11)

In this appendix, we shall show how (3.11) is derived from the previous considerations.

From (3.6), we have:

$$
\begin{aligned}
& \left(\left.\frac{\partial^t \tilde{S}}{\partial X}\right|_{X} - \left.\frac{\partial^t \tilde{S}}{\partial X}\right|_{X^{in}} \right) \mathcal{F}_X^{in} \\
= & \begin{bmatrix} \frac{1}{T} - \frac{1}{T^{in}} \\ -\frac{\mu_A}{T} + \frac{\mu_A^{in}}{T^{in}} \\ -\frac{\mu_B}{T} + \frac{\mu_B^{in}}{T^{in}} \\ -\frac{\mu_I}{T} + \frac{\mu_I^{in}}{T^{in}} \end{bmatrix}^t \begin{bmatrix} q_l \mathscr{C}_p^{in} \left(T^{in} - T_0\right) + q_l \left(C_A^{in} h_{0_A} + C_I h_{0_I}\right) \\ q_l C_A^{in} \\ 0 \\ q_l C_I \end{bmatrix} \\
= & \left(\frac{1}{T} - \frac{1}{T^{in}}\right) q_l \mathscr{C}_p^{in} \left(T^{in} - T_0\right) \\
& + \left(\frac{1}{T} - \frac{1}{T^{in}}\right) q_l C_A^{in} h_{0_A} + \left(\frac{1}{T} - \frac{1}{T^{in}}\right) q_l C_I h_{0_I} \\
& + \left(-\frac{\mu_A}{T} + \frac{\mu_A^{in}}{T^{in}}\right) q_l C_A^{in} + \left(-\frac{\mu_I}{T} + \frac{\mu_I^{in}}{T^{in}}\right) q_l C_I
\end{aligned}
\tag{B.1}
$$

In an ideal liquid mixture, the chemical potential of species i is given as follows (see (3.9)):

$$
\frac{\mu_i}{T} = -C_{p_i} \ln\left(\frac{T}{T_0}\right) + R \ln\left(\frac{n_i}{N}\right) - s_{i_0} + C_{p_i} \frac{T - T_0}{T} + \frac{h_{0_i}}{T}
$$

so that we can write the following relation:

$$\begin{aligned}
-\frac{\mu_i}{T}+\frac{\mu_i^{in}}{T^{in}} &= C_{p_i}\ln\left(\frac{T}{T_0}\right)-R\ln\left(\frac{n_i}{N}\right)+s_{0_i}-C_{p_i}\frac{T-T_0}{T}-\frac{h_{0_i}}{T}\\
&\quad -C_{p_i}\ln\left(\frac{T^{in}}{T_0}\right)+R\ln\left(\frac{C_i^{in}}{C_A^{in}+C_I}\right)-s_{0_i}\\
&\quad +C_{p_i}\frac{T^{in}-T_0}{T^{in}}+\frac{h_{0_i}}{T^{in}}\\
&= C_{p_i}\ln\left(\frac{T}{T^{in}}\right)+R\left[\ln\left(\frac{C_i^{in}}{C_A^{in}+C_I}\right)-\ln\left(\frac{n_i}{N}\right)\right]\\
&\quad -C_{p_i}\left(\frac{T-T_0}{T}-\frac{T^{in}-T_0}{T^{in}}\right)-\left(\frac{1}{T}-\frac{1}{T^{in}}\right)h_{0_i} \qquad \text{(B.2)}
\end{aligned}$$

As a consequence the terms in h_{0_A} and h_{0_I} are canceled out when replacing (B.2) into (B.1). (B.1) can be written as follows:

$$\begin{aligned}
&\left(\left.\frac{\partial^t\tilde{S}}{\partial X}\right|_X-\left.\frac{\partial^t\tilde{S}}{\partial X}\right|_{X^{in}}\right)\mathcal{F}_X^{in}\\
= &\left(\frac{1}{T}-\frac{1}{T^{in}}\right)q_l\mathscr{C}_p^{in}\left(T^{in}-T_0\right)\\
&-q_l\left(C_{p_A}C_A^{in}+C_{p_I}C_I\right)\left(\frac{T-T_0}{T}-\frac{T^{in}-T_0}{T^{in}}\right)\\
&+q_lC_A^{in}\left[C_{p_A}\ln\left(\frac{T}{T^{in}}\right)+R\left[\ln\left(\frac{C_A^{in}}{C_A^{in}+C_I}\right)-\ln\left(\frac{n_A}{N}\right)\right]\right]\\
&+q_lC_i^{in}\left[C_{p_i}\ln\left(\frac{T}{T^{in}}\right)+R\left[\ln\left(\frac{C_I}{C_A^{in}+C_I}\right)-\ln\left(\frac{n_I}{N}\right)\right]\right] \qquad \text{(B.3)}
\end{aligned}$$

Let us consider the first two terms. As defined in (2.4), the constant pressure volumetric heat capacity of the inlet is given by the following relation:

$$\mathscr{C}_p^{in}=C_A^{in}C_{p_A}+C_IC_{p_I}$$

The two first terms of (B.3) can be rewritten as follows:

$$\begin{aligned}
& \left(\frac{1}{T}-\frac{1}{T^{in}}\right) q_l \mathscr{C}_p^{in}\left(T^{in}-T_0\right) \\
& -q_l\left(C_{p_A} C_A^{in}+C_{p_I} C_I\right)\left(\frac{T-T_0}{T}-\frac{T^{in}-T_0}{T^{in}}\right) \\
= \; & q_l \mathscr{C}_p^{in}\left(\frac{T^{in}}{T}-\frac{T_0}{T}-1+\frac{T_0}{T^{in}}-1+\frac{T_0}{T}+1-\frac{T_0}{T^{in}}\right) \\
= \; & q_l \mathscr{C}_p^{in}\left(\frac{T^{in}-T}{T}\right)
\end{aligned}$$

As a consequence we finally have:

$$\begin{aligned}
& \left(\left.\frac{\partial^t \tilde{S}}{\partial X}\right|_X-\left.\frac{\partial^t \tilde{S}}{\partial X}\right|_{X^{in}}\right) \mathcal{F}_X^{in} \\
= \; & q_l \mathscr{C}_p^{in}\left(\frac{T^{in}-T}{T}\right) \\
& +q_l C_A^{in}\left[C_{p_A} \ln\left(\frac{T}{T^{in}}\right)+R\left[\ln\left(\frac{C_A^{in}}{C_A^{in}+C_I}\right)-\ln\left(\frac{n_A}{N}\right)\right]\right] \\
& +q_l C_I^{in}\left[C_{p_I} \ln\left(\frac{T}{T^{in}}\right)+R\left[\ln\left(\frac{C_I}{C_A^{in}+C_I}\right)-\ln\left(\frac{n_I}{N}\right)\right]\right] \\
= \; & q_l \mathscr{C}_p^{in}\left[\frac{T^{in}-T}{T}+\ln\left(\frac{T}{T^{in}}\right)\right] \\
& +q_l R C_A^{in}\left[\ln\left(\frac{C_A^{in}}{C_I+C_A^{in}}\right)-\ln\left(\frac{n_A}{N}\right)\right] \\
& +q_l R C_I\left[\ln\left(\frac{C_I}{C_I+C_A^{in}}\right)-\ln\left(\frac{n_I}{N}\right)\right]
\end{aligned}$$

which is indeed the relation given in (3.11).

Appendix C

Numerical values used for the simulations

In this appendix, we give the numerical values which have been used to generate the graphs of Chapter 4.

The temperature dependence of the kinetics have been chosen to be of Arrhenius type, i.e.:

$$k\left(T\right) = k_0 e^{-\frac{A}{T}}$$

The following numerical values are common to all the figures of the chapter (except Figure 4.2 which is schematic):

Parameter	**Value**	**Parameter**	**Value**
V	100 l	C_A^{in}	1 $^{\text{mol}}/_{\text{l}}$
q_l	100 $^{\text{l}}/_{\text{min}}$	T_w	350 K [1]
k_0	$10^4\,\text{min}^{-1}$	T^{in}	293,15 K
A	$4 \cdot 10^3$ K	$\mathscr{C}_p$	1 $^{\text{J}}/_{\text{l}\cdot\text{K}}$
$(-\Delta_r H)$	$-2,8 \cdot 10^5\,^{\text{J}}/_{\text{mol}}$		

[1] Except in Figure 4.6 where $T_w = 290$ K.

With these numerical values, the open-loop system has three equilibria at the following states:

	$\bar{n}_A$	$\bar{T}$
low temperature stable equilibrium $\left(\bar{n}_{A_1}, \bar{T}_1\right)$	98,6 mol	297,1 K
intermediate unstable equilibrium $\left(\bar{n}_{A_2}, \bar{T}_2\right)$	48,7 mol	436,7 K
high temperature stable equilibrium $\left(\bar{n}_{A_3}, \bar{T}_3\right)$	16,6 mol	526,8 K

In all the figures, the parameter q_{12} has been set equal to -0,1 and the parameter α has been set equal to 0,5 (except in Figure 4.8). The other values are specific to each figure and are listed below:

Figure	ω	**Set point**	**Initial conditions**	
		T^*	$n_A(0)$	$T(0)$
Figure 4.1	-	-	-	-
Figure 4.3	[0; 0,25; 0,3; 0,4; 1]	450 K	-	-
Figure 4.4	0,3	480 K	-	-
Figure 4.5	10	480 K	-	-
Figure 4.6	0,3	480 K	30 mol	[420 K; 530 K]
Figure 4.7	[0,5; 1; 1,5; 2; 3]	480 K	40 mol	450 K
Figure 4.8	5	480 K	40 mol	450 K
Figure 4.9	5	480 K	40 mol	450 K
Figure 4.10	5	480 K	40 mol	465 K
Figure 4.11	3	480 K	0 mol	460 K

Furthermore in Figure 4.6, the lower and upper bounds on the input u_c have been set to 0 and $2\,u_c^*$, respectively. In Figure 4.9, the modelling error is on the activation energy A of the Arrhenius law. The converging curves correspond to 10% (blue), 5% (green) and -10% error (cyan) on A whereas the diverging curve corresponds to -18% error on A. In Figure 4.11, the errors on n_A^* and u_c^* are respectively 10% and 5%. The integral gain τ_I was set equal to -300.

Appendix D

The Brayton-Moser formulation of the CSTR: some particular cases

In this appendix, we shall present in details the solution of the algebraic equation system given by the equations (4.17a) and (4.17b) in some particular cases. The obtained matrix $\boldsymbol{Q}(x)$ can then be used to express the dynamics using the Brayton-Moser formulation, and consequently to find a Lyapunov function for the open-loop system or to apply the power-shaping control methodology. We shall consider successively the particular cases of parallel reactions, of one reaction with two reacting species and of consecutive reactions.

D.1 Parallel reactions

The reaction scheme is given as follows[1]:

$$\begin{array}{ll} A & \overset{r_1(n_A,T)}{\rightarrow} \quad \ldots \\ A & \overset{r_2(n_A,T)}{\rightarrow} \quad \ldots \end{array}$$

with $r_1(n_A,T) = k_1(T)\,\phi^{(1)}(n_A)$ and $r_2(n_A,T) = k_2(T)\,\phi^{(2)}(n_A)$.

In this case, (4.17b) is given by the following equation[2]:

$$\begin{aligned} &-\frac{q_l}{V}q_{12}(n_A) + \phi^{(1)}(n_A)\frac{dk_1}{dT}\left(-q_{11}(n_A) + \gamma_1 q_{12}(n_A)\right) \\ &+ \phi^{(2)}(n_A)\frac{dk_2}{dT}\left(-q_{11}(n_A) + \gamma_2 q_{12}(n_A)\right) \\ &= -\frac{q_l}{V}q_{21}(T) + k_1(T)\frac{d\phi^{(1)}}{dn_A}\left(-q_{21}(T) + q_{22}(T)\,\gamma_1\right) \\ &+ k_2(T)\frac{d\phi^{(2)}}{dn_A}\left(-q_{21}(T) + q_{22}(T)\,\gamma_2\right) \end{aligned} \tag{D.1}$$

By taking the limit of (D.1) for T tending to zero, we find that the following relation has to be satisfied:

$$\begin{aligned} -\frac{q_l}{V}q_{12}(n_A) = -\frac{q_l}{V}\lim_{T\to 0} q_{21}(T) &+ \frac{\partial\phi^{(1)}}{\partial n_A}\lim_{T\to 0}\left[k_1(T)\left(-q_{21}(T) + q_{22}(T)\,\gamma_1\right)\right] \\ &+ \frac{\partial\phi^{(2)}}{\partial n_A}\lim_{T\to 0}\left[k_2(T)\left(-q_{21}(T) + q_{22}(T)\,\gamma_2\right)\right] \end{aligned}$$

This implies obviously that $q_{12}(n_A)$ has to be of the following form:

$$q_{12}(n_A) = \alpha + \beta_1\frac{\partial\phi^{(1)}}{\partial n_A} + \beta_2\frac{\partial\phi^{(2)}}{\partial n_A} \tag{D.2}$$

with

$$\begin{aligned} \alpha &= \lim_{T\to 0} q_{21}(T) \\ -\frac{q_l}{V}\beta_1 &= \lim_{T\to 0}\left[k_1(T)\left(-q_{21}(T) + q_{22}(T)\,\gamma_1\right)\right] \\ -\frac{q_l}{V}\beta_2 &= \lim_{T\to 0}\left[k_2(T)\left(-q_{21}(T) + q_{22}(T)\,\gamma_2\right)\right] \end{aligned}$$

[1] It is always possible to normalize the stoichiometric coefficients so that the coefficient of species A is equal to 1 in the two reactions.

[2] (4.17a) does not exist in this case because $N_c = 1$.

Assumption D.1. The functions $\phi^{(1)}(n_A)$ and $\phi^{(2)}(n_A)$ are powers of n_A as follows ($\zeta_1, \zeta_2 \in \mathbb{R}^{*+}$):

$$\begin{aligned}\phi^{(1)}(n_A) &= (n_A)^{\zeta_1} \\ \phi^{(2)}(n_A) &= (n_A)^{\zeta_2}\end{aligned}$$

Remark D.1. *This assumption obviously restricts the class of considered kinetics. But it still encompasses a large class of chemical reactions, and in particular those which follow the mass action law kinetics.*

By taking Assumption D.1 into account, (D.2) becomes as follows:

$$q_{12}(n_A) = \alpha + \beta_1\zeta_1 (n_A)^{\zeta_1 - 1} + \beta_2\zeta_2 (n_A)^{\zeta_2 - 1}$$

This relation can be inserted into (D.1):

$$\begin{aligned}&- \frac{q_l}{V}\alpha - \frac{q_l}{V}\beta_1\zeta_1 (n_A)^{\zeta_1-1} - \frac{q_l}{V}\beta_2\zeta_2 (n_A)^{\zeta_2-1} \\ &+ (n_A)^{\zeta_1}\frac{dk_1}{dT}\left(-q_{11}(n_A) + \gamma_1\alpha + \gamma_1\beta_1\zeta_1 (n_A)^{\zeta_1-1} + \gamma_1\beta_2\zeta_2 (n_A)^{\zeta_2-1}\right) \\ &+ (n_A)^{\zeta_2}\frac{dk_2}{dT}\left(-q_{11}(n_A) + \gamma_2\alpha + \gamma_2\beta_1\zeta_1 (n_A)^{\zeta_1-1} + \gamma_2\beta_2\zeta_2 (n_A)^{\zeta_2-1}\right) \\ &= -\frac{q_l}{V}q_{21}(T) + k_1(T)\zeta_1 (n_A)^{\zeta_1-1}(-q_{21}(T) + \gamma_1 q_{22}(T)) \\ &+ k_2(T)\zeta_2 (n_A)^{\zeta_2-1}(-q_{21}(T) + \gamma_2 q_{22}(T))\end{aligned} \tag{D.3}$$

or by regrouping the terms of same power on the left-hand side:

$$\begin{aligned}&- \frac{q_l}{V}\alpha - \frac{q_l}{V}\beta_1\zeta_1 (n_A)^{\zeta_1-1} - \frac{q_l}{V}\beta_2\zeta_2 (n_A)^{\zeta_2-1} + \gamma_1\alpha\frac{dk_1}{dT}(n_A)^{\zeta_1} \\ &+ \gamma_2\alpha\frac{\partial k_2}{\partial T}(n_A)^{\zeta_2} + \gamma_1\beta_1\zeta_1\frac{dk_1}{dT}(n_A)^{2\zeta_1-1} + \gamma_2\beta_2\zeta_2\frac{dk_2}{dT}(n_A)^{2\zeta_2-1} \\ &+ (n_A)^{\zeta_1+\zeta_2-1}\left(\gamma_1\beta_2\zeta_2\frac{dk_1}{dT} + \gamma_2\beta_1\zeta_1\frac{dk_2}{dT}\right) \\ &- q_{11}(n_A)\left((n_A)^{\zeta_1}\frac{dk_1}{dT} + (n_A)^{\zeta_2}\frac{dk_2}{dT}\right) \\ &= -\frac{q_l}{V}q_{21}(T) + k_1(T)\zeta_1 (n_A)^{\zeta_1-1}(-q_{21}(T) + \gamma_1 q_{22}(T)) \\ &+ k_2(T)\zeta_2 (n_A)^{\zeta_2-1}(-q_{21}(T) + \gamma_2 q_{22}(T))\end{aligned}$$

On the left-hand side, there is a term of power $\zeta_1 + \zeta_2 - 1$, but there is no corresponding term on the right-hand side. As a consequence the following relation has to be fulfilled:

$$\gamma_2 \beta_1 \zeta_1 \frac{dk_2}{dT} = -\gamma_1 \beta_2 \zeta_2 \frac{dk_1}{dT} \tag{D.4}$$

There is no reason in general for $\frac{dk_2}{dT}$ to be proportional to $\frac{dk_1}{dT}$, and therefore the only possibility is to set $\beta_1 = \beta_2 = 0$. As a consequence q_{12} is a constant and (D.3) becomes as follows:

$$\begin{aligned} &- \frac{q_l}{V} q_{12} - q_{11}(n_A)\, n_A \left((n_A)^{\zeta_1 - 1} \frac{dk_1}{dT} + (n_A)^{\zeta_2 - 1} \frac{dk_2}{dT} \right) \\ &+ q_{12} n_A \left(\gamma_1 (n_A)^{\zeta_1 - 1} \frac{dk_1}{dT} + \gamma_2 (n_A)^{\zeta_2 - 1} \frac{dk_2}{dT} \right) \\ = &- \frac{q_l}{V} q_{21}(T) + \zeta_1 k_1(T) (n_A)^{\zeta_1 - 1} (-q_{21}(T) + q_{22}(T) \gamma_1) \\ &+ \zeta_2 k_2(T) (n_A)^{\zeta_2 - 1} (-q_{21}(T) + q_{22}(T) \gamma_2) \end{aligned} \tag{D.5}$$

There exist different solutions of the above equation depending on the values of ζ_1 and ζ_2.

Case 1: $\zeta_1 \neq 1$ and $\zeta_2 \neq 1$, with $\zeta_1 \neq \zeta_2$

The relation (D.5) has to be fulfilled for any values (n_A, T) and in particular for $n_A = 0$. Since $\zeta_1 - 1 \neq 0$, (D.5) becomes as follows when setting n_A equal to zero:

$$-\frac{q_l}{V} q_{12} = -\frac{q_l}{V} q_{21}(T)$$

This obviously implies that $q_{21}(T)$ is a constant with $q_{12} = q_{21}$. Using this result, (D.5) can now be written as follows:

$$\begin{aligned} &- q_{11}(n_A)\, n_A \left((n_A)^{\zeta_1 - 1} \frac{dk_1}{dT} + (n_A)^{\zeta_2 - 1} \frac{dk_2}{dT} \right) \\ &+ q_{12} n_A \left(\gamma_1 (n_A)^{\zeta_1 - 1} \frac{dk_1}{dT} + \gamma_2 (n_A)^{\zeta_2 - 1} \frac{dk_2}{dT} \right) \\ = &\zeta_1 k_1(T) (n_A)^{\zeta_1 - 1} (-q_{21} + q_{22}(T) \gamma_1) \\ &+ \zeta_2 k_2(T) (n_A)^{\zeta_2 - 1} (-q_{21} + q_{22}(T) \gamma_2) \end{aligned} \tag{D.6}$$

The only possibility for obtaining the same dependence on n_A in both sides of (D.6) is to set $q_{12} = 0$ and $q_{11}(n_A) = -\frac{\omega}{n_A}$, where $\omega \in \mathbb{R}^*$. Since $q_{21} = q_{12} = 0$, (D.6) becomes now as follows:

$$\omega\left((n_A)^{\zeta_1-1}\frac{dk_1}{dT} + (n_A)^{\zeta_2-1}\frac{dk_2}{dT}\right) = \zeta_1 k_1(T)(n_A)^{\zeta_1-1} q_{22}(T)\gamma_1 + \zeta_2 k_2(T)(n_A)^{\zeta_2-1} q_{22}(T)\gamma_2$$

This equality is satisfied if and only if the following relations are fulfilled:

$$\begin{aligned}\omega\frac{dk_1}{dT} &= \zeta_1\gamma_1 k_1(T) q_{22}(T)\\ \omega\frac{dk_2}{dT} &= \zeta_2\gamma_2 k_2(T) q_{22}(T)\end{aligned}$$

It is obvious that these relations can be fulfilled with $\omega \neq 0$ and $q_{22}(T) \neq 0$ only in the very particular cases where:

$$\frac{dk_1}{dT}\frac{1}{\zeta_1\gamma_1 k_1(T)} = \frac{dk_2}{dT}\frac{1}{\zeta_2\gamma_2 k_2(T)}$$

However in the general case, the above relations can be fulfilled only if $\omega = 0$ and $q_{22}(T) = 0$, but then the matrix $\boldsymbol{Q}(n_A, T)$ is the null-matrix.

Case 2: $\zeta_1 \neq 1$ and $\zeta_2 \neq 1$, with $\zeta_1 = \zeta_2$

Case 2 is the same as Case 1 and (D.6) has also to be fulfilled. Nevertheless in this particular case (D.6) is written as follows:

$$\begin{aligned}&-q_{11}(n_A)\,n_A\,(n_A)^{\zeta_1-1}\left(\frac{dk_1}{dT}+\frac{dk_2}{dT}\right) + q_{12}n_A\,(n_A)^{\zeta_1-1}\left(\gamma_1\frac{dk_1}{dT}+\gamma_2\frac{dk_2}{dT}\right)\\ &= \zeta_1(n_A)^{\zeta_1-1}\left[k_1(T)\left(-q_{21}+q_{22}(T)\gamma_1\right) + k_2(T)\left(-q_{21}+q_{22}(T)\gamma_2\right)\right]\end{aligned} \tag{D.7}$$

The only possibility for obtaining the same dependence on n_A in both sides of (D.7) is to set $q_{12} = 0$ and $q_{11}(n_A) = -\frac{\omega}{n_A}$, where $\omega \in \mathbb{R}^*$. Since $q_{21} = q_{12} = 0$, (D.7) becomes now as follows (by dividing by $(n_A)^{\zeta_1-1}$):

$$\omega\left(\frac{dk_1}{dT}+\frac{dk_2}{dT}\right) = \zeta_1\left[k_1(T)\,q_{22}(T)\,\gamma_1 + k_2(T)\,q_{22}(T)\,\gamma_2\right]$$

and the corresponding matrix $\boldsymbol{Q}(n_A, T)$ is given by the following expression:

$$\boldsymbol{Q}(n_A, T) = \begin{pmatrix} -\frac{\omega}{n_A} & 0 \\ 0 & \frac{\omega}{\zeta_1}\left(\frac{dk_1}{dT} + \frac{dk_2}{dT}\right)\left[k_1(T)\gamma_1 + k_2(T)\gamma_2\right]^{-1} \end{pmatrix}$$

It can be seen immediately that this matrix is indefinite if γ_1 and γ_2 are both positive, i.e. if both reactions are exothermic. If both reactions are endothermic, $\boldsymbol{Q}(n_A, T)$ is negative definite for $\omega > 0$. If γ_1 and γ_2 have different signs, $\boldsymbol{Q}(n_A, T)$ can be either indefinite or negative definite depending on the numerical values of the parameters.

Case 3: $\zeta_1 = 1$

In this case (D.5) becomes as follows:

$$\begin{aligned} &-\frac{q_l}{V}q_{12} - q_{11}(n_A)\, n_A\left(\frac{dk_1}{dT} + (n_A)^{\zeta_2 - 1}\frac{dk_2}{dT}\right) \\ &+ q_{12} n_A\left(\gamma_1\frac{dk_1}{dT} + \gamma_2(n_A)^{\zeta_2 - 1}\frac{dk_2}{dT}\right) \\ &= -\frac{q_l}{V}q_{21}(T) + k_1(T)\left(-q_{21}(T) + q_{22}(T)\gamma_1\right) \\ &+ \zeta_2 k_2(T)(n_A)^{\zeta_2 - 1}\left(-q_{21}(T) + q_{22}(T)\gamma_2\right) \end{aligned}$$

The same dependence on n_A in the two sides of the above equation is obtained by choosing the elements of $\boldsymbol{Q}(n_A, T)$ as follows:

$$\begin{aligned} q_{11}(n_A) &= -\frac{\omega}{n_A} \\ q_{12} &= 0 \\ \omega\frac{dk_1}{dT} &= -q_{21}(T)\left(k_1(T) + \frac{q_l}{V}\right) + q_{22}(T)\gamma_1 k_1(T) \\ \omega\frac{dk_2}{dT} &= \zeta_2 k_2(T)\left(-q_{21}(T) + q_{22}(T)\gamma_2\right) \end{aligned}$$

where $\omega \in \mathbb{R}^*$. The corresponding matrix is given as follows:

$$\boldsymbol{Q}(n_A, T) = \begin{pmatrix} -\frac{\omega}{n_A} & 0 \\ q_{21}(T) & q_{22}(T) \end{pmatrix}$$

with

$$\begin{aligned} q_{21}(T) &= \frac{\omega}{\zeta_2 k_2\left[-\frac{q_l}{V}\gamma_2 + k_1(\gamma_1-\gamma_2)\right]}\left(\zeta_2\gamma_2 k_2(T)\frac{dk_1}{dT} - \gamma_1 k_1(T)\frac{dk_2}{dT}\right) \\ q_{22}(T) &= \frac{\omega}{\zeta_2 k_2\left[-\frac{q_l}{V}\gamma_2 + k_1(\gamma_1-\gamma_2)\right]}\left(\zeta_2 k_2(T)\frac{dk_1}{dT} - \left(\frac{q_l}{V}+k_1(T)\right)\frac{dk_2}{dT}\right) \end{aligned}$$

A necessary condition for the symmetric part of $\boldsymbol{Q}(n_A, T)$ to be negative semi-definite is given by the following relation:

$$\begin{aligned} 0 &\geq \operatorname{tr}\left(\boldsymbol{Q}(n_A,T) + \boldsymbol{Q}^t(n_A,T)\right) \\ &= -\frac{2\omega}{n_A} + \frac{2\omega}{\zeta_2 k_2\left[-\frac{q_l}{V}\gamma_2 + k_1(\gamma_1-\gamma_2)\right]}\left(\zeta_2 k_2(T)\frac{dk_1}{dT} - \left(\frac{q_l}{V}+k_1(T)\right)\frac{dk_2}{dT}\right) \end{aligned}$$

The first term of the sum is obviously negative if $\omega > 0$. Nothing can be said in general about the second term because it depends on the numerical parameters of the two reactions, namely their reaction heat, their kinetic coefficient and on the dilution rate $\frac{q_l}{V}$.

There exists a function $\mathscr{P}(n_A, T)$ such that the dynamics of the system can be written in the Brayton-Moser form (4.1). But the condition (4.2) on the negativity of the symmetric part of the matrix given cannot be guaranteed anymore. The potential function $\mathscr{P}(n_A, T)$ may be non-decreasing along the system trajectories and consequently cannot be used as a Lyapunov function for the open-loop system.

Remark D.2. *If $\zeta_1 = \zeta_2 = 1$, condition* (D.4) *is only sufficient and not necessary. Indeed the following non-singular matrix is then another solution of* (D.3) *(with $q_{12} \neq 0$):*

$$\boldsymbol{Q}(n_A,T) = \begin{pmatrix} \gamma_1 q_{12} & q_{12} \\ \frac{[\gamma_1 k_1(T)+\gamma_2 k_2(T)]q_{22}(T)+\frac{q_l}{V}q_{12}}{\frac{q_l}{V}+k_1(T)+k_2(T)} & q_{22}(T) \end{pmatrix}$$

One may note the similarity with the form of the matrix proposed in Lemma 4.1. This seems to indicate that the matrix $\boldsymbol{Q}(n_A, T)$ that has been used in Chapter 4 is a particular solution of (4.20) *that exists only in the case of first-order kinetics.*

Conclusion

As a conclusion, we have found a solution to (4.15) only in the case where at least one of the kinetics is of the first order or if the reactions are of the same order. However the obtained matrix may have a non-negative symmetric part. In the more general case (4.15) has no non-trivial solution. This does not mean that the dynamics cannot be put into the Brayton-Moser form. But if the Brayton-Moser form exists, then the relation (4.14) is not fulfilled and the partial differential equation (4.13) has to be solved.

D.2 Reaction with 2 reactants

The reaction scheme is given as follows:

$$A + \nu_B B \overset{r(T,n_A,n_B)}{\rightarrow} \dots$$

where ν_B is the stoichiometric coefficient of the species B.

In this case, (4.17a) and (4.17b) are given by the following equations:

- for $i = 1$ and $j = 2$:

$$\begin{aligned} &-\frac{q_l}{V} q_{12}(n_A) + k(T)\,\phi_A(n_A)\,\frac{d\phi_B}{dn_B}\left(-q_{11}(n_A) - \nu_B q_{12}(n_A) + \gamma q_{13}(n_A)\right) \\ &= -\frac{q_l}{V} q_{21}(n_B) + k(T)\,\phi_B(n_B)\,\frac{d\phi_A}{dn_A}\left(-q_{21}(n_B) - \nu_B q_{22}(n_B) + \gamma q_{23}(n_A)\right) \end{aligned} \tag{D.8a}$$

- for $i = 1$ and $j = 3$:

$$\begin{aligned} &-\frac{q_l}{V} q_{13}(n_A) + \phi_A(n_A)\,\phi_B(n_B)\,\frac{dk}{dT}\left(-q_{11}(n_A) - \nu_B q_{12}(n_A) + \gamma q_{13}(n_A)\right) \\ &= -\frac{q_l}{V} q_{31}(T) + k(T)\,\phi_B(n_B)\,\frac{d\phi_A}{dn_A}\left(-q_{31}(T) - \nu_B q_{32}(T) + \gamma q_{33}(T)\right) \end{aligned} \tag{D.8b}$$

- for $i = 2$ and $j = 3$:

$$\begin{aligned} &-\frac{q_l}{V} q_{23}(n_B) + \phi_A(n_A)\,\phi_B(n_B)\,\frac{dk}{dT}\left(-q_{21}(n_B) - q_{22}(n_B) + \gamma q_{23}(n_B)\right) \\ &= -\frac{q_l}{V} q_{32}(T) + k(T)\,\phi_A(n_A)\,\frac{d\phi_B}{dn_B}\left(-q_{31}(T) - \nu_B q_{32}(T) + \gamma q_{33}(T)\right) \end{aligned} \tag{D.8c}$$

By taking the limit for T tending to zero of (D.8a), we find that the following relation has to be fulfilled:

$$-\frac{q_l}{V}q_{12}\left(n_A\right) = -\frac{q_l}{V}q_{21}\left(n_B\right) \tag{D.9}$$

This relation implies that q_{12} and q_{21} have to be constants. Moreover we have $q_{12} = q_{21}$. (D.8b) and (D.8c) have to be satisfied for any (n_A, n_B, T) and in particular if $n_A = 0$ or $n_B = 0$. As a consequence, by taking (D.8b) (resp. (D.8c)) at n_B (resp. n_A) equal to 0, we find that the following relations have to be fulfilled[1]:

$$-\frac{q_l}{V}q_{13}\left(n_A\right) = -\frac{q_l}{V}q_{31}\left(T\right) \tag{D.10}$$

$$-\frac{q_l}{V}q_{23}\left(n_B\right) = -\frac{q_l}{V}q_{32}\left(T\right) \tag{D.11}$$

Thus q_{13}, q_{23}, q_{31} and q_{32} have to be constants with $q_{13} = q_{31}$ and $q_{23} = q_{32}$.

Remark D.3. *An immediate consequence of* (D.9)*,* (D.10) *and* (D.11) *is that the matrix* $\boldsymbol{Q}\left(n_A, n_B, T\right)$ *that solves the equations* (D.8a) *to* (D.8c) *is symmetric.*

Let us now consider the following assumption on the reaction kinetics:

Assumption D.2. The functions $\phi_A\left(n_A\right)$ and $\phi_B\left(n_B\right)$ are powers of n_A and n_B, respectively, as follows $(\zeta_A, \zeta_B \in \mathbb{R}^{*+})$:

$$\begin{aligned}\phi_A\left(n_A\right) &= \left(n_A\right)^{\zeta_A}\\ \phi_B\left(n_A\right) &= \left(n_B\right)^{\zeta_B}\end{aligned}$$

Remark D.4. *The above assumption is the analogue of Assumption D.1 in the case of parallel reactions.*

Using the above assumption, (D.8b) can be written as follows:

$$\begin{aligned}&\left(n_A\right)^{\zeta_A}\frac{dk}{dT}\left(-q_{11}\left(n_A\right) - \nu_B q_{12} + \gamma q_{13}\right)\\ &= \zeta_A k\left(T\right)\left(n_A\right)^{\zeta_A - 1}\left(-q_{13} - \nu_B q_{23} + \gamma q_{33}\left(T\right)\right)\end{aligned}$$

[1]Indeed from Assumption 4.4, $\phi_A\left(0\right) = 0$ and $\phi_B\left(0\right) = 0$.

A possible solution of this equation is given by the following relations:

$$\begin{aligned} q_{11}(n_A) &= -\frac{\omega\zeta_A}{n_A} \\ \nu_B q_{12} &= \gamma q_{13} \\ \omega\frac{dk}{dT} &= k(T)\left(-q_{13} - \nu_B q_{22} + \gamma q_{33}(T)\right) \end{aligned}$$

Remark D.5. *Actually this is the unique non-singular solution. Indeed there are two possibilities to obtain the same dependence on n_A in both sides. The first one is the above solution, the other one is to set:*

$$q_{11}(n_A) = -\nu_B q_{12} + \gamma q_{13}$$

which implies obviously:

$$\gamma q_{33}(T) = q_{13} + \nu_B q_{23}$$

(D.8c) *becomes then as follows:*

$$\begin{aligned} &(n_B)^{\zeta_B}\frac{dk}{dT}\left(-q_{21} - \nu_B q_{22}(n_B) + \gamma q_{23}\right) \\ &= \zeta_B (n_B)^{\zeta_B - 1} k(T)\left(-q_{13} - \nu_B q_{23} + \gamma q_{33}\right) = 0 \end{aligned}$$

and hence:

$$q_{12} = q_{21} = -\nu_B q_{22}(n_B) + \gamma q_{23}$$

and

$$q_{11} = \gamma q_{13} - \nu_B\left(-\nu_B q_{22} + \gamma q_{23}\right)$$

The obtained matrix has the following form:

$$\begin{aligned} &\boldsymbol{Q}(n_A, n_B, T) \\ &= \begin{pmatrix} \gamma q_{13} - \nu_B\left(-\nu_B q_{22} + \gamma q_{23}\right) & -\nu_B q_{22} + \gamma q_{23} & q_{13} \\ -\nu_B q_{22} + \gamma q_{23} & q_{22} & q_{23} \\ q_{13} & q_{23} & \frac{1}{\gamma}\left(q_{13} + \nu_B q_{23}\right) \end{pmatrix} \end{aligned}$$

The third line is a linear combination of the first two and this matrix is obviously singular.

As a consequence (D.8c) becomes as follows:

$$\begin{aligned}&(n_B)^{\zeta_B}\,\frac{dk}{dT}\left(-q_{21}-\nu_B q_{22}\left(n_B\right)+\gamma q_{23}\right)\\ =\;&\zeta_B\left(n_B\right)^{\zeta_B-1}\omega\frac{dk}{dT}\end{aligned}$$

A possible solution of this equation is given by the following relations:

$$\begin{aligned}q_{22}\left(n_B\right) &= -\frac{\omega\zeta_B}{\nu_B n_B}\\ q_{21} &= \gamma q_{23}\end{aligned}$$

Finally the matrix $\boldsymbol{Q}\left(n_A,n_B,T\right)$ is given as follows:

$$\boldsymbol{Q}\left(n_A,n_B,T\right)=\begin{pmatrix}-\frac{\omega\zeta_A}{n_A} & \gamma q_{23} & \nu_B q_{23}\\ \gamma q_{23} & -\frac{\omega\zeta_B}{\nu_B n_B} & q_{23}\\ \nu_B q_{23} & q_{23} & \frac{1}{\gamma}\left(\omega\frac{1}{k(T)}\frac{dk}{dT}+2\nu_B q_{23}\right)\end{pmatrix} \tag{D.12}$$

A necessary condition for this symmetric matrix to be negative semi-definite is given as follows[1]:

$$\begin{aligned}-\frac{\omega\zeta_A}{n_A} &\leq 0 \quad \Rightarrow \omega>0\\ \frac{\omega^2\zeta_A\zeta_B}{\nu_B n_A n_B}-\gamma^2 q_{23}^2 &\geq 0\end{aligned}$$

The second condition cannot be fulfilled for any pair (n_A,n_B) and the above matrix is not negative semi-definite in the whole phase plane.

In this case the dynamics of the system can be written in the Brayton-Moser form (4.1). But the matrix given in (D.12) is not negative semi-definite. The comment is consequently the same as for the case with parallel reactions.

D.3 Consecutive reactions

The reaction scheme is given as follows:

$$\begin{aligned}A &\overset{r_1(n_A,T)}{\rightarrow} \nu_B\quad B+\ldots\\ B &\overset{r_2(n_B,T)}{\rightarrow}\quad \ldots\end{aligned}$$

[1] We consider the principal minors of the matrix.

We assume that the second reaction does not produce A. This implies in particular that we do not consider here the case of reversible reactions.

In this particular case, (4.17a) and (4.17b) are given by the following equations:

- for $i = 1$ and $j = 2$:

$$\begin{aligned} &-\frac{q_l}{V} q_{12}(n_A) + k_2(T)\frac{d\phi_B^{(2)}}{dn_B}\left(-q_{12}(n_A) + \gamma_2 q_{13}(n_A)\right) \\ &= -\frac{q_l}{V} q_{21}(n_B) + k_1(T)\frac{d\phi_A^{(1)}}{dn_A}\left(-q_{21}(n_B) + \nu_B q_{22}(n_B) + \gamma_1 q_{23}(n_A)\right) \end{aligned} \tag{D.13a}$$

- for $i = 1$ and $j = 3$:

$$\begin{aligned} &-\frac{q_l}{V} q_{13}(n_A) + \phi_A^{(1)}(n_A)\frac{dk_1}{dT}\left(-q_{11}(n_A) + \nu_B q_{12}(n_A) + \gamma_1 q_{13}(n_A)\right) \\ &+ \phi_B^{(2)}(n_B)\frac{dk_2}{dT}\left(-q_{12}(n_A) + \gamma_2 q_{13}(n_A)\right) \\ &= -\frac{q_l}{V} q_{31}(T) + k_1(T)\frac{d\phi_A^{(1)}}{dn_A}\left(-q_{31}(T) + \nu_B q_{32}(T) + \gamma_1 q_{33}(T)\right) \end{aligned} \tag{D.13b}$$

- for $i = 2$ and $j = 3$:

$$\begin{aligned} &-\frac{q_l}{V} q_{23}(n_B) + \phi_A^{(1)}(n_A)\frac{dk_1}{dT}\left(-q_{21}(n_B) + \nu_B q_{22}(n_B) + \gamma_1 q_{23}(n_B)\right) \\ &+ \phi_B^{(2)}(n_B)\frac{dk_2}{dT}\left(-q_{22}(n_B) + \gamma_2 q_{23}(n_B)\right) \\ &= -\frac{q_l}{V} q_{32}(T) + k_2(T)\frac{d\phi_B^{(2)}}{dn_B}\left(-q_{32}(T) + \gamma_2 q_{33}(T)\right) \end{aligned} \tag{D.13c}$$

By taking the limit for T tending to zero of (D.13a), we find that the following relation has to be satisfied:

$$-\frac{q_l}{V} q_{12}(n_A) = -\frac{q_l}{V} q_{21}(n_B)$$

It is obvious that q_{12} and q_{21} have to be constants with $q_{12} = q_{21}$.

The left-hand side of (D.13b) (resp. (D.13c)) depends on n_B (resp. n_A) but the right-hand side does not. Suppressing the dependence on n_B (resp. n_A) in

the left-hand side of (D.13b) (resp. (D.13c)) results in the following relation:

$$\begin{aligned} q_{21} &= q_{12} = \gamma_2 q_{13}\left(n_A\right) \\ &= \nu_B q_{22}\left(n_B\right) + \gamma_1 q_{23}\left(n_B\right) \end{aligned} \tag{D.14}$$

q_{13} is obviously a constant.

By taking the limit of (D.13c) for T tending to 0, we find that the following relation has to be satisfied:

$$-\frac{q_l}{V} q_{23}\left(n_B\right) = -\frac{q_l}{V} \lim_{T\to 0} q_{32}\left(T\right) + \frac{d\phi_B^{(2)}}{dn_B} \lim_{T\to 0} \left[k_2\left(T\right)\left(-q_{32}\left(T\right) + \gamma_2 q_{33}\left(T\right)\right)\right]$$

This implies that the function $q_{23}\left(n_B\right)$ must be of the following form:

$$q_{23}\left(n_B\right) = \alpha + \beta \frac{d\phi_B^{(2)}}{dn_B} \tag{D.15}$$

where $\alpha, \beta \in \mathbb{R}$:

$$\begin{aligned} \alpha &= \lim_{T\to 0} q_{32}\left(T\right) \\ -\frac{q_l}{V}\beta &= \lim_{T\to 0} \left[k_2\left(T\right)\left(-q_{32}\left(T\right) + \gamma_2 q_{33}\left(T\right)\right)\right] \end{aligned}$$

Assumption D.3. The function $\phi_B^{(2)}\left(n_B\right)$ is a power of n_B as follows (where $\zeta_B \in \mathbb{R}^{*+}$):

$$\phi_B^{(2)}\left(n_B\right) = \left(n_B\right)^{\zeta_B}$$

Case 1: $\zeta_B \neq 1$

In this case, we have:

$$q_{23}\left(n_B\right) = \alpha + \beta\zeta_B \left(n_B\right)^{\zeta_B - 1}$$

and by inserting this relation into (D.14) we obtain the following expression:

$$\begin{aligned} q_{22}\left(n_B\right) &= \frac{1}{\nu_B}\left(\gamma_2 q_{13} - \gamma_1 q_{23}\left(n_B\right)\right) \\ &= \frac{1}{\nu_B}\left(\gamma_2 q_{13} - \gamma_1\alpha - \gamma_1\beta\zeta_B \left(n_B\right)^{\zeta_B - 1}\right) \end{aligned}$$

(D.13c) becomes then as follows:

$$\begin{aligned} &-\frac{q_l}{V}\alpha-\frac{q_l}{V}\beta\zeta_B\left(n_B\right)^{\zeta_B-1}+\left(n_B\right)^{\zeta_B}\frac{dk_2}{dT}\left(-\frac{\gamma_2}{\nu_B}q_{13}+\frac{\gamma_1\alpha}{\nu_B}+\gamma_2\alpha\right)\\ &+\left(n_B\right)^{2\zeta_B-1}\frac{dk_2}{dT}\left(\frac{\gamma_1}{\nu_B}\beta\zeta_B+\gamma_2\beta\zeta_B\right)\\ =&-\frac{q_l}{V}q_{32}\left(T\right)+k_2\left(T\right)\zeta_B\left(n_B\right)^{\zeta_B-1}\left(-q_{32}\left(T\right)+\gamma_2q_{33}\left(T\right)\right)\end{aligned} \tag{D.16}$$

We have to suppress the dependence in the terms of order $2\zeta_B-1$ and in ζ_B on the left-hand side. Since $\zeta_B\neq 1$, $2\zeta_B-1\neq\zeta_B$. The only possibility is to set $\left(\gamma_1+\nu_B\gamma_2\right)\alpha=\gamma_2q_{13}$ and $\beta=0$, i.e. q_{23} is a constant. It follows directly that:

$$\nu_Bq_{22}=\gamma_2q_{13}-\gamma_1\alpha=\gamma_2q_{13}-\gamma_1\frac{\gamma_2q_{13}}{\gamma_1+\nu_B\gamma_2}=\nu_B\gamma_2q_{23}$$

(D.16) becomes as follows:

$$-\frac{q_l}{V}\alpha=-\frac{q_l}{V}q_{32}\left(T\right)+k_2\left(T\right)\zeta_B\left(n_B\right)^{\zeta_B-1}\left(-q_{32}\left(T\right)+\gamma_2q_{33}\left(T\right)\right)$$

This implies that:

$$q_{32}\left(T\right)=\gamma_2q_{33}\left(T\right)$$

Finally the matrix $\boldsymbol{Q}\left(n_A,n_B,T\right)$ is as follows:

$$\boldsymbol{Q}\left(n_A,n_B,T\right)=\begin{pmatrix}q_{11}&\gamma_2q_{13}&q_{13}\\ q_{21}&\gamma_2q_{23}&q_{23}\\ q_{31}&\gamma_2q_{33}\left(T\right)&q_{33}\left(T\right)\end{pmatrix}$$

which is obviously singular since the second and the third column are proportional.

Case 2: $\zeta_B=1$

In this case, (D.15) implies directly that q_{23} is a constant. From (D.14), q_{22} is a constant, too.

Now (D.13c) becomes as follows:

$$\begin{aligned} &-\frac{q_l}{V}q_{23}+n_B\frac{dk_2}{dT}\left(-q_{22}+\gamma_2q_{23}\right)\\ =&-\frac{q_l}{V}q_{32}\left(T\right)+k_2\left(T\right)\left(-q_{32}\left(T\right)+\gamma_2q_{33}\left(T\right)\right)\end{aligned} \tag{D.17}$$

The second term of the left-hand side of (D.17) has a term with a higher power in n_B than the right-hand side. As a consequence, we have to set:

$$-q_{22} + \gamma_2 q_{23} = 0 \tag{D.18}$$

Let us now consider (D.13b):

$$\begin{aligned} &-\frac{q_l}{V} q_{13} + \phi_A^{(1)}(n_A) \frac{dk_1}{dT} \left(-q_{11}(n_A) + (\nu_B \gamma_2 + \gamma_1) q_{13}\right) \\ &= -\frac{q_l}{V} q_{31}(T) + k_1(T) \frac{d\phi_A^{(1)}}{dn_A} \left(-q_{31}(T) + \nu_B q_{32}(T) + \gamma_1 q_{33}(T)\right) \end{aligned} \tag{D.19}$$

Assumption D.4. The function $\phi_A^{(1)}(n_A)$ is a power of n_A as follows (with $\zeta_A \in \mathbb{R}^{*+}$):

$$\phi_A^{(1)}(n_A) = (n_A)^{\zeta_A}$$

Using this assumption, (D.19) can be rewritten as follows:

$$\begin{aligned} &-\frac{q_l}{V} q_{13} + (n_A)^{\zeta_A} \frac{dk_1}{dT} \left(-q_{11}(n_A) + (\nu_B \gamma_2 + \gamma_1) q_{13}\right) \\ &= -\frac{q_l}{V} q_{31}(T) + \zeta_A k_1(T) (n_A)^{\zeta_A - 1} \left(-q_{31}(T) + \nu_B q_{32}(T) + \gamma_1 q_{33}(T)\right) \end{aligned}$$

Thus the second term of the left-hand side of (D.19) has a term with a higher power of n_A than the right-hand side. There are two possibilities to solve (D.19):

Possibility 1: We set

$$-q_{11}(n_A) + (\nu_B \gamma_2 + \gamma_1) q_{13} = 0$$

From the previous considerations, the obtained matrix $\boldsymbol{Q}(n_A, n_B, T)$ is then of the following form:

$$\boldsymbol{Q}(n_A, n_B, T) = \begin{pmatrix} (\nu_B \gamma_2 + \gamma_1) q_{13} & \gamma_2 q_{13} & q_{13} \\ (\nu_B \gamma_2 + \gamma_1) q_{23} & \gamma_2 q_{23} & q_{23} \\ q_{31}(T) & q_{32}(T) & q_{33}(T) \end{pmatrix}$$

with

$$q_{12} = \gamma_2 q_{13} = q_{21} = (\nu_B \gamma_2 + \gamma_1) q_{23}$$

This matrix is singular because q_{13} is proportional to q_{23}. The first and the second lines of the above matrix are thus proportional.

Possibility 2: We set:

$$q_{13} = 0 \quad \text{and} \quad q_{11}\left(n_A\right) = -\frac{\omega \zeta_A}{n_A}$$

where ω is some constant. Then using (D.14) and (D.18) we have the following relations:

$$\begin{aligned} \nu_B q_{22} = \nu_B \gamma_2 q_{23} &= -\gamma_1 q_{23} + q_{21} \\ &= -\gamma_1 q_{23} + q_{12} \\ &= -\gamma_1 q_{23} + \gamma_2 q_{13} \end{aligned}$$

Since $q_{13} = 0$, these relations imply[1] $q_{23} = 0$. As a consequence $q_{22} = 0$ and $q_{21} = q_{12} = \gamma_2 q_{13} = 0$. It is obvious that the matrix $\boldsymbol{Q}\left(n_A, n_B, T\right)$ is singular.

Conclusion The system composed of the equations (D.13a) to (D.13c) has no non-singular solution. This does not mean that the dynamics cannot be put into the Brayton-Moser form. But if the Brayton-Moser form exists, then the relation (4.14) is not fulfilled and the partial differential equation (4.13) has to be solved.

[1] except if $\nu_B \gamma_2 = -\gamma_1$, which is not very likely to happen. We have $\nu_B \gamma_2 = -\gamma_1$ when the second reaction is the reverse reaction of the first one. But this is not the case here, since we have assumed that the second reaction does not produce A.

Appendix E

Some elements of differential geometry

In this appendix, we shall explain some of the basic concepts of differential geometry which are used in this thesis, especially in Part II. Intuitively differential geometry provides tools that allow to apply the usual concepts of differential calculus in $\mathbb{R}^d$ to more "complex" surfaces (e.g. the derivative of a function that is defined on a sphere, or even on a set of matrices). We state here some definitions and fundamental properties without any proof. For a more detailed introduction to differential geometry, the reader can refer for instance to [45][64][66][71].

E.1 Manifolds and tangent spaces

E.1.1 Manifolds and submanifolds

Instead of working with $\mathbb{R}^d$, differential geometry considers more complex objects, namely manifolds. Manifolds are sets where the neighbourhood of each of its point has a structure that is "similar" to $\mathbb{R}^d$, and more exactly is homeomorphic to $\mathbb{R}^d$. A more formal definition can be given using the notion of charts and atlases. In order to define these notions, let us consider a set $\mathscr{M}$.

Definition E.1 (Homeomorphism)**.** A function φ between two topological spaces is called a homeomorphism if it has the following properties:

- φ is a bijection (one-to-one and onto)
- φ is continuous
- the inverse function φ^{-1} is continuous

Definition E.2 (Chart)**.** A homeomorphism φ from a subset $\mathcal{U}$ of $\mathscr{M}$ onto an open subset of $\mathbb{R}^d$ is a d-dimensional *chart* of the set $\mathscr{M}$, denoted by $(\mathcal{U}, \varphi)$ (see Figure E.1).

Definition E.3 (Coordinates)**.** Given a chart $(\mathcal{U}, \varphi)$ and an element $x \in \mathcal{U}$, the elements $\varphi(x) \in \mathbb{R}^d$ are called the *coordinates* of x in the chart $(\mathcal{U}, \varphi)$.

Example E.1. *Consider the set $\mathcal{S}^2$ containing all the points $(x, y, z) \in \mathbb{R}^3$ that are located at a distance 1 from the origin:*

$$\mathcal{S}^2 = \left\{(x, y, z) \in \mathbb{R}^3 \middle|\, x^2 + y^2 + z^2 = 1\right\}$$

$\mathcal{S}^2$ is the sphere centred at the origin with radius equal to 1. Let us now consider the following open subset of $\mathcal{S}^2$:

$$\mathcal{U}_{(1)} = \mathcal{S}^2 \setminus \{(0, 0, 1)\}$$

and the following mapping:

$$\begin{aligned} \varphi_{(1)} : \mathcal{U}_{(1)} &\rightarrow \mathbb{R}^2 \\ (x, y, z) &\mapsto (X, Y) = \left(\frac{x}{1 - z}, \frac{y}{1 - z}\right) \end{aligned}$$

$\varphi_{(1)}$ gives the north pole stereographic projection, i.e. $\varphi_{(1)}(x, y, z)$ is the intersection of the line through the north pole $(0, 0, 1)$ and the point (x, y, z) with the plane $z = 0$ (see Figure E.2). $\varphi_{(1)}$ is a homeomorphism and the inverse mapping is given as follows

$$\begin{aligned} \varphi_{(1)}^{-1} : \mathbb{R}^2 &\rightarrow \mathcal{U}_{(1)} \\ (X, Y) &\mapsto \left(\frac{2X}{1 + X^2 + Y^2}, \frac{2Y}{1 + X^2 + Y^2}, \frac{\left(X^2 + Y^2\right) - 1}{1 + X^2 + Y^2}\right) \end{aligned}$$

$(\mathcal{U}_1, \varphi_1)$ is a 2-dimensional chart of $\mathcal{S}^2$ and the coordinates are given by (X, Y).

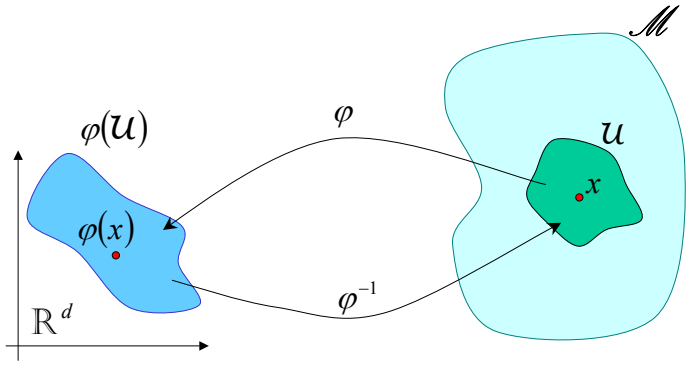


Figure E.1: Chart

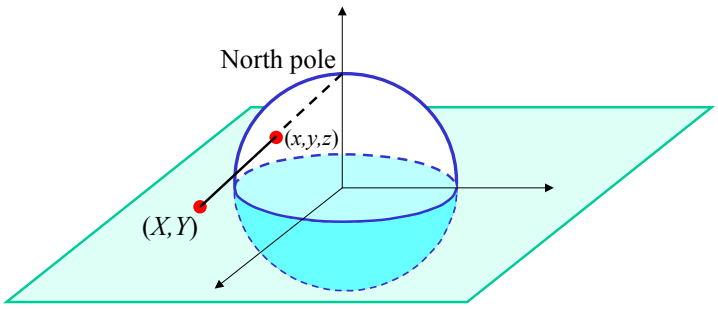


Figure E.2: North pole stereographic projection

The notions of chart and of coordinates allow to bring the elements of $\mathscr{M}$ into the more usual space $\mathbb{R}^d$. But in order to be able to compare $\mathscr{M}$ to $\mathbb{R}^d$, some conditions have to be fulfilled. First, each element of $\mathscr{M}$ has to belong to at least one chart. If two charts $\left(\mathcal{U}_{(1)}, \varphi_{(1)}\right)$ and $\left(\mathcal{U}_{(2)}, \varphi_{(2)}\right)$ intersect (i.e. $\mathcal{U}_{(1)} \cap \mathcal{U}_{(2)} \neq \emptyset$), then the two charts must give compatible information.

These considerations are formalized in the concept of an atlas, defined as follows:

Definition E.4 (Compatible charts [66])**.** Two charts $\left(\mathcal{U}_{(1)}, \varphi_{(1)}\right)$ and $\left(\mathcal{U}_{(2)}, \varphi_{(2)}\right)$ of a set $\mathscr{M}$ are *compatible of order* k (with $1 \leq k \leq \infty$) if $\mathcal{U}_{(1)} \cap \mathcal{U}_{(2)} = \emptyset$ or if the mapping

$$\varphi_{(2)} \circ \varphi_{(1)}^{-1} : \ \varphi_{(1)}\left(\mathcal{U}_{(1)} \cap \mathcal{U}_{(2)}\right) \rightarrow \varphi_{(2)}\left(\mathcal{U}_{(1)} \cap \mathcal{U}_{(2)}\right)$$

is a $\mathcal{C}^k$-diffeomorphism (i.e. the mapping and its inverse are k times continuously differentiable).

Definition E.5 (Atlas [66])**.** A $\mathcal{C}^k$*-atlas* $\mathcal{A}$ of $\mathscr{M}$ is a collection of charts $\left(\mathcal{U}_{(i)}, \varphi_{(i)}\right)$ of $\mathscr{M}$ such that:

- $\bigcup_i \mathcal{U}_{(i)} = \mathscr{M}$, i.e. each element of $\mathscr{M}$ is contained at least in one chart of $\mathcal{A}$.
- for any pair of charts $\left(\mathcal{U}_{(i)}, \varphi_{(i)}\right)$ and $\left(\mathcal{U}_{(j)}, \varphi_{(j)}\right)$ of the atlas $\mathcal{A}$, the charts $\left(\mathcal{U}_{(i)}, \varphi_{(i)}\right)$ and $\left(\mathcal{U}_{(j)}, \varphi_{(j)}\right)$ are compatible of order k.

Now let us consider some $\mathcal{C}^k$-atlas $\mathcal{A}$ of $\mathscr{M}$ and the set $\mathcal{A}^+$ of all the charts $(\mathcal{U}, \varphi)$ such that $\mathcal{A} \cup (\mathcal{U}, \varphi)$ is also an atlas. The set $\mathcal{A}^+$ is also an atlas and is called the *maximal atlas* of $\mathscr{M}$ generated by $\mathcal{A}$ [1]. A maximal atlas is also called a *differential structure* of class $\mathcal{C}^k$ [66].

Example E.1 (continued)**.** *In addition to* $\mathcal{U}_{(1)}$ *and* $\varphi_{(1)}$ *let us consider the following set:*

$$\mathcal{U}_{(2)} = \mathcal{S}^2 \setminus \{(0, 0, -1)\}$$

and the associated mapping:

$$\begin{aligned} \varphi_{(2)} : \mathcal{U}_{(2)} &\rightarrow \mathbb{R}^2 \\ (x, y, z) &\mapsto (\chi, \Upsilon) = \left(\frac{x}{1+z}, \frac{y}{1+z}\right) \end{aligned}$$

$\varphi_{(2)}$ gives the south pole stereographic projection, i.e. $\varphi_{(2)}(x,y,z)$ is the intersection of the line through the south pole $(0,0,-1)$ and the point (x,y,z) with the plane $z=0$. It can be easily seen that $\left(\mathcal{U}_{(2)},\varphi_{(2)}\right)$ is a 2-dimensional chart of $\mathcal{S}^2$. Moreover $\mathcal{U}_1 \cup \mathcal{U}_{(2)} = \mathcal{S}^2$.

Let us now consider the two charts $\left(\mathcal{U}_{(1)},\varphi_{(1)}\right)$ and $\left(\mathcal{U}_{(2)},\varphi_{(2)}\right)$. The intersection of $\mathcal{U}_{(1)}$ and $\mathcal{U}_{(2)}$ is given as follows:

$$\mathcal{U}_{(1)} \cap \mathcal{U}_{(2)} = \mathcal{S}^2 \setminus \{(0,0,1),(0,0,-1)\}$$

The images of $\mathcal{U}_{(1)} \cap \mathcal{U}_{(2)}$ by $\varphi_{(1)}$ and $\varphi_{(2)}$ are open sets of $\mathbb{R}$:

$$\varphi_{(1)}\left(\mathcal{U}_{(1)} \cap \mathcal{U}_{(2)}\right) = \mathbb{R}^2 \setminus \{(0,0)\} \quad \textit{and} \quad \varphi_{(2)}\left(\mathcal{U}_{(1)} \cap \mathcal{U}_{(2)}\right) = \mathbb{R}^2 \setminus \{(0,0)\}$$

The mapping $\varphi_{(2)} \circ \varphi_{(1)}^{-1} : \mathbb{R}^2 \setminus \{(0,0)\} \to \mathbb{R}^2 \setminus \{(0,0)\}$

$$\varphi_{(2)} \circ \varphi_{(1)}^{-1}(X,Y) = \left(\frac{X}{X^2+Y^2}, \frac{Y}{X^2+Y^2}\right)$$

and its inverse $\varphi_{(1)} \circ \varphi_{(2)}^{-1} : \mathbb{R}^2 \setminus \{(0,0)\} \to \mathbb{R}^2 \setminus \{(0,0)\}$

$$\varphi_{(1)} \circ \varphi_{(2)}^{-1}(\chi,\Upsilon) = \left(\frac{\chi}{\chi^2+\Upsilon^2}, \frac{\Upsilon}{\chi^2+\Upsilon^2}\right)$$

are $\mathcal{C}^\infty$-diffeomorphisms. As a conclusion, the collection of charts

$$\left(\mathcal{U}_{(1)},\varphi_{(1)}\right) \cup \left(\mathcal{U}_{(2)},\varphi_{(2)}\right)$$

is a $\mathcal{C}^\infty$-atlas of $\mathcal{S}^2$.

Definition E.6 (Topological manifold [66])**.** A topological manifold of dimension d is a Hausdorff topological space (i.e. two distinct points have two disjoint neighbourhoods) that is locally homeomorphic to an open subset of $\mathbb{R}^d$.

Definition E.7 (Differentiable manifold [66])**.** A d-dimensional *differentiable manifold* of class $\mathcal{C}^k$ is a d-dimensional topological manifold $\mathscr{M}$ provided with a differentiable structure of class $\mathcal{C}^k$.

Example E.1 (continued)**.** *The sphere $\mathcal{S}^2$ is a 2-dimensional manifold.*

Definition E.8 (Submanifold [66])**.** Let $\mathscr{N}$ be a subset of a d_M-dimensional manifold $\mathscr{M}$. $\mathscr{N}$ is a d_N-dimensional *submanifold* of $\mathscr{M}$ (with $d_N < d_M$) if for any element $x \in \mathscr{N}$ there exists open neighbourhoods $\mathcal{U} \in \mathscr{M}$ and $\mathcal{V} \in \mathbb{R}^{d_M}$ of x and 0, respectively and a diffeomorphism $\phi : \mathcal{U} \to \mathcal{V}$ such that:

$$\phi\left(\mathcal{U} \cap \mathscr{N}\right) = \mathcal{V} \cap \left(\mathbb{R}^{d_N} \times \{0\}\right)$$

Example E.1 (continued)**.** *Let us consider the subset $\mathcal{S}^1$ of $\mathcal{S}^2$ defined as follows:*

$$\mathcal{S}^1 = \left\{(x, y, z) \in \mathbb{R}^3 | z^2 + y^2 = 1, x = 0\right\}$$

First let x be an element of $\mathcal{S}^1 \setminus \{0, 0, 1\}$. Let us consider the following open neighbourhoods of x and 0, respectively:

$$\mathcal{U}_{(1)} = \mathbb{R}^3 \setminus \{0, 0, 1\} \quad \textit{and} \quad \mathcal{V}_{(1)} = \mathbb{R}^2$$

Let us consider the following diffeomorphism:

$$\begin{array}{rcl} \phi_{(1)} : \mathcal{U}_{(1)} & \to & \mathcal{V}_{(1)} \\ (x, y, z) & \mapsto & (X, Y) = \left(\dfrac{x}{1-z}, \dfrac{y}{1-z}\right) \end{array}$$

We have:

$$\begin{array}{rcl} \phi_{(1)}\left(\mathcal{U}_{(1)} \cap \mathcal{S}^1\right) & = & \phi_{(1)}\left(\mathcal{S}^1 \setminus \{0, 0, 1\}\right) \\ & = & \left\{(X, Y) \in \mathbb{R}^2 | X = 0\right\} = \mathbb{R} \times \{0\} = \mathcal{V}_{(1)} \cap (\mathbb{R} \times \{0\}) \end{array}$$

Now let x be an element of $\mathcal{S}^1 \setminus \{0, 0, -1\}$. Let us consider the following open neighbourhoods of x and 0, respectively:

$$\mathcal{U}_{(2)} = \mathbb{R}^3 \setminus \{0, 0, -1\} \quad \textit{and} \quad \mathcal{V}_{(2)} = \mathbb{R}^2$$

Consider the following diffeomorphism:

$$\begin{array}{rcl} \phi_{(2)} : \mathcal{U}_{(2)} & \to & \mathcal{V}_{(2)} \\ (x, y, z) & \mapsto & (\chi, \Upsilon) = \left(\dfrac{x}{1+z}, \dfrac{y}{1+z}\right) \end{array}$$

We have:

$$\begin{aligned}\phi_{(2)}\left(\mathcal{U}_{(2)} \cap \mathcal{S}^1\right) &= \phi_{(2)}\left(\mathcal{S}^1 \setminus \{0,0,-1\}\right) \\ &= \left\{(\chi,\Upsilon) \in \mathbb{R}^2 | \chi = 0\right\} = \mathbb{R} \times \{0\} = \mathcal{V}_{(2)} \cap (\mathbb{R} \times \{0\})\end{aligned}$$

Each element x of $\mathcal{S}^1$ is contained either in $\mathcal{S}^1 \setminus \{(0,0,1)\}$ or in $\mathcal{S}^1 \setminus \{(0,0,-1)\}$. Since $\varphi_{(1)}$ and $\varphi_{(2)}$ are diffeomorphisms, it follows from Definition E.8 that $\mathcal{S}^1$ is a 1-dimensional submanifold of $\mathcal{S}^2$.

E.1.2 Tangent vectors and tangent space

Let us consider a d-dimensional manifold $\mathscr{M}$ and let x be an element of $\mathscr{M}$.

Definition E.9 (Tangent curves [66])**.** Let $(\mathcal{U}, \varphi)$ be a chart of $\mathscr{M}$ such that $x \in \mathcal{U}$. Consider two smooth curves on $\mathscr{M}$, γ_1 and γ_2, defined on open intervals of $\mathbb{R}$ containing 0, and such that $\gamma_1(0) = \gamma_2(0) = x$. Then γ_1 and γ_2 are said to be tangent at x if the ordinary derivatives of $\varphi \circ \gamma_1$ and $\varphi \circ \gamma_2$ at 0 are equal:

$$\left.\frac{d\left(\varphi \circ \gamma_1\right)}{ds}\right|_{s=0} = \left.\frac{d\left(\varphi \circ \gamma_2\right)}{ds}\right|_{s=0}$$

This definition does not depend on the chosen chart and the above definition defines an equivalence relation.

Definition E.10 (Tangent vector [66])**.** An equivalence class of the equivalence relation defined in Definition E.9 is a tangent vector of $\mathscr{M}$ at the point x.

In other words a tangent vector can be seen as the set of smooth curves on $\mathscr{M}$ through x that are tangent to each other.

Example E.1 (continued)**.** *Let us consider the two following curves on $\mathcal{S}^2$:*

$$\gamma_1 : \left\{ \begin{array}{l} \left]-\frac{\pi}{2}, \frac{\pi}{2}\right[\to \mathcal{S}^2 \\ \qquad s \mapsto \left(\frac{\sqrt{3}}{2}\cos s, \frac{\sqrt{3}}{2}\sin s, \frac{1}{2}\right) \end{array} \right.$$

and

$$\gamma_2 : \left\{ \begin{array}{l} \mathbb{R} \to \mathcal{S}^2 \\ s \mapsto \left(\frac{2\sqrt{3}}{4+3s^2}, \frac{2\sqrt{3}\,s}{4+3s^2}, \frac{2+3s^2}{4+3s^2}\right) \end{array} \right.$$

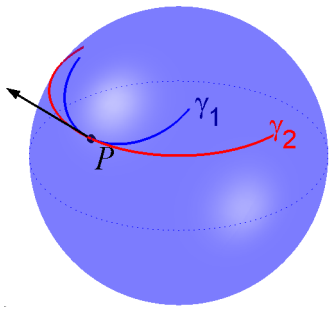


Figure E.3: Tangent curves and tangent vectors

Let us now take the chart $\left(\mathcal{U}_{(1)}, \varphi_{(1)}\right)$ *and the point* $P = \left(\frac{\sqrt{3}}{2}, 0, \frac{1}{2}\right)$. *It can be easily checked that* $P \in \mathcal{S}^2$ *and that* $\gamma_1(0) = \gamma_2(0) = P$. *We have:*

$$\varphi_{(1)} \circ \gamma_1 = \begin{pmatrix} \sqrt{3}\cos s \\ \sqrt{3}\sin s \end{pmatrix} \qquad \left.\frac{d\left(\varphi_{(1)} \circ \gamma_1\right)}{ds}\right|_{s=0} = \begin{pmatrix} 0 \\ \sqrt{3} \end{pmatrix}$$

$$\varphi_{(1)} \circ \gamma_2 = \begin{pmatrix} \sqrt{3} \\ \sqrt{3}s \end{pmatrix} \qquad \left.\frac{d\left(\varphi_{(1)} \circ \gamma_2\right)}{ds}\right|_{s=0} = \begin{pmatrix} 0 \\ \sqrt{3} \end{pmatrix}$$

It follows from Definition E.9 that γ_1 *and* γ_2 *are tangent curves* P. *The corresponding tangent vector is given by the following set of curves:*

$$\left\{ \gamma \in \mathcal{C}_P\left(\mathcal{S}^2\right) \text{ such that } \left.\frac{d\left(\varphi_{(1)} \circ \gamma\right)}{ds}\right|_{s=0} = \begin{pmatrix} 0 \\ \sqrt{3} \end{pmatrix} \right\}$$

where $\mathcal{C}_P\left(\mathcal{S}^2\right)$ *is the set of smooth curves on* $\mathcal{S}^2$, *defined on an open interval* $I \subset \mathbb{R}$ *with* $\{0\} \in I$ *such that* $\gamma(0) = P$.

Figure E.3 shows the curves γ_1 *and* γ_2. *It can be seen that they indeed define a tangent vector to the sphere that corresponds to the intuition.*

Definition E.11 (Tangent space)**.** The tangent space $\mathrm{T}_x\mathscr{M}$ of $\mathscr{M}$ at x is the set of all the tangent vectors of $\mathscr{M}$ at x.

Lemma E.1. *The tangent space* $T_x\mathscr{M}$ *of a* d*-dimensional manifold* $\mathscr{M}$ *is a* d*-dimensional vector space.*

Let v_1 and v_2 be two tangent vectors of $\mathscr{M}$ at x and let α be a scalar. The operations on $\mathrm{T}_x\mathscr{M}$ are defined as follows [64]:

$$\alpha v_1 = \left\{ \gamma \in \mathcal{C}_x(\mathscr{M}) \text{ such that } \left.\frac{d(\varphi\circ\gamma)}{ds}\right|_{s=0} = \alpha \left.\frac{d(\varphi\circ\gamma_1)}{ds}\right|_{s=0} \right\}$$

$$v_1+v_2 = \left\{ \gamma \in \mathcal{C}_x(\mathscr{M}) \text{ s. th. } \left.\frac{d(\varphi\circ\gamma)}{ds}\right|_{s=0} = \left.\frac{d(\varphi\circ\gamma_1)}{ds}\right|_{s=0} + \left.\frac{d(\varphi\circ\gamma_2)}{ds}\right|_{s=0} \right\}$$

where γ_1 and γ_2 are any curves of the equivalence class corresponding to v_1 and v_2, respectively. $\mathcal{C}_x(\mathscr{M})$ is the set of smooth curves on $\mathscr{M}$, defined on an open interval $I \subset \mathbb{R}$ with $\{0\} \in I$ such that $\gamma(0) = x$.

For a particular choice of chart $(\mathcal{U}, \varphi)$ the following tangent vectors form a basis for $\mathrm{T}_x\mathscr{M}$:

$$\xi_i = \left\{ \gamma \in \mathcal{C}_x(\mathscr{M}) \text{ such that } \left.\frac{d(\varphi\circ\gamma)}{ds}\right|_{s=0} = e_i \right\} \tag{E.1}$$

where e_i is the i^{th} basis vector of the canonical basis of $\mathbb{R}^n$ (i.e. $e_i = (0,\cdots,0,1,0,\cdots,0)^t$ where 1 is the i^{th} entry.). Given a chart φ, ξ_i corresponds to the set of curves that are tangent to the following curve:

$$\varphi^{-1}(\varphi_1(x),\ldots,\varphi_{i-1}(x),\varphi_i(x)+s,\varphi_{i+1}(x),\cdots,\varphi_n(x))$$

i.e. the image on $\mathscr{M}$ of the straight line in $\varphi(\mathcal{U}) \subset \mathbb{R}^n$ that is parallel to the X_i-axis and going through $\varphi(x)$. As a consequence the basis vectors depend on the chosen chart.

Let us consider some tangent vector $v \in \mathrm{T}_x\mathscr{M}$. Since $(e_1,\ldots,e_n)$ is a basis of $\mathbb{R}^n$, we can express v as follows:

$$\begin{aligned} v &= \left\{ \gamma \in \mathcal{C}_x(\mathscr{M}) \text{ such that } \left.\frac{d(\varphi\circ\gamma)}{ds}\right|_{s=0} = \sum_{i=1}^n \alpha_i e_i \right\} \\ &= \sum_{i=1}^n \alpha_i \left\{ \gamma \in \mathcal{C}_x(\mathscr{M}) \text{ such that } \left.\frac{d(\varphi\circ\gamma)}{ds}\right|_{s=0} = e_i \right\} \\ &= \sum_{i=1}^n \alpha_i \xi_i \end{aligned}$$

which shows indeed that any vector $v \in \mathrm{T}_x\mathscr{M}$ can be expressed as a linear combination of the tangent vectors $\xi_1,\ldots,\xi_n$. The scalars α_i are the coordinates

of v in the basis $(\xi_1, \ldots, \xi_n)$. Let us mention that the definition of a tangent vector does not depend on the chart, but the coordinates are depending on the basis of $\mathrm{T}_x\mathscr{M}$ and therefore of the corresponding chart.

Definition E.12 (Tangent bundle [66])**.** The *tangent bundle* $\mathrm{T}\mathscr{M}$ is build from the tangent spaces at each point of $\mathscr{M}$, and more precisely is the disjoint union of the tangent spaces at each point:

$$\mathrm{T}\mathscr{M} = \bigcup_{x \in \mathscr{M}} \mathrm{T}_x\mathscr{M}$$

Lemma E.2. *The tangent fibre bundle $T\mathscr{M}$ is a $2d$-dimensional manifold.*

Definition E.13 (Vector field [1])**.** A *vector field* $\mathcal{X}$ on a manifold $\mathscr{M}$ is a smooth mapping from $\mathscr{M}$ to the tangent bundle $\mathrm{T}\mathscr{M}$ that assigns to each point $x \in \mathscr{M}$ a tangent vector $\xi_x \in \mathrm{T}_x\mathscr{M}$. In other words, a vector field is a section of the tangent fibre bundle.

Let us denote by $\mathfrak{F}_x(\mathscr{M})$ the set of real-valued $\mathcal{C}^\infty$-functions defined in a neighbourhood of x.

Definition E.14 (Derivation)**.** Let $g \in \mathfrak{F}_x(\mathscr{M})$. A derivation at the point x is a mapping $\mathrm{D} : \mathfrak{F}_x(\mathscr{M}) \to \mathbb{R}$ with the following characteristics:

$$\begin{aligned} \mathrm{D}(\alpha g_1 + \beta g_2) &= \alpha \mathrm{D}(g_1) + \beta \mathrm{D}(g_2) \\ \mathrm{D}(g_1 g_2) &= g_1 \mathrm{D}(g_2) + g_2 \mathrm{D}(g_1) \end{aligned}$$

where $g_1, g_2 \in \mathfrak{F}_x(\mathscr{M})$ and $\alpha, \beta \in \mathbb{R}$.

Actually there is an isomorphism between the set of derivations and the tangent space [66]. To each derivation there corresponds one tangent vector (and conversely) as follows:

$$\mathrm{D}_v(g) = \left.\frac{d(g \circ \gamma)}{ds}\right|_{s=0} \tag{E.2}$$

where $v \in \mathrm{T}_x\mathscr{M}$ and γ is any curve of the equivalence class corresponding to v.

Remark E.1. *Applying $\mathrm{D}_v(\cdot)$ to the i^{th} coordinate function φ_i of a given chart $(\mathcal{U}, \varphi)$ gives the i^{th} coordinate of the vector v in the basis of $T_x\mathscr{M}$ given by* (E.1)*.*

E.2 Differential forms

E.2.1 Cotangent fibre bundle

Definition E.15 (Cotangent vector)**.** A *cotangent vector* ω to $\mathscr{M}$ at the point $x \in \mathscr{M}$ is a linear mapping from $\mathrm{T}_x\mathscr{M}$ into $\mathbb{R}$.

Definition E.16 (Cotangent space)**.** The set of all cotangent vectors to $\mathscr{M}$ at the point $x \in \mathscr{M}$ is the *cotangent space* $\mathrm{T}_x^*\mathscr{M}$ of $\mathscr{M}$ at the point x.

Lemma E.3. *The cotangent space is a vector space.*

Definition E.17 (Differential)**.** Let $g \in \mathfrak{F}_x(\mathscr{M})$, i.e. a real-valued $\mathcal{C}^\infty$-function defined in a neighbourhood of x. The differential of g at the point x is an element of $\mathrm{T}_x^*\mathscr{M}$, denoted $\mathrm{d}g$ defined as follows:

$$\begin{aligned} \mathrm{d}g : \mathrm{T}_x\mathscr{M} &\to \mathbb{R} \\ v &\mapsto \mathrm{D}_v(g) \end{aligned}$$

where $\mathrm{D}_v(g)$ has been defined in (E.2).

Actually the cotangent vector space is the dual space of the tangent space $\mathrm{T}_x\mathscr{M}$. An element of $\mathrm{T}_x^*\mathscr{M}$ belongs to a special class of mappings, namely the so-called 1-forms on $\mathrm{T}_x\mathscr{M}$. Let us consider a chart $(\mathcal{U}, \varphi)$ of $\mathscr{M}$ such that $x \in \mathcal{U}$. For this choice of chart a basis of $\mathrm{T}_x\mathscr{M}$ is given by (E.1). In a first time, let us denote the dual basis to $(\xi_1, \ldots, \xi_n)$ of $\mathrm{T}_x^*\mathscr{M}$ by $\left(\hat{\xi}_1, \ldots, \hat{\xi}_n\right)$. By definition of the dual basis:

$$\hat{\xi}_i(v) = \alpha_i \tag{E.3}$$

where $v \in \mathrm{T}_x\mathscr{M}$ is a tangent vector and α_i its i^{th} coordinate in the basis $(\xi_1, \ldots, \xi_n)$. From Remark E.1 we can write the following relation:

$$\hat{\xi}_i(v) = \mathrm{D}_v(\varphi_i) = \mathrm{d}\varphi_i(v)$$

This explains why the basis vector of the cotangent space are often denoted as $(\mathrm{d}X_1, \ldots, \mathrm{d}X_d)$. This notation obviously implies the choice of a chart.

Definition E.18 (Cotangent bundle)**.** The *cotangent bundle* $\mathrm{T}^*\mathscr{M}$ is build from the cotangent vector spaces at each point of $\mathscr{M}$:

$$\mathrm{T}^*\mathscr{M} = \bigcup_{x\in\mathscr{M}} \mathrm{T}_x^*\mathscr{M}$$

E.2.2 Exterior product

Definition E.19 (k-form)**.** Let E be a vector space. A k-form is a k-linear alternating mapping defined on:

$$\theta : \underbrace{E \times \ldots \times E}_{k \text{ times}} \to \mathbb{R}$$

i.e. $\forall i = 1\ldots, k$ and for any $e_1, \ldots, e_k, \hat{e}_i \in E$, $\alpha, \beta \in \mathbb{R}$:

$$\theta\left(e_1, \ldots, e_i, e_{i+1}, \ldots, e_k\right) = -\theta\left(e_1, \ldots, e_{i+1}, e_i, \ldots, e_k\right) \tag{E.4}$$

and

$$\theta\left(e_1, \ldots, \alpha e_i + \beta\hat{e}_i, \ldots, e_k\right) = \alpha\theta\left(e_1, \ldots, e_i, \ldots, e_k\right) + \beta\theta\left(e_1, \ldots, \hat{e}_i, \ldots, e_k\right) \tag{E.5}$$

As it has already been mentioned, the elements of the cotangent space of $\mathscr{M}$ at x is a special case of 1-form, namely a differential 1-form. Let $\hat{v}$ be a cotangent vector of $\mathscr{M}$ at x. $\hat{v}$ is a linear mapping from $\mathrm{T}_x\mathscr{M}$ into $\mathbb{R}$ and hence (E.5) is trivially satisfied. (E.4) is also trivially satisfied by setting $k = 1$.

Definition E.20 (Exterior product)**.** The wedge product (denoted $\wedge$) is a mapping that associates to a k-form θ and a l-form ω on a vector space a $k + l$-form as follows:

$$\begin{aligned}\theta\left(e_1, \ldots, e_k\right) \wedge \omega\left(e_{k+1}, \ldots, e_{k+l}\right) \\ = \frac{1}{k!l!} \sum_{\sigma\in S_{k+l}} \epsilon\left(\sigma\right) \theta\left(e_{\sigma(1)}, \ldots, e_{\sigma(k)}\right) \omega\left(e_{\sigma(k+1)}, \ldots, e_{\sigma(k+l)}\right)\end{aligned}$$

where S_{k+l} is the group of permutation of $k + l$ elements and $\epsilon\left(\sigma\right)$ is the signature of the permutation.

Example E.2. *Let θ and ω be two 1-forms. The permutation of 2 elements are:*

$$\begin{aligned} \sigma_1 &= \{1,2\} \quad \epsilon(\sigma_1) = 1 \\ \sigma_2 &= \{2,1\} \quad \epsilon(\sigma_2) = -1 \end{aligned}$$

As a consequence the wedge product of two 1-forms is given as follows:

$$\theta(e_1) \wedge \omega(e_2) = \theta(e_1)\,\omega(e_2) - \theta(e_2)\,\omega(e_1)$$

It can be checked that the result is indeed a 2-form.

E.2.3 Pfaffian equation

Definition E.21 (Pfaffian equation)**.** Let θ be a 1-form defined on the tangent vector space of the d-dimensional manifold $\mathscr{M}$. Let us consider the set of tangent vectors v such that $\theta(v) = 0$. This set is a vector subspace of $\mathrm{T}_x\mathscr{M}$ and it is the solution of $\theta = 0$ which is called a *Pfaffian equation*.

Definition E.22 (Class of a 1-form [69])**.** Let θ be a 1-form defined on the tangent vector space of the d-dimensional manifold $\mathscr{M}$. Let $s \leq \frac{d-1}{2}$ be an integer. Then θ is said to be:

- of class 0 if $\theta = 0$ on $\mathscr{M}$.
- of class $2s+1$ if on: $\mathscr{M}$: $\theta \wedge (\mathrm{d}\theta)^s \neq 0$ and $(\mathrm{d}\theta)^{s+1} = 0$.
- of class $2s+2$ if on $\mathscr{M}$: $\theta \wedge (\mathrm{d}\theta)^s \neq 0$, $(\mathrm{d}\theta)^{s+1} \neq 0$ and $\theta \wedge (\mathrm{d}\theta)^{s+1} = 0$.

Definition E.23 (Integral submanifold)**.** Let θ be a 1-form defined on the tangent vector spaces of the d-dimensional manifold $\mathscr{M}$. Then the submanifold $\mathscr{N} \subset \mathscr{M}$ is an integral manifold of the Pfaffian equation $\theta = 0$ if the tangent vectors of $\mathscr{N}$ are solutions of $\theta = 0$, i.e.:

$$\forall v \in \mathrm{T}\mathscr{N}, \quad \theta(v) = 0$$

Example E.3. *Let us consider the sphere $\mathcal{S}^2$ in $\mathbb{R}^3$ endowed with the maximal atlas generated by $\left(\mathcal{U}_{(1)},\varphi_{(1)}\right)$ and $\left(\mathcal{U}_{(2)},\varphi_{(2)}\right)$. Let us consider the following 1-form, expressed in the local coordinates:*

$$\begin{array}{rcl}\theta & \overset{\left(\mathcal{U}_{(1)},\varphi_{(1)}\right)}{=} & X\mathrm{d}X+Y\mathrm{d}Y \\ & \overset{\left(\mathcal{U}_{(2)},\varphi_{(2)}\right)}{=} & \chi\mathrm{d}\chi+\Upsilon\mathrm{d}\Upsilon\end{array}$$

Each horizontal circle situated on $\mathcal{S}^2$, i.e.:

$$\left\{(x,y,z)\,|x^2+y^2=1-h^2,\,z=h,h\in\,]-1;1[\right\}$$

is an integral manifold of the Pfaffian expression $\theta=0$.

Indeed, let us consider for instance the horizontal circle $\mathcal{S}^1$ at the height $z=0$.

Consider an element $P\in\mathcal{S}^1$ and a chart $(\mathcal{V},\phi)$ that contains P. Using this chart, the tangent space to $\mathcal{S}^1$ at P is given as follows:

$$\mathrm{T}_P\mathcal{S}^1=\bigcup_{c\in\mathbb{R}}\left(v_c=\left\{\gamma\in\mathcal{C}_P\left(\mathcal{S}^1\right)\ \textit{such that}\ \left.\frac{d\left(\phi\circ\gamma\right)}{ds}\right|_{s=0}=c\right\}\right)$$

By definition of a tangent vector, the curves of any tangent vector v_c are equivalent on $\mathcal{S}^1$ at P, but in fact they are also equivalent on $\mathcal{S}^2$. Indeed, take two curves γ_1 and γ_2 that are tangent at P on $\mathcal{S}_1$ and let us consider a chart $(\mathcal{U},\varphi)$ of $\mathcal{S}^2$ that contains P. Indeed we have the following equalities:

$$\begin{array}{rcl}\left.\frac{d\left(\varphi\circ\gamma_1\right)}{ds}\right|_{s=0} & = & \left.\frac{d\left(\varphi\circ\phi^{-1}\right)}{dt}\right|_{t=\phi(P)}\left.\frac{d\left(\phi\circ\gamma_1\right)}{ds}\right|_{s=0}=c\left.\frac{d\left(\varphi\circ\phi^{-1}\right)}{dt}\right|_{t=\phi(P)} \\ \left.\frac{d\left(\varphi\circ\gamma_2\right)}{ds}\right|_{s=0} & = & \left.\frac{d\left(\varphi\circ\phi^{-1}\right)}{dt}\right|_{t=\phi(P)}\left.\frac{d\left(\phi\circ\gamma_2\right)}{ds}\right|_{s=0}=c\left.\frac{d\left(\varphi\circ\phi^{-1}\right)}{dt}\right|_{t=\phi(P)}\end{array}$$

and consequently:

$$\left.\frac{d\left(\varphi\circ\gamma_1\right)}{ds}\right|_{s=0}=\left.\frac{d\left(\varphi\circ\gamma_2\right)}{ds}\right|_{s=0}$$

Let us consider the two following charts for $\mathcal{S}^1$ (here given by the inverse of the chart):

$$\begin{array}{rcl}\phi_{(1)}^{-1}:\,]-\pi,\pi[& \rightarrow & \mathcal{S}^1\setminus\{(-1,0,0)\} \\ t & \mapsto & (\cos t,\sin t,0)\end{array}$$

$$\begin{aligned} \phi_{(2)}^{-1} :]0, 2\pi[&\rightarrow \mathcal{S}^1 \setminus \{(1,0,0)\} \\ t &\mapsto (\cos t, \sin t, 0) \end{aligned}$$

Using these charts and the chart $\left(\mathcal{U}_{(1)}, \varphi_{(1)}\right)$ *for* $\mathcal{S}^2$*, a tangent vector* $v_c \in \mathrm{T}_P\mathcal{S}^1$ *is given as follows:*

$$v_c = \left\{ \gamma \in \mathcal{C}_P\left(\mathcal{S}^1\right) \text{ such that } \left.\frac{d\left(\varphi_{(1)} \circ \gamma\right)}{ds}\right|_{s=0} = c \begin{pmatrix} -\sin\left(\phi_{(i)}(P)\right) \\ \cos\left(\phi_{(i)}(P)\right) \end{pmatrix} \right\}$$

where $\phi_{(i)}$ *can be either* $\phi_{(1)}$ *or* $\phi_{(2)}$*. Applying* (E.3) *to* v_c*, we have:*

$$\begin{aligned} \theta(v_c) &= X\mathrm{d}X(v_c) + Y\mathrm{d}Y(v_c) \\ &= \cos\left(\phi_{(i)}(P)\right) c\left(-\sin\left(\phi_{(i)}(P)\right)\right) + \sin\left(\phi_{(i)}(P)\right) c\cos\left(\phi_{(i)}(P)\right) \\ &= 0 \end{aligned}$$

E.3 Contact manifolds

Let us consider an odd-dimensional, connected, differentiable manifold $\mathscr{M}$ of dimension $2d_M + 1$. Assume there exists a 1-form θ fulfilling the following condition:

$$\theta \wedge (\mathrm{d}\theta)^{d_M} \neq 0 \quad \text{and} \quad (\mathrm{d}\theta)^{d_M+1} = 0 \tag{E.6}$$

where $(2d_M + 1)$ is the dimension of $\mathscr{M}$ and $\wedge$ denotes the exterior product. Then θ is called a *contact form* and the manifold $(\mathscr{M}, \theta)$ endowed with the contact form θ is called a *contact manifold*. In other words a contact form is a 1-form of maximal class, namely $2d_M + 1$ (see Definition E.22).

Proposition E.1 (Darboux's theorem)**.** *Consider a contact manifold* $(\mathscr{M}, \theta)$ *where* $\mathscr{M}$ *is a differentiable manifold of dimension* $2d_M+1$ *(i.e. odd-dimensional). Since* θ *fulfills condition* (E.6)*, there exists a local set of coordinates* $(x_0, x_1, \ldots, x_{d_M}, p_1, \ldots, p_{d_M})$ *such that* θ *can be expressed in the following way in a neighbourhood* $\mathscr{V}$ *of every point of* $\mathscr{M}$*:*

$$\theta|_{\mathscr{V}} = \mathrm{d}x_0 - p^t\mathrm{d}x$$

where $x = [x_1, \ldots, x_{d_M}]^t$*,* $p = [p_1, \ldots, p_{d_M}]^t$ *and* $|_{\mathscr{V}}$ *indicates the restriction to* $\mathscr{V}$*.*

Remark E.2. *Darboux's theorem is a generalization of Frobenius's theorem [52] for 1-forms of class greater than 1 [69]. Frobenius's theorem states that a non-zero 1-form θ defined on some differentiable manifold $\mathscr{M}$ of dimension d has an integral manifold of dimension $d-1$ if $\mathrm{d}\theta = 0$ (i.e. θ is of class 1), which means that there exists a set of local coordinates $(X_1, \ldots, X_d)$ such that in these coordinates $\theta = \mathrm{d}X_1$ [69]. As a consequence Frobenius's theorem is the particular case of Darboux's theorem for 1-forms of class 1.*

The d_M-dimensional integral manifolds $\mathscr{L} \subset \mathscr{M}$ of the Pfaffian equation $\theta = 0$ (associated to the contact manifold $(\mathscr{M}, \theta)$) are called *Legendre submanifolds* of $(\mathscr{M}, \theta)$.

Proposition E.2. *In the set of local coordinates, each Legendre submanifold can be generated by a differentiable function $F(x_I, p_J)$ of d_M variables where $I \cup J = \{1, \ldots, d_M\}$ is a disjoint partition of the set of indices. The coordinates of each point of the Legendre submanifold $\mathscr{L}$ fulfill then the following relations:*

$$x_0 \overset{\mathscr{L}}{=} F(x_I, p_J) - p_J^t \frac{\partial F}{\partial p_J}, \quad x_J \overset{\mathscr{L}}{=} -\frac{\partial F}{\partial p_J}, \quad p_I \overset{\mathscr{L}}{=} \frac{\partial F}{\partial x_I} \tag{E.7}$$

Conversely, given a set of coordinates and any disjoint partition $I \cup J$ of the set of indices $\{1, ..., d_F\}$ and a differentiable function $F(x_I, p_J)$ of d_M variables, the relations (E.7) *define a Legendre submanifold.*

Example E.4. *The Euclidean space $\mathbb{R}^3$ is a manifold. Let us consider the chart $\left(\mathbb{R}^3, \varphi\right)$ that to each point of $x \in \mathbb{R}^3$ associates its canonical coordinates (X, Y, Z). Let us consider the following 1-form:*

$$\theta = Z - Y\mathrm{d}X$$

Let us choose the following generating function: $F(X) = -X^2$ with the partition $I = \{1\}$ and $J = \emptyset$. As suggested by (E.7)*, we consider the following subset of $\mathbb{R}^3$:*

$$\mathscr{L} = \left\{(X, Y, Z) \,|\, Y = -2X,\, Z = -X^2\right\}$$

It can be easily seen that $\mathscr{L}$ is indeed a submanifold of $\mathbb{R}^3$ and a chart $(\mathscr{L}, \phi)$

is given as follows:

$$\begin{array}{ll} \phi: & \mathscr{L} \to \mathbb{R} \\ & (X,Y,Z) \mapsto t = X \end{array} \qquad \begin{array}{l} \phi^{-1}: \mathbb{R} \to \mathscr{L} \\ t \mapsto \left(t, -2t, -t^2\right) \end{array}$$

By a similar development as in Example E.3, it can be seen that a tangent vector v_c of $\mathscr{L}$ at a point $P \in \mathscr{L}$ is given as follows:

$$v_c = \left\{ \gamma \in \mathcal{C}_P\left(\mathscr{L}\right) \text{ such that } \left.\frac{d\left(\varphi \circ \gamma\right)}{ds}\right|_{s=0} = c \begin{pmatrix} 1 \\ -2 \\ -2\phi\left(P\right) \end{pmatrix} \right\}$$

Let us now apply the 1-form θ to v_c:

$$\theta\left(v_c\right) = \mathrm{d}Z - Y\mathrm{d}X = -2c\phi\left(P\right) - \left(-2\phi\left(P\right)\right)c = 0$$

As a consequence $\mathscr{L}$ is indeed an integral manifold of θ of dimension 1 and is hence a Legendre submanifold of $\left(\mathbb{R}^3, \theta\right)$. Graphically, $\mathscr{L}$ is a curve in $\mathbb{R}^3$.

Definition E.24 (Legendre transform)**.** The Legendre transform allows to express a scalar function $F\left(X,Y\right)$ as a different function, whose arguments are the partial derivatives of $F\left(X,Y\right)$ instead of Y. Let $F\left(X,Y\right)$ be some scalar differentiable function (X and Y are vectors). The Legendre transform $F^\star\left(X,p\right)$ is given by the following expression:

$$F^\star\left(X,p\right) = \left[F\left(X,Y\right) - Y^t p\right]_{p=\frac{\partial F}{\partial Y}}$$

The Legendre transforms of the generating function from a given Legendre submanifold is another generating function corresponding to another partition of the indices.

Example E.4 (continued)**.** *Let us now consider the Legendre transform of the previous generating function $F\left(X\right) = -X^2$:*

$$\begin{aligned} F^\star\left(Y\right) &= \left[F\left(X\right) - \frac{dF}{dX}X\right]_{Y=\frac{dF}{dX}} = \left[-X^2 - \left(-2X\right)X\right]_{Y=\frac{dF}{dX}} \\ &= \left[X^2\right]_{Y=\frac{dF}{dX}} = \frac{Y^2}{4} \end{aligned}$$

Let us now apply (E.7) *with the partition* $I = \emptyset$ *and* $J = \{1\}$. *The obtained set is given as follows:*

$$\mathscr{L}_2 = \left\{ (X, Y, Z) \,|X = -\frac{Y}{2},\, Z = \frac{Y^2}{4} - Y\frac{Y}{2} = -\frac{Y^2}{4} \right\}$$

It is obvious that $\mathscr{L}_2 = \mathscr{L}$, *i.e. that* $F(X)$ *and* $F^\star(Y)$ *generate the same Legendre submanifold provided that the partitions of the indices are chosen adequately.*