



Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

An entropy-based formulation of irreversible processes based on contact structures

A. Favache^a, D. Dochain^{b,*}, B. Maschke^c

^a Institute of Mechanics, Materials, and Civil Engineering, Université catholique de Louvain, 2 place Sainte Barbe, B-1348 Louvain-la-Neuve, Belgium

^b CESAME, Université catholique de Louvain, 4-6 avenue G. Lemaître, B-1348 Louvain-la-Neuve, Belgium

^c LAGEP, UMR CNRS 5007, Université de Lyon, Université Lyon 1, F-69622 Villeurbanne, France

ARTICLE INFO

Article history:

Received 10 July 2009

Received in revised form

5 February 2010

Accepted 18 June 2010

Available online 7 July 2010

Keywords:

Irreversible thermodynamics

GENERIC

Matrix

Contact structures

Entropy

System theory

ABSTRACT

In this paper we propose an analytical formulation of the dynamical behaviour of complex and open physical systems which is formulated on the total thermodynamic phase space using the contact form associated with Gibbs' relation. Starting from balance equations we construct control contact systems by using the entropy function to represent the thermodynamic properties. The contact Hamiltonian function generating the dynamical behaviour has then the units of an entropy variation. We consider complex thermodynamic systems, described by compartmental systems, and we construct the associated control contact system by composing the control contact formulation of every compartment. The contact Hamiltonian functions generating the dynamical behaviour are discussed with respect to two alternative formalisms used for describing coupled sets of reversible and irreversible processes, namely the GENERIC formulation and the Matrix formulation. This analysis is then illustrated on the elementary example of a coupled mechanical and thermodynamic system.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Physics-based control design is an approach for the control of physical systems for which a growing interest has risen in the recent years. The design of the control systems is based on the understanding of the physical phenomena that give rise to the dynamical behaviour. For electro-mechanical systems, this approach has been largely studied with the use of the Lagrangian or Hamiltonian formalism. However with regard to chemical processes and more generally to thermodynamic systems in the large (i.e. systems where reversible and irreversible phenomena take place), this area is only in its early stages. Some results in interpreting physical properties in terms of nonlinear dynamical system theory and control have been already achieved. For instance quantities related to the entropy (e.g. the entropy itself, the entropy production, the availability) have been considered as Lyapunov function candidates (Alonso and Ydstie, 2001; Favache, 2009; Favache and Dochain, 2009a, b; Ydstie, 2002). In this paper we shall develop an analytical formulation adapted to modelling thermodynamic systems with the perspective of formalizing the previous results and extend them in a systematic way.

* Corresponding author.

E-mail addresses: audrey.favache@uclouvain.be (A. Favache), denis.dochain@uclouvain.be (D. Dochain), maschke@lagep.univ-lyon1.fr (B. Maschke).

The modelling of complex transport phenomena as they arise in the analysis of rheological fluids, multiphase fluids, meteorological systems for instance, is greatly enhanced by the use of structural properties associated with the basic physical modelling assumptions. They result from the main physical modelling assumptions that encompass the formulation of conservation laws, the thermodynamic properties of matter and the reversible and irreversible phenomena. This leads to dynamical behaviours that possess dynamical invariants or preserve some geometric structures for instance whose flows are symplectic transformations. The main issue is to express the dynamical equations in such a way to explicitly embed the physical properties. Considering for instance complex fluids, the aim is to embed the thermodynamic properties of the fluid, as well as the structure of the fluid dynamics and the irreversible phenomena in the formulation of the dynamical system. The thermodynamic properties are captured in the definition of one or several thermodynamic functions (such as the internal energy or any of its Legendre transformations). The reversible processes are captured in the definition of some differential geometric structures such as Poisson brackets (for mechanical systems or fluid dynamics) (Arnold, 1989; Olver, 1993) and the irreversible processes are defined using a symmetric bracket (Grmela and Öttinger, 1997; Ortega and Planas-Bielsa, 2004). Physical systems subject simultaneously to reversible and irreversible processes are expressed as the sum of gradient and pseudo-Hamiltonian dynamical systems (Dalsmo and van der Schaft, 1999; Grmela and

Öttinger, 1997; Öttinger and Grmela, 1997). In order to include the interaction with their environment (i.e. open systems), or for their control, these systems have been extended in two ways. A first extension consists in rendering the Hamiltonian functions or the generating potential of gradient systems depending not only on the state but also on some input variables (Cortés et al., 2005; van der Schaft, 1989). The second extension consisted in the description of the interaction with the environment, in terms of a geometric structure called Dirac structure (Courant, 1990), a generalization of the Poisson bracket, defined on manifolds including the input and output spaces (Dalsmo and van der Schaft, 1999; van der Schaft and Maschke, 1995; Yoshimura and Marsden, 2006).

In this paper we suggest to use an alternative formulation, based on contact forms, another geometrical structure, arising from the differential geometric formulation of the thermodynamic properties of matter as it has been developed in Carathéodory (1909) and Mrugała et al. (1991) according to the geometrical definition suggested by Gibbs (1873b). Recent work has shown that the same structure might be used in order to describe reversible thermodynamic transformations (Mrugała, 2000) and irreversible dynamical processes (Eberard et al., 2007; Grmela, 2002b; Grmela and Öttinger, 1997). In the present paper we propose a formulation based on the entropy form of Gibbs' equation and suggest a general formulation of a class of compartmental systems as the composition of elementary models.

In order to discuss the advantages of the suggested contact formulation, we shall analyze two alternative formal frameworks for modelling thermodynamic systems: the GENERIC formalism (general equation for the non-equilibrium reversible-irreversible coupling) by Grmela and Öttinger (1997) and Öttinger and Grmela (1997) as well as the Matrix formalism developed by Jongschaap (2001) and Jongschaap and Öttinger (2004).

In Section 2 we shall recall the definition of the contact structure associated with a thermodynamic system and the definition of reversible and irreversible systems on this structure using contact vector fields. We shall also show how one may formulate open thermodynamic systems in this framework. In Section 3, after a brief exposition of the GENERIC and Matrix formalisms, we shall show how they can be related to the contact formulation. Section 4 illustrates the contact formalism in comparison with GENERIC and Matrix by considering the simple example of a gas-piston system also treated in Jongschaap and Öttinger (2004).

2. Contact formulation of open and irreversible systems using the entropy

In this section we first recall how the geometric definition of the thermodynamic properties of simple systems introduced by Gibbs (1873a) using tangent planes is formalized in a differential-geometric way using Pfaffian equations and the contact geometry (Arnold, 1989; Carathéodory, 1909; Herman, 1973). Secondly we recall how the reversible and irreversible transformations of a thermodynamic system may be expressed by a contact vector field generated by some contact Hamiltonian function defining the transformation (Eberard et al., 2007; Grmela, 2002b; Mrugała, 1993, 2000). However we shall depart from the cited work in the sense that we shall use the fundamental thermodynamic equation in terms of the entropy function instead of the energy function. Thirdly we shall consider complex thermodynamic systems, in the sense of compartmental systems, and show that the contact systems of every subsystem may be composed to obtain the contact system of the complex system.

2.1. Gibbs' relation in the thermodynamic phase space

Let us first consider a simple thermodynamic system¹ (Callen, 1960) consisting of a mixture of N chemical species. Its thermodynamic properties may be described in the thermodynamic phase space composed of $2\delta+1$ state variables, where $\delta=N+2$. They are composed of $\delta+1$ extensive quantities (the internal energy U , the volume V , the number of moles n_i of the species $i=1, \dots, N$, the entropy S) and δ intensive quantities (the pressure P , the temperature T and the chemical potential μ_i of the species i). If several chemical species are present in the subsystem, then we denote by n and μ the N -dimensional vectors with entry i for each species. According to the Gibbs' phase theorem, only δ of these quantities are independent since they have to obey Gibbs' relation:

$$dS - \frac{1}{T}dU - \frac{P}{T}dV + \frac{\mu^t}{T}dn = 0 \quad (1)$$

The thermodynamic properties may be derived from a fundamental thermodynamic equation (Gibbs, 1873a) relating the set of extensive variables and which may be defined in an equivalent way as the energy function: $U = \tilde{U}(S, V, n)$ or preferably in this paper, the entropy function:

$$S = \tilde{S}(U, V, n) \quad (2)$$

The δ dependent quantities are then obtained by writing the differential of the entropy function (2):

$$\frac{1}{T} = \frac{\partial \tilde{S}}{\partial U}, \quad \frac{P}{T} = \frac{\partial \tilde{S}}{\partial V}, \quad -\frac{\mu}{T} = \frac{\partial \tilde{S}}{\partial n} \quad (3)$$

Hence the entropy conjugate variable to the internal energy, to the volume and to the number of moles n_i of species i are $1/T$, P/T and $-\mu_i/T$, respectively.

This thermodynamic perspective may be extended in order to include other physical domains, the mechanical domain if the system or some part of it undergoes some motion, or the electromagnetic domain if some species are charged for instance.

In his work, Gibbs developed a geometrical approach of thermodynamics (Gibbs, 1873a, b). The fundamental relation (2) of a subsystem can be represented by an hypersurface in a $(\delta+1)$ -dimensional space of the extensive variables. This hypersurface is called the thermodynamic surface. The relation (3) indicates that the intensive variables define the tangent hyperplanes to the thermodynamic surface. Actually the structure of Gibbs' relations (1) endows the thermodynamic phase space with a canonical geometric structure, called *contact structure*, in the same way as Lagrangian and Hamiltonian formulations endow their state space with a symplectic form or Poisson bracket (Arnold, 1989; Herman, 1973). In the remainder of this paragraph we shall briefly recall some basic notions of contact geometry useful for thermodynamic systems and refer the reader to the books (Arnold, 1989; Herman, 1973) for a detailed mathematical exposition and to Chen (1999), Eberard (2006), Mrugała (1978), and Mrugała et al. (1991) for the application to equilibrium thermodynamics. For the sake of simplicity we shall restrict ourselves to a presentation in some coordinates and hence identify the thermodynamic phase space with the real vector space $\mathcal{T} = \mathbb{R}^{2\delta+1}$, $\delta \in \mathbb{N}$.

Gibbs' relation and the definition of the equilibrium thermodynamic properties have been defined in a differential-geometric way in the fundamental paper of Carathéodory (1909) who formulated them in terms of a Pfaffian equation. This Pfaffian equation is expressed in terms of a 1-form, called *contact form*, which in a set of canonical coordinates $(x_0, x_1, \dots, x_\delta, p_1, \dots, p_\delta)$ is

¹ I.e. a macroscopically homogeneous, isotropic and uncharged system.

written as follows:

$$\theta = dx_0 - \sum_{i=1}^{\delta} p_i dx_i \quad (4)$$

and defines locally a 1-form of class $2\delta+1$ (Arnold, 1989; Herman, 1973).

The solution of the Pfaffian equation $\theta = 0$ with θ being Gibbs' contact form (4) (for instance (1)), is a δ -dimensional integral manifold of the thermodynamic phase space $\mathbb{R}^{2\delta+1}$, called *Legendre submanifold*. Any point of this Legendre submanifold corresponds to state variables compatible with the thermodynamic properties of the considered system. It may be shown that in a set of canonical coordinates $(x_0, x_1, \dots, x_\delta, p_1, \dots, p_\delta)$, a Legendre submanifold is defined by a *generating function* $\mathcal{F}(x_i, p_j)$ using the following relations:

$$x_0 = \mathcal{F}(x_i, p_j) - p_j \frac{\partial \mathcal{F}}{\partial p_j}, \quad x_j = -\frac{\partial \mathcal{F}}{\partial p_j}, \quad p_l = \frac{\partial \mathcal{F}}{\partial x_l} \quad (5)$$

for any disjoint partition $I \cup J = \{1, \dots, \delta\}$ of the set of indices. Furthermore the generating functions for the different partitions are partial Legendre transformations of each other.

Example 1. Consider the example of a simple thermodynamic system consisting of a mixture of N species, and choose canonical coordinates such that restricted on the Legendre submanifold, we have the following equivalence:

$$\begin{cases} x_0 \equiv S \\ \mathbf{x} \equiv [U, V, n]^t \\ \mathbf{p} \equiv [p_U, p_V, p_n]^t \end{cases} \quad (6)$$

and the partition $I = \{1, \dots, \delta\}$ and $J = \emptyset$, then the generating equation (5) is simply the entropy function $\tilde{S}(x_i)$ of the fundamental thermodynamic equation (2) and the identification on the Legendre submanifold with the energy-conjugated intensive variables is explicitly written as follows:

$$x_0 = \tilde{S}(x_i) \quad \text{and} \quad p_l = \frac{\partial \tilde{S}}{\partial x_l}(x_i) = \left[\frac{1}{T}, \frac{P}{T}, -\frac{\mu}{T} \right]^t$$

Other choices of partition correspond to choose as generating function some partial Legendre transformations of the entropy function also called *Massieu-Planck functions*.

2.2. Reversible and irreversible transformations as contact vector fields

It appears that the transformations of thermodynamic systems may also be formulated in this geometric framework as transformations that leave the contact structure invariant. Indeed if the transformations undergone by the system define a quasi-static process, the transient states are all thermodynamic equilibrium states, and the state variables fulfill the fundamental relation. Such infinitesimal transformations may be defined in terms of *contact vector fields* \mathfrak{X} on the thermodynamic phase space \mathcal{T} (Arnold, 1989; Herman, 1973). Furthermore it may be shown that contact vector field are uniquely defined by a real-valued function f called contact Hamiltonian (and actually the reverse is also true). In the sequel we shall denote by \mathfrak{X}_f the contact vector field generated by the contact Hamiltonian function f . In a set of canonical coordinates $(x_0, x_1, \dots, x_\delta, p_1, \dots, p_\delta)$, the contact vector

field is expressed by

$$\mathfrak{X}_f = \begin{pmatrix} f \\ 0 \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & -p^t \\ 0 & 0 & -I_\delta \\ p & I_\delta & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial f}{\partial x_0} \\ \frac{\partial f}{\partial \mathbf{x}} \\ \frac{\partial f}{\partial \mathbf{p}} \end{pmatrix} \quad (7)$$

where I_δ denotes the $\delta \times \delta$ identity matrix.

Contact vector fields usually appear in the framework of time-varying Hamiltonian systems and also, however much less used, for the formulation of thermodynamic transformations (Eberard et al., 2007; Grmela, 2002b; Mrugała, 1993, 2000; Mrugała et al., 1991). For (quasi-static) transformations of a thermodynamic system, a trivial condition on the contact vector field is that it should leave the Legendre submanifold characterizing its thermodynamic properties invariant. This leads to a condition on the contact Hamiltonian function given in Mrugała et al. (1991) and that states that a contact vector field \mathfrak{X}_f , generated by the contact Hamiltonian f , is tangent to a given Legendre submanifold \mathcal{L} if and only if the contact Hamiltonian function f is identically zero on \mathcal{L} :

$$\mathcal{L} \subset f^{-1}(0) \quad (8)$$

In this paper we are interested in the contact formulations of irreversible processes in the continuation of the formulation suggested in Grmela (2002b) and the formulation of the so-called *conservative contact systems* suggested in Eberard et al. (2006, 2007). This allows to generalize the contact Hamiltonians from the state equations used to generate reversible transformations to contact Hamiltonians generating irreversible transformations and defined by the constitutive relations of the irreversible phenomena.

Definition 1. A *conservative contact system* is defined as a quadruple composed of a contact manifold \mathcal{T} endowed with the contact form θ , a Legendre submanifold \mathcal{L} characterizing some thermodynamic properties, a contact Hamiltonian function f_0 satisfying the invariance condition (8) and the differential equation: $(dx/dt)(t) = \mathfrak{X}_{f_0}$.

In this paper we shall use the entropy form of Gibbs' relation (1) which leads in the case of a mixture of N species, to the identification of the canonical coordinates relations (6). Indeed with the entropy 1-form, the conservative extensive quantities are gathered in the vector \mathbf{x} , the intensive quantities are gathered in the vector \mathbf{p} and the non-conserved entropy is given by x_0 . The time variation dx/dt of the conserved variables corresponds to the balance equations on the energy, the volume and the matter which are the base equations of models in chemical engineering. As will be shown in the sequel this choice of coordinates is well adapted for the derivation of the contact formulation (see also Favache et al., 2009). A striking feature of this formulation is that the total entropy balance equation is then derived directly from the contact Hamiltonian function. This departs from the work of Eberard et al. (2005, 2007) who used the internal energy form $dU - T dS + P dV - \mu^n dn = 0$. The formulation in Eberard et al. (2005, 2007) has indeed been developed as an extension of controlled Hamiltonian systems and is well adapted to electro-mechanical systems for which the entropy is not expressed. Hence the entropy formulation is better adapted for thermodynamic systems in general, especially if heat exchanges or chemical reactions occur.

When dealing with open thermodynamic systems, the conservative Hamiltonian systems of Definition 1 is extended to *control contact systems* following the definition suggested in Eberard et al. (2007).

Definition 2 (Eberard et al., 2007). A conservative control contact system is defined as a quintuple composed of a contact manifold \mathcal{L} endowed with the contact form θ , a Legendre submanifold \mathcal{L} characterizing the system's thermodynamic properties, $\mathcal{U} = \mathbb{R}^m \ni u = (u_1, \dots, u_m)$ the input space, and an internal contact Hamiltonian f_0 with m control contact Hamiltonians $f_j(x, u_j)$, $j = 1, \dots, m$ satisfying the invariance condition (8). The dynamics are given by the differential equation:

$$\frac{dx}{dt} = \dot{x}_0(x) + \sum_{j=1}^m \dot{x}_j(x, u_j) = \dot{x}(x, u) \quad (9)$$

As an elementary illustration, consider the example of an open simple thermodynamic system undergoing some irreversible transformation due to thermodynamic non-equilibrium conditions with its environment.

Example 2. Consider a simple mono-constituent thermodynamic system with thermodynamic properties given by the fundamental relation with some entropy function as the generating function (2). Define its thermodynamic properties by the Legendre submanifold according to Example 1. Let us assume that the system is closed and isochore and may only exchange a heat flux due to conduction through the wall separating it from the environment being at some temperature T_{env} . Let us consider the following contact Hamiltonian function:

$$f(x_U, p_U, T_{env}) = - \left(p_U - \frac{\partial \tilde{S}}{\partial U} \right) \dot{Q}(p_U, T_{env})$$

where $(\partial \tilde{S} / \partial U)(U, V, N) = 1/T$, \dot{Q} denotes the heat flux through the wall: $\dot{Q}(p_U, T_{env}) = \kappa(T_{env} - 1/p_U)$ and κ denotes the heat conduction coefficient. As the contact Hamiltonian function does not depend on P/T and μ^t/T , i.e. the entropy-conjugated intensive variables to the volume and the number of moles, it generates an isochore and closed transformation. Let us now compute the time evolution of the internal energy, its conjugated variable and the entropy using (7) and restricted to the Legendre submanifold:

$$\left. \frac{dS}{dt} \right|_{\mathcal{L}} = -p_U \left. \frac{\partial f}{\partial p_U} \right|_{\mathcal{L}} = \frac{\dot{Q}}{T}$$

$$\left. \frac{dU}{dt} \right|_{\mathcal{L}} = - \left. \frac{\partial f}{\partial p_U} \right|_{\mathcal{L}} = \dot{Q}$$

$$\frac{d}{dt} \left(\frac{1}{T} \right) = \left. \frac{dp_U}{dt} \right|_{\mathcal{L}} = \left. \frac{\partial f}{\partial U} \right|_{\mathcal{L}} = \dot{Q} \frac{\partial^2 S}{\partial U^2}$$

It may be noted that in the above example, the Hessian matrix of the entropy function appears in the dynamic equation on the intensive variable. Following the second principle of thermodynamics this function is concave. A stability analysis of the above dynamical system would show that the concavity leads to a stability criterion. In Favache et al. (2009) a stability criterion for contact systems has been established and has been given a physical interpretation using the concavity of the entropy function.

2.3. Complex systems

In this section we shall give the formulation of systems consisting of sets of coupled conservation laws (Favache et al., 2007) generalizing systems appearing in chemical and biological systems under the name of compartmental models.

Such a system is composed of K compartments consisting of simple thermodynamic systems exchanging fluxes of their extensive variables. Let us assume that the dynamics of each compartment, indexed by $i = 1, \dots, K$, is described by the balance

equations on the extensive variables, $x^{(i)} = [U^{(i)}, V^{(i)}, n^{(i)}]^t$. The total flux for each extensive variable, denoted by $\mathcal{N}_x^{(i)}$, is the variation of the quantity x due to the incoming/outcoming fluxes and to the consumption/production term (for $n^{(i)}$); it depends on the thermodynamic state $(x^{(i)}, p^{(i)})$ of the subsystem i , the variables

$$\eta^{(i)} = \Psi \left(\left[G_{ij} \left(\begin{matrix} x^{(j)} \\ p^{(j)} \end{matrix} \right) \right]_{j=1, \dots, n}^t \right) \quad (10)$$

that refer to the state of the other compartments interacting with the compartment i and where G_{ij} is the adjacency matrix of the graph defining the compartmental system and the variables ξ_{ext} that refer to the state of environment of the compartmental system. For instance ξ_{ext} could be the temperature of the environment whereas $\eta^{(i)}$ could be the temperature of the subsystem $j \neq i$. The dynamics are given by the following balance equations on the energy, the volume and the mass, respectively:

$$\frac{dU^{(i)}}{dt} = \mathcal{N}_E^{(i)}(x^{(i)}, p^{(i)}, \eta^{(i)}, \xi_{ext}) \quad (11a)$$

$$\frac{dV^{(i)}}{dt} = \mathcal{N}_V^{(i)}(x^{(i)}, p^{(i)}, \eta^{(i)}, \xi_{ext}) \quad (11b)$$

$$\frac{dn^{(i)}}{dt} = \mathcal{N}_n^{(i)}(x^{(i)}, p^{(i)}, \eta^{(i)}, \xi_{ext}) \quad (11c)$$

Consider the following contact Hamiltonian function:

$$f^{(i)}(x^{(i)}, p^{(i)}, \eta^{(i)}, \xi_{ext}) = \left(\frac{\partial \mathcal{F}^{(i)}}{\partial x^{(i)}} - p^{(i)} \right)^t \mathcal{N}^{(i)}(x^{(i)}, p^{(i)}, \eta^{(i)}, \xi_{ext}) \quad (12)$$

where $\mathcal{N}^{(i)} = [\mathcal{N}_E^{(i)}, \mathcal{N}_V^{(i)}, \mathcal{N}_n^{(i)}]^t$ and $\mathcal{F}^{(i)}(x^{(i)})$ is the generating function of the Legendre submanifold generating the thermodynamic model of the compartment i . By construction, this contact Hamiltonian satisfies the invariance condition (8) and defines a conservative contact system according to Definition 2 (for a proof, see Favache, 2009; Favache et al., 2007).

Let us now consider the dynamics of the K interconnected compartments. First we shall define the thermodynamic properties of the total compartmental system. Therefore similarly as suggested in Eberard et al. (2006) and Favache et al. (2007), we shall define the thermodynamic phase space of the compartmental system on the product space of the pairs of entropy-conjugated variables of each compartment augmented by the total entropy of the compartmental system. The thermodynamic phase space of the compartmental system is defined by the $(2 \sum_{i=1}^K \delta^{(i)} + 1)$ -dimensional real vector space endowed with the entropy contact form

$$\theta = dx_0^{tot} - \sum_{i=1}^K (p^{(i)})^t dx^{(i)} = dx_0^{tot} - p^t dx \quad (13)$$

with the following canonical coordinates:

$$x_0^{tot}, x = [x^{(1)}, \dots, x^{(K)}]^t, \quad p = [p^{(1)}, \dots, p^{(K)}]^t$$

The thermodynamic properties of the compartmental system are defined as the $(\sum_{i=1}^K \delta^{(i)})$ -dimensional Legendre submanifold \mathcal{L} generated by the function $\mathcal{F}(x)$ which is the sum of the generating functions of each subsystem:

$$\mathcal{F}(x) = \sum_{i=1}^K \mathcal{F}^{(i)}(x^{(i)}) \quad (14)$$

It is easy to see from (5) that on the Legendre submanifold \mathcal{L} , the total entropy satisfies $x_0^{tot} = \sum_{i=1}^K x_0^{(i)}$ where $(x_0^{(i)}, x^{(i)}, p^{(i)}) \in \mathcal{L}^{(i)}$ for all $i \in \{1, \dots, K\}$ and that, due to the separation property of the generating function (i.e. the entropy of each subsystem depends only on the state of the subsystem itself and not on the state of

the other subsystems), setting $\mathcal{F}^{(j)} = 0, j \neq i$, one recovers $(x_0^{tot}, x^{(i)}, p^{(i)}) \in \mathcal{L}^{(i)}$.

The contact Hamiltonian function generating the dynamics of the global system is given by the sum of the contact Hamiltonian of each compartment:

$$f(x_0^{tot}, x, p, \xi_{ext}) = \sum_{i=1}^K f^{(i)}(x^{(i)}, p^{(i)}, \eta^{(i)}, \xi_{ext}) \quad (15)$$

with

$$\eta^{(i)} = \Psi \left(\left[G_{ij} \begin{pmatrix} x^{(j)} \\ p^{(j)} \end{pmatrix} \right]_{j=1, \dots, n}^t \right)$$

3. Contact formulation of GENERIC and Matrix

In the preceding section, we did not specify the general expression of the fluxes in the balance equations on the extensive variables (11a)–(11c). However following the theories of irreversible thermodynamics near equilibrium, these fluxes are in general expressed as semi-linear functions of the generating forces giving rise to dynamical phenomena (Bird et al., 2002; Callen, 1960; deGroot and Mazur, 1962; Jou et al., 2001; Prigogine, 1962).

In order to discuss the structure of the balance equations, we shall recall two other formalisms based on the axioms of irreversible thermodynamics in the definition of the state space and the generating functions as thermodynamic state variables and potentials. The first one is called GENERIC (general equation for the non-equilibrium reversible-irreversible coupling) and consists in the sum of an Hamiltonian and a pseudo-gradient dynamical system generated by two different generating functions, namely the entropy and the energy (Grmela, 2002b; Grmela and Öttinger, 1997; Öttinger and Grmela, 1997). We shall recall its definition for isolated systems defined on the extensive variables subject to conservation laws and its lift to a contact formulation on the thermodynamic phase space. We shall then discuss the representation of the interaction with the environment. The second formalism is called Matrix and is based on defining a structured (semi-)linear mapping which is composed of skew-symmetric and a symmetric part, on thermodynamic force and flux variables (Jongschaap, 2001; Jongschaap et al., 1994; Jongschaap and Öttinger, 2004). We shall recall its definition and give its contact formulation on the thermodynamic phase space.

3.1. The GENERIC formalism

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 both reversible and irreversible physical systems in a single framework (Grmela and Öttinger, 1997; Öttinger, 1999; Öttinger and Grmela, 1997). It has been first developed for isolated thermodynamic systems, but Muschik and Jongschaap have proposed two different approaches to extend it to open systems (Jongschaap and Öttinger, 2004; Muschik et al., 2000). Therefore we shall first present the GENERIC formalism as it was initially developed for isolated systems in Section 3.1.1, then show how to extend it to open systems in Section 3.1.2.

3.1.1. Representation of isolated systems

In the GENERIC formalism, the time evolution of the δ independent variables required for the description of the system, denoted by $Z \in \mathbb{R}^\delta$, of a complex thermodynamic system is expressed as the sum of a Hamiltonian system and a dissipative

system. The Hamiltonian system is defined with respect to a Poisson bracket (with structure matrix denoted by $L(Z)$) 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 $M(Z)$ 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 3. A GENERIC system on the vector space $\mathbb{R}^\delta \ni Z$ is defined by a Poisson bracket denoted by $\{, \}$ with structure matrix $L(Z)$ and a pseudo-Riemannian metric a Ginzburg–Landau dissipative bracket denoted by $[,]$, with semi-definite positive symmetric structure matrix $M(Z)$. The GENERIC system is generated by two functions $E^{tot}(Z)$ and $S^{tot}(Z)$ fulfilling the following conditions:

$$\forall g(Z) \in C^\infty(\mathbb{R}^\delta) : [g(Z), E^{tot}(Z)] = 0 \quad \text{i.e.} \quad M(Z) \frac{\partial E^{tot}}{\partial Z} = 0 \quad (16a)$$

$$\forall g(Z) \in C^\infty(\mathbb{R}^\delta) : \{g(Z), S^{tot}(Z)\} = 0 \quad \text{i.e.} \quad L(Z) \frac{\partial S^{tot}}{\partial Z} = 0 \quad (16b)$$

The system dynamics are then given by the following differential equation:

$$\frac{dZ}{dt} = \{Z, E_{tot}\} + [Z, S_{tot}] \quad \text{i.e.} \quad \frac{dZ}{dt} = L(Z) \frac{\partial E^{tot}}{\partial Z} + M(Z) \frac{\partial S^{tot}}{\partial Z} \quad (17)$$

Remark 1. The bracket $[,]$ is called the Ginzburg–Landau dissipative bracket (Grmela and Öttinger, 1997). The Ginzburg–Landau dissipative bracket is symmetric (i.e. for all $A, B \in C^\infty(Z)$, $[A(Z), B(Z)] = [B(Z), A(Z)]$) and satisfies the positivity condition $[A(Z), A(Z)] \geq 0$ for all $A \in C^\infty(\mathbb{R}^\delta)$.

This definition is justified for models where the reversible phenomena are generated by the gradient of the total energy function $E^{tot}(Z)$ and the irreversible phenomena are generated by the gradient of the total entropy function $S^{tot}(Z)$ of some complex thermodynamic system (Grmela, 2002a, b; Grmela and Öttinger, 1997; Öttinger and Grmela, 1997). It could seem that the two generating functions $E^{tot}(Z)$ and $S^{tot}(Z)$ are chosen independently. However when considering quasi-static processes for the subsystems they both are the sum of entropy and energy functions characterizing the thermodynamic equilibrium states of the subsystems. Thus they are linked by the fundamental relation (2) of each of the subsystems. However when considering quasi-static processes for the complex system and each of its components, they are related by the fundamental relation (2).

The condition (16a) expresses that the energy function is a Casimir function of the (Ginzburg–Landau) dissipative bracket.² As a consequence, using also the skew-symmetry of the Poisson bracket, the total energy is conserved:

$$\frac{dE^{tot}}{dt} = \{E^{tot}, E^{tot}\} + [E^{tot}, S^{tot}] = 0$$

Condition (16b) expresses that the entropy function is a Casimir function of the Poisson bracket. Hence, using the positivity of the dissipative bracket, the entropy balance equation becomes as follows:

$$\frac{dS^{tot}}{dt} = \{S^{tot}, E^{tot}\} + [S^{tot}, S^{tot}] = [S^{tot}, S^{tot}] \geq 0$$

Therefore by using two different generating functions satisfying the conditions (16a) and (16b), one may express simultaneously the energy conservation and the irreversible entropy production.

² I.e. a function $f(Z) \in C^\infty$ such that $\{f(Z), g(Z)\} = 0$ for any function $g(Z) \in C^\infty$.

Remark 2. The Hamiltonian part of dynamics (i.e. the Poisson bracket) in (17) 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:

$$\sigma_S = \frac{dS^{tot}}{dt} = \frac{\partial^t S^{tot}}{\partial Z} \mathbf{M}(Z) \frac{\partial S^{tot}}{\partial Z}$$

Defining the thermodynamic forces by $Y_k = \partial S^{tot} / \partial Z_k$ with $k = 1, 2, \dots, \delta$ and defining the flux variable J_k by the law of fluxes as $J_k = \sum_{l=1}^{\delta} M_{kl}(Z) \partial S^{tot} / \partial Z_l$, the entropy production σ_S can be written as a bilinear product of the thermodynamic forces and the conjugated fluxes (deGroot and Mazur, 1962):

$$\sigma_S = \sum_{k=1}^{d_F} J_k Y_k = Y^t J$$

If the selected pairs (Y_k, J_k) are such that they follow the Onsager reciprocal relations, then the matrix $\mathbf{M}(Z)$ is a matrix in which the entries are equal to the parameters appearing in the phenomenological laws.

3.1.2. Extension to open systems

In order to apply the GENERIC formulation to open systems, two approaches can be found in the literature (Jongschaap and Öttinger, 2004; Muschik et al., 2000). 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 (Eberard et al., 2007). The second approach, developed in Jongschaap and Öttinger (2004), 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 environment as they appear for dissipative control systems (Brogliato et al., 2007; van der Schaft, 2000; Willems, 1972), input–output Hamiltonian-systems, (van der Schaft, 1989) and port Hamiltonian systems (van der Schaft and Maschke, 1995, 1997). 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 (van der Schaft and Maschke, 1995) and a dissipative system (Cortés et al., 2005) as follows.

Definition 4. An open GENERIC system on the vector space \mathbb{R}^{δ} 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:

$$\tilde{\mathbf{L}}(Z) = \begin{pmatrix} 0 & 0 & \Gamma(Z) \\ 0 & 0 & 0 \\ -\Gamma^t(Z) & 0 & \mathbf{L}(Z) \end{pmatrix}$$

and a symmetric tensor with the following positive structure

matrix:

$$\tilde{\mathbf{M}}(Z) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \mathbf{\Pi}(Z) \\ 0 & \mathbf{\Pi}^t(Z) & \mathbf{M}(Z) \end{pmatrix}$$

with $\Gamma(Z) \in \mathbb{R}^{m_1} \times \mathbb{R}^{\delta}$ and $\mathbf{\Pi}(Z) \in \mathbb{R}^{m_2} \times \mathbb{R}^{\delta}$. The dynamics is generated by two functions $E^{tot}(Z)$ and $S^{tot}(Z)$ satisfying the conditions (16a) and (16b) and the system of algebro-differential equations:

$$\begin{pmatrix} -\dot{X}_{ham} \\ \dot{X}_{diss} \\ \frac{dZ}{dt} \end{pmatrix} = \tilde{\mathbf{L}}(Z) \begin{pmatrix} F_{ham} \\ 0 \\ \frac{\partial E^{tot}}{\partial Z} \end{pmatrix} + \tilde{\mathbf{M}}(Z) \begin{pmatrix} 0 \\ F_{diss} \\ \frac{\partial S^{tot}}{\partial Z} \end{pmatrix} \quad (18)$$

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 $(\partial^t E^{tot} / \partial Z) dZ / dt$:

$$\frac{dE^{tot}}{dt} = F_{ham}^t \dot{X}_{ham} + \frac{\partial^t E^{tot}}{\partial Z} \mathbf{\Pi}(Z) F_{diss} \quad (19)$$

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 $(\partial^t S^{tot} / \partial Z) dZ / dt$:

$$\frac{dS^{tot}}{dt} = \frac{\partial^t S^{tot}}{\partial Z} \mathbf{M}(Z) \frac{\partial S^{tot}}{\partial Z} + \dot{X}_{diss}^t F_{diss} - \frac{\partial^t S^{tot}}{\partial Z} \Gamma^t(Z) F_{ham}$$

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 3. The extension of Remark 2 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 $\tilde{\mathbf{L}}$ fulfills (16b), i.e. the following condition should be fulfilled:

$$\Gamma(Z) \frac{\partial S^{tot}}{\partial Z} = 0$$

The pair of conjugated external variables (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 $\tilde{\mathbf{L}}$ fulfills (16b), i.e. the following condition should be fulfilled:

$$\Gamma(Z) \frac{\partial S^{tot}}{\partial Z} = 0$$

The entropy balance involves only the pair of external variables $(F_{diss}, \dot{X}_{diss})$ and can finally be written as follows:

$$\frac{dS^{tot}}{dt} = \frac{\partial^t S^{tot}}{\partial Z} \mathbf{M}(Z) \frac{\partial S^{tot}}{\partial Z} + \dot{X}_{diss}^t F_{diss}$$

Yet $\tilde{\mathbf{M}}$ does not fulfill (16a) since $(\partial^t E^{tot} / \partial Z) \mathbf{\Pi}(Z) F_{diss} \neq 0$. In the energy balance equation (19) not only the pair (F_{ham}, \dot{X}_{ham}) appears

but also the external force F_{diss} related to irreversible phenomena as these indeed may result in an energy flow.

Example 3. 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 2. 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:

$$\frac{\partial S^{tot}}{\partial Z} = \frac{\partial \tilde{S}}{\partial U} = \frac{1}{T}$$

3.1.3. Contact formulation of the GENERIC models

The contact formulation of GENERIC models for closed systems has already been suggested in Grmela (2002a, b) and Grmela and Öttinger (1997). In this section we shall briefly recall the contact formulation for closed systems and suggest the contact formulation of GENERIC models of open systems according to Definition 4. Starting from the dynamic equations expressed on the variables $Z \in \mathbb{R}^\delta$ and using a procedure called *lift* (Eberard et al., 2007), the contact system is defined on the whole thermodynamic phase space $\mathbb{R}^{2\delta+1} \ni (x_0, Z, p_Z)$ endowed with the contact form $\theta = dx_0 - p_Z dZ$. This results in the definition of a Legendre submanifold (actually its generating function) and a contact Hamiltonian function generating a conservative contact system such that its restriction to the Legendre submanifold is precisely the system expressed in the Z coordinates. At that point it should be noticed that there is no unique solution as it has been discussed in Favache et al. (2009). For GENERIC models of closed systems (Definition 3), it is easy to check that the lift is a conservative contact system with Legendre submanifold generated by the total entropy function S_{tot} and the contact Hamiltonian function:

$$f_0(Z, p_Z) = -p_Z^t \mathbf{L}(Z) \frac{\partial E^{tot}}{\partial Z}(Z) - \left(p_Z - \frac{\partial S^{tot}}{\partial Z}(Z) \right)^t \mathbf{M}(Z) \frac{\partial S^{tot}}{\partial Z}(Z) \quad (20)$$

Now consider the differential equation of an open GENERIC system (18). Its lift to the thermodynamic phase space is again easily seen to be a control contact system according to Definition 2 with Legendre submanifold generated by the total entropy function $S^{tot}(Z)$ and the contact Hamiltonian, sum of the internal contact Hamiltonian (20) and an interaction contact Hamiltonian function f_{int} :

$$f_{int}(Z, p_Z, F_{ham}, F_{diss}) = - \left(p_Z - \frac{\partial S^{tot}}{\partial Z} \right)^t \left(-\mathbf{\Gamma}^t(Z) F_{ham} + \mathbf{\Pi}^t(Z) F_{diss} \right) \quad (21)$$

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 (Eberard et al., 2006, 2007).

3.2. The matrix formalism

3.2.1. Definition

The Matrix model was developed by Jongschaap to describe the thermodynamics of complex fluids (Edwards et al., 1997; Jongschaap, 2001; Jongschaap and Öttinger, 2004). The Matrix formalism distinguishes between two kinds of variables: on one side the internal variables characterizing the state of the subsystems and the external variables referring to the environment of the subsystems.

The state 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

$$\mathcal{P}_{int} = F_{th}^t \frac{dX}{dt}$$

where $F_{th} = \partial \tilde{U} / \partial X$ 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 relations:

$$\frac{dU}{dt} = F_{th}^t \frac{dX}{dt} + T \frac{dS}{dt} \quad (22a)$$

$$\frac{dU}{dt} = F_e^t \dot{X}_e + \dot{Q} \quad (22b)$$

where \dot{Q} is the heat provided to the system. Using the Principle of Macroscopic Time Reversal (Jongschaap, 2001), the dynamics can finally be expressed as the sum of a non-dissipative and a dissipative coupling as follows:

$$\begin{pmatrix} F_e \\ \frac{dX}{dt} \end{pmatrix} = \begin{pmatrix} 0 & -\mathbf{\Upsilon}^t \\ \mathbf{\Upsilon} & 0 \end{pmatrix} \begin{pmatrix} \dot{X}_e \\ -F_{th} \end{pmatrix} + \begin{pmatrix} \boldsymbol{\eta} & 0 \\ 0 & \boldsymbol{\beta} \end{pmatrix} \begin{pmatrix} \dot{X}_e \\ -F_{th} \end{pmatrix} \quad (23)$$

where $\mathbf{\Upsilon}$ 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 to remark 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 (16b) of the GENERIC formalism. This matrix is not associated to the operator \mathbf{L} of the GENERIC formalism, whose skew-symmetry was inherited from the Poisson structure of classical mechanics.

The dissipation Δ 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.:

$$\Delta = F_e^t \dot{X}_e - F_{th}^t \frac{dX}{dt} = (\dot{X}_e)^t \boldsymbol{\eta} \dot{X}_e + F_{th}^t \boldsymbol{\beta} F_{th} \quad (24)$$

3.2.2. Contact formulation of the Matrix model

The contact formulation of the Matrix system (23) may be obtained by lifting the system on the extended space $\mathbb{R}^{2(\delta-1)+1} \approx \mathbb{R} \times \mathbb{T}\mathbb{R}^{(\delta-1)}$ of dimension $2\delta-1$. However this space would not be the physical thermodynamic space associated with Gibbs' equation (22a) which includes the entropy and energy variables. We shall define the thermodynamic phase space $\mathbb{R}^{2\delta+1} \ni (x_0, x, p)$ with the following identification:

$$\begin{cases} x_0 = S \\ x = [U, X]^t \\ p = [p_U, p_X]^t \end{cases} \quad (25)$$

The thermodynamic properties of the system are defined by the generating function given by the fundamental relation (2) given in entropy form. On the Legendre submanifold \mathcal{L} , generated by $\tilde{S}(U, X)$, one has the following relations: $p_U|_{\mathcal{L}} = \partial \tilde{S} / \partial U = 1/T$ and $p_X|_{\mathcal{L}} = \partial \tilde{S} / \partial X = -F_{th}/T$. Proceeding by analogy with (12) on the balance equations (22b)–(23) allows to define the following

internal contact Hamiltonian function:

$$f_0 = - \left(\frac{\partial \tilde{S}}{\partial X} - p_X \right)^t \beta F_{th}$$

and the following interaction contact Hamiltonian function:

$$\begin{aligned} f_{int} &= \left(\frac{\partial \tilde{S}}{\partial U} - p_U \right) [(\dot{X}_e)^t \eta \dot{X}_e + \dot{Q} + F_{th} \Upsilon \dot{X}_e] + \left(\frac{\partial \tilde{S}}{\partial X} - p_X \right)^t \Upsilon \dot{X}_e \\ &= \left(\frac{\partial \tilde{S}}{\partial U} - p_U \right) [(\dot{X}_e)^t \eta \dot{X}_e + \dot{Q}] - (p_X + p_U F_{th})^t \Upsilon \dot{X}_e \end{aligned}$$

It should be noted again that the contact Hamiltonian functions are tensor products, defined by the matrix β for the internal contact Hamiltonian function and by the matrix Υ for the control contact Hamiltonian function, both with the dimension of an entropy flow. The term containing Υ 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 (7):

$$\begin{aligned} \frac{dS}{dt} &= \frac{dx_0}{dt} \Big|_c = -p_U \frac{\partial(f_0 + f_{int})}{\partial p_U} \Big|_c - p_X \frac{\partial(f_0 + f_{int})}{\partial p_X} \Big|_c \\ &= \frac{1}{T} [(\dot{X}_e)^t \eta \dot{X}_e + \dot{Q} + F_{th}^t \beta F_{th}] \end{aligned}$$

As expected, the entropy variation is due to the dissipative effects (via the terms containing β and η) and to the heat exchange. By comparison with (24), the dissipation Δ represents the entropy variation that is not due to heat transfer.

4. Case study: the adiabatic piston

In this section, we shall illustrate the contact formalism by considering the example of a gas in an adiabatic isolated cylinder closed by a piston (Fig. 1). When the piston moves, friction effects cause 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.

This example has already been used in order to illustrate the GENERIC and Matrix formalism and to emphasize some relations with dissipative port-Hamiltonian systems in Jongschaap and Öttinger (2004). It is a very simple example and hence the contact, GENERIC and Matrix models of this system are easy to build. However it is sufficient to illustrate the differences and to highlight the advantages of the contact model from the point of view of control. Indeed it is an open system and it can be seen as a complex system composed of two subsystems: the piston and the enclosed gas.

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. Finally we assume that the temperature

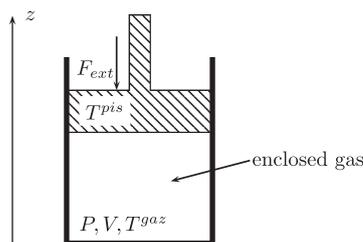


Fig. 1. Study case: the adiabatic piston.

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 $\delta = 5$ 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 4. 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} .

4.1. Contact formulation as a compartmental system

We shall consider the gas–piston system as a compartmental system composed of the piston and the gas in the cylinder. According to Section 2.3, we first give the contact formulation of each subsystem and then gather them through interconnection relations. Both subsystems, the gas and the piston, are considered as simple homogeneous thermodynamic systems.

4.1.1. The compartment gas

The thermodynamic model and its description in the thermodynamic phase space has been given in Example 1. However considering that there is no mass exchange with the environment, and for the sake of simplicity, the vector of extensive variable may be reduced to $x^{gas} = (U^{gas}, V^{gas})$ with the internal energy U^{gas} and volume V^{gas} . The thermodynamic phase space becomes $\mathbb{R}^5 \ni (x_0, U^{gas}, V^{gas}, p_U, p_V)$ with intensive variable of the gas $p^{gas} = (p_U, p_V)$ and the entropy function of the gas: $S^{gas}(U^{gas}, V^{gas})$ may be used as generating function of the Legendre submanifold associated with the thermodynamic properties of the gas.

The dynamical model is given by the balance equation on the extensive variables $x^{gas} = (U^{gas}, V^{gas})$. The internal energy balance equation is the sum of the heat flow coming from the piston and the mechanical power due to the displacement of the piston:

$$\frac{dU^{gas}}{dt} = \dot{Q}_{p \rightarrow g} - Av_{wall}P \quad (26a)$$

where v_{wall} denotes the velocity of the surface, of area A , in contact with the piston and P denotes the pressure of the gas:

$$P = - \frac{\partial S^{gas}}{\partial V} \left(\frac{\partial S^{gas}}{\partial U^{gas}} \right)^{-1}$$

The “balance” equation on the volume is equal to

$$\frac{dV}{dt} = Av_{wall} \quad (26b)$$

The formulation as a control contact system on the whole thermodynamic phase space is then obtained in accordance with Section 2.3 by using the balance equation in the definition of generated by the contact Hamiltonian function:

$$f^{gas}(x^{gas}, p^{gas}, \eta^{gas}) = \left(\frac{\partial \tilde{S}^{gas}}{\partial U^{gas}} - p_U^{gas} \right) (\dot{Q}_{p \rightarrow g} - v_{wall}AP)$$

$$+ \left(\frac{\partial \tilde{S}^{gas}}{\partial V} - p_V^{gas} \right) (Av_{wall}) \quad (27)$$

with the interconnection variables with the piston being: $\eta^{gas} = [\dot{Q}_{p \rightarrow g}, v_{wall}]$.

4.1.2. The compartment piston

The contact formulation of thermodynamic systems has been derived based on the Gibbs' equation in Section 2 for systems at rest. But the piston is a mechanical system in motion and Gibbs' relation has to be extended to its displacement and momentum variable.

Assuming that the piston does not exchange matter ($dn^{pis} = 0$) and is undeformable ($dV^{pis} = 0$) its thermodynamic model is defined by the restricted relation:

$$dS^{pis} = \frac{1}{T^{pis}} dU^{pis} \quad (28)$$

Furthermore the total energy of the piston is

$$\tilde{E}^{pis}(U^{pis}, q, z) = U^{pis} + \tilde{E}^{kin}(q) + \tilde{E}^{pot}(z)$$

the sum of the kinetic energy depending on the kinetic momentum q of the piston: $\tilde{E}^{kin}(q) = q^2/2m$, the gravity potential energy depending on the position z of the piston: $\tilde{E}^{pot}(z) = mgz$ and its internal energy U^{pis} .

Combining the differential of the total energy:

$$dE^{pis} = dU^{pis} + v dq - F_{pot} dz$$

where $v = q/m$ is the velocity of the piston and $F_{pot} = -mg$ is the gravity force, with (28), one obtains the extended form of the Gibbs' relation:

$$dS^{pis} = \frac{1}{T} dE^{pis} - \frac{v}{T} dq + \frac{F_{pot}}{T} dz \quad (29)$$

In the same way as Gibbs' relation (28) is equivalent to the fundamental relation defined by the entropy function $\tilde{S}_0^{pis}(U^{pis})$, the extended Gibbs' relation (29) is equivalent to the fundamental relation:

$$S^{pis} = \tilde{S}(E^{pis}, q, z) = \tilde{S}_0^{pis} \left(E^{pis} - \frac{q^2}{m} - mgz \right) \quad (30)$$

The contact formalism can now be applied directly by using (29) as the 1-form for endowing the thermodynamic phase space with a contact structure and (30) as the generating function of the Legendre manifold \mathcal{L}^{pis} . In the case of the piston the thermodynamic phase space can be taken as \mathbb{R}^7 with the local coordinates $(x_0^{pis}, x^{pis}, p^{pis})$ which have the following physical interpretation on the Legendre submanifold:

$$\begin{cases} x_0^{pis} \stackrel{\mathcal{L}^{pis}}{=} S^{pis} \\ x^{pis} = [x_E^{pis}, x_q^{pis}, x_z^{pis}] \stackrel{\mathcal{L}^{pis}}{=} [E^{pis}, q, z]^t \\ p^{pis} = [p_E^{pis}, p_q^{pis}, p_z^{pis}] \stackrel{\mathcal{L}^{pis}}{=} \left[\frac{1}{T^{pis}}, -\frac{v}{T^{pis}}, \frac{F_{pot}}{T^{pis}} \right]^t \end{cases}$$

The dynamical model is given by the balance equation of the total energy, the momentum (Newton's equation) and the displacement (kinematic relation):

$$\frac{dE^{pis}}{dt} = \dot{Q}_{g \rightarrow p} + (F_{gas} - F_{ext})v \quad (31a)$$

$$\frac{dq}{dt} = F_{gas} - F_{ext} - F_{pot} - \alpha v \quad (31b)$$

$$\frac{dz}{dt} = v \quad (31c)$$

where $F_{fric} = \alpha v$ is the force due to friction with α the friction coefficient. The heat transfer rate from the gas to the piston $\dot{Q}_{g \rightarrow p}$ and the force F_{gas} exerted by the gas on the piston compose the vector of interaction variables of the piston: $\eta^{pis} = [\dot{Q}_{g \rightarrow p}, F_{gas}]$. The external interaction variable with the environment of the gas-piston system is the force exerted by the environment on the piston $F_{ext} = \zeta_{ext}$.

The control contact system on the whole thermodynamic phase space is generated by the following contact Hamiltonian function defined in accordance with Section 2 as follows:

$$\begin{aligned} f^{pis}(x, p, \eta^{pis}, F_{ext}) &= \left(\frac{\partial \tilde{S}^{pis}}{\partial E^{pis}} - p_E^{pis} \right) \left(\dot{Q}_{g \rightarrow p} - (F_{gas} - F_{ext}) \frac{p_q^{pis}}{p_E^{pis}} \right) \\ &+ \left(\frac{\partial \tilde{S}^{pis}}{\partial q} - p_q^{pis} \right) \left(F_{gas} - F_{ext} - \frac{p_z^{pis}}{p_E^{pis}} + \alpha \frac{p_q^{pis}}{p_E^{pis}} \right) \\ &- \left(\frac{\partial \tilde{S}^{pis}}{\partial z} - p_z^{pis} \right) \frac{p_q^{pis}}{p_E^{pis}} \end{aligned} \quad (32)$$

4.1.3. The gas-piston system

The thermodynamic properties of the composed system are obtained according to Section 2.3 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 simply defined by the Legendre submanifold with generating function being the sum of the generating functions:

$$\mathcal{F}(x) = \tilde{S}^{pis}(x^{pis}) + \tilde{S}^{gas}(x^{gas}) \quad (33)$$

The interconnection relations (10) defining the variables η^{pis} and η^{gas} are defined as follows:

- the heat exchange due to conduction:

$$\dot{Q}_{p \rightarrow g} = -\dot{Q}_{g \rightarrow p} = \kappa \left(\frac{1}{p_E^{pis}} - \frac{1}{p_E^{gas}} \right) \quad (34a)$$

- the kinematic relation relating the velocity of the piston with the velocity of displacement of the moving wall:

$$v_{wall} = v = -\frac{p_q^{pis}}{p_E^{pis}} \quad (34b)$$

- the static equilibrium:

$$F^{gas} = AP = Ap_V^{gas} \quad (34c)$$

The contact system for the composed system is then simply generated by the sum of the contact Hamiltonian functions (27) and (32) with the interconnection relations (34a)–(34c):

$$f(x, p, \zeta_{ext}) = f^{pis}(x, p, \zeta_{ext}) + f^{gas}(x, p, \zeta_{ext}) \quad (35)$$

We may illustrate now an important property of the contact formulation, namely that it embeds not only the balance equation on the conserved quantities but also that one may simply deduce from the contact Hamiltonian the dynamics of their conjugated intensive variables as well as of all thermodynamic potentials in particular the total entropy balance equation. As the system is isolated, there is no external entropy flux, and the variation of the total entropy of the system is thus equal to the entropy production σ_S . The variation of the total entropy is obtained by computing the x_0 -component of the vector field generated by the

contact Hamiltonian function (35) and then restricting it to the Legendre submanifold generated by $\mathcal{F}(x)$ and one obtains

$$\sigma_S = \frac{dx_{0tot}}{dt} \Big|_{\mathcal{L}} = \dot{Q}_{g \rightarrow p} \left(\frac{\tilde{S}^{gas}}{\partial U^{gas}} - \frac{\tilde{S}^{pis}}{\partial E} \right) + \frac{\tilde{S}^{pis}}{\partial q} \alpha \frac{\partial E^{kin}}{\partial q}(q)$$

In terms of the usual thermodynamic quantities, this is equal to the following relation:

$$\sigma_S = \dot{Q}_{g \rightarrow p} \left(\frac{1}{T^{gas}} - \frac{1}{T^{pis}} \right) + \alpha \frac{v^2}{T^{pis}} \quad (36)$$

We can clearly recover the two sources of irreversibility: the heat transfer and the viscous dissipation.

4.2. The GENERIC model

In this section we shall recall how the complete piston–gas system would be modelled using GENERIC according to Section 3.1.2. We shall comment in detail the construction of the structure matrices \mathbf{L} and \mathbf{M} of the dynamic equation (18).

The state space may be chosen to be the set of conserved extensive variables of each subsystem:

$$Z = [U^{pis}, z, q, U^{gas}, V]$$

The two generating functions (or potentials in thermodynamic terms) are the total energy, that is the sum of the total energy of the piston and the gas:

$$E^{tot}(Z) = \frac{1}{2m} q^2 + mgz + U^{pis} + U^{gas}$$

and the total entropy function of the system, that is the sum of the entropy functions of the piston and of the gas:

$$S^{tot}(Z) = \tilde{S}_0^{pis}(U^{pis}) + \tilde{S}^{gas}(U^{gas}, V)$$

The gradient of these potentials define the two vectors of generating forces $\partial E^{tot}/\partial Z$ for the reversible phenomena and $\partial S^{tot}/\partial Z$ for the irreversible phenomena:

$$\frac{\partial E^{tot}}{\partial Z} = \left(1, \frac{\partial E^{pot}}{\partial z}, \frac{\partial E^{kin}}{\partial q}, 1, 0 \right)^t = (1, -F_{pot}, v, 1, 0)^t \quad (37a)$$

$$\frac{\partial S^{tot}}{\partial Z} = \left(\frac{\tilde{S}^{pis}}{\partial U^{pis}}, 0, 0, \frac{\tilde{S}^{gas}}{\partial U^{gas}}, \frac{\tilde{S}^{gas}}{\partial V} \right)^t = \left(\frac{1}{T^{pis}}, 0, 0, \frac{1}{T^{gas}}, \frac{P}{T^{gas}} \right)^t \quad (37b)$$

The vector $\partial E^{tot}/\partial Z$ contains only the mechanical co-energy variables as independent variables, and the vector $\partial S^{tot}/\partial Z$ 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 $\partial E^{tot}/\partial Z$ 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 (26) and (31) into two vector fields; the first one, denoted by \mathfrak{X}_{ham} , corresponding to a Hamiltonian vector field, and the second one, denoted by \mathfrak{X}_{grad} , to the dissipative vector field in (17). The suggested choice corresponds to split it into a vector field corresponding to the reversible phenomena and the other one to the irreversible

phenomena as follows:

$$\begin{pmatrix} \frac{dU^{pis}}{dt} \\ \frac{dz}{dt} \\ \frac{dq}{dt} \\ \frac{dU^{gas}}{dt} \\ \frac{dV}{dt} \end{pmatrix} = \underbrace{\begin{pmatrix} 0 \\ v \\ F^{gas} + F_{pot} \\ -PAv \\ Av \end{pmatrix}}_{\mathfrak{X}_{ham}} + \underbrace{\begin{pmatrix} \dot{Q}_{g \rightarrow p} + \alpha v^2 \\ 0 \\ -\alpha v \\ -\dot{Q}_{g \rightarrow p} \\ 0 \end{pmatrix}}_{\mathfrak{X}_{grad}} \quad (38)$$

For the Hamiltonian vector field, it appears that there exists a unique skew-symmetric matrix \mathbf{L} that corresponds to the Poisson bracket such that the total energy $E^{tot}(Z)$ generates the Hamiltonian vector field \mathfrak{X}_{ham} and such that the total entropy is a Casimir function:

$$\mathbf{L} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & -1 & 0 & AP & -A \\ 0 & 0 & -AP & 0 & 0 \\ 0 & 0 & A & 0 & 0 \end{pmatrix} \quad (39)$$

where $P = (\partial \tilde{S}^{gas}/\partial V)(U^{gas}, V)$.

The matrix \mathbf{L} defines indeed a Poisson bracket as it is skew-symmetric and it satisfies the Jacobi identities which will be proven by giving a complete set of Casimir functions. Note first that, as the pressure satisfies $P > 0$ for any state, the rank of \mathbf{L} 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 $C_2(Z) = S^{gas}(U^{gas}, V)$, 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 invariance of $S^{tot}(Z)$ and S^{gas} proves that 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 \mathbf{M} as it has been noted e.g. in Muschik et al. (2000). One possible semi-definite positive symmetric matrix \mathbf{M} that generates the vector field \mathfrak{X}_{grad} and admits the total energy $E^{tot}(Z)$ as Casimir function is the following one:

$$\mathbf{M} = \begin{pmatrix} \kappa T^{gas} T^{pis} + T^{pis} \alpha v^2 & 0 & -\alpha T^{pis} v & -\kappa T^{gas} T^{pis} & 0 \\ 0 & 0 & 0 & 0 & 0 \\ -\kappa T^{pis} v & 0 & \kappa T^{pis} & 0 & 0 \\ -\kappa T^{gas} T^{pis} & 0 & 0 & \kappa T^{gas} T^{pis} & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (40)$$

with

$$T^{pis} = \left(\frac{\tilde{S}^{pis}}{\partial U^{pis}} \right)^{-1} (U^{pis})$$

$$T^{gas} = \left(\frac{\tilde{S}^{gas}}{\partial U^{gas}} \right)^{-1} (U^{gas}, V)$$

$$v = \frac{\partial E^{kin}}{\partial q}(q)$$

The matrix \mathbf{M} is symmetric and semi-definite *positive* as the friction and conduction coefficients α and λ 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 $D_2(Z) = V$ which implies that the dissipative vector field corresponds to isochore transformations and the third Casimir function is, by construction, the total energy $E^{tot}(Z)$.

This model may be extended in order to account for the interactions with the environment due to the external force F_{ext} . As this interaction consists of a reversible phenomenon, it is sufficient to augment the Hamiltonian vector field and the GENERIC formulation of the open system can then be written as follows:

$$\begin{pmatrix} -\dot{X}_{ham} \\ \frac{dZ_{open}}{dt} \end{pmatrix} = \begin{pmatrix} 0 & \mathbf{\Gamma}(Z) \\ -\mathbf{\Gamma}^t(Z) & \mathbf{L}(Z) \end{pmatrix} \begin{pmatrix} F_{ext} \\ \frac{\partial E^{tot}}{\partial Z} \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & \mathbf{M}(Z) \end{pmatrix} \begin{pmatrix} 0 \\ \frac{\partial S^{tot}}{\partial Z} \end{pmatrix}$$

The second row can be developed and the following expression is obtained:

$$\frac{dZ}{dt} = -\mathbf{\Gamma}^t(Z)F_{ext} + \mathbf{L}(Z)\frac{\partial E^{tot}}{\partial Z} + \mathbf{M}(Z)\frac{\partial S^{tot}}{\partial Z} \quad (41)$$

Actually the external force appears solely in the momentum balance (31b), hence it is easy to define the interaction matrix $\mathbf{\Gamma}$:

$$\mathbf{\Gamma}(Z) = (0 \ 0 \ 1 \ 0 \ 0)$$

The conjugated port variable \dot{X}_{ham} associated to F_{ext} is consequently equal to the velocity of the piston:

$$-\dot{X}_{ham} = \mathbf{\Gamma} \frac{\partial E^{tot}}{\partial Z} = v$$

4.3. The Matrix model

We have recalled in Section 3.2 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 energy form may be generalized to encompass the thermodynamic states of the piston and the gas:

$$dU^{tot} = T^{pis} dS^{pis} + T^{gas} dS^{gas} - P dV$$

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 this implies that the conjugated pair of extensive variables and intensive variables 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:

$$\frac{dU^{tot}}{dt} = \frac{dU^{pis}}{dt} + \frac{dU^{gas}}{dt} \quad (42)$$

The internal energy balance of the piston is obtained from the energy balance (31a) as follows:

$$\begin{aligned} \frac{dU^{pis}}{dt} &= \frac{dE^{pis}}{dt} - \frac{dE^{kin}}{dt} - \frac{dE^{pot}}{dt} \\ &= \dot{Q}_{g \rightarrow p} + (F_{gas} - F_{ext})v - \dot{\partial} \frac{\tilde{E}^{pot}}{\partial Z} v \\ &\quad - \dot{\partial} \frac{\tilde{E}^{kin}}{\partial q} (F_{gas} - F_{ext} - F_{pot} - \alpha v) \\ &= \dot{Q}_{g \rightarrow p} + \alpha v^2 \end{aligned}$$

By combining with (26a) we finally obtain

$$\frac{dU^{tot}}{dt} = \frac{dU^{pis}}{dt} + \frac{dU^{gas}}{dt} = (\alpha v - AP)v$$

which, according to (22b), 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 (23) lead to the Matrix model of the piston–gas system:

$$\begin{pmatrix} \alpha v - AP \\ \frac{dV}{dt} \end{pmatrix} = \begin{pmatrix} \alpha & -A \\ A & 0 \end{pmatrix} \begin{pmatrix} v \\ P \end{pmatrix} \quad (43)$$

Note that (43) reduces to a single balance equation on the volume corresponding the conservation of space. This result is indeed analogous to that presented in Jongschaap and Öttinger (2004).

Note also that the final formulation of the Matrix model (43) does not include explicitly the energy balance.

The total dissipation can now be calculated using (24):

$$\Delta = \dot{X}_e \eta \dot{X}_e = \alpha v^2 \quad (44)$$

As shown in Section 3.2, the dissipation is related to the entropy variation which is not due to heat effects. Indeed by comparing with (36), we have

$$\sigma_S = \left(\frac{1}{T^{gas}} - \frac{1}{T^{pis}} \right) \dot{Q}_{g \rightarrow p} + \frac{\Delta}{T^{pis}}$$

4.4. Concluding comments

On the example of a gas–piston subject to an external force we have illustrated the construction of the conservative control contact system, of the GENERIC and of the Matrix models starting from the balance equations of an independent set of extensive variables. The control contact system has been constructed by considering the gas–piston system as a compartmental system composed of the gas and the piston according to Section 2.3. The GENERIC and Matrix models have been constructed for the total system. We have discussed in detail the construction and the properties of the two structure matrices of the GENERIC model from the balance equations and have interpreted the Casimir functions of the skew-symmetric structure matrix as isentropic transformations and the Casimir functions of the symmetric structure matrix in terms of isochore transformations. It may be noticed that the kinematic interconnection relation between the gas and the piston corresponds precisely to one of the Casimir functions of the skew-symmetric structure matrix. By definition the Matrix model represents basically the balance equations by considering the mechanical part of the system: its structure matrix has been shown to be composed of a symplectic part corresponding to the usual mechanical model augmented with some symmetric terms associated with the dissipative phenomena. However the interconnection relation cannot appear in this formulation as only the mechanical part of the systems is explicitly represented.

Both the conservative control contact and the GENERIC formulation are based on some differential-geometric structure. The GENERIC imposes some differential-geometric structure on the space of the n independent extensive variables: the skew-symmetric structure matrix defines (in coordinates) a Poisson bracket as it arises in mechanical systems and the positive symmetric structure matrix defines a pseudo-Riemannian structure associated with the dissipative phenomena. The control contact formulation uses the contact structure associated with Gibbs' relation on the whole $(2n+1)$ -dimensional thermodynamic phase space containing all the extensive and the intensive variables.

This contact structure is canonical, in the same way as the symplectic structure for Lagrangian systems, however the

structure matrices of the GENERIC formulation are not. They have to be constructed for each system of balance equations and are in general not uniquely defined. In our example, there is a unique solution for the skew-symmetric structure matrix but a non-unique solution for the symmetric matrix.

Furthermore by construction, the gradient of the total energy or the total entropy functions should be in the kernel of the structure matrices (see Eqs. (16a) and (16b)). Hence the structure matrices depend explicitly on the intensive variables: in the example the skew-symmetric matrix L depends on the pressure and the symmetric structure matrix M on the temperatures and the velocity. If this dependence is left explicit and not expressed as functions of the extensive variables by using the thermodynamic properties of the system, the structure matrices do not really define a Poisson bracket or a Riemannian metric. This is a sharp contrast with the situation in mechanical systems where the Poisson structure matrix may be defined in a canonical way from the structure of the configuration space of the mechanical system.

When considering the contact formulation of the GENERIC model on the thermodynamic phase space, this implies that the contact Hamiltonian is no more defined as the tensor product on the space of intensive variables (as Poisson bracket would do) but rather functions, eventually semi-linear, on the whole thermodynamic phase space. This was indeed one of the major motivations to consider contact structures and contact vector fields defined on the whole thermodynamic phase space (Eberard et al., 2005, 2007).

Let us also emphasize the fact that the considered system is an interconnection of two subsystems. In the above study case the advantage of the contact formulation appears clearly. Indeed the contact model has been built first for each subsystem individually (the gas and the piston) and the total model has been deduced from the two previous ones. In the GENERIC and in the Matrix formulations, the interconnection of two systems would require to recompute the structure matrices for the whole system and check their kernel, which can become very tedious as the dimension increases. With the contact formalism, the total model is obtained simply by adding a term in the already computed contact Hamiltonian function (35). Hence one of the major forces of the contact formalism compared to the two other formalisms for expressing thermodynamic systems is the easy handling of interconnected systems.

5. Conclusion

In this paper we have been considering the differential-geometric structure of the dynamic systems associated with thermodynamic systems such as the GENERIC, the Matrix or the control contact system formulations. The first two formalisms are based on defining some Poisson and Riemannian metric matrices on the state space of independent extensive thermodynamic variables. The third one defines the dynamics as a contact vector field on the complete thermodynamic phase space endowed with the canonical contact form associated with Gibbs' relation.

All the 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 Matrix formulations lead to contact Hamiltonian functions being tensor products of the thermodynamic forces whereas the control contact system admits more general expressions which allows for a more general expression of fluxes.

An important feature of considering the dynamics on the thermodynamic phase space is to allow for a simplified expression of the tensors arising in the contact Hamiltonian function.

Indeed one may express the generating forces as simple functions of the extensive variables instead of using their expression in terms of the intensive variables via the state equation necessary to define the Poisson and Riemann tensor on the space of extensive variables.

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 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, and especially of interconnected systems such as chemical processes for example.

The GENERIC and Matrix formalism can also be applied to distributed parameter systems. The case of distributed systems has not been considered in this paper, 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 it has been described in Grmela (2002b) for instance.

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.

The use of the physical and thermodynamic properties such as the convexity of the entropy function (Hangos et al., 1999; Ydstie, 2002) or some pseudo-Hamiltonian formulations (Ramírez et al., 2009) has been used recently for the control of open thermodynamic systems such as chemical reactors. The contact formulation based on the entropy form of Gibbs' equations, opens the road for some alternative approach to the control problem by shifting the control design from energy shaping and IDA-PBC methods to the design of closed-loop entropy and entropy variation (the closed-loop contact Hamiltonian).

Acknowledgements

This paper presents research results of the Belgian Network DYSCO (Dynamical Systems, Control, and Optimization), funded by the Interuniversity Attraction Poles Programme, initiated by the Belgian State, Science Policy Office. The scientific responsibility rests with its authors. The authors acknowledge also the support of the Hubert Curien collaborative project Tournesol nr.18091VJ. Audrey Favache is a fellow student of the Belgian Fonds National de la Recherche Scientifique (FNRS).

References

- Alonso, A.A., Ydstie, B.E., 2001. Stabilization of distributed systems using irreversible thermodynamics. *Automatica* 37, 1739–1755.

- Arnold, V., 1989. *Mathematical Methods of Classical Mechanics*, second ed. Springer.
- Bird, R., Stewart, W., Lightfoot, E., 2002. *Transport Phenomena*, second ed. John Wiley.
- Brogliato, B., Lozano, R., Maschke, B., Egeland, O., 2007. *Dissipative Systems Analysis and Control, Communications and Control Engineering Series*, second ed. Springer Verlag, London.
- Callen, H., 1960. *Thermodynamics*. Wiley, New-York.
- Carathéodory, C., 1909. Untersuchungen über die Grundlagen der Thermodynamik. *Mathematische Annalen* 67, 355–386.
- Chen, M., 1999. On the geometric structure of thermodynamics. *Journal of Mathematical Physics* 40 (2), 830–837.
- Cortés, J., van der Schaft, A., Crouch, P.E., 2005. Characterization of gradient control systems. *SIAM Journal of Control and Optimization* 44 (4), 1192–1214.
- Courant, T., 1990. Dirac manifolds. *Transactions of the American Mathematical Society* 319, 631–661.
- Dalsmo, M., van der Schaft, A., 1999. On representations and integrability of mathematical structures in energy-conserving physical systems. *SIAM Journal of Control and Optimization* 37 (1), 54–91.
- de Groot, S., Mazur, P., 1962. *Non-equilibrium Thermodynamics*. North-Holland, Amsterdam.
- Eberard, D., 2006. Extensions des systèmes hamiltoniens à ports aux systèmes irréversibles: une approche par la géométrie de contact. Ph.D. Thesis, Université Claude Bernard, Lyon 1, France.
- Eberard, D., Maschke, B., van der Schaft, A., 2005. Conservative systems with ports on contact manifolds. In: *Proceedings of the IFAC World Congress, Prague, Czech Republic*.
- Eberard, D., Maschke, B., van der Schaft, A., 2006. On the interconnection structures of open physical systems. In: *Proceedings of the 3rd IFAC Workshop on Lagrangian and Hamiltonian Methods for Nonlinear Control (LHMNLC'06)*, Nagoya, Japan.
- Eberard, D., Maschke, B., van der Schaft, A., 2007. An extension of pseudo-hamiltonian systems to the thermodynamic space: towards a geometry of non-equilibrium thermodynamics. *Reports on Mathematical Physics* 60 (2), 175–198.
- Edwards, B., Öttinger, H., Jongschaap, R., 1997. On the relationship between thermodynamic formalisms for complex fluids. *Journal of Non-Equilibrium Thermodynamics* 22, 356–373.
- Favache, A., 2009. *Thermodynamics and process control*. Ph.D. Thesis, Université catholique de Louvain, Belgium. URL <<http://hdl.handle.net/2078.1/23872>>.
- Favache, A., Dochain, D., 2009a. Analysis and control of the exothermic continuous stirred tank reactor: the power-shaping approach. In: *Proceedings of the 48th IEEE Conference on Decision and Control, Shanghai, China*.
- Favache, A., Dochain, D., 2009b. Thermodynamics and chemical systems stability: the CSTR case study revisited. *Journal of Process Control* 19 (3), 371–379.
- Favache, A., Dos Santos Martins, V.S., Dochain, D., Maschke, B., 2009. Some properties of conservative port contact systems. *IEEE Transactions on Automatic Control* 54, 2341–2351.
- Favache, A., Maschke, B., Dochain, D., 2007. Contact structures: application to interconnected thermodynamical systems. In: *Proceedings of the European Control Conference 2007, Kos, Greece*.
- Gibbs, J., 1873a. Graphical methods in the thermodynamics of fluids. *Transactions of the Connecticut Academy* 2, 309–342.
- Gibbs, J., 1873b. Method of geometrical representation of the thermodynamic properties of substances by means of surfaces. *Transactions of the Connecticut Academy* 2, 382–404.
- Grmela, M., 2002a. Lagrange hydrodynamics as extended Euler hydrodynamics: Hamiltonian and GENERIC structures. *Physics Letters A* 296, 97–104.
- Grmela, M., 2002b. Reciprocity relations in thermodynamics. *Physica A* 309, 304–328.
- Grmela, M., Öttinger, H., 1997. Dynamics and thermodynamics of complex fluids. I. Development of a general formalism. *Physical Review E* 56 (6), 6620–6632.
- Hangos, K.M., Alonso, A.A., Perkins, J.D., Ydstie, B.E., 1999. Thermodynamic approach to the structural stability of process plants. *AIChE Journal* 45 (4), 802–816.
- Herman, R., 1973. *Geometry Physics and Systems*. Dekker, New-York.
- Jongschaap, R., 2001. The matrix model, a driven state variables approach to non-equilibrium thermodynamics. *Journal of Non-Newtonian Fluid Mechanics* 96, 63–76.
- Jongschaap, R., de Haas, K., Damen, C., 1994. A generic matrix representation of configuration tensor rheological models. *Journal of Rheology* 38, 769–795.
- Jongschaap, R., Öttinger, H., 2004. The mathematical representation of driven thermodynamical systems. *Journal of Non-Newtonian Fluid Mechanics* 120, 3–9.
- Jou, D., Casa-Vasquez, J., Lebon, G., 2001. *Extended Irreversible Thermodynamics*, third ed. Springer.
- Mrugała, R., 1978. Geometrical formulation of equilibrium phenomenological thermodynamics. *Reports on Mathematical Physics* 14 (3), 419–427.
- Mrugała, R., 1993. Continuous contact transformations in thermodynamics. *Reports in Mathematical Physics* 33 (1/2), 149–154.
- Mrugała, R., 2000. On a special family of thermodynamic processes and their invariants. *Reports in Mathematical Physics* 46 (3), 461–468.
- Mrugała, R., Nulton, J., Schon, J., Salamon, P., 1991. Contact structure in thermodynamic theory. *Reports in Mathematical Physics* 29 (1), 109–121.
- Muschik, W., Gumbel, S., Kröger, M., Öttinger, H., 2000. A simple example for comparing GENERIC with rational non-equilibrium thermodynamics. *Physica A* 285, 448–466.
- Olver, P., 1993. *Applications of Lie Groups to Differential Equations*. Graduate Texts in Mathematics, vol. 107, second ed. Springer, New-York.
- Ortega, J.-P., Planas-Bielsa, V., 2004. Dynamics on Leibniz manifolds. *Journal of Geometry and Physics* 52, 1–27.
- Öttinger, H., 1999. Nonequilibrium Thermodynamics—a tool for applied rheologists. *Applied Rheology* 9, 17–26.
- Öttinger, H., Grmela, M., 1997. Dynamics and thermodynamics of complex fluids. ii. Illustrations of a general formalism. *Physical Review E* 56 (6), 6633–6655.
- Prigogine, I., 1962. *Introduction to Thermodynamics of Irreversible Processes*. John Wiley.
- Ramírez, H., Sbarbaro, D., Ortega, R., 2009. On the control of non-linear processes: an IDA-PBC approach. *Journal of Process Control* 19, 405–414.
- van der Schaft, A., 1989. *System theory and mechanics*. Three Decades of Mathematical System Theory. Lecture Notes in Control and Information Sciences, vol. 135. Springer, Berlin, pp. 426–452.
- van der Schaft, A., 2000. *L₂-gain and Passivity Techniques in Nonlinear Control*. Springer Communications and Control Engineering Series, second ed. Springer-Verlag, London.
- van der Schaft, A., Maschke, B., 1995. The Hamiltonian formulation of energy conserving physical systems with external ports. *Archiv für Elektronik und Übertragungstechnik* 49 (5/6), 362–371.
- van der Schaft, A., Maschke, B., 1997. Interconnected mechanical systems. Part 1: geometry of interconnection and implicit Hamiltonian systems. In: *Modelling and Control of Mechanical Systems*. Imperial College Press, London, pp. 1–16.
- Willems, J., 1972. Dissipative dynamical systems, Part 1: general theory. *Archive for Rational Mechanics and Analysis* 45, 321–351.
- Ydstie, B.E., 2002. Passivity based control via the second law. *Computers & Chemical Engineering* 26 (7–8), 1037–1048.
- Yoshimura, H., Marsden, J., 2006. Dirac structures in lagrangian mechanics part i: implicit lagrangian systems. *Journal of Geometry and Physics* 57 (1), 133–156.