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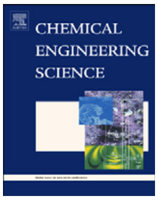

An entropy-based formulation of irreversible processes based on contact structures

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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.

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.

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

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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 system*[1] (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 $i=1,..,N$, 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:

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

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:

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

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

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

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 $(x_0,x_1,\ldots,x_\delta,p_1,\ldots,p_\delta)$ is

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