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Two Approaches to the Description of the Evolution of Thermodynamic Systems [⋆]

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Abstract: This paper analyses two approaches to the description of thermodynamic evolution. The first approach describes the dynamics of a thermodynamic system by contact vector fields extended with inputs and outputs while the second one interprets the thermodynamic vector field as a smooth section of the tangent bundle of the respective Legendre manifold parametrized by n functions, called thermodynamic controls. It is shown that there is a duality between these two approaches similar to the one found in the symplectic case. However, there are still many open questions which present a waste opportunity for further research.

Keywords: Mathematical modeling, Thermodynamics, Contact geometry

1. INTRODUCTION

During the last decades there has been a constant interest in developing the system-theoretic foundations of thermodynamics. A representation of thermodynamic systems by stochastic models was first proposed in Brockett and Willems (1979) and later developed in Sandberg et al. (2011, 2014). Haddad et al. (2005) proposed a non-linear compartmental model which exhibits many features typical for thermodynamic systems such as equipartition of energy and irreversibility phenomena. These ideas were later extended (see Berg et al. (2013) and references therein).

One particularly interesting direction of research is based on the use of the geometric structure of thermodynamic state spaces. Within this framework, pioneered in Hermann (1973) and adopted in this contribution, the state space of a thermodynamic system is associated with an n-dimensional Legendre sub-manifold of the $(2n + 1)$-dimensional contact space. Within this framework, we are particularly interested in defining the dynamics of a thermodynamic system.

There are two main approaches to the definition of thermodynamic evolution. The first approach, following Mrugała et al. (1991), consists in describing the dynamics of a thermodynamic system by contact vector fields extended with inputs and outputs (see Eberard et al. (2007); Favache et al. (2009)). This leads to the definition of port contact systems which can be seen as a contact counterpart of port Hamiltonian systems (van der Schaft, 2004). An alternative approach, proposed in Gromov and Caines (2011a,b), describes the thermodynamic vector field as a smooth section of the tangent bundle of the respective Legendre manifold parametrized by n functions, called thermodynamic controls. Both frameworks allow describing interconnected thermodynamic systems and studying their basic properties.

Obviously, the coexistence of two different approaches raises questions regarding their validity or the domain of their applicability. This paper attempts to resolve this issue. Apart from that, we hope to stimulate the discussion on *"what is the dynamics of a thermodynamic system?"*

The paper is organized as follows. Section 2 gives a brief overview of the necessary background. Section 3 describes two approaches to the description of thermodynamic evolution. A number of results related to these approaches is presented in Sec. 4 while Sec. 5 outlines directions for further research.

2. GEOMETRIC DESCRIPTION OF THERMODYNAMICS

In this section, we present some basic facts regarding the thermodynamic notation and conventions as well as the geometric (contact) description of thermodynamic phase space. For a more detailed treatment see Callen (1985); Kondepudi and Prigogine (1998) for thermodynamics, Geiges (2008); Arnold (1989) for contact geometry, and Mrugała et al. (1991); Gromov and Caines (2015) for the contact description of thermodynamics.

In the following, we will restrict ourselves to the study of single phase, single component homogeneous thermodynamic systems that do not undergo any chemical transformations. Furthermore, when considering interactions between thermodynamic systems we restrict ourselves to the interactions accompanied by any form of energy or matter transfer. Thus, we do not consider processes driven by the elimination of constraints imposed on the system.

2.1 Reversible and irreversible quasi-static processes

The central postulate of equilibrium thermodynamics is that the system is *spatially homogeneous*, i.e., each part of the system has the same properties as any other. This implies that the whole system can be described by a small

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number of state variables which completely characterize the respective equilibrium state. Within this framework, the system's evolution is considered to be a temporally ordered dense sequence of equilibrium states which the system passes through at a sufficiently slow pace such that the spatial inhomogeneities can be neglected. This class of thermodynamic processes is referred to as *quasi-static*.

We can say that a thermodynamic system has infinite-dimensional unmodeled drift dynamics. The system is in an equilibrium state if this dynamics have settled down. Quasi-static evolution would then mean that this infinite-dimensional drift dynamics is sufficiently fast such that we can neglect it and consider only the lumped response to the control actions. Obviously, this drift dynamics must be stable – this is referred to as the *thermodynamic stability*.

A quasi-static process evolves on the set of equilibrium states which is assumed to be a smooth manifold embedded in the space of state variables. Such manifold is naturally called the *equilibrium manifold*.

There are two types of quasi-static processes: reversible and irreversible ones. The notion of (ir)reversibility is intimately related to the concept of time arrow which says that any real life process can evolve only in the direction characterized by the growth of the total entropy of the system and its environment. A reversible process does not increase the total entropy and is therefore an idealization which sets a limit to the set of physically realizable processes.

We note at this point that both reversible and irreversible quasi-static processes obey the same rules. Thus the property of the process to be reversible (resp. irreversible) depends on the type of interaction occurring between the system and its environment (or between two subsystems). For instance, a frictionless mechanical process (e.g. sufficiently slow compression of a gas by a frictionless piston) does not increase the total entropy and is hence reversible. On the other hand, any process involving heat transfer at finite rate inevitably leads to the increase of the total entropy and is therefore irreversible.

Some processes, however, cannot be described within the quasi-static framework. One classical example is the expansion of a gas in an (otherwise isolated) evacuated chamber. While the initial and the final states are well defined, the intermediate states cannot be described by lumped parameters. Using our geometrical picture, we can say that the state disappears from one point on the equilibrium manifold to appear at another one after some time. During this transition the system's entropy increases while energy remains constant as the process is not accompanied by any heat or work transfer.

2.2 Thermodynamic basics

In an *equilibrium state*, a thermodynamic system can be completely described by a number of parameters. For the considered class of systems the system's state can be described by four parameters: the *internal energy* U, the *entropy* S, the *volume* V, and the *mole number* N. All these are *extensive* parameters, i.e. they satisfy the *additivity property*. The state variables also satisfy the *state equation*

$$U = U(S, V, N). \tag{1}$$

Note that $U(S, V, N)$ is a smooth, positive homogeneous function of order 1 which implies that it can be rewritten using the Euler homogeneous function theorem:

$$U = TS - pV + \mu N, \tag{2}$$

where T, p, and μ are the conjugate variables, $T = \frac{\partial U}{\partial S}$, $p = -\frac{\partial U}{\partial V}$, and $\mu = \frac{\partial U}{\partial N}$, called the *temperature*, the *internal pressure* (note the minus sign), and the *chemical potential*, respectively. These variables are *intensive parameters*, i.e. they are invariant with respect to the partitioning of the system (put differently, they are positive homogeneous functions of order 0). Note that all intensive and extensive variables take on only positive values.

Alternatively, instead of the energy representation of the main relationship (1) one can use the entropy formulation

$$S = S(U, V, N). \tag{3}$$

It can be readily seen that the conjugate variables are now $\left(\frac{1}{T},\ \frac{p}{T},\ -\frac{\mu}{T}\right)$. Along with the energy and entropy representations of the state equation one often uses different state equations obtained as partial Legendre transformations of (1) yielding, e.g., the Gibbs energy, the enthalpy etc. or the Legendre transformations of (3) resulting in the Massieu-functions (see, e.g., (Callen, 1985, Ch. 5)).

Definition 1. An *equilibrium energy manifold* of a thermodynamic system is defined as the graph $\mathcal{U}$ of the energy function $U(S, V, N)$. Correspondingly, an *equilibrium entropy manifold* $\mathcal{S}$ is defined as the graph of the entropy function $S(U, V, N)$.

Remark 2. In the same way one can define equilibrium manifolds corresponding to the different state functions. Note though that while energy and entropy representations result in the same equilibrium manifold up to the permutation of coordinates, the equilibrium manifolds derived from other state functions are not directly comparable to $\mathcal{U}$ or $\mathcal{S}$ because these are expressed in different coordinates (both extensive and intensive variables). On the other hand, these equilibrium manifolds represent the same substance. To unify all descriptions of a given thermodynamic system, it proves to be helpful to lift the equilibrium manifold into the higher-dimensional space of extensive and intensive coordinates as described in Subsection 2.3.

The behavior of a thermodynamic system is governed by the *First* and the *Second Law of Thermodynamics* (Callen (1985); Kondepudi and Prigogine (1998)). The First Law states that the infinitesimal variation of energy, dU, in a thermodynamic process[1] can be written as

$$dU = \Delta Q + \Delta W + \Delta C, \tag{4}$$

where ΔQ, ΔW, ΔC are the path-dependent infinitesimal quantities describing the amount of heat transferred to the system, the work done on the system, and the change of the internal energy due to the matter flow. In contrast to the latter quantities, dU is path-independent and thus is identified with the differential of the internal energy function. For a quasi-static process (4) can be rewritten in terms of state variables and their conjugates to yield

$$dU = TdS - pdV + \mu dN. \tag{5}$$

Of particular importance is the first term in the r.h.s. of (5) which is addressed by the Second Law. It states that

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[1] This result holds true for any class of thermodynamic processes, whether equilibrium or non-equilibrium ones.