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A Hamiltonian approach to Thermodynamics

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HIGHLIGHTS

- A strictly Hamiltonian approach to Thermodynamics is proposed.
- Dirac's theory of constrained systems is extensively used.
- Thermodynamic equations of state are realized as constraints.
- Thermodynamic potentials are related by canonical transformations.

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ABSTRACT

In the present work we develop a strictly Hamiltonian approach to Thermodynamics. A thermodynamic description based on symplectic geometry is introduced, where all thermodynamic processes can be described within the framework of Analytic Mechanics. Our proposal is constructed on top of a usual symplectic manifold, where phase space is even dimensional and one has well-defined Poisson brackets. The main idea is the introduction of an extended phase space where thermodynamic equations of state are realized as constraints. We are then able to apply the canonical transformation toolkit to thermodynamic problems. Throughout this development, Dirac's theory of constrained systems is extensively used. To illustrate the formalism, we consider paradigmatic examples, namely, the ideal, van der Waals and Clausius gases.

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1. Introduction

The use of the theoretical structure of Analytic Mechanics, with the introduction of a principle of stationary action and a Lagrangian description, allowed a unification of many areas of Classical Physics, including General Relativity. Also, this structure provides a more straightforward way to the quantum description of important physical systems. Both in the classical and quantum treatment, Dirac's theory of constrained systems [1] has a central role. In this sense, Analytic Mechanics provides a unified language for much of the Physics landscape.

The same degree of generalization, albeit in a different path, is given by Thermodynamics. This theory ignores the internal (microscopic) structure of the system to be described, treating it as a "black box". The final states of a given system can be described by a reduced number of variables which effectively implement the interaction of the black box with its environment. In this way, the description provided by Thermodynamics is generally adequate, even if the system of interest is a gas in a recipient or a black hole (which is fundamentally a true black box, at least in classical terms).

Previous attempts at unifying the theoretical framework of Analytic Mechanics and Thermodynamics followed two distinct paths, one alongside a more physical standpoint, and another towards a geometrical unification. As an example of the first, one can cite [2], where Poisson brackets (PB) between thermodynamic variables are defined, but the issue of the invariance of the new PB with respect to canonical transformations is not completely clarified. The second approach has its origin with Gibbs [3] and Caratheodory [4], and culminated with the work of Hermann [5]. In a nutshell, the geometric approach assigns a contact structure to the thermodynamic phase space, such that the Legendre submanifolds describe equilibrium states. One then defines a pseudo-Riemannian metric on the phase space which is compatible with the contact structure. The contact structure is responsible for encoding the first law, while the metric structure encodes the second law [6]. Notwithstanding the conceptual clarity of the geometric approach, the meaning of the of length of curves in the thermodynamic state space is not completely understood given the various proposals and interpretations [7,6,8,9], as well as the physical meaning of contact symmetries and contact vector field flow, analogs of symplectomorphisms and Hamiltonian flow in Mechanics [10,9].

Another important development on the subject was presented in [11]. In this work, a Hamilton–Jacobi formalism is proposed starting from the geometric approach, i.e., a contact manifold. By solving the Hamilton–Jacobi equation, one is able to recover all equations of state. In a different work [12], the author quantizes the previous approach in the framework of deformation quantization of contact manifolds. However, the presence of non-conventional structures, such as the odd thermodynamic phase space, Lagrange brackets and the resulting non-standard algebra of observables, make it difficult to obtain recognizable physical features, e.g., thermodynamic uncertainty relations.

Contrasting with previous developments, we present a strictly Hamiltonian approach to Thermodynamics. Our proposal sets aside the contact manifold framework and is constructed on top of a usual symplectic manifold, where phase space is even dimensional and one has well-defined Poisson brackets. The main idea is the introduction of an extended phase space where thermodynamic equations of state are realized as constraints. We are then able to apply the canonical transformation toolkit to thermodynamic problems, and with little effort we solve van der Waals and Clausius gases from the much simpler ideal gas. Finally, our approach allows a Lagrangian description of Thermodynamics.

The structure of this work is as follows. In Section 2 we consider the symplectic structure involving thermodynamic variables in the present approach, introducing suitable Poisson brackets and analyzing related integrability issues. In Section 3 the formal structure for the extended phase space is rigorously developed. The constraint structure of our formalism and Lagrangian description of thermodynamic systems in the context introduced here are discussed in Section 4. To illustrate the formalism, we consider paradigmatic examples in Section 5, namely ideal, van der Waals and Clausius gases. Final considerations and some perspectives of future developments are presented in Section 6.

2. Integrability and Poisson brackets

There have been works dedicated to the attempt of establishing a symplectic structure involving thermodynamic variables [2,13]. In fact, the duality between mechanics and Thermodynamics is