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Bracket formulation of nonequilibrium thermodynamics for systems interacting with the environment☆

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Abstract

In this work we show how to naturally modify the expressions for the total time derivatives of functionals of the field variables in complex systems, expressed originally using generalized brackets in the bracket formulation of nonequilibrium thermodynamics for non-interacting systems, in order to account for the interactions of the systems with the environment. After a short description of the problem, the approach is illustrated in a simple example involving the flow of a non-isothermal incompressible viscous fluid in a fixed domain. We examine here exclusively classical but possibly non-local (i.e. where higher derivatives may be involved in the definition of extended thermodynamic quantities) hydrodynamics. We also use the "extended equilibrium" or "quasi-equilibrium" assumption: it is assumed that an extended entropy can be defined as a state variable of the system. The resulting surface terms in the final expression can then be used to fully identify the fluxes describing the surface interactions of the system with the environment. In this way, it is shown that the generalized bracket formalism as described before, i.e. in terms of bracket equations applicable only for non-interacting (isolated) systems, is nevertheless complete. Although those original bracket equations cannot be directly used to describe the evolution equations for functionals defined for complex interacting systems, those can be derived in a straightforward fashion from the governing dynamic equations of the field variables that have themselves been derived from the original generalized bracket equations. The final equations are then automatically compatible with thermodynamics and duly comply with both the first and the second law of thermodynamics. Additional long range interactions can also be taken into account naturally though a modification of the system's Hamiltonian. This work parallels and extends to open systems involving constrained variables recent work [Öttinger, Phys. Rev. E 73:036126 (2006)] that also addresses the treatment of surface excess variables.

Keywords: Bracket formalism; Nonequilibrium thermodynamics; Open system; Interacting system; Functional evolution

1. Introduction

During the last 20 years considerable effort has been placed in developing a systematic framework for the generation of the equations governing the dynamics of continuum media—see [1–11] and references therein. This entails the consistent extension of equilibrium thermodynamics under nonequilibrium conditions. Following the pioneering work by Truesdell and Toupin in the axiomatic foundation of continuum mechanics [12], the new approaches emphasize more the physical content (namely, thermodynamics) and the existing interconnections between various formalisms applied at different scales of length and time, thus offering a systematic way for multiscale analysis [10,11].

The use of thermodynamics enters at different levels. First of all, equilibrium thermodynamics suggests the minimum variables for an adequate description of the continuum system: those are the ones that are required for the description of the equilibrium thermodynamic system, like the density, entropy, etc. Of course, in addition to those, one needs more variables in order to describe

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departures from equilibrium, at a minimum the velocity (or, equivalently, the momentum density) and on many occasions, other variables necessary to describe the nonequilibrium structure of the system, like the conformation tensor, **c**, for polymer dynamics.

Second, thermodynamics imposes strict relations for the evolution of key extensive thermodynamic quantities, like the total energy of the system, H, (which is customarily called the Hamiltonian) and the total entropy of the system, S. Namely, the first law of thermodynamics can be written for a closed system interacting with the environment

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \dot{Q} - \dot{W}, \tag{1}$$

where $\dot{Q}$ is the rate of heat transfer from the environment to the system, and $\dot{W}$ the rate of work performed by the system to the environment. On the other hand, the second law of thermodynamics can be described by the inequality

$$\dot{S} \geq 0, \tag{2}$$

where $\dot{S}$ is the total rate of entropy production within the system and its environment; this automatically also implies that the local rate of entropy production also has to be a non-negative quantity. Eqs. (1) and (2) impose stringent conditions on the dynamics that need to be satisfied in any models.

2. The bracket formulation

To achieve further contributions, it is necessary to make additional assumptions regarding the structure of the dynamic equations. Various nonequilibrium thermodynamic extensions have been developed over the last 20 years. The very first one, originating from the pioneering work of Morrison [2] and Grmela [3], is based on an extension of the Poisson bracket to accommodate dissipation and irreversibility. The Poisson bracket is a mathematical quantity that it is alternatively used for the expression of conservative, Hamiltonian dynamics [7]. It is defined for both discrete and continuum systems. For example, for a particle moving within a given potential field, $V(\mathbf{x})$, the Poisson bracket $\{F, G\}$ corresponding to two arbitrary functions of the particle's position, $\mathbf{x}$, and the particle's momentum, $\mathbf{p}$, $F(\mathbf{x},\mathbf{p})$ and $G(\mathbf{x},\mathbf{p})$, is given as [7,8]

$$\{F, G\} \equiv \frac{\partial F}{\partial \mathbf{x}} \cdot \frac{\partial G}{\partial \mathbf{p}} - \frac{\partial G}{\partial \mathbf{x}} \cdot \frac{\partial F}{\partial \mathbf{p}}. \tag{3}$$

This definition of the Poisson bracket exhibits all its generic properties: namely that is bilinear and antisymmetric with respect to F and G, and that is satisfies the Jacobi equality

$$\{F, \{G, H\}\} + \{G, \{H, F\}\} + \{H, \{F, G\}\} = 0, \tag{4}$$

for any three arbitrary functions F, G and H. The key property of the Poisson bracket is that it can be used in an alternative formulation of the particle dynamics. This is generated by the following general equation, valid for any arbitrary function F:

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \{F, H\}, \tag{5}$$

where H is the total energy, Hamiltonian, of the system, which for a particle in a potential field is simply the sum of its kinetic and potential energies:

$$H = \frac{1}{(2m)}\mathbf{p}^2 + V(\mathbf{x}), \tag{6}$$

where m is the mass of the particle. Indeed, it can be easily shown that the traditional Hamiltonian equations for particle dynamics can be recovered simply by substituting into the master equation, Eq. (5), the expression for the particle's Hamiltonian provided by Eq. (6), and by requiring that the final result is, for all functions $F = F(\mathbf{x},\mathbf{p})$, the same as that obtained by evaluating the left hand side of Eq. (5) using differentiation by parts:

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \frac{\partial F}{\partial \mathbf{x}} \cdot \frac{\partial \mathbf{x}}{\partial t} + \frac{\partial F}{\partial \mathbf{p}} \cdot \frac{\partial \mathbf{p}}{\partial t}. \tag{7}$$

The very interesting fact is that the Poisson structure can also be extended to describe the conservative Hamiltonian dynamics of continua. This extension is accomplished simply by switching from a set of low dimensionality vectors (for example, $\mathbf{x}$, and $\mathbf{p}$ in the example above) to a set of continuum field variables (such as the mass density $\rho(\mathbf{x})$) in describing the state of the system. Correspondingly, the arbitrary functions, F, G and H are replaced by functionals of those field variables whereas the partial derivatives of the functions, entering the definition of the Poisson bracket – see Eq. (7) – are to be replaced by Volterra (or functional) derivatives [8] (for functionals represented as simple integrals involving functions of unconstrained variables these are simply the partial derivatives of these functions). It is possible to show then that suitable expressions for the Poisson bracket exist (which now is expressed as a bilinear functional) so that the dynamics can still be described using the master equation, Eq. (5) and the corresponding Hamiltonian