A RIEMANNIAN GEOMETRY FOR THERMODYNAMIC STATE SPACE

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Received 3 March 1992

We consider a class of thermodynamic systems in which the dynamics of the spontaneous approach to equilibrium is governed by the gradient of negentropy, where the gradient is taken with respect to a Riemannian metric. In open systems (dissipative structures) this gradient field is superposed with a vector field of interactions with environment. We consider three characteristics of the "economy" of dissipative structures: negentropy inflow (income), negentropy consumption (i.e. entropy production), and negentropy surplus (reserves). We derive explicit formulas for these characteristics and for the relations between them.

1. Introduction

The conceptual foundations of thermodynamics have been clarified in the last thirty years by a number of authors (see e.g. [2, 8-10]). A fundamental concept of any thermodynamic theory is the state space, on which thermodynamic variables are defined. Thermodynamic processes are paths in the state space, while work and heat are functionals acting on processes, usually via integration of differential forms. Thermodynamic theories introduce constraints on possible processes, for example Clausius-Duhem inequality.

For the theory of dissipative structures, which are open thermodynamic systems far from equilibrium (see [4]), it seems desirable to inquire into the structure of processes in more detail. Thus the spontaneous process of the approach to equilibrium should be distinguished from that forced by the flows from environment. For example, the entropy production is a property of the former, while the entropy flow is a property of the latter. Both these processes require a theory. Spontaneous thermodynamic processes possess Lyapunov functions, e.g. entropy or another thermodynamic potential. A wide class of dynamical systems possessing Lyapunov functions are gradient systems, so it is tempting to postulate that the thermodynamic vector field is the gradient field of entropy. However, the simplest thermodynamic systems show that the dynamics of spontaneous processes cannot be determined by the entropy alone. For example, diffusion or rate constants are not derivable from it. Rather, they are geometric properties of the state space.
Nevertheless, gradient is a metric concept and besides Euclidean metric there are many Riemannian metrics which yield other gradients. This is the idea behind Shahshahani metric in population genetics: The selection vector field is the negative gradient of fitness function with respect to Shahshahani metric (see [1]). It seems that non-Euclidean metrics may be workable for some thermodynamic processes too. Thus we recognize in entropy the basic driving force behind the spontaneous approach to equilibrium. This force, however, is canalized by the geometry of the state space.

From another point of view, we can arrive at the same standpoint by a generalization of linear nonequilibrium thermodynamics. We postulate, that the thermodynamic fluxes are determined from the thermodynamic forces via a positive definite matrix of phenomenological coefficients but we assume that these coefficients are state dependent. There is also a formal analogy with classical mechanics. While a Hamiltonian vector field is obtained from the energy function and symplectic geometry, a thermodynamic vector field is obtained from the entropy function and Riemannian geometry.

In the present paper we develop this approach in abstract setting. We adopt the approach of [2], which recognizes the prime importance of entropy. Because of formal reasons, however, we use negentropy (negative entropy) introduced by Schrödinger in [7]. All thermodynamic data might be encoded in the negentropy function, which is an extensive, convex function of extensive and conservative variables like energy, volume and quantities of components. These extensive variables form the state space (compare with [9]). The intensive variables like temperature or pressure may be obtained through differentiation of negentropy or by taking ratio of extensive variables. Thus energy has no privileged position. It is only one of the variables defining the state space.

We add to this structure a space of (spontaneous) processes, and for each state a positive definite bilinear form which determines the rates of processes in the current state. The processes lift the form to a positive semidefinite bilinear form on the state space which in turn determines a Riemannian metric on some of its subspaces. The negative gradient of negentropy with respect to this metric is then the vector field of closed system. In an open system we adjoin a vector field of interactions with environment. This field is subject to condition that the resulting vector field conserves some intensive variables.

While this approach of gradient field is not completely general (for example negentropy is required to be differentiable, which excludes phase transitions), it seems to work in chemical kinetics which is the proper domain of dissipative structures. We obtain in this way the mass action law with conservation laws as linear constraints. This conforms to the treatment of chemical kinetics in [10] and [3]. However, since we consider the flows from environment explicitly, we restrict ourselves to the detailed balanced systems.

This approach enables us to investigate the “economy” of dissipative structures. This is based on Schrödinger’s insight, later worked out by the Brussels School of I. Prigogine that it is the negentropy that the living organisms (and dissipative structures) feed on. Thus negentropy is regarded as a value which is consumed in all