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Thermodynamics of dissipative systems

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Abstract. A new model of phenomenological thermodynamics unifying classical mechanics and thermodynamics is presented. This model can be used to describe dissipative mechanical systems. Precise statements for the first and the second law of thermodynamics are given in the context of dynamical systems. An equilibrium principle connecting the concept of entropy to thermodynamical equilibrium is stated, and the problem of the existence of an equilibrium set is examined. The emphasis is laid on the conceptual difficulties encountered if entropy and temperature are introduced in the phenomenological description of dynamical systems. This dynamical model is shown to be compatible with classical thermodynamics. The presentation is restricted to the study of discrete systems (finite number of degrees of freedom).

Key-words: Thermodynamics, Dynamical systems, Dissipative mechanics, Equilibrium.

1. Introduction

The mechanics of dissipative systems has been discussed in several papers [1, 2]. Usually, the starting point of these models is the Raleigh's dissipation function, introduced in the context of symplectic mechanics.

However, we think that a natural description of these systems should make use of the two principles of thermodynamics: the principle of conservation of energy and, in the case of closed systems, the principle of nondecrease of entropy.

The existence of entropy for systems out of equilibrium cannot be established without the additional principle of "local equilibrium". Indeed, the zeroth principle of thermostatics teaches us that temperature can only be defined for systems in equilibrium. Consequently, the entropy is meaningful only for the equilibrium states of a system.

This difficulty becomes essential when we are dealing with phenomenological thermodynamics out of equilibrium (in opposition with statistical thermodynamics). The more common argument used to bypass this problem is the local equilibrium hypothesis: in the thermodynamical models of continuous media, a temperature scalar field is assumed to exist as well as an entropy density. Basically, thermostatics is assumed to hold for the infinitesimal parts of fluid composing the whole system. Several examples of thermodynamical models can be found in the mechanics of continuous media [3, 4]; a lot of other papers use statistical mechanics as a starting point [5, 6].

Actually, from a phenomenological point of view, the second law of thermodynamics does not lead naturally to an unambiguous definition of entropy for systems out of equilibrium. Indeed, the introduction of entropy and temperature in the framework of dynamical systems raises several conceptual difficulties that we are going to examine in this paper. More precisely, our aim is threefold:

i). Emphasize the physical and mathematical postulates that we found necessary to use in order to conserve the concepts of entropy and temperature in the phenomenological description of dynamical systems.
ii). Give a precise statement of the two principles in the context of dynamical systems, and build a dynamics for dissipative mechanical systems consistent with the two principles.
iii). Give a simple criterion to be satisfied by thermodynamic systems in order to respect the equilibrium principle (this principle asserts that an isolated system must tend to an invariant set for $t \rightarrow +\infty$).

The resulting model unifies classical mechanics and thermodynamics. Our model is consistent with Caratheodory's ideas [7], and is also an extension of Stueckelberg's approach to the same subject [8]. Essentially, we will suppose that it is always possible to break up a thermodynamic system into several "simple systems"; these simple systems are totally specified by a single variable of non-geometrical nature (e.g. energy, temperature or entropy) and by several geometrical variables (e.g. position, speed). We will see that this model allows us to deal rather easily with the crucial problem of the interactions between different systems.

We restricted our attention to discrete systems, in opposition to continuous systems, in order to simplify the mathematical description and to emphasize the logical structure of the theory. The existence of entropy in our description of a dissipative system modifies completely the symplectic scheme which is proper to mechanics. In particular, the adjunction of this additional variable in the description of the states of the mechanical system transforms the state space into a manifold of odd and not even dimension: it questions therefore the existence of the symplectic form. The resulting mathematical structure will be, in comparison with the usual symplectic structure of mechanics, relatively poor but will give rise to new situations.

We will see that our model reduces to thermostatics when appropriate constraints are imposed to the vector field which defines the motion: the 'quasi-static' process happens to be a very artificial evolution in which the states of constrained equilibrium play an essential rôle.

2. Thermodynamics

Classical thermodynamics is confined to the study of the equilibrium states of a system; only quasi-static processes between two equilibrium states can be described. For this reason "thermostatics" is a more suitable name for classical thermodynamics. Following Gibbs, Tisza [9] and Falk [10] developed a geometrical thermostatics in which energy and entropy are introduced in a axiomatic way. Another point of view, inspired by Caratheodory's ideas, was presented by Jauch [11].

However, thermodynamics is the science of motion, and we believe that both thermodynamics and thermostatics should be inbedded in a same general mathematical frame.

As for thermostatics, we will postulate that the set of all states of a thermodynamical system is a differentiable manifold E. For simplicity, we will assume that the dimension of E is finite.

In addition, we assume that a closed system is a dynamical system. In other words, the evolution is defined by a semi-flow

$$U : R_+ \times E \to E$$

generated by the vector field

$$Z(e) = \frac{d}{dt} U(t, e)\Big|_{t=0}, \quad e \in E.$$

The vector field does not depend explicitly on time, which means that the system is autonomous, or equivalently, is closed.

Moreover, this dynamical system must satisfy the two principles of thermodynamics. To begin with, we will assume that there exists an energy state function $H : E \to R$, such that

$$Z \lrcorner dH = 0.$$

This is only a restatement of the conservation of energy principle.

Next, we need a phenomenological formulation of the second principle, which is a more delicate problem. Our point of view is that the second principle, in a phenomenological context, cannot be stated without referring to the concept of temperature. Indeed, how could we say that heat flows from hot to cold if it were not possible to assign two temperatures to systems under consideration?

This perspective leads us to study systems composed of many interacting 'simple systems', each of them having its own temperature. These simple systems will be assumed to have a temperature without being necessarily in a static equilibrium. This state of affair could seem very artificial and paradoxal, but it is currently encountered in fluid dynamics, where a temperature scalar field is always assumed to exist; to go further with this analogy, we could say that the infinitesimal amount of fluid actually plays the rôle of an simple system in fluid thermodynamics.

Historically, the idea of systems composed of simple systems as well as the postulates of extensivity of energy were introduced by Caratheodory in thermostatics [7].

Following Caratheodory and especially Stueckelberg [8], we are going to define, for thermodynamical system, the notion of simple system.

3. Simple systems

We will assume that in the atlas of the manifold E, there exist coordinate systems in which the state functions are naturally divided in two classes: geometrical and non-geometrical state functions. To the first class belongs for example state functions such as the position or the velocity of a point, and the second one contains for example the energy or the temperature of the system. The essential difference between a thermodynamical and a mechanical system is that the last one can be fully described without using non-geometrical state functions.

We will say that a system is simple if, for each choice of these special coordinate systems, the class of its non-geometrical state functions contains only one element.

For inessential reasons of simplicity, we will assume that the state space has a structure of cartesian product

$$E = M \times R.$$

Remembering our motivations for the introduction of simple systems, it seems natural, at first, to choose the temperature as the unique non-geometrical state variable. We will restrict ourselves to the study of systems with positive temperature, hence

$$E = M \times R_+ = \{(m, T)\}, \quad T > 0.$$

We are recovering here one of the classical Caratheodory's idea: for a simple system, only one non-geometrical state variable is necessary in order to describe all the non-geometrical internal phenomena.

Taking into account the cartesian product structure, a vector field of $T_{(m,T)}E$ is given by a couple $X = (X_1, x_0)$, where $X_1 \in T_m M$ and $x_0 \in R$. We will frequently use the decomposition $df = \mathbf{d}f + \partial f/\partial T\, dT$ and therefore $X \lrcorner df = X_1 \lrcorner \mathbf{d}f + \partial f/\partial T\, x_0$.

The first principle can easily be extended to simple systems interacting with the outside world. We will restrict ourselves to the two classical interactions: work and heat.

The work will be defined by a differential 1-form, possibly depending on time

$$\omega : R \times E \to T^*E.$$

But work can only be produced by a change in the geometrical state variables of the system; this leads us to impose an essential restriction to ω:

$$\forall x_0 \in R, \quad (0, x_0) \lrcorner \omega = 0.$$

Introducing for the work and for the vector field Z the following notations

$$\omega_t(m, T) = \omega(t, m, T)$$

$$\begin{cases} Z : R \times E \to TE \\ Z_t(m, T) = Z(t, m, T) = (X_t(m, T), \dot{T}_t(m, T)) \end{cases}$$

we can write the first principle for an adiabatically closed system

$$Z_t \lrcorner\, dH = X_t \lrcorner\, \omega.$$

The heat entering the system is a function, possibly depending on time

$$Q: R \times E \rightarrow R$$

defined by

$$Q(t, m, T) = Z_t \lrcorner\, dH - X_t \lrcorner\, \omega_t.$$

Introducing the notation

$$Q_t(m, T) = Q(t, m, T)$$

the first law takes the general form

$$Z_t \lrcorner\, dH = X_t \lrcorner\, \omega_t + Q_t.$$

Now that the definition of a simple system is completed, we can give a statement of the second principle for a simple system. Afterwards, the motivation for this principle will be discussed.

Second principle (*second law 2a*))

There exists a non-geometrical state function $S: E \rightarrow R$, the entropy, such that

1) $\partial H / \partial S > 0$
2) $Z_t \lrcorner\, dS = \dot{S}_t \geq 0$ if the system is adiabatically closed.

This postulate is motivated by the Kelvin–Planck principle. Basically, this last principle asserts that if we 'force' the geometrical state variables of an adiabatically closed system to perform a cycle, the total amount of work done on the system is positive. In other words, we cannot recover entirely the work put into the system because a part of it is always wasted by friction. Because $\int \omega = \int dH$ for an adiabatically closed system, the net result is an increase of the total energy of the system.

Let us check that systems satisfying the second law 2a) also satisfy the Kelvin–Planck principle. Assume first that we choose the entropy as the non-geometrical coordinate, instead of the temperature. Next, imagine that we can find a suitable 1-form of work ω_t such that the trajectory $U_t(e)$ describes a 'quasi-closed' path $C: [t_1, t_2] \rightarrow E$ (a quasi-closed path between two instants t_1 and t_2 is such that $m(t_1) = m(t_2)$, i.e. such that the geometrical variables perform a cycle [11]). The total increase of energy on C is given by $\Delta H = \int_C dH$. But H is a state function, hence ΔH can be calculated along any path connecting the end points of C. If we denote by γ the path such that $m = \text{const.}$ (see Fig. 1), then ΔH reduces to

$$\Delta H = \int_\gamma \frac{\partial H}{\partial S} \dot{S}_t \, dt$$

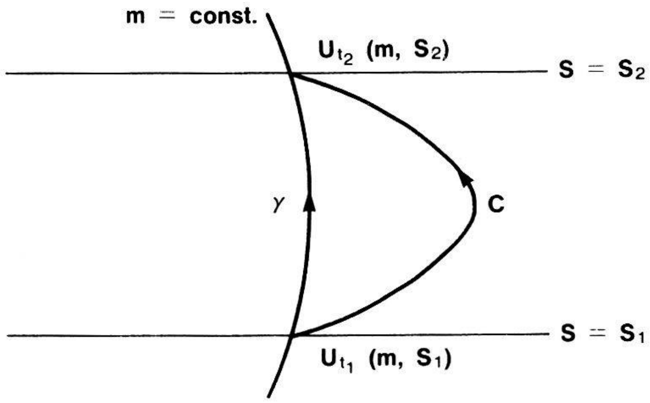

Figure 1

According to the second law 2a), $\partial H/\partial S > 0$ and $\dot{S}_t \geq 0$, hence the Kelvin–Planck principle is satisfied.

Our last problem is to define the entropy state function. We wish to define this function in such a way that it reduces to the classical entropy on the static states of E (i.e. states $e^* \in E \mid Z(e^*) = 0$). In thermostatics, entropy and temperature are linked by the well known relationship $T = \partial H/\partial S$. A very simple way to build an appropriate entropy is to impose the following constraint on S:

$$\forall e \in E, \ \frac{\partial H}{\partial S} = T(e) > 0.$$

Obviously, $T = \partial H/\partial S$ will be satisfied for the static states, since it is satisfied for all states. In addition, this relation allows us to find an expression for entropy once the energy $H(m, T)$ is known; indeed

$$T = \frac{\partial H}{\partial S} = \frac{\partial H}{\partial T}\frac{\partial T}{\partial S} = \frac{\partial H}{\partial T}\Big/\frac{\partial S}{\partial T}$$

provided $(\partial S/\partial T) = (1/T)(\partial H/\partial T)$ is not equal to zero, which is the case if the heat capacity $c = \partial H/\partial T$ is always positive. Then we obtain an expression of S which satisfies the third principle of thermodynamics ($S(m, 0) = 0$)

$$S(m, T) = \int_0^T \frac{1}{T}\frac{\partial H}{\partial T}\, dT.$$

3. Equations of motion of simple systems

In this section, the vector field $Z = (X, \dot{S})$ of a simple system will be defined in such a way that the two principles of thermodynamics will be respected. For convenience, we will always use the entropy as the non-geometrical state variable.

We will begin with a closed simple system. The first law reduces to

$$Z \lrcorner\, dH = X \lrcorner\, \mathbf{d}H + T\dot{S} = 0$$

hence

$$\dot{S} = -\frac{1}{T} X \lrcorner \mathbf{d}H.$$

The second law 2a) imposes $\dot{S} \geq 0$. In order to satisfy this inequality, we will adopt the Onsager's hypothesis by setting

$$\dot{S} = \frac{1}{T} \Lambda_S(X, X) \tag{1}$$

where $\Lambda_S(X, X)$ is a positive semidefinite quadratic form (the subscript "S" indicates that Λ_S is symmetric). Consequently, we have $X \lrcorner \mathbf{d}H = -\Lambda_S(X, X)$.

Actually, we are going to postulate that the field X is defined by

$$\mathbf{d}H = -\Lambda(X) \tag{2}$$

where $\Lambda : E \to (TE)_2^0$ is a bilinear form on TE. In addition, we assume that the null space of Λ contains only vectors of the form $(0, x_0)$ and that the symmetric part of Λ is positive semidefinite. Restricted to T_mM, this bilinear form is regular and equation (2) can always be solved for X, provided the couple (H, Λ) is known.

Since a bilinear form Λ can always be decomposed in a sum of a symmetric and an antisymmetric form, i.e.

$$\Lambda = \Lambda_S + \Lambda_A$$

then equation (2) allows us to recover equation (1). Indeed

$$\dot{S} = \frac{1}{T} \Lambda(X, X) = \frac{1}{T} \{\Lambda_S(X, X) + \Lambda_A(X, X)\} = \frac{1}{T} \Lambda_S(X, X).$$

Equations (1) and (2) define completely the vector field Z; as we wished, Z satisfies the two principles. In Section 4, we will see that an additional restriction must be imposed on (H, Λ) if we want an equilibrium set to exist.

In the field of symplectic mechanics, where the state space reduces to the submanifold M, we know that the vector field X is defined by

$$dH = -\Omega(X)$$

where Ω is a symplectic 2-form [1]. From this point of view, our model appears like a generalization of mechanics. Indeed the symmetric form, absent in mechanics, has been introduced to take into account dissipation.

If the simple system is not isolated, the vector field X_t is simply defined by

$$\mathbf{d}H = -\Lambda(X_t) + \omega_t. \tag{2'}$$

The first principle

$$Z_t \lrcorner dH = X_t \lrcorner \mathbf{d}H + T\dot{S} = X_t \lrcorner \omega_t + Q_t.$$

consequently gives

$$\dot{S}_t = \frac{1}{T} \Lambda_S(X_t, X_t) + \frac{1}{T} Q_t.$$

Again, the second law 2a) is respected. Indeed, even if X is modified by ω_t, the first term of $\dot{S}$ remains positive because Λ_S is positive semidefinite. Hence, if $Q_t = 0$, i.e. if the system is adiabatically closed, then we recover $\dot{S}_t \geq 0$. Usually, the quantity $(1/T)\Lambda_S(X_t, X_t)$ is called the internal irreversibility of the system.

Remark. A system in a constrained equilibrium is a special case of the above general model. The motion is quasi-static, which means that $X \approx 0$. Therefore, the equation (2′) reduces to (for a time independant external work)

$$\mathbf{d}H = \omega.$$

This equation defines a submanifold of E: the manifold of the constrained equilibrium states of classical thermodynamics. On this submanifold, we have

$$dH = \mathbf{d}H + T dS = \omega + T dS$$

which is the classical form of the first principle. Notice that the interpretation of this last equation is somewhat different from the dynamical meaning of the first law.

Dissipative mechanical simple systems

A dissipative mechanical system is defined by the manifold

$$M = T^*N$$

where N is the configuration manifold. The energy H and the bilinear form Λ are given by

$$H(q, p, S) = E_{\mathrm{kin}}(p) + U(q, S)$$
$$\Lambda(q, p, S) = \Omega(p) + \Lambda_S(q, p, S)$$

where $E_{\mathrm{kin}}(p)$ is the kinetic energy term, $U(q, S)$ is the internal energy, i.e. the thermostatic energy of the same system but in constrained equilibrium (see the above remark), $\Omega(p)$ is the symplectic form on T^*M[1] and $\Lambda_S(q, p, S)$ is a positive semidefinite symmetric bilinear form operating only on the vectors of TN.

Notice that

$$\frac{\partial H}{\partial S} = \frac{\partial U}{\partial S} = T.$$

Temperature is independent of the state of motion of the system: it is the temperature of the corresponding thermostatic system, obtained with the use of suitable external constraints.

Example. A damped harmonic oscillator is defined by

$$E = M \times R = R^2 \times R = \{(q, p), S\}$$

with

$$H(q, p, S) = \frac{1}{2M} p^2 + \tfrac{1}{2} k(S) q^2 + f(S)$$

$$\Lambda(q, p, S) = dq \Lambda\, dp + \Lambda_S(q, S)\, dq\, dq$$

where $M > 0$ is the mass, $k(S)$ is the spring constant, $f(S)$ is a purely thermal energy and $\Lambda_S(q, S) \geq 0$ is interpreted as the friction coefficient.

With the notation $Z = (\dot{q}, \dot{p}, \dot{S})$, the equation $\mathbf{d}H = -\Lambda(X)$ gives

$$\frac{1}{M} p\, dp + k(S) q\, dq = -\dot{p}\, dq + \dot{q}\, dp - \Lambda_S(q, S) \dot{q}\, dq,$$

from which we get

$$\dot{q} = \frac{1}{M} p$$

$$\dot{p} = -\Lambda_S(q, S) \frac{1}{M} p - k(S) q.$$

The equation for the entropy, $\dot{S} = (1/T) \Lambda_S(X, X)$, reduces to

$$\dot{S} = \frac{1}{TM^2} \Lambda_S(q, S) p^2 \geq 0.$$

The system gives the motion of a material point set in a fluid for which the interaction with the point is described by Λ_S and f.

4. Equilibrium principle for simple systems

An isolated thermodynamic system naturally evolves toward an equilibrium state, or more generally toward a motion such that the entropy remains constant. According to the principle 2a), this constant value of the entropy has to be a maximum in the sense that $S \circ U_t(e) \leq S_{\mathrm{MAX}}$. During the motion, the energy is constant: $H \circ U_t(e) = H(e)$. Hence, the system always stays on a subset of constant energy and tends to a constant value of S. This does not mean that the equilibrium states are states for which the entropy is a constrained maximum: in general, the equilibrium states may depend on the initial conditions.

Basically, the equilibrium principle states that for any initial state e, the closed system evolves toward states of bounded entropy:

Equilibrium principle for a closed simple system (*second law* 2*b*))

$$\lim_{t \to \infty} S \circ U_t(e) = \hat{S}(e) < \infty$$

where $\hat{S} : E \to R$ is a state function and $U_t(e) = U(t, e)$.

A sufficient condition to impose to the system in order to satisfy the above principle is to assume that the entropy always has an upper bound on each energy level set [12, 13]. If it is the case, then the infinitesimal version of this principle is [14]

$$\lim_{t\to\infty} (Z \circ dS) \circ U_t = 0$$

which means that $U_t(e)$ evolves toward a subset such that $Z \lrcorner dS = \dot{S} = 0$. Since $\dot{S} = (1/T)\Lambda_S(X, X)$, this subset is defined by $\Lambda_S(X, X) = 0$ or $\Lambda_S(X) = 0$ (using the symmetry of Λ_S). Consequently, the system tends to the submanifold

$$D = \{(m, S) \in E \mid \Lambda_S(X)\,|_{(m,S)} = 0\}.$$

According to the equilibrium principle, the system cannot quit this submanifold once it has approached it: this means that for an equilibrium state (m, S), the field $X(m, S)$ is tangent to D. We will call equilibrium states of the system the states belonging to the submanifold

$$G = \{(m, S) \in D \mid X(m, S) \in TD\}.$$

G is an invariant set of U_t on which $dH = -\Lambda_A(X)$. If $\dim(G) \neq 0$, the equilibrium motion is purely mechanical.

The following example illustrates this phenomenon.

Example [12]. Consider a dissipative coupled oscillator defined by

$$M = R^4 = \{(q_1, q_2, p_1, p_2)\}$$

with

$$H = p_1^2/2 + p_2^2/2 + \tfrac{1}{2}k(q_1 - q_2)^2 + f(S)$$

$$\Lambda = dq_1 \Lambda dp_1 + dq_2 \Lambda dp_2 + \Lambda_S$$

$$\Lambda_S(X) = \lambda(\dot{q}_1 - \dot{q}_2)(dq_1 - dq_2),\ \lambda \geq 0.$$

The equation $\mathbf{d}H = -\Lambda(X)$ gives the vector field

$$X = (p_1, k(q_1 - q_2) + \lambda(p_1 - p_2), p_2, -k(q_1 - q_2) - \lambda(p_1 - p_2)).$$

The condition $\Lambda_S(X) = 0$ tells us that D is defined by the equation $p_1 - p_2 = 0$. The tangency of X to D is expressed by $d(p_1 - p_2)(X) = 0$ and gives $q_1 - q_2 = 0$. On G, the vector field reduces to

$$X = (p, 0, p, 0)$$

which generates a free motion. This simply means that the two masses are moving with a constant momentum, without any relative velocity; the friction forces due to the relative motion of these masses consequently vanished. This is an example of an equilibrium state realizing a perpetual motion.

5. Composite systems

In our model, a thermodynamic system will always be assumed to be decomposable in a finite number N of simple systems, exchanging heat and work with each other. More precisely, the state space of a thermodynamical system will be defined by

$$E = \underbrace{R \times R \times \cdots \times R}_{N} \times M$$

where $R \times M$ is the state space of one of these simple systems. It is important to notice that, in general, the simple systems will share their geometrical variables; on the other hand, each simple system will have its own "personal" non-geometrical variable: the entropy.

Each simple system is characterized by an energy H_i, a positive semidefinite bilinear form Λ_i, not necessarily regular on TM, and by a work term ω_i and a heat term Q_i related by

$$\mathbf{d}H_i = -\Lambda_i(X) + \omega_i \tag{3}$$

$$Z \lrcorner\, dH_i = X \lrcorner\, \omega_i + Q_i, \tag{4}$$

where $Z = (\dot{S}_1, \dot{S}_2, \ldots, \dot{S}_N, X)$ denotes the vector field generating the motion of the total system.

We will define the total energy H of the system by

$$H = \sum_{i=1}^{i=N} H_i.$$

This definition may seem surprising because it does not involve any interaction energy. This does not mean that we neglect the effects of the interactions: actually, H can always be interpreted as the energy of the simple systems contained in the total system (by "total system" we mean the composite system plus the internal interactions described by the ω_i's and the Q_i's). The following example illustrates this idea:

Example. A coupled oscillator can be described by

$$H_1 = p_1^2/2 + f_1(S_1),\ H_2 = p_2^2/2 + f_2(S_2)$$

$$\Lambda_1 = dq_1 \Lambda dp_1 + \Lambda_{1S},\ \Lambda_2 = dq_2 \Lambda dp_2 + \Lambda_{2S}$$

$$\omega_1 = k_1(S_1, S_2)(q_2 - q_1)dq_1,\ \omega_2 = k_2(S_1, S_2)(q_1 - q_2)dq_2,$$

In this description, the spring is treated as two "external" state dependant forms of work.

Notice that we can imagine purely thermal simple systems, i.e systems which does not depend of geometrical variables (for example a heat reservoir).

We assume that the vector field X is determined by the equation

$$\mathbf{d}H = \sum_{i=1}^{i=N} \mathbf{d}H_i = -\sum_{i=1}^{i=N} \Lambda_i(X) + \sum_{i=1}^{i=N} \omega_i,$$

which implies that the bilinear form

$$\Lambda(X) = \sum_{i=1}^{i=N} \Lambda_i(X)$$

is regular on TM.

Hence, the remaining components of Z are given by the equations (4)

$$Z \lrcorner dS_i = \dot{S}_i = \frac{1}{T_i} \Lambda_i(X, X) + \frac{1}{T_i} Q_i. \tag{5}$$

We will say that the system is adiabatically closed if

$$Q = \sum_{i=1}^{i=N} Q_i = 0.$$

The system will be closed if, in addition, we have:

$$\omega = \sum_{i=1}^{i=N} \omega_i = 0,$$

from which follows at once the first law $Z \lrcorner dH = 0$.

Now, let us restrict our attention to a closed system. Our last problem is to express the fact that the second principle imposes some limitations on the possible interactions between the simple systems. Actually, the second principle for composite systems rests on two assumptions.

Firstly, we assume that heat is a current, i.e.

$$Q_i = \sum_{j=1}^{j=N} Q_{ji} \quad \text{with} \quad Q_{ji} = -Q_{ij} \tag{6}$$

where Q_{ji} denotes the heat flowing from system "j" to system "i". Secondly, we suppose that heat flows from hot to cold and, in a first approximation, we admit that the following discretization of Fourier's conduction law is valid

$$Q_{ji} = \measuredangle_{ji}(T_j - T_i) \quad \text{with} \quad \measuredangle_{ji} = \measuredangle_{ij} > 0. \tag{7}$$

The state function $\measuredangle_{ji}$ is the thermal conductivity coefficient between system "j" and system "i". Usually this is the content of zeroth principle of thermodynamics.

Finally, we can define the entropy of the total system to be

$$S = \sum_{i=1}^{i=N} S_i.$$

In other words, we define the entropy as an extensive function with respect to the decomposition of the system. The motivation for this definition is that $Z \lrcorner dS = \sum_{i=1}^{i=N} \dot{S}_i \geq 0$. Indeed, we easily obtain from equations (5), (6) and (7):

$$Z \lrcorner dS = \sum_{i=1}^{i=N} \frac{1}{T_i} \Lambda_i(X, X) + \frac{1}{2} \sum_{i=1}^{i=N} \sum_{j=1}^{j=N} \frac{\measuredangle_{ji}}{T_i T_j} (T_j - T_i)^2 \geq 0. \tag{8}$$

We recognize here the Clausius-Duhem inequality.

6. Equilibrium principle for composite systems

For a closed system, the energy $H = \sum_{i=1}^{i=N} H_i$ is constant. However, the energies H_i of the subsystems are not constant because of the exchanges of work and of heat. If we assume, what seems very natural, that these terms of exchange remain bounded, the values of the H_i's will remain bounded too. A simple example of a composite system with bounded exchanges of energy is obtained if we assume that the energies H_i have a lower bound [12]: in this case, the conservation of the total energy H actually implies the boundedness of each H_i. In Section 4, we admitted that, on each level set of the energy of a simple system, the entropy has an upper bound; accordingly, $S_i < S_{i\mathrm{MAX}}$ follows from the boundedness of H_i and consequently

$$S = \sum_{i=1}^{i=N} S_i < \sum_{i=1}^{i=N} S_{i\mathrm{MAX}} = S_{\mathrm{MAX}}.$$

Since, $Z \lrcorner\, dS \geq 0$, we see that the composite system will also obey an equilibrium principle. In addition, it follows that

$$\lim_{t \to \infty} (Z \lrcorner\, dS) \circ U_t = 0.$$

This infinitesimal version of the equilibrium principle implies the equality of the temperatures. Indeed, the formula (8) being a sum of non-negative terms, the condition $Z \lrcorner\, dS = 0$ implies

$$i, j = 1, 2, \ldots, N : T_i = T_j.$$

The argumentation of Section 4 is also valid here and allows us to state that the system will tend toward an invariant submanifold G where the motion is purely mechanical.

Conclusion

Our presentation of thermodynamics is remarkable for its simplicity and for its ability to unify in a single model classical mechanics and thermodynamics. Besides its pedagogical interest, this paper emphasizes the conceptual difficulties encountered when we try to include thermodynamics in the framework of dynamical systems.

We would like to mention that the structure of the invariant set G is worthwhile to study and will be investigated in a future publication.

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