The Interaction of Bodies in Thermodynamics

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Abstract

Dynamic laws are established for thermodynamic bodies that interact with each other and their environment. The trend to equilibrium (asymptotic stability) of processes of such systems is examined. The role of entropy is discussed.

Key words: system of homogenous bodies, irreversibility, trend to equilibrium, Onsager formalism

1. INTRODUCTION

In a previous paper[1] a theory of *ordinary thermodynamics* was detailed in which *processes* are considered functions defined in time, a *dynamic law* (a system of differential equations that contains the usual first law) is established to determine processes, and *formative laws* and the *second law* (restrictions) are imposed on the constitutive relations appearing in the dynamic law to have equilibria and to assure the trend to equilibrium.

The same paper treated in that framework the simplest thermodynamic system: a body in a fixed environment.

Now I continue this theory by considering systems consisting of interacting bodies, applying the previously[1] introduced notions.

The specific volume and temperature of a body are simple notions and form a base for the description of processes. They are indispensable for determining fundamental formulas from analogies with continuum thermodynamics, and they supply the formative laws for the body constitutive relations in a simple form. However, in order to describe processes, it is often more appropriate to use the specific internal energy as an independent variable instead of the temperature.

In this paper n bodies will be considered, and $n \geq 2$. The specific internal energy e_i and the specific volume v_i of the ith body are taken as independant variables. Then the temperature and the pressure of the ith body are given by continuously differentiable constitutive functions:

$$T_i = \mathbf{T}_i(e_i, v_i), \quad p_i = \mathbf{p}_i(e_i, v_i), \tag{1}$$

for which the formative laws hold[2]:

$$\begin{gathered}\frac{\partial \mathbf{T}_i}{\partial e_i} > 0, \quad \frac{\partial \mathbf{T}_i}{\partial e_i}\frac{\partial \mathbf{p}_i}{\partial v_i} - \frac{\partial \mathbf{T}_i}{\partial v_i}\frac{\partial \mathbf{p}_i}{\partial e_i} < 0, \\ \left[\mathbf{p}_i \frac{\partial \mathbf{T}_i}{\partial e_i} - \frac{\partial \mathbf{T}_i}{\partial v_i}\right] \frac{\partial \mathbf{p}_i}{\partial e_i} \geq 0.\end{gathered} \tag{2}$$

A process of the bodies is $(e_1, v_1, \ldots, e_n, v_n)$ as a function depending on time.

The *dynamic law* for the processes has the form

$$\begin{aligned}\dot{e}_i &= q_i + w_i \quad (i = 1, \ldots, n) \\ \dot{v}_i &= f_i \qquad\quad (i = 1, \ldots, n)\end{aligned} \tag{3}$$

where the "heating" q_i, the "springing" f_i, and the "working"[1]

$$w_i = -z_i f_i \tag{4}$$

are given by continuously differentiable constitutive relations satisfying some *formative laws* that will be specified according to the system that includes the bodies.

The *classical case* means the constitutive relations

$$z_i = p_i, \text{ that is, } w_i = -p_i f_i, \tag{5}$$

and the existence of the twice continuously differentiable specific entropies $s_i = \mathbf{s}_i(e_i, v_i)$ with the well-known properties

$$\frac{\partial \mathbf{s}_i}{\partial e_i} = \frac{1}{\mathbf{T}_i}, \quad \frac{\partial \mathbf{s}_i}{\partial v_i} = \frac{\mathbf{p}_i}{\mathbf{T}_i}. \tag{6}$$

Then (2) implies that the second derivative of $\mathbf{s}_i$ is negative definite.

Let m_i be the mass of the ith body. Then the *total entropy* of the bodies together is the function

$$S = \mathbf{S}(e_1, v_1, \ldots, e_n, v_n) := \sum_{i=1}^{N} m_1 \mathbf{s}_i(e_i, v_i). \tag{7}$$

It has the second derivative (in a block matrix form)

$$\mathbf{S}''(e_1, v_1, \dots, e_n, v_n) = \begin{bmatrix} m_1\mathbf{s}_1''(e_1, v_1) & & \\ & \ddots & \\ & & m_n\mathbf{s}_n''(e_n, v_n) \end{bmatrix}, \tag{8}$$

which is evidently negative definite as well.

2. BODIES IN A FIXED ENVIRONMENT

Let us suppose that the n bodies interacting with each other are put into an environment of fixed temperature T_a and fixed pressure p_a.

The constitutive relations for q_i, f_i, and z_i ($i = 1, \dots, n$) are required to satisfy the formative laws

$$\begin{aligned} 0 \neq q_i &= \mathbf{q}_i(T_1, p_1, \dots, T_n, p_n, T_a, p_a), \\ 0 \neq f_i &= \mathbf{f}_i(T_1, p_1, \dots, T_n, p_n, T_a, p_a), \\ z_i &= \mathbf{z}_i(T_1, p_1, \dots, T_n, p_n, T_a, p_a); \end{aligned} \tag{9}$$

that is, the quantities in question depend on $(e_1, v_1, \dots, e_n, v_n)$ through the temperatures and pressures of the bodies and depend on the ambient temperature and pressure. Furthermore,

$$\begin{aligned} \mathbf{q}_i(T_a, p_a, \dots, T_a, p_a, T_a, p_a) &= 0, \\ \mathbf{f}_i(T_a, p_a, \dots, T_a, p_a, T_a, p_a) &= 0, \\ \mathbf{z}_i(T_a, p_a, \dots, T_a, p_a, T_a, p_a) &= p_a. \end{aligned} \tag{10}$$

Recall that an expression of the form

$$-\frac{q}{t}(T - T_a) - \frac{w}{p}(p - p_a) \tag{11}$$

was accepted as a basis of the second law for a one-body system.[3] Divided by T_a, it is transformed into

$$(q + w)\left[\frac{1}{T} - \frac{1}{T_a}\right] - \frac{w}{p}\left[\frac{p}{T} - \frac{p_a}{T_a}\right], \tag{12}$$

which proves to be more opportune regarding the new variables (specific internal energy and specific volume).

The *second law* for the present system is formulated as follows:

$$\sum_{i=1}^{n} m_i\left[(q_i + w_i)\left[\frac{1}{T_i} - \frac{1}{T_a}\right] - \frac{w_i}{p_i}\left[\frac{p_i}{T_i} - \frac{p_a}{T_a}\right]\right] \geq 0, \tag{13}$$

and equality holds if and only if $T_i = T_a$ and $p_i = p_a$ for all $i = 1, \dots, n$. If

$$\begin{aligned} \mathbf{T}_i(e_{i,0}, v_{i,0}) &= T_a \quad (i = 1, \dots, n), \\ \mathbf{p}_i(e_{i,0}, v_{i,0}) &= p_a \quad (i = 1, \dots, n), \end{aligned} \tag{14}$$

then the constant process $(e_{1,0}, v_{1,0}, \dots, e_{n,0}, v_{n,0})$ is an equilibrium of the dynamic law (3). Observe that the second relation in (2) implies that the above equations determine the equilibrium locally uniquely, which means that equilibria, if they exist, form a discrete set.

Now we are interested in the trend to equilibrium (i.e., in asymptotic stability[4]).

Proposition 1: In the classical case an equilibrium is asymptotically stable.

Proof: The first derivative of the function

$$\mathbf{L}(e_1, v_1, \dots, e_n, v_n) := \mathbf{S}(e_1, v_1, \dots, e_n, v_n) - \sum_{i=1}^{n} m_i \frac{e_i + p_a v_i}{T_a} \tag{15}$$

at $(e_{1,0}, v_{1,0}, \dots, e_{n,0}, v_{n,0})$ is zero, and its second derivative equals the second derivative of $\mathbf{S}$, which is negative definite. Consequently, $\mathbf{L}$ has a strict maximum at the equilibrium. The derivative of $\mathbf{L}$ along the dynamic law (3) equals the left-hand side of 13; thus it has a strict minimum at the equilibrium: $\mathbf{L}$ is a Lyapunov function assuring asymptotic stability.

3. BODIES IN A RIGID BOX

Let us suppose that the n bodies interacting with each other have a fixed total volume,

$$\sum_{i=1}^{n} m_i v_i = V_0 = \text{const}, \tag{16}$$

and they are in an environment of fixed temperature T_a (in this case the ambient pressure is irrelevant). Then we require the relations for $i = 1, \dots, n$:

$$\begin{aligned} 0 \neq q_i &= \mathbf{q}_i(T_1, p_1, \dots, T_n, p_n, T_a), \\ 0 \neq f_i &= \mathbf{f}_i(T_1, p_1, \dots, T_n, p_n, T_a), \\ z_i &= \mathbf{z}_i(T_1, p_1, \dots, T_n, p_n, T_a) \end{aligned} \tag{17}$$

with the properties

$$\begin{aligned} \mathbf{q}_i(T_a, p_i, \dots, T_a, p_i, T_a) &= 0, \\ \mathbf{f}_i(T_a, p_i, \dots, T_a, p_i, T_a) &= 0, \\ \mathbf{z}_i(T_a, p_i, \dots, T_a, p_i, T_a) &= p_i, \end{aligned} \tag{18}$$

$$\sum_{i=1}^{N} m_i f_i = 0. \tag{19}$$

For the *second law* we set

$$\sum_{i=1}^{n} m_i \left[(q_i + w_i) \left[\frac{1}{T_i} - \frac{1}{T_a} \right] - \frac{w_i}{p_i} \left[\frac{p_i}{T_i} - \frac{p_k}{T_k} \right] \right] \geq 0$$
$$(k = 1, \ldots, n), \tag{20}$$

and equality is allowed if and only if $T_i = T_a$ and $p_i = p_k$ for all i, $k = 1, \ldots, n$.

Equilibria of the system are determined by

$$\begin{aligned} \mathbf{T}_i(e_{i,0}, v_{i,0}) &= T_a, \\ \mathbf{p}_i(e_{i,0}, v_{i,0}) &= \mathbf{p}_k(e_{k,0}, v_{k,0}) \end{aligned} \tag{21}$$

for all i, $k = 1, \ldots, n$. Equilibria are not unique even locally, because we have only $2n - 1$ independent equations. Attaching to them Eq. (16) (for $v_i = v_{i,0}$) we get locally unique equilibrium. In other words, for every volume value V_0,

$$\mathrm{H}_{V0} := \{e_1, v_1, \ldots, e_n, v_n) \mid \sum_{i=1}^{n} m_i v_i = V_0\} \tag{22}$$

is a $2n-1$ dimensional submanifold which is invariant under the dynamic law (3) because of (19), and equilibria in V_0 are locally unique,

Since we imposed (16) as a constraint on the processes, we are interested in asymptotic stability with the condition H_{V0}.

Proposition 2: In the classical case for all V_0, an equilibrium in H_{V0} is asymptotically stable with the condition H_{V0}.[4]

Proof: Let us parametrize H_{V0} by $(e_1, v_1 \ldots, e_{n-1}, v_{n-1}, e_n)$; then

$$v_n = \frac{1}{m_n} [V_0 - \sum_{i=1}^{n-1} m_i v_i]$$

and the reduced dynamic law becomes

$$\begin{aligned} \dot{e}_i &= q_i + w_i \quad (i = 1, \ldots, n), \\ \dot{v}_i &= f_i \qquad (i = 1, \ldots, n-1). \end{aligned} \tag{23}$$

It is easily shown that

$$\begin{aligned} &\mathbf{L}(e_1, v_1, \ldots, e_{n-1}, v_{n-1}, e_n) \\ &:= \mathbf{S}[e_1, v_1, \ldots, e_{n-1}, v_{n-1}, e_n, (1/m_n) [V_0 - \sum_{i=1}^{n-1} m_i v_i] \\ &\qquad - \sum_{i=1}^{n} m_i \frac{e_i}{T_a} \end{aligned} \tag{24}$$

is a Lyapunov function assuring the asymptotic stability of an equilibrium of (23).

4. BODIES IN A HEAT-INSULATED RIGID BOX

Now both the total internal energy and the total volume are fixed:

$$\sum_{i=1}^{n} m_i e_i = E_0 = \text{const}, \tag{25}$$

$$\sum_{i=1}^{n} m_i v_i = V_0 = \text{const}. \tag{26}$$

Then we assume the relations

$$\begin{aligned} 0 \not\equiv q_i &= \mathbf{q}_i(T_1, p_1, \ldots, T_n, p_n), \\ 0 \not\equiv f_i &= \mathbf{f}_i(T_1, p_1, \ldots, T_n, p_n), \\ z_i &= \mathbf{z}_i(T_1, p_1, \ldots, T_n, p_n) \end{aligned} \tag{27}$$

for $i = 1, \ldots, n$ with the properties

$$\begin{aligned} \mathbf{q}_i(T_i, p_i, \ldots, T_i, p_i) &= 0, \\ \mathbf{f}_i(T_i, p_i, \ldots, T_i, p_i) &= 0, \\ \mathbf{z}_i(T_i, p_i, \ldots, T_i, p_i) &= p_i, \end{aligned} \tag{18}$$

and

$$\sum_{i=1}^{n} m_i(q_i + w_i) = 0, \tag{29}$$

$$\sum_{i=1}^{n} m_i f_i = 0. \tag{30}$$

For the *second law* we set

$$\sum_{i=1}^{n} m_i \left[(q_i + w_i) \left[\frac{1}{T_i} - \frac{1}{T_k} \right] - \frac{w_i}{p_i} \left[\frac{p_i}{T_i} - \frac{p_k}{T_k} \right] \right] \geq 0$$
$$(k = 1, \ldots, n), \tag{31}$$

and equality is allowed if and only if $T_i = T_k$ and $p_i = p_k$ for all i, $k = 1, \ldots, n$.

Equilibria of the system are determined by

$$\begin{aligned} \mathbf{T}_i(e_{i,0}, v_{i,0}) &= \mathbf{T}_k(e_{k,0}, v_{k,0}), \\ \mathbf{p}_i(e_{i,0}, v_{i,0}) &= \mathbf{p}_k(e_{k,0}, v_{k,0}) \end{aligned} \tag{32}$$

for all i, $k = 1, \ldots, n$. Equilibria are not unique even locally, because we have only $2n - 2$ independent equations. Attaching to them equalities (25) and (26) for $e_i = ei_0$ and $v_i = v_{i,0}$, we get locally unique equilibrium. More closely, for every energy value E_0 and for every volume value V_0,

$$\mathrm{H}_{E_0,\,V_0} := \{e_1, v_1, \dots, e_n, v_n) \mid \sum_{i=1}^{n} m_i e_i = E_0,\ \sum_{i=1}^{n} m_i v_i = V_0\} \quad (33)$$

is a $2n-2$ dimensional submanifold which is invariant under the dynamic law (3) because of (29) and (30), and equilibria in $\mathrm{H}_{E_0,\,V_0}$ are locally unique.

Since we imposed (29) and (30) as constraints on the processes, we are interested in asymptotic stability with the condition $\mathrm{H}_{E_0,\,V_0}$.

Proposition 3: In the classical case for all E_0 and V_0, an equilibrium in $\mathrm{H}_{E_0,\,V_0}$ is asymptotically stable with the condition $\mathrm{H}_{E_0,\,V_0}$.

Proof: Let us parametrize $\mathrm{H}_{E_0,\,V_0}$ by $(e_1, v_1, \dots, e_{n-1}, v_{n-1})$; then

$$e_n = \frac{1}{m_n}[E_0 - \sum_{i=1}^{n-1} m_i e_i], \quad v_n = \frac{1}{m_n}[V_0 - \sum_{i=1}^{n-1} m_i v_i],$$

and the reduced dynamic law becomes

$$\begin{aligned} \dot{e}_i &= q_i + w_i \quad (i = 1, \dots, n-1), \\ \dot{v}_i &= f_i \qquad (i = 1, \dots, n-1). \end{aligned} \quad (34)$$

It is easily shown that

$$\mathbf{L}(e_1, v_1, \dots, e_{n-1}, v_{n-1})$$
$$:= \mathbf{S}\left[e_1, v_1, \dots, e_{n-1}, v_{n-1}, (1/m_n)[E_0 - \sum_{i=1}^{n-1} m_i e_i], (1/m_n)[V_0 - \sum_{i=1}^{n-1} m_i v_i]\right] \quad (35)$$

is a Lyapunov function assuring the asymptotic stability of an equilibrium of (34).

5. A GENERAL FORMULA

The fundamental cases were treated in the preceding paragraphs. Evidently, there are many other interesting cases as well, for example, if each body has a fixed volume, and the bodies are in an environment of given temperature or they are heat insulated.

We would like to have a general formula that covers all these cases. However, we can hardly expect that all the possibilities of interactions can be dealt with on the same line; indeed, in general, the description of heat insulation is questionable (see Sec. 7).

A general case including the cases treated above and many others can be formulated as follows.

Let r be a positive integer, $r \le n$, and for all $\alpha = 1, \dots, r$, let d_α be a positive integer. We define a family

$$(\mathrm{A}_{\alpha\beta} \mid \alpha = 1, \dots, r,\ \beta = 1, \dots, d_\alpha) \quad (36)$$

of disjoint subsets of $\{1, \dots, n\}$. Set

$$\begin{aligned} \mathrm{B}_\alpha &:= \bigcup_{\beta=1}^{d_\alpha} \mathrm{A}_{\alpha\beta} \quad (\alpha = 1, \dots, r), \\ \mathrm{B}_0 &:= \{1, \dots, n\} \setminus \bigcup_{\alpha=1}^{n} \mathrm{B}_\alpha. \end{aligned} \quad (37)$$

For every $\alpha = 1, \dots, r$ and for every $\beta = 1, \dots, d_\alpha$ let E_α and $V_{\alpha\beta}$ be an energy value and a volume value, respectively, and suppose

$$\sum_{i\in \mathrm{A}_{\alpha\beta}} m_i v_i = V_{\alpha\beta}, \quad \sum_{i\in \mathrm{B}_\alpha} m_i e_i = E_\alpha. \quad (38)$$

[We have grouped the n bodies: there is no constraint on the bodies in B_0, the total volume of the bodies in $\mathrm{A}_{\alpha\beta}$ is fixed (together they are in a rigid box), and the total internal energy of the bodies in B_α is fixed (together they are heat insulated from the other bodies and the environment.]

The formative laws for the "heatings," etc., will not be detailed, because it is obvious how we shall set them.

The second law reads as follows. Let $k(\alpha)$ and $j(\alpha\beta)$ be arbitrarily chosen elements of B_α and $\mathrm{A}_{\alpha\beta}$, respectively. Then we require

$$\begin{aligned} &\sum_{i\in \mathrm{B}_0} m_i \left[(q_i + w_i)\left[\frac{1}{T_i} - \frac{1}{T_a}\right] - \frac{w_i}{p_i}\left[\frac{p_i}{T_i} - \frac{p_a}{T_a}\right]\right] \\ &+ \sum_{\alpha=1}^{r} \sum_{i\in \mathrm{B}_\alpha} m_i \left[(q_i + w_i)\left[\frac{1}{T_i} - \frac{1}{T_{k(\alpha)}}\right]\right] \\ &- \sum_{\alpha=1}^{r} \sum_{\beta=1}^{d_\alpha} \sum_{i\in \mathrm{A}_{\alpha\beta}} m_i \frac{w_i}{p_i}\left[\frac{p_i}{T_i} - \frac{p_{j(\alpha\beta)}}{T_{j(\alpha\beta)}}\right] \ge 0. \end{aligned} \quad (39)$$

Asymptotic stability with condition (38) is proved in the classical case as previously.

6. THE ONSAGER FORMALISM

Consider the n bodies isolated from the environment, that is, the case treated in Sec. 4. Suppose the temperature value T_0 and the pressure value p_0 correspond to an equilibrium $[T_0 = \mathbf{T}_i(e_{i,0}, v_{i,0})$ and $p_0 = p_i(e_{i,0}, v_{i,0})$ for all $i = 1, \dots, n]$. Since the constitutive relations are supposed to be continuously differentiable funcitons, equalities in (29) and Lagrange's mean value theorem yield that in a neighborhood of the equilibrium

$$q_i = \sum_{k=1}^{n} \left[a_{ik}\left[\frac{1}{T_k} - \frac{1}{T_0}\right] + b_{ik}\left[\frac{p_k}{T_k} - \frac{p_0}{T_0}\right]\right],$$

$$f_i = \sum_{k=1}^{n} \left[c_{ik}\left[\frac{1}{T_k} - \frac{1}{T_0}\right] + d_{ik}\left[\frac{p_k}{T_k} - \frac{p_0}{T_0}\right]\right], \tag{40}$$

where $a_{ik} = \mathbf{a}_{ik}(T_1, p_1, \ldots T_n, p_n)$, etc., $(i, k = 1, \ldots, n)$ are continuous functions.

Then the dynamic law becomes

$$\dot{e}_i = \sum_{k=1}^{n} \left[(a_{ik} - z_i c_{ik})\left[\frac{1}{T_k} - \frac{1}{T_0}\right] + (b_{ik} - z_i d_{ik})\left[\frac{p_k}{T_k} - \frac{p_0}{T_0}\right]\right]$$

$$\dot{v}_i = \sum_{k=1}^{n} \left[c_{ik}\left[\frac{1}{T_k} - \frac{1}{T_0}\right] + d_{ik}\left[\frac{p_k}{T_k} - \frac{p_0}{T_0}\right]\right]. \tag{41}$$

Introducing

$$Y_r := \begin{cases} m_r \dot{e}_r & \text{for } r = 1, \ldots, n \\ m_{r-n}\dot{v}_{r-n} & \text{for } r = n+1, \ldots, 2n, \end{cases} \tag{42}$$

$$X_r := \begin{cases} \dfrac{1}{T_r} - \dfrac{1}{T_0} & \text{for } r = 1, \ldots, n \\ \dfrac{p_{r-n}}{T_{r-n}} - \dfrac{p_0}{T_0} & \text{for } r = n+1, \ldots, 2n, \end{cases} \tag{43}$$

we can write (41) in the form

$$Y_r = \sum_{s=1}^{2n} L_{rs} X_s \quad (r = 1, \ldots, 2n), \tag{44}$$

where $L_{rs} = \mathbf{L}_{rs}(T_1, p_1, \ldots, T_n, p_n)$ $(r, s = 1, \ldots, 2n)$ are continuous functions.

In the classical case we have for the total entropy (by the constraints $\sum_{i=1}^{n} m_i\dot{e}_i = 0$, $\sum_{i=1}^{n} m_i\dot{v}_i = 0$)

$$\dot{S} = \sum_{i=1}^{n} \left[\left[\frac{1}{T_i} - \frac{1}{T_0}\right] m_i\dot{e}_i + \left[\frac{p_i}{T_i} - \frac{p_0}{T_0}\right] m_i\dot{v}_i \right]$$

$$= \sum_{r=1}^{2n} X_r Y_r = \sum_{r,s=1}^{2n} L_{rs} X_r X_s. \tag{45}$$

Almost the same formulas are deduced for the other two cases treated in Secs. 2 and 3; the only difference is that the corresponding Lyapunov functions (15) and (24) appear in (45) instead of the total entropy:

$$\dot{L} = \sum_{r=1}^{2n} X_r Y_r. \tag{46}$$

We recognize the Onsager formalism for "fluxes and forces." More precisely, the usual formalism corresponds to the approximation that the equilibrium value $\Lambda_{rs} := \mathbf{L}_{rs}(T_0, p_0, \ldots, T_0, p_0)$ is taken instead of L_{rs}.

Let me remark that the usual derivation and applications of the Onsager formalism are not completely clear. One starts with the entropy production in continuum thermodynamics, so forces and fluxes are functions defined in space and time. Then one considers fluxes as ordinary time derivatives of extensive variables describing the system.[5] The formalism is applied to homogeneous bodies as well as for inhomogeneous bodies,[6] and sometimes care is not taken that a flux be a time derivative. Moreover, one always gets the equality (45) regardless of whether or not the system is closed whereas we have seen in our rigorous framework that for nonclosed systems, equality (46) is valid.

7. DISCUSSION

First of all, let us make a few remarks about heat insulation, which is an everyday notion, important in applications but questionable in theory.

We usually consider heating as conduction of internal energy. If the n bodies are heat insulated from the environment, internal energy is conducted between the bodies only. So it seems evident that the bodies are heat insulated from the environment if and only if the total heating is zero:

$$\sum_{i=1}^{n} m_i q_i = 0. \tag{47}$$

On the other hand, it seems evident as well that if the bodies have a fixed total volume, then they are heat insulated if and only if the total internal energy is constant.

It is a simple fact that relations (25) and (26) are not equivalent to (26) and (47): the two pieces of "evidence" contradict each other. Which of them shall we prefer?

To clarify the situation, let us consider two classical bodies with fixed total volume. For convenience, set

$$E_i := m_i e_i, \quad V_i := m_i v_i, \quad Q_i := m_i q_i \quad (i = 1,2). \tag{48}$$

Then

$$\dot{E}_i = Q_i - p_i \dot{V}_i \quad (i = 1,2) \tag{49}$$

and

$$\dot{V}_1 + \dot{V}_2 = 0. \tag{50}$$

If we require the total heating to be zero, then

$$Q_1 + Q_2 = 0, \quad \dot{E}_1 + \dot{E}_2 = -(p_1 - p_2)\dot{V}_1; \tag{51}$$

if we require the total energy to be fixed, then

$$\dot{E}_1 + \dot{E}_2 = 0, \quad Q_1 + Q_2 = (p_1 - p_2)\dot{V}_1. \tag{52}$$

Equations (51) and (52) are equivalent if and only if $(p_1 - p_2)\dot{V}_1 = 0$ for all possible processes, that is, if and only if $(p_1 - p_2)\mathbf{f}_1(T_1, p_1, T_2, p_2) = 0$ for all T_1, p_1, T_2, p_2, which does not hold in general; for example, in the simplest case $f_1 = \beta(p_1 - p_2)$ with a positive β we have $(p_1 - p_2)\dot{V}_1 = \beta(p_1 - p_2)^2 \geq 0$, and equality holds if and only if $p_1 = p_2$.

Thus if the total heating vanishes, in general, the total internal energy is not conserved (decreases monotonically in the simplest case); if the total internal energy is conserved, the total heating does not vanish, in general (is non-negative in the simplest case). Which of (51) and (52) corresponds to the heat insulation of the bodies together?

To get an answer, let us examine the approximation upon which "ordinary"[1] thermodynamics is based: the bodies are considered homogeneous and internal motion is neglected. In fact, if the two bodies interact with each other, changing volumes (the volumes of the bodies can change, although the total volume is fixed), then internal motion appears to which kinetic energy belongs; so a part of the internal energy is converted into kinetic energy. In fact, the total internal energy is not constant in a process. However, the kinetic energy of internal motion will dissipate into internal energy, and, finally (in equilibrium), the value of the total internal energy will equal the original one. In ordinary thermodynamics our models do not consider the kinetic energy of internal motion, so we have to understand what happens by means of the internal energy. The total internal energy varies slightly in the process, but its initial and final values coincide: a monotone decrease of the total internal energy is incorrect; hence (51) cannot be accepted.

On the other hand, we can consider the total internal energy to be constant in the whole process (to such an extent that the body is homogeneous), and we have to modify our conception of heating. In addition to the direct conduction of internal energy, heating includes the indirect conduction as well: internal energy $\rightarrow$ kinetic energy $\rightarrow$ internal energy. In this way it is comprehensible why the total heating is not necessarily zero in a heat-insulated system.

Thus we can accept that if the total volume is fixed, then heat insulation is described by the conservation of the total internal energy.

On the other hand, if the total volume is not fixed, the conservation of energy does not mean heat insulation. It is clear from the above that zero total heating can express heat insulation in particular cases only, when indirect heat conduction is not considered. Thus we are left with the important open question: which mathematical relation describes heat insulation in general?

Second, the present theory of ordinary thermodynamics does not include the notion of entropy, which appears now only as an auxiliary quantity; *in this context entropy has no conceptual importance* (of course, this assertion does not concern the role of entropy in other aspects, e.g., in statistical physics). If entropy exists, we can easily construct a Lyapunov function; hence asymptotic stability is proved immediately. The role of entropy is similar to that of a potential in mechanics. The axioms of mechanics concern forces and do not use the notion of potentials; however, some formulas, calculations, and deductions are much simpler if the force has a potential.

Note that, even if entropy exists, the Lyapunov function is the total entropy if and only if the bodies together are isolated from the environment (see Sec. 4). In other cases the Lyapunov function is the total entropy plus a convenient term (see Secs. 2 and 3). In the literature entropy often appears as a Lyapunov function.[7] However, in those instances continuous media are described by partial differential equations for which the extension of Lyapunov's theory is questionable. The corresponding formulas are obscure from a mathematical point of view.

Third, in usual equilibrium thermodynamics the first law – implicitly or explicitly – is degraded to define the heating[8]; even in a new approach it is utilized only to rule out the heating from the constitutive relations.[9]

After having pronounced the existence of entropy, the first law is used merely to fix the properties of the entropy listed in (6).

In usual theories the second law postulates some extremal property of the entropy. Henceforth the conditions and circumstances are confused. Namely, up to now a single homogeneous body has been considered, and the general formulation of the second law suggests that we continue to consider a single homogeneous body.

Clausius' inequality $dS \geq \delta Q/T$, a common form of the usual second law, obviously must refer to a single homogeneous body because it contains a single temperature value. However, the assertion "the entropy of an isolated system cannot decrease,"[10] deduced from the above inequality for $\delta Q = 0$, tacitly concerns an inhomogeneous body (which lies outside the competence of equilibrium theory) or a system of homogeneous bodies, because no change can occur at all in a single isolated homogeneous body. Unfortunately, even if the entropy increase is postulated explicitly for a system of homogeneous bodies,[11] the entropy increase for a single body appears surprisingly and without justification.[12]

Furthermore, according to the common conception, $dS = \delta Q/T$ if and only if the process is reversible. Nevertheless, we find the following assertion as well: "in a quasi-static process the increase in entropy is given by $dS = \delta Q/T$."[12] Perhaps the obscure content of such statements suggests the different opinion that "there is no special relation between entropy change and heat flow for general irreversible changes."[13]

I suspect that Clausius' inequality is a consequence of tacitly supposed and incompatible "evidence."

Let us take two classical bodies isolated together and use the notations of (48). The isolation is described by the "evidence" (50) and (52). The first body will be regarded as the body submitted to our investigation and the second one as the tool of investigation (experimental instrument). Let us omit the subscript 1 and substitute a prime for the subscript 2. Accepting the "evidence" $(p - p')\dot{V} \geq 0$, we have $Q + Q' \geq 0$. Here, $T\dot{S}$ is substituted for Q, where S is the entropy of the investigated body: $T\dot{S} + Q' \geq 0$. In practice, we can control the heat $-Q'$ supplied by the experimental instrument. Supposing the "evidence," that is, the heat absorbed by the body equals the supplied heat, $Q = -Q'$, we arrive at the inequality $T\dot{S} \geq Q$. Furthermore, for a "quasi-static process," that is, for a "process in which the body is always in equilibrium with the experimental device," thus for a process in which $T = T'$ and $p = p'$, we should have $Q + Q' = 0$, or with the above manipulation, $T\dot{S} = Q$.

Fourth, in the present theory of ordinary thermodynamics the troubles with Clausius' inequality are removed. As it has been pointed out,[14] for a *single* classical body in a given environment, we *always* have $T\dot{s} = q$ – or $\dot{S} = Q/T$ with $Q := mq$, $S = ms$, where m is the mass of the body – and this *equality* is strictly related to asymptotic stability, that is, *irreversibility*. In a process, entropy can decrease or increase. If the single body is isolated, then no change can occur; there is no nonconstant process. Of course, then entropy is constant as well.

For a *system* of classical bodies we now have that

$$\dot{S} = \sum_{i=1}^{n} \dot{S}_i = \sum_{i=1}^{n} \frac{Q_i}{T_i};$$

entropy can increase or decrease, in general.

The basic property of a Lyapunov function assuring asymptotic stability is that in a nonequilibrium process, it is strictly monotone increasing (its derivative along the differential equation has a strict maximum at an equilibrium). If the bodies together are *isolated* from the environment, then the total entropy is the Lyapunov function; thus the *total entropy increases* in a nonequilibrium process (see Sec. 4).

Fifth, usual equilibrium thermodynamics abounds in tacit assumptions that do not follow form the axioms. For instance, consider "two simple systems within a closed cylinder, separated from each other by an internal piston." Then one "frees the piston," "strips the adiabatic coating," etc., and as a consequence, "various internal processes are induced."[15] These considerations are based on "evidence"; there is no formulation in the axioms describing what happens under given circumstances, what causes changes, why and how a process comes into being.

The formative laws and the dynamic laws in the present theory of ordinary thermodynamics are destined to answer these questions, that is, to formulate mathematically the tacit assumptions.

A typical piece of "evidence" that does not follow from the usual axioms is that "the induced pressure difference tends to move the piston inward,"[15] that is, in our notations at the beginning of Sec. 7, if $p_1 - p_2 < 0$, then $\dot{V}_1 < 0$. This seems plausible from a pure mechanical point of view, but even if it were correct, it should be part of the axioms of thermodynamics. However, since thermal and mechanical effects are now coupled, one can doubt the truth of this "evidence." Another well-known piece of "evidence" is that "heat flows from hot to cold."

The second law in the present theory of ordinary thermodynamics is destined to incorporate the tendencies of processes that correspond to the "evidence" described in this paper into the foundation of thermodynamics.

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Résumé

Les lois dynamiques pour des corps thermodynamiques en interaction l'un avec l'autre et avec leur environnement sont établies. La tendence à l'équilibre (stabilité asymptotique) du processus de tels systèmes est examinée et le rôle de l'entropie discuté.

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