Reservoirs in Thermodynamics

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Abstract
Dynamic law is defined for isothermal processes and for isobaric processes in ordinary thermodynamics, and asymptotic stability is examined.

Key words: isothermal process, isobaric process, stability, trend to equilibrium

1. INTRODUCTION

A theory of thermodynamics of homogeneous bodies has recently[1] been suggested — called "ordinary thermodynamics" — in which the fundamental notion is that a *process* is a function that depends on time. Processes are governed by a *dynamic law* which is a differential equation, as in the other areas of physics. *Equilibrium* is a constant process. *Trend to equilibrium* means asymptotic stability of equilibria. The usual *first law* is involved in the dynamic law, and the *second law* is formulated as an inequality playing a fundamental role in assuring asymptotic stability.

The process of a single body in a given environment[1] and processes of interacting bodies[2] have been treated. Now we shall deal with isothermal processes and isobaric processes which are not covered by those investigations.

It is commonly taken for granted in the literature of thermodynamics that a body placed in contact with a heat reservoir (put into an environment of given constant temperature) changes its volume isothermally.[3-6] However, anyone who has pumped air into a tire knows that this is not true: materials under compression become warmer even if they are in an environment of constant temperature. Nevertheless, we may think that if the "compression is slow compared to the heat conduction" or "the heat conduction is fast compared to the compression," then the process can be considered to be isothermal. The two phrases within quotation marks have the same meaning; in an exaggerated formulation they read, "the compression is infinitely slow" or "the heat conduction is infinitely fast."

Now we are interested in whether the latter conditions within quotation marks can be formulated in a mathematically exact way.

Let us take a body in an environment of given temperature T_a and pressure p_a described in ordinary thermodynamics according to Ref. 1. Assume the simplest constitutive relations

$$e = cT, \quad p = \mathrm{p}(T,v), \tag{1}$$

$$q = -\lambda(T - T_a), \quad f = \delta(p - p_a), \quad w = -pf, \tag{2}$$

where λ, δ, and c are positive constants. Then the dynamic law becomes

$$\begin{aligned} c\dot{T} &= -\lambda(T - T_a) - \delta p(p - p_a), \\ \dot{v} &= \delta(p - p_a). \end{aligned} \tag{3}$$

It is evident that if the temperature is constant, $T = T_a$, then $\dot{T} = 0$, thus $p = p_a$ as well, which implies $\dot{v} = 0$, $v = \text{const}$. Consequently, the process is an equilibrium; hence nonequilibrium isothermal processes do not exist.

Now let us suppose that the compression, that is, the volume change, is "infinitely slow," which means that δ is "infinitely small." Setting $\delta = 0$ in the first equation of (3) and taking into account the initial condition $T(0) = T_a$, we get $T = T_a$; however, this does not mean that the process is isothermal; $\delta = 0$ in the second equation results in $v = \text{const}$, that is, nothing changes in the process, it is an equilibrium. It is not possible to get a correct mathematical interpretation of an "infinitely slow" compression.

Now let us suppose that the heat conduction is "infinitely fast," which means that λ is "infinitely large." Dividing the first equation in (3) by λ and then letting λ tend to infinity, we get formally $T = T_a$ without any effect on the second equation. This offers a good possibility for describing isothermal processes. It is emphasized that the mentioned limit procedure is not completely correct from a mathematical point of view. More precisely, we can formulate the problem as follows.

For each $\lambda > 0$, let (v_λ, T_λ) be the solution of the differential Eq. (3) with initial values $v_\lambda(0) = v_0$, $T_\lambda(0) = T_a$. Moreover, let v be the solution of the initial value problem

$$\begin{aligned} \dot{v} &= \delta[\mathrm{p}(v,T_a) - p_a], \\ v(0) &= v_0. \end{aligned} \tag{4}$$

Then under not too strong conditions (which are satisfied in the present case) we have[7]

$$\begin{aligned} \lim_{\lambda\to\infty} v_\lambda(t) &= v(t)\,, \\ \lim_{\lambda\to\infty} T_\lambda(t) &= T_a \end{aligned} \tag{5}$$

for all $t > 0$.

Now we shall *postulate* that isothermal processes are described by an equation of type (4) *regardless* of the conditions that imply (5). A similar reasoning leads us to isobaric processes which correspond to an "infinitely fast" volume change (δ is "infinitely large" in the example).

2. SOME FUNDAMENTAL NOTIONS AND NOTATIONS

We shall consider n bodies in several circumstances, where n is an arbitrary positive integer ($n = 1$ is allowed). The subscript i refers to the ith body; if $n = 1$, the subscript 1 is omitted. The mass of the ith body is denoted by m_i. The bodies will be described by their temperature and specific volume; the specific internal energy and the pressure of each body are given by a differentiable constitutive relation:

$$e_i = \mathrm{e}_i(T_i,v_i),\quad p_i = \mathrm{p}_i(T_i,v_i) \tag{6}$$

for which the inequalities

$$\frac{\partial \mathrm{e}_i}{\partial T_i} > 0\,,\quad \frac{\partial \mathrm{p}_i}{\partial v_i} < 0\,,\quad \left[\frac{\partial \mathrm{e}_i}{\partial v_i} + \mathrm{p}_i\right]\frac{\partial \mathrm{p}_i}{\partial T_i} \geq 0 \tag{7}$$

hold.

The classical case means the existence of twice differentiable specific entropies $s_i = \mathrm{s}_i(T_i,v_i)$ such that

$$T_i\frac{\partial \mathrm{s}_i}{\partial T_i} = \frac{\partial \mathrm{e}_i}{\partial T_i}\,,\quad T_i\frac{\partial \mathrm{s}_i}{\partial v_i} = \frac{\partial \mathrm{e}_i}{\partial v_i} + \mathrm{p}_i\,. \tag{8}$$

Theorems given in the Appendix of Ref. 1 will be used regarding asymptotic stability.

3. ISOTHERMAL PROCESSES

Now we give a model for a system consisting of n bodies in an environment of given temperature T_a and pressure p_a, supposing that the environment acts as a *thermal reservoir*, that is, the temperature of the bodies always coincides with T_a.

Since the temperature is constant, we have only one variable for each body: the specific volume. A *process* is $(v_1, \dots ,v_n)$ as a function of time. Corresponding to the investigations in Refs. 1 and 2, we assume that the *dynamic law* takes the form (in the sequel $i = 1, \dots ,n$)

$$\dot{v}_i = f_i, \tag{9}$$

where the *formative laws*

$$0 \not\equiv f_i = \mathrm{f}_i(p_1,p_2, \dots ,p_n,p_a,T_a),$$
$$\mathrm{f}_i(p_a,p_a, \dots ,p_a,p_a,T_a) = 0 \tag{10}$$

are required. Assuming the workings

$$w_i = -p_i f_i, \tag{11}$$

we impose the second law as follows:

$$\sum_{i=1}^{n} m_i\left[-\frac{w_i}{p_i}(p_i - p_a)\right] \geq 0\,, \tag{12}$$

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

If $v_{i,0}$ is a specific volume value such that

$$\mathrm{p}_i(T_a,v_{i,0}) = p_a \quad (i = 1, \dots ,n), \tag{13}$$

then the constant process $(v_{1,0}, \dots ,v_{n,0})$ is an equilibrium of the dynamic law (9). The above equalities determine equilibrium in a locally unique way.

Proposition 1: For $n = 1$, an equilibrium process v_0 of the dynamic law (9) is asymptotically stable.

Proof: The function $v \to \mathrm{p}(T_a,v)$ is strictly monotone decreasing because $\partial\mathrm{p}/\partial v < 0$; thus $v \to L(v) := [\mathrm{p}(T_a,v) - p_a]^2$ has a strict minimum at v_0. Its derivative along the dynamic law,

$$2(p - p_a)(\partial\mathrm{p}/\partial v)f = 2(-\partial\mathrm{p}/\partial v)[-(w/p)(p - p_a)],$$

has a strict maximum at v_0 in virtue of the second law.

Proposition 2: For $n \geq 1$, in the classical case, an equilibrium process $(v_{1,0}, \dots ,v_{n,0})$ is asymptotically stable.

Proof:

$$L(v_1, \dots ,v_n) := \sum_{i=1}^{n} m_i\left[\mathrm{s}_i(T_a,v_i) - \frac{\mathrm{e}_i(T_a,v_i) + p_a v_i}{T_a}\right] \tag{14}$$

is a Lyapunov function: (1) it has a strict maximum at the equilibrium because its first derivative equals $[m_i(p_i/T_a - p_a/T_a) \mid i = 1, \dots ,n]$ which is zero at the equilibrium, and its second derivative is the diagonal matrix having the diagonal $(\partial\mathrm{p}_i/\partial v_i \mid i = 1, \dots ,n)$, which is negative definite; (2) its derivative along the dynamic law (9) equals $\sum_{i=1}^{n} m_i(p_i/T_a - p_a/T_a)f_i$, which, according to the second law (12), has a strict minimum at the equilibrium.

Remark: Now the first law $\dot{e}_i = q_i + w_i$ does not appear in the dynamic law. Since v_i as a function of time is determined by the differential equation (9), $e_i = \mathrm{e}_i(v_i,T_a)$, $p_i = \mathrm{p}_i(v_i,T_a)$, and consequently the workings w_i as functions of time in the process are determined as well. Thus if we adhere to the first law, $\dot{e}_i$ and w_i being determined in our model of isothermal processes, the heat transfers cannot be given by independent constitutive relations. In this case the first law can serve to define the heat transfers q_i.

4. ISOBARIC PROCESSES

Now we suppose that the environment with given temperature T_a and pressure p_a acts as a *mechanical reservoir*, that is, the pressure of the bodies always coincides with p_a.

The second inequality in (7) implies that from the equations

$$\mathrm{p}_i(T_i, v_i) = p_a \tag{15}$$

we can express v_i (at least locally) as a function of T_i,

$$v_i = v_i(T_i); \tag{16}$$

we have again a single variable for each body: the temperature. A process is $(T_1, \dots, T_n)$ as a function of time.

Note that from (15) and (16) we have

$$\dot{v}_i = -\left[\frac{\partial \mathrm{p}_i}{\partial T_i} \Big/ \frac{\partial \mathrm{p}_i}{\partial v_i}\right](T_i, v_i(T_i))\dot{T}_i, \tag{17}$$

that is, $\dot{v}_i$ is determined by the process.

We assume the dynamic law in the form (in the sequel $i = 1, \dots, n$)

$$\dot{e}_i = q_i + w_i, \tag{18}$$

where the formative laws

$$0 \neq q_i = \mathbf{q}_i(T_1, \dots, T_n, p_a, T_a),$$
$$\mathbf{q}_i(T_a, \dots, T_a, p_a, T_a) = 0, \tag{19}$$

$$w_i = -p_a \dot{v}_i \tag{20}$$

are required.

We impose the second law in the form

$$\sum_{i=1}^{n} m_i \left[-\frac{q_i}{T_i}(T_i - T_a)\right] \geq 0, \tag{21}$$

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

Let us introduce the specific heat capacities at constant pressure

$$\mathrm{C}_i := \frac{\partial \mathrm{e}_i}{\partial T_i} - \left[\frac{\partial \mathrm{e}_i}{\partial v_i} + \mathrm{p}_i\right]\left[\frac{\partial \mathrm{p}_i}{\partial T_i} \Big/ \frac{\partial \mathrm{p}_i}{\partial v_i}\right], \tag{22}$$

which are positive. With the notation

$$C_i(T_i) := \mathrm{C}_i[T_i, v_i(T_i)] \tag{23}$$

we can write the dynamic law in the form

$$C_i(T_i)\dot{T}_i = q_i \quad (i = 1, \dots, n) \tag{24}$$

Evidently, $(T_a, \dots, T_a)$ is an equilibrium process of this dynamic law.

Proposition 3: For $n = 1$, the equilibrium process T_a is asymptotically stable.

Proof: $L(T) := (T - T_a)^2$ is evidently a Lyapunov function.

Proposition 4: For $n \geq 1$, the equilibrium process $(T_a, \dots, T_a)$ is asymptotically stable (1) if e_i, p_i, and consequently C_i are the same for all i ("all the bodies consist of the same material"); (2) if C_i is constant (independent of temperature) for all i; and (3) in the classical case.

Proof: The following functions are Lyapunov functions:

$$(1) \quad L(T_1, \dots, T_n) := \sum_{i=1}^{n} m_i (T_i - T_a)^2, \tag{25}$$

$$(2) \quad L(T_1, \dots, T_n) := \sum_{i=1}^{n} m_i C_i (T_i - T_a)^2, \tag{26}$$

where C_i denotes the constant value of C_i, and

(3) $L(T_1, \dots, T_n) :=$

$$\sum_{i=1}^{n} m_i \left[\mathrm{s}_i(T_i, v_i(T_i)) - \frac{\mathrm{e}_i(T_i, v_i(T_i)) + p_a v_i(T_i)}{T_a}\right]. \tag{27}$$

5. ISOBARIC PROCESSES OF A HEAT-INSULATED SYSTEM

Suppose now that $n \geq 2$, and the n bodies are put into a mechanical reservoir, and they are heat-insulated from the environment. (Such systems are taken in adiabatic calorimetry.)

According to our previous considerations, the first condition means that we are to construct a model in which the pressure of each body is the same constant throughout the process. Heat insulation is a delicate matter: the right mathematical expression of heat insulation is questionable, in general.[2] Now we can argue as follows. Each body can extend or contract freely in such a way that its pressure constantly equals the pressure of the environment; hence we can consider that the bodies do not act mechanically on each other; they work only on the environment. The reasoning in Ref. 2 shows that then there is no indirect heating between the bodies, and so we can describe heat insulation by the requirement that the total heating is zero:

$$\sum_{i=1}^{n} m_i q_i = 0. \tag{28}$$

Moreover, heat insulation of the bodies means that the ambient temperature does not play any role.

Thus we accept relations (15) and (16), and so a process will again be $(T_1, \dots, T_n)$, and we have relation (17) as well. Furthermore, putting the formative laws

$$0 \not\equiv q_i = \mathbf{q}_i(T_1, \ldots, T_n, p_a),$$
$$\mathbf{q}_i(T_i, \ldots, T_i, p_a) = 0, \tag{29}$$

we require relation (28); accepting equality (20) we assume the dynamic law (18), which can be written in the form (24) as well. The second law becomes

$$\sum_{i=1}^{n} m_i \left[-\frac{q_i}{T_i}(T_i - T_k) \right] \geq 0 \quad (k = 1, \ldots, n), \tag{30}$$

where equality holds if and only if $T_i = T_k$ for all $i,k = 1, \ldots, n$.

We see from (29) that $(T_{1,0}, \ldots, T_{n,0})$ is an equilibrium process if

$$T_{i,0} = T_{k,0} \quad (i,k = 1, \ldots, n). \tag{31}$$

These are only $n - 1$ independent equalities for the n variables; thus they do not determine equilibrium in locally unique way. A further equality comes from the relation (28) of heat insulation as follows.

Introducing

$$h_i(T_i) := \mathrm{e}_i[T_i, v_i(T_i)] + \mathrm{p}_i[T_i, v_i(T_i)] v_i(T_i) \tag{32}$$

(the specific enthalpies corresponding to the constant pressure), we easily find that

$$C_i(T_i) = dh_i(T_i)/dT_i \tag{33}$$

(which is well known from usual equilibrium thermodynamics as well). Consequently, the dynamic law (24) becomes

$$h_i(T_i)^{\cdot} = q_i \tag{34}$$

from which we deduce by equality (28) that

$$\sum_{i=1}^{n} m_i h_i(T_i) = \text{const.} \tag{35}$$

Thus for a given enthalpy value H_0, the equation

$$\sum_{i=1}^{n} m_i h_i(T_{i,0}) = H_0 \tag{36}$$

supplements (31), assuring the (local) uniqueness of equilibrium.

Proposition 5: For every enthalpy value H_0,

$$H_{H_0} := \{(T_1, \ldots, T_n) \mid \sum_{i=1}^{n} m_i h(T_i) = H_0\} \tag{37}$$

is a submanifold invariant under the dynamic law (34). In the classical case an equilibrium $(T_{1,0}, \ldots, T_{n,0})$ in H_{H_0} is asymptotically stable with condition H_{H_0}.

Proof: The submanifold in question can be parametrized by $(T_1, \ldots, T_{n-1})$. Then T_n is expressed (at least locally) as a function of the parameters,

$$T_n = \tau_n(T_1, \ldots, T_{n-1}), \tag{38}$$

and the reduced dynamic law becomes

$$C_i(T_i)\dot{T}_i = q_i \quad (i = 1, \ldots, n-1). \tag{39}$$

We can easily verify that $L[T_1, \ldots, T_{n-1}, \tau_n(T_1, \ldots, T_{n-1})]$ is a Lyapunov function, where L is the function introduced in the Proof of item (3) in Proposition 4.

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Résumé

La loi dynamique est définie pour des processus isothermes et pour des processus isobares dans la thermodynamique ordinaire. En plus, la stabilité asymptotique est examinée.

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