Dynamical Laws in Thermodynamics

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Abstract
A theory of thermodynamics is proposed in which processes are time-dependent functions governed by a dynamical law (a system of differential equations), equilibrium is defined as a constant solution of the dynamical law, and the trend to equilibrium is formulated as the asymptotic stability of equilibrium.

1. INTRODUCTION

Thermodynamics is one of the most discussed areas of physics, because its formulation, especially the notion of entropy and the content of the second law, is not crystal clear. In the vast literature concerning thermodynamics, different points of view and newer approaches appear, which keep challenging researchers.

In comparing thermodynamics with other theories of physics that are commonly accepted and well developed, we see an important difference: thermodynamics lacks a *dynamical law*, that is, (a system of) differential equations whose solution with given initial and surface conditions describe processes uniquely.

More precisely, the Newtonian equation in classical mechanics, the Maxwell equations in electromagnetism, and the Schrödinger equation in quantum mechanics are dynamical laws. Physical theories possessing dynamical laws are firmly founded and have powerful applications. Thermodynamics in its present state is not such a theory. A body is left free, it falls – the process in time of falling is accurately described by mechanics. A hot body is left on the table, it cools – the process in time of cooling has not yet been described by thermodynamics.

There have been attempts to establish dynamical laws in nonequilibrium thermodynamics, which in usual treatments include two theories: the theory of continuous media, which I shall call "continuum thermodynamics," and the theory of "nonequilibrium processes of homogeneous bodies." The balances of mass, momentum, and energy in continuum thermodynamics[1,2] are well formulated and (together with constitutive relations) make up a dynamical law: they are partial differential equations that determine processes from given initial and boundary conditions. In this sense continuum thermodynamics is also a complete theory.

On the other hand, the theory of nonequilibrium processes of homogeneous bodies is based on the notions of equilibrium theory and formulates only approximate equations near equilibrium ("linear phenomenological equations for the description of the state parameters."[3,4]) Since the starting point is an equilibrium theory, that is, only equilibria are considered meaningful, such an approach would be acceptable only if it defined what nonequilibria are and which of them are near equilibrium. I think we have to proceed in the opposite direction: to define processes in general and to distinguish equilibria among them.

To do so, we have to overcome the common objection that the thermodynamical quantities (pressure, temperature, etc.) can be defined only in equilibrium. Of course, they can be measured with a reliable accuracy only "near equilibrium," that is, when they do not change too fast. But the same is true for other quantities in other branches of physics as well. How can we measure the instantaneous energy of a body moving irregularly and very quickly? Or the instantaneous value of the electric field in a light beam? The impossibility of such measurements does not refrain us from considering the quantities in question as physically meaningful. Note that no objection is raised to the Navier-Stokes equation, because it concerns nonequilibrium flows, and so the pressure in the equation must also be defined out of equilibrium and even far from equilibrium.

We shall use the term "ordinary thermodynamics" for such a theory of

homogenous bodies in which thermodynamical quantities are supposed to be defined independently of processes.

An essential property of processes in physics is that they are functions defined either in time (classical mechanics, quantum mechanics) or in space-time (electromagnetism and continuum thermodynamics). Processes in ordinary thermodynamics are time-dependent functions. Then we must have ordinary differential equations for determining processes in this theory.

The trend to equilibrium (or irreversibility) and the stability of equilibrium are basic problems of thermodynamics. In ordinary thermostatics we try to solve this problem by a variational principle.[5,6] However, we find that "Statics is a theory designed to avoid commitment to equation of motion yet determine directly (and alone) the figure of equilibrium and in the same time condition of stability for it. ... The variation principle is sufficient for its purposes, which is to solve a problem of statics; for dynamical ends it is useless."[7]

For dynamical ends the theory of differential equations offers a powerful and suitable notion for describing the trend to equilibrium: asymptotic stability. A short survey of definitions and results of stability theory that are necessary for our purpose can be found in the Appendix. For further details we refer the reader to Ref. 8.

The purposes of the present paper are to introduce a complete dynamical law (system of differential equations) in ordinary thermodynamics and to find conditions assuring the trend to equilibrium (asymptotic stability).

To illustrate the way to establish a working theory based on ordinary differential equations, let us look briefly at classical mechanics.

2. THE DYNAMICAL LAWS IN CLASSICAL MECHANICS

The fundamental principle of classical mechanics is Newton's second axiom: the product of mass and acceleration equals force, $m\mathbf{a} = \mathbf{f}$. However, this is only a general framework that must be (1) correctly interpreted and (2) adapted to special cases, because in this form it is suitable and sufficient only for point masses. The other cases are spinning particles, bodies with variable mass (rockets), and rigid bodies.

A process of a point mass is $(\mathbf{r}, \mathbf{v})$, the space-time position and velocity as a function of time. If the point mass exists under an external action, then the action is described by a force $\mathbf{f}$ that depends on $(\mathbf{r}, \mathbf{v})$, and so we have the dynamical equation

$$m\dot{\mathbf{v}} = \mathbf{f}(\mathbf{r}, \mathbf{v}). \qquad (1)$$

In general, we do not stress (and it is not obvious from the vague form $m\mathbf{a} = \mathbf{f}$) that the *force does not depend on derivatives* of $(\mathbf{r}, \mathbf{v})$, although this is a fundamental fact. We say that force is a functional of processes by saying that force is given by a *constitutive relation*.

Equation (1) is a single vector equation for the pair $(\mathbf{r}, \mathbf{v})$ of vector functions. Hence it is not sufficient for determining processes from initial values. Another equation is to be established in addition. Fortunately, we need not look for it yet. Since velocity is the derivative of position, the trivial equation

$$\dot{\mathbf{r}} = \mathbf{v} \qquad (2)$$

supplements (1); together they form a complete dynamical law.

I emphasize that in a correct interpretation Eq. (1) is a dynamical law, that is, a differential equation, and it is not the definition of force.

Let us now consider a rocket. Its process is $(m, \mathbf{r}, \mathbf{v})$, the mass, space-time position, and velocity as a function of time, and the dynamical law has the form

$$\dot{m} = b(m, \mathbf{r}, \mathbf{v}), \qquad \dot{\mathbf{r}} = \mathbf{v},$$

$$m\dot{\mathbf{v}} = \mathbf{f}(m, \mathbf{r}, v) + \dot{m}\mathbf{w}(m, \mathbf{r}, \mathbf{v}), \qquad (3)$$

where $\mathbf{f}$ is the external force, b is the time rate of fuel decrease, and $\mathbf{w}$ is the relative velocity of the burnt material leaving the rocket, all three given by constitutive relations.

In a similar way we can consider several point masses, spinning particles, and rockets together, interacting among themselves, and then rigid bodies, point masses under constraints, etc. First we have to determine *what a process is* (which uniquely characterizes what happens) and then establish *as many differential equations as necessary* for unique solutions with given initial values.

We see that there is no general form of the Newtonian equation, and there is no axiom that would give such a general form. The only tacit general principle in mechanics is that we must have sufficiently many differential equations – we shall call them here the "dynamical laws of mechanics" – for a unique description of the processes.

3. THE FIRST LAW IN THERMODYNAMICS

The usual first law of ordinary thermodynamics can be considered as a counterpart of Newton's second axiom.[9] The first law says that the time rate of internal energy change equals the sum of work and heat. This statement, too, must be (1) correctly interpreted and (2) adapted to special cases, because in this form it is suitable only for the simplest bodies that participate only in mechanical and thermal interactions. Material interaction (diffusion, chemical reaction) and electromagnetic interaction also change the internal energy (for example, hydrochloric acid dissolving in water, burning, and electric currents raise the temperature, i.e., cause an increase in the internal energy).

Let us begin the treatise of ordinary thermodynamics with the simplest body, as we begin mechanics, with a point mass. The simplest thermodynamical body participating only in mechanical and thermal interaction is characterized by two quantities: the specific volume v and the temperature T. In other words, a process is (v, T) as a function of time.

We accept that we are given the specific internal energy e, work w, and heat q by constitutive relations as functionals of the processes, $e = e(v, T)$, $w = w(v, T)$, $q = q(v, T)$, and the first law,

$$\dot{e} = w + q, \qquad (4)$$

is valid. The first law is not a definition of internal energy or work or heat. Usually one utilizes the first law for omitting the heat from the list of quantities given by constitutive relations[10]; however, doing so deprives it of being a counterpart of the Newtonian equation, which serves to describe processes and not omit the force from the list of quantities.

I think we correctly interpret the first law by regarding it as a dynamical law, that is, as a differential equation for (v, T). As in mechanics, where it is stated that force does not depend on acceleration, here it is assumed that the dependence of e, w, and q on (v, T) *excludes higher-order derivatives*, so the more precise form

$$e(v, T)^{\cdot} = w(v, T) + q(v, T) \qquad (5)$$

of (4) [where $e(v, T)^{\cdot}$ denotes the function $t \rightarrow (d/dt)\, e(v(t), T(t))$] shows clearly that we have a first-order implicit differential equation for (v, T).

However, the first law is only a single differential equation for the two quantities v and T. So we should have another equation, too. To find the missing equation, we turn to continuum mechanics.

4. ANALOGIES WITH CONTINUUM THERMODYNAMICS

A process of a medium consisting of identical, spinless, chargeless particles is a field $(\mathbf{u}, v, T)$, that is, the velocity, specific volume, and temperature as a function defined in space-time. The balances of mass, momentum, and energy yield the partial differential equations

$$D_{\mathbf{u}} v = v \nabla \cdot \mathbf{u}, \qquad D_{\mathbf{u}} \mathbf{u} = -v \nabla \cdot \mathbf{P},$$

$$D_{\mathbf{u}} e = -v\,(\mathbf{P}{:}\nabla \mathbf{u} + \nabla \cdot \mathbf{k}), \tag{6}$$

where $D_{\mathbf{u}}$ denotes the "substantial time derivative" with respect to the velocity field $\mathbf{u}$, the body force and body heat are taken to be zero, and $\mathbf{P}, e, \mathbf{k}$ are the pressure tensor, the specific internal energy, and the heating flux, respectively, given by constitutive relations as functionals of $(\mathbf{u}, v, T)$.

The process $(\mathbf{u}, v, T)$ can be determined, at least in theory, from initial and surface values by these balance equations that form a complete dynamical law.

What is the relation between continuum thermodynamics and ordinary thermodynamics? The latter theory considers the bodies as homogeneous, that is, all quantities depend only on time, not on space. Let us insert the conditions $\nabla \mathbf{u} = 0$, $\nabla v = 0$, $\nabla T = 0$, $\nabla e = 0$, $\nabla \mathbf{P} = 0$, $\nabla \mathbf{k} = 0$ into the equations of continuum thermodynamics. We find that the quantities do not depend on time either, that is, nothing happens. *There is no nonconstant homogeneous process.* Ordinary thermodynamics cannot be obtained from continuum thermodynamics as a special case. Perhaps one could even say, then, that the theory of homogeneous bodies is meaningless, because it is an experimental fact as well that bodies out of equilibrium are never homogeneous; for example, the temperature of a cooling body is always lower on the surface than in the interior of the body. However, we also know that a rigid body does not exist: all bodies are deformed under forces. Still, certain bodies in certain circumstances can be considered as rigid. The rigid body model is simple, much simpler than the model of deformable bodies, and it is suitable for many purposes. Similarly, ordinary thermodynamics offers simpler models than continuum thermodynamics, and they are applicable for a large class of phenomena.

The main condition of the applicability of ordinary thermodynamics is that the inner motion of the body is insignificant. From the point of view of continuum thermodynamics, this means that $\mathbf{u}$ is taken to be constant, and thus the balance of momentum becomes uninteresting. Of course, if $\mathbf{u}$ was constant, indeed, then v would be constant in time, but we wish to keep v variable. So $\mathbf{u}$ is not constant; it is only considered as constant. To solve the problems, let us argue as follows. According to momentum balance, $\mathbf{u}$ is determined by $\nabla \cdot \mathbf{P}$, which is given as a functional of $(\mathbf{u}, v, T)$. According to mass balance, the change of v is determined by $\nabla \cdot \mathbf{u}$. Consequently, the change of v is determined indirectly by $\mathbf{P}$, that is, by $(\mathbf{u}, v, T)$ through a constitutive relation. If we want to eliminate $\mathbf{u}$, we have to provide a direct constitutive relation for the change of v. This is proposed to be done in ordinary thermodynamics.

A process of a continuous medium is $(\mathbf{u}, v, T)$ as a function of space-time. A process of a homogeneous body is (v, T) as a function of time.

The balance equations determine $(\mathbf{u}, v, T)$ from initial and surface values. The energy balance corresponds clearly to the usual first law of ordinary thermodynamics. The momentum balance has no counterpart in ordinary thermodynamics. A counterpart of mass balance will supplement the first law to form a complete system of dynamical equations. The substantial time derivatives $D_{\mathbf{u}} v$ and $D_{\mathbf{u}} e$ are to be replaced by ordinary time derivatives $\dot{v}$ and $\dot{e}$, and so the correspondence is schemed as follows:

$$
\begin{aligned}
D_{\mathbf{u}} v &= v \nabla \cdot \mathbf{u}, & \dot{v} &= f \\
D_{\mathbf{u}} \mathbf{u} &= -v \nabla \cdot \mathbf{P}, & & \\
D_{\mathbf{u}} e &= -v\,(\mathbf{P}{:}\nabla \mathbf{u} + \nabla \cdot \mathbf{k}), & \dot{e} &= w + q.
\end{aligned} \tag{7}
$$

According to this paper, we suggest accepting that f – called "springing" – can be given by a constitutive relation as a functional of (v, T), $f = f(v, T)$. In this way we get two differential equations,

$$
\begin{aligned}
\dot{v} &= f(v, T), \\
e(v, T)^{\cdot} &= w(v, T) + q(v, T),
\end{aligned} \tag{8}
$$

for determining the two quantities v and T. They form a *dynamical law in ordinary thermodynamics*.

"Springing" expresses some visco-elastic properties. Its physical meaning will be clarified in Sec. 6.

5. THE FORMATIVE LAWS

Usually several conditions are imposed on forces in mechanics. One of them is Newton's well-known action-reaction principle; the others are used in general tacitly, without being formulated as principles, although they are of vital importance. Here are some of them:

(1) The interaction force of two point masses depends only on the relative position of the point masses and is parallel to the relative position vector (this ensures conservation of angular momentum).

(2) The interaction force between two spinning particles depends only on the relative position and the relative velocity of the particles.

(3) The torque acting on a spinning particle is always orthogonal to the spin of the particle.

We call such conditions imposed on the constitutive relations the "formative laws of mechanics."

It is not surprising, then, that we meet similar conditions, called the "formative laws," in ordinary thermodynamics, too.

Up to now we have spoken about bodies and processes of a body. The processes of a body originate from interactions of the body with its environment or with other bodies. It is useful to distinguish between a *body* and a *system*: the latter is a body and its environment together or several bodies and their environments together. The same body under different circumstances is a part of different systems. Dealing with the processes of a body we have to take into consideration the system to which the body belongs. This is so in mechanics as well.

Let us examine the simplest system: a body under the action of an environment with given constant temperature T_a and pressure p_a. The formative laws for such a system are formulated as follows.

All the functionals in question are supposed to be continuously differentiable functions. The customary (ambiguous, but useful) notations will be applied in which v, T, etc., denote both functions of time and possible values of such functions which are variables of the constitutive relations.

A.1: Besides the specific internal energy e, the pressure p (which plays a fundamental role in connection with constitutive relations, as is clarified below) characterizes the body. Both are given as functions defined on a connected open set of points (v, T), called the "constitutive domain": $e = e(v, T)$, $p = p(v, T)$, and[11]

$$\partial e/\partial T > 0, \quad \partial p/\partial v < 0, \quad (\partial e/\partial v + p)\partial p/\partial T \geq 0. \quad (9)$$

A.2: Springing, work, and heat characterize the interaction between the body and the environment. They are functions of (v, T) that depend on v implicitly through p; they depend on the ambient pressure p_a and the ambient temperature T_a:

$$f = \mathbf{f}(p, T, p_a, T_a),$$
$$w = \mathbf{w}(p, T, p_a, T_a), \quad (10)$$
$$q = \mathbf{q}(p, T, p_a, T_a).$$

A.3: Work is proportional to springing:

$$w = -zf, \quad (11)$$

where $z = \mathbf{z}(p, T, p_a, T_a)$ is such that

$$\mathbf{z}(p_a, T_a, p_a, T_a) = p_a. \quad (12)$$

[If the pressure and temperature of the body are near the pressure and temperature, respectively, of the environment (i.e., near equilibrium, as we shall see), then we require that working nearly coincides with the classical $-pf (= -p\dot{v})$.] Evidently we can write $z = p + r$, where $r = \mathbf{r}(p, T, p_a, T_a)$ and $\mathbf{r}(p_a, T_a, p_a, T_a) = 0$.

A.4: If the temperature and pressure of the body coincide with those of the environment, then springing and heat (and work, because of the previous condition) are zero:

$$\mathbf{f}(p_a, T_a, p_a, T_a) = 0,$$
$$\mathbf{q}(p_a, T_a, p_a, T_a) = 0. \quad (13)$$

A.5: (1) If $\mathbf{q}$ is identically zero, then springing does not depend on T_a, $f = \mathbf{f}(p, T, p_a)$, and $\mathbf{f}(p_a, T, p_a) = 0$ for all T. (2) If $\mathbf{f}$ is identically zero, then heating does not depend on p_a, $q = \mathbf{q}(p, T, T_a)$, and $\mathbf{q}(p, T_a, T_a) = 0$ for all p.

A.6: The dynamical law in the notations introduced above takes the form

$$\dot{v} = \mathbf{f}(p, T, p_a, T_a),$$
$$e(v, T)^{\cdot} = \mathbf{w}(p, T, p_a, T_a) + \mathbf{q}(p, T, p_a, T_a), \quad (14)$$
$$p = p(v, T).$$

Definition. A constant solution of the above dynamical equation is called an "equilibrium process."

Observe that if there is a volume value v_0 such that (v_0, T_a) is in the constitutive domain and $p(v_0, T_a) = p_a$, then the constant function (v_0, T_a) is an equilibrium process.

6. AN EXAMPLE

Newton's heating law

$$q = -\beta(T - T_a) \quad (\beta > 0 \text{ is a given constant}) \quad (15)$$

is a well-known constitutive relation satisfying the conditions listed in A.1 to A.5. The simplest springing can be written in a similar form:

$$f = \delta(p - p_a) \quad (\delta > 0 \text{ is a given constant}). \quad (16)$$

The larger the pressure difference, the faster the volume changes. The smaller the δ, the more slowly the volume changes. From a physical point of view the more viscous the body and its environment, the more slowly the volume changes. Hence δ is something similar to the inverse of viscosity.

Besides these constitutive relations, let us suppose that $z = p$, that is,

$$w = -pf (= -p\dot{v}). \quad (17)$$

Furthermore, let e and p be arbitrary (of course, subjected to the conditions listed in A.1).

With the notations

$$c := \partial e/\partial T, \quad n := \partial e/\partial v, \quad (18)$$

the dynamical equations are written in the form

$$\dot{v} = \delta(p - p_a),$$
$$\dot{T} = \frac{1}{c}[-(n + p)\delta(p - p_a) - \beta(T - T_a)], \quad (19)$$
$$p = p(v, T), \quad n = p(v, T), \quad c = c(v, T).$$

We are interested in the trend to equilibrium: does the above dynamical law describe the everyday phenomenon that a body takes on the temperature and the pressure of its environment? In mathematical terms, Is an equilibrium process (v_0, T_a) asymptotically stable? Recall that asymptotic stability implies $\lim_{t \to \infty}[v(t), T(t)] = (v_0, T_a)$ for every process (v, T) in a neighborhood of (v_0, T_a).

Proposition: If (v_0, T_a) is an equilibrium process of the dynamical Eq. (19), then it is asymptotically stable.

PROOF: The linearization of the right-hand side of the differential equations yields the matrix

$$\begin{pmatrix} -\delta\rho & \delta\xi \\ \rho(\nu + p_a)\delta/\gamma & -[(\nu + p_a)\delta\xi + \beta]/\gamma \end{pmatrix}, \quad (20)$$

where

$$\rho := -\frac{\partial p}{\partial v}(v_0, T_a) > 0, \quad \gamma := c(v_0, T_a) > 0,$$

(21)

$$\xi := \frac{\partial p}{\partial T}(v_0, T_a), \quad v := n(v_0, T_a), \quad (v + p_a)\xi \geq 0.$$

It is easy to check that the eigenvalues of (20) are negative.

7. THE SECOND LAW

For special cases of heat and springing we obtained asymptotic stability. However, asymptotic stability does not follow from our general assumptions; namely, the formative laws permit negative β and negative δ, and then asymptotic stability fails.

The positivity of β reflects the well-known fact that "heat flows from hot to cold"; the positivity of δ has a similar evident meaning: a body expands if its pressure exceeds that of the environment. We should like to formulate a general condition that assures such "irreversibility," that is, roughly speaking, that excludes negative β and negative δ.

In this way we arrive at the second law, which is a crucial point of thermodynamics. It was previously based on the notion of entropy which has no crystal clear meaning. Some have tried to eliminate entropy; the latest axiomatic foundations formulate the second law with the aid of cycles considered as primitive concepts.[12] Unfortunately, I cannot see an application of such a second law to a system described by the proposed dynamical equations. Namely, the system has no nonconstant cyclic processes. The notion of cycles is a delicate matter. In general, to realize a cycle of a *body*, we have to change the *system* several times, for example, put the body in an environment of given temperature supplying some "amount of heat," then make an adiabatic isolation letting the body work, and then put the body in a new environment, etc. Moreover, a body that is not of the simplest type has very few cyclic processes. For instance, how can we realize a cycle of a diffusing or chemically reacting medium? How can we make cycles such as "flour with water – paste – flour with water" and "paste – pastry – paste"?

We prefer the opinion that the second law is to be a restriction on the constitutive relations. To find a convenient setting, let us study the working $-v\,\mathbf{P}{:}\nabla\mathbf{u}$ and the heating $-v\,\nabla{\cdot}\mathbf{k}$ in the energy balance of continuum thermodynamics. According to experience, we can decompose the pressure tensor into two parts: elastic and viscous, $\mathbf{P} = \mathbf{E} + \mathbf{V}$. Both $\mathbf{E}$ and $\mathbf{V}$ are given by constitutive relations. We conceive that $-v\,\mathbf{E}{:}\nabla\mathbf{u}$ and $-v\,\mathbf{V}{:}\nabla\mathbf{u}$ are "reversible" and "irreversible" parts of work. Similarly, we are convinced by experience that heat, too, can be decomposed into reversible and irreversible parts. A decomposition is suggested by usual treatments of continuous media: $-\nabla{\cdot}\mathbf{k} = -T\nabla{\cdot}\mathbf{k}/T - (\mathbf{k}/T)\cdot\nabla T$.

The Clausius-Duhem inequality in the simplest case is equivalent to

$$-\mathbf{V}{:}\nabla\mathbf{u} - \frac{\mathbf{k}}{T}\cdot\nabla T \geq 0,$$

(22)

which has a clear meaning: the sum of the irreversible parts of work and heat is non-negative.

A straightforward analogy of $-(\mathbf{k}/T)\cdot\nabla T$ in ordinary thermodynamics is $-(q/T)(T - T_a)$, which we accept as the irreversible part of heat. We encounter some difficulties regarding work, because in ordinary thermodynamics the inner motion of bodies is not taken into account, and the

irreversible part of work in continuum thermodynamics concerns just the inner motion. Let us argue as follows. Work is strongly related to the volume change; the larger the difference between the pressures of the body and its environment, the faster the volume changes; the faster the volume changes, the more intensive the inner motion. The kinetic energy of the inner motion dissipates into internal energy. Thus the irreversible part of work, which is strongly related to the dissipated inner motion, seems to be proportional to work and the pressure difference. Therefore, impelled also by the form of irreversible heat, we accept $-(w/p)(p - p_a)$ as the irreversible part of work in ordinary thermodynamics.

Now I formulate the *second law* as a restriction imposed on the constitutive relations:

$$-\frac{w}{p}(p - p_a) - \frac{q}{T}(T - T_a) \geq 0.$$

(23)

More precisely, the following is required.

A.7: Work and heat satisfy

$$-\frac{\mathbf{w}(p, T, p_a, T_a)}{p}(p - p_a)$$
$$-\frac{\mathbf{q}(p, T, p_a, T_a)}{T}(T - T_a) \geq 0 \quad (24)$$

and, excluding the trivial case $\mathbf{w} = 0$, $\mathbf{q} = 0$, equality holds if and only if

(1) $T = T_a$ in the case when $\mathbf{w}$ is identically zero.
(2) $p = p_a$ in the case when $\mathbf{q}$ is identically zero.
(3) $T = T_a$ and $p = p_a$ in the case when neither $\mathbf{w}$ nor $\mathbf{q}$ is identically zero.

The dynamical law (14) (which includes the first law), the formative laws (9) to (13), and the second law (24) (which are restrictions on the constitutive relations), that is, conditions A.1 to A.7, form a set of axioms for the simplest systems in ordinary thermodynamics.

8. TREND TO EQUILIBRIUM

Now we can state satisfactory theorems on the asymptotic stability of equilibrium processes. The reader is advised to consult the Appendix.

(1) If neither $\mathbf{f}$ nor $\mathbf{q}$ is zero, the formative law A.2, together with Lagrange's mean value theorem, yield

$$f = d(p - p_a) + j(T - T_a),$$
$$q = -i(p - p_a) - b(T - T_a),$$

(25)

where d, j, i, b are supposed to be continuous functions of (p, p_a, T, T_a), $d = \mathbf{d}(p, p_a, T, T_a)$, etc.

Then the second law has the form

$$\frac{dz}{p}(p - p_a)^2 + \left[\frac{jz}{p} + \frac{i}{T}\right](p - p_a)(T - T_a)$$
$$+ \frac{b}{T}(T - T_a)^2 \geq 0, \quad (26)$$

and equality holds if and only if $p = p_a$, $T = T_a$. It is not difficult to see that this implies that the matrix

$$\begin{pmatrix} \delta & \frac{1}{2}\left(\eta + \frac{\iota}{T_a}\right) \\ \frac{1}{2}\left(\eta + \frac{\iota}{T_a}\right) & \frac{\beta}{T_a} \end{pmatrix} \qquad (27)$$

is positive semidefinite, in particular, $\delta \geq 0$, $\beta \geq 0$, where

$$\delta := \mathbf{d}(p_a, T_a, p_a, T_a), \quad \eta := \mathbf{j}(p_a, T_a, p_a, T_a),$$

$$\iota := \mathbf{i}(p_a, T_a, p_a, T_a), \quad \beta := \mathbf{b}(p_a, T_a, p_a, T_a). \qquad (28)$$

It is straightforward to assume that in a neighborhood of an equilibrium process (v_0, T_a), the dependence of springing on $T - T_a$ is of less order than the dependence on $p - p_a$, and the dependence of heat on $p - p_a$ is of less order than the dependence on $T - T_a$. Thus the assumptions of the following proposition do not seem too difficult to accept.

Proposition 1: If $\delta > 0$, $\beta > 0$, $\eta = 0$, $\iota = 0$, then an equilibrium process is asymptotically stable.

PROOF: In this case the linearization of the right-hand side of the dynamical law coincides with the matrix in (20).

(2) Because of the first relation in (9), a change of variables can be performed, at least locally; the specific internal energy e can be used as an independent variable instead of the temperature T. Then a process becomes (e, v) as a function of time, and the dynamical law (14) takes the form

$$\dot{e} = \mathbf{w}(p, T, p_a, T_a) + \mathbf{q}(p, T, p_a, T_a),$$

$$\dot{v} = \mathbf{f}(p, T, p_a, T_a), \qquad (29)$$

$$p = \mathbf{p}(e, v), \quad T = \mathbf{T}(e, v).$$

If $\mathbf{T}(e_0, v_0) = T_a$, $\mathbf{p}(e_0, v_0) = p_a$, then the constant function (e_0, v_0) is an equilibrium process.

Let us take the classical case when (17) holds and a two times differentiable specific entropy $s = \mathbf{s}(e, v)$ exists such that

$$\partial \mathbf{s}/\partial e = 1/\mathbf{T}, \quad \partial \mathbf{s}/\partial v = \mathbf{p}/\mathbf{T}. \qquad (30)$$

As is well known, the second derivative of $\mathbf{s}$ is negative definite because of the relations in (9). Then the function

$$L(e, v) := \mathbf{s}(e, v) - e/T_a - p_a v/T_a \qquad (31)$$

has a strict maximum at (e_0, v_0), because its first derivative at (e_0, v_0) is zero, and its second derivative, being equal to the second derivative of $\mathbf{s}$, is negative definite. Furthermore, the derivative of L along the differential Eq. (29) (with $w = pf$) is

$$\left(\frac{1}{T} - \frac{1}{T_a}\right)(q + w) + \left(\frac{p}{T} - \frac{p_a}{T_a}\right)f$$

$$= -\frac{q}{T}(T - T_a) - \frac{w}{p}(p - p_a). \qquad (32)$$

According to (23), it has a strict minimum at (e_0, v_0). Thus we have proved:

Proposition 2: Equilibrium processes in the classical case given by (17) and (30) are asymptotically stable.

(3) If $\mathbf{f} = 0$, that is, in the case of isochoric processes, we have $\dot{v} = 0$, then $w = 0$ as well and for all specific volume values v_0 the set $\mathrm{H}_{v_0} := \{(v, T) \mid v = v_0\}$ is a one-dimensional submanifold (a line) invariant under the dynamical law.

Proposition 3: For all v_0, (v_0, T_a) is an equilibrium process, asymptotically stable with the condition H_{v_0}.

PROOF: With the aid of the parametrization $T \to (v_0, T)$ of H_{v_0}, the reduced dynamical law becomes

$$\dot{T} = \frac{1}{c(v_0, T)} \mathbf{q}[\, p(v_0, T), T, p_a, T_a\,] \qquad (33)$$

for T, where $c := \partial e/\partial T > 0$. The second law (24) reads as follows:

$$-\mathbf{q}[\, p(v_0, T), T, p_a, T_a\,](T - T_a) \geq 0, \qquad (34)$$

and equality holds if and only if $T = T_a$.

The function $L(T) := -(T - T_a)^2$ is a Lyapunov function: as a function of T it has a strict maximum at T_a, and its derivative along the differential Eq. (33) is $-2(T - T_a)(q/c)$, which, according to (34), has a strict minimum at T_a.

(4) If $\mathbf{q} = 0$, that is, in the case of adiabatic processes, the dynamical law takes the form

$$\dot{v} = f, \quad \dot{T} = -[(n + z)/c]f, \qquad (35)$$

where $f = \mathbf{f}(\, p(v, T), T, p_a, T_a)$, $n = n(v, T) = (\partial e/\partial v)(v, T)$, etc.

In view of A.5, (v_0, T_0) is an equilibrium process if $p(v_0, T_0) = p_a$. Because of the second relation in (9), there is a function v, at least locally, such that $v_0 = v(T_0)$.

Let $\mathcal{T}_0$ be the solution of the differential equation [which arises from the formal quotient of the two equations in (35)]

$$\frac{d\mathcal{T}}{dv} = -\frac{n(v, T) + z[\, p(v, \mathcal{T}), \mathcal{T}, p_a, T_a\,]}{c(v, \mathcal{T})} \qquad (36)$$

with the initial condition $\mathcal{T}_0(v(T_0)) = T_0$. Then for all temperature values T_0, $\mathrm{H}_{T_0} := \{(v, T) \mid T = \mathcal{T}_0(v)\}$ (the adiabat passing through $(v(T_0), T_0)$) is a one-dimensional submanifold (a curve) invariant under the dynamical law.

Proposition 4: For all T_0, $(v(T_0), T_0)$ is an equilibrium process, asymptotically stable with condition H_{T_0}.

PROOF: With the aid of the parametrization $v \to (v, \mathcal{T}_0(v))$ of H_{T_0}, the reduced dynamical law takes the form

$$\dot{v} = \mathbf{f}[\, p(v, \mathcal{T}_0(v)), \mathcal{T}_0(v), p_a, T_a\,]. \qquad (37)$$

Observe that

$$\frac{d}{dv} p[v, \mathcal{T}_0(v)]\bigg|_{v=v_0} = \frac{\partial p}{\partial v} + \frac{\partial p}{\partial T}\frac{d\mathcal{T}_0}{dv}\bigg|_{v=v_0}$$

$$= -\rho - \frac{\xi(v + p_a)}{\gamma} < 0, \quad (38)$$

where the notations introduced in Sec. 6 are used, and $v_0 := v(T_0)$. Consequently, the derivative (supposed to be continuous) is negative in a neighborhood of v_0 as well; thus $p(v, \mathcal{T}_0(v))$ as a function of v is strictly montonically decreasing and so injective in a neighborhood of v_0. Hence the second law (24) can be formulated as follows:

$$[zf][\ p(v, \mathcal{T}_0(v)), \mathcal{T}_0(v), p_a, T_a]$$
$$\times [\ p(v, \mathcal{T}_0(v)) - p_a] \geq 0, \quad (39)$$

and equality holds in a neighborhood of v_0 if and only if $v = v_0$.

By the same reason, $L(v) := -\{p(v, T_0(v)) - p_a\}^2$ as a function of v has a strict maximum at v_0. Its derivative along the differential Eq. (38),

$$2(p - p_a)\left(\frac{\partial p}{\partial v} + \frac{\partial p}{\partial T}\frac{d\mathcal{T}_0}{\partial v}\right)f$$

$$= \frac{2}{z}\left(\frac{\partial p}{\partial v} + \frac{\partial p}{\partial T}\frac{d\mathcal{T}_0}{dv}\right)[zf(p - p_a)], \quad (40)$$

has a strict minimum at v_0 because of (38), (39), and (12).

9. DISCUSSION

Asymptotic stability is a convenient mathematical notion for the trend to equilibrium, or irreversibility. A nonequilibrium process is irreversible if it tends to equilibrium. The previous propositions tell us that processes in a neighborhood of equilibrium are irreversible. It would be interesting to know how large such a neighborhood can be.

The present second law is a convenient reformulation of the Clausius-Duhem inequality. Usually the second law is conceived as the law of irreversibility. This is so, but it is clear now that the second law alone does not involve asymptotic stability; the second law and the formative laws together do. Namely, the strict maximum of a Lyapunov function and the strict minimum of its derivative along the dynamical law together call forth asymptotic stability. The cases treated in items (2), (3), and (4) of Sec. 8 show that the strict maximum is assured by the formative laws given in A.1, which concern the body only, and the strict minimum is assured by the second law, which concerns the system.

Observe that the existence of equilibrium is also a consequence of formative laws that concern the system (see A.2 to A.5).

The classical case treated in item (2) of Sec. 8 has a special interest. Then $Ts = q$ holds and asymptotic stability, that is, irreversibility, occurs. $Ts = q$ does not mean reversibility.

The second law is formulated and, in general, the trend to equilibrium is proved without the notion of entropy. The existence of entropy with the classical properties is irrelevant to the present results. The role of entropy will be discussed in a forthcoming paper.

Finally, the reader is reminded that only the simplest bodies have been treated in this paper. To proceed further we must deal with systems of interacting bodies, with diffusing and chemically reacting systems, phase transitions, etc.. We have to find the actual formative laws, the dynamical law and the second law, to create an effective theory of ordinary thermodynamics.

APPENDIX

Let n be a positive integer, and suppose F is a continuously differentiable function from $\mathbf{R}^n$ into $\mathbf{R}^n$, and consider the differential equation

$$\dot{x} = F(x). \quad (A1)$$

Moreover, suppose that x_0 is in the domain of F and

$$F(x_0) = 0. \quad (A2)$$

Then the constant function $x(t) = x_0$ ($t \in \mathbf{R}$) is a solution of the differential equation; we call it an "equilibrium."

We say that a solution r *starts* from a subset H of the domain of F if $r(0)$ is in H. The solution *proceeds* in H if $r(t) \in$ H for all $t \geq 0$.

Definition A1: The equilibrium x_0 is *stable* if for each neighborhood N of x_0 there is a neighborhood U of x_0, such that for every solution r starting from U proceeds in N.

The equilibrium x_0 is *asymptotically stable* if it is stable and there is a neighborhood V of x_0 such that for all solutions r starting from V we have $\lim_{t \to \infty} r(t) = x_0$.

If L is a differentiable real valued function defined in $\mathbf{R}^n$, then its derivative (gradient) L' is a function from $\mathbf{R}^n$ into $\mathbf{R}^n$. The real valued function $L' \cdot F$ defined in $\mathbf{R}^n$ by $x \longrightarrow L'(x) \cdot F(x)$ (where the dot represents the inner product in $\mathbf{R}^n$) is called the *derivative of F along the differential equation*.

Proposition A1: If there is a continuously differentiable function L, defined in a neighborhood of x_0 and having real values, such that (1) L has a strict maximum at x_0, that is, $L(x) < L(x_0)$ for all x in a neighborhood of x_0, and (2) $L' \cdot F$ has a (strict) minimum at x_0, then the equilibrium x_0 is (asymptotically) stable.

Function L is usually referred to as a Lyapunov function.

The derivative of F at x_0, denoted by $F'(x_0)$, is a linear map from $\mathbf{R}^n$ into $\mathbf{R}^n$ (the Jacobian matrix of F at x_0). We call it the "linearization" of F at x_0.

Proposition A2: If all eigenvalues of $F'(x_0)$ have negative real parts, then the equilibrium x_0 is asymptotically stable.

A subset H of $\mathbf{R}^n$ is an *m-dimensional submanifold*, if for every $b \in$ H there is a function p from $\mathbf{R}^m$ into $\mathbf{R}^n$, called a "parametrization" of H at b, such that (1) p is continuously differentiable, and (2) $p'(\xi)$ (the derivative of p at ξ, which is a linear map from $\mathbf{R}^m$ into $\mathbf{R}^n$) is injective for all ξ in the domain of p, (3) p is injective and its inverse is continuous, and (4) the range of p is a neighborhood of b in H.

A submanifold H is called "invariant" under the differential Eq. (A1) if every solution starting from H proceeds in H.

Definition A2: Let H be a submanifold invariant under the differential Eq. (A1). An equilibrium x_0 in H is called "stable with condition" H if for each neighborhood N of x_0 there is a neighborhood U of x_0, such that for every solution starting from U ∩ H proceeds in N ∩ H.

The equilibrium x_0 is *asymptotically stable with condition* H if it is stable with condition H and there is a neighborhood V of x_0, such that for all solutions starting from V ∩ H we have $\lim_{t \to \infty} r(t) = x_0$.

If p is a parametrization of the m-dimensional submanifold H at x_0, then we can define the *reduced* differential equation

$$\dot{\xi} = p'(\xi)^{-1} F(\xi) \tag{A3}$$

in $\mathbf{R}^m$.

Proposition A3: The equilibrium x_0 is (asymptotically) stable with condition H if and only if the equilibrium $\xi_0 := p^{-1}(x_0)$ of the reduced differential equation is (asymptotically) stable.

Résumé

Une théorie de la thermodynamique est proposée dans laquelle les processus sont gouvernés par une loi dynamique (un système d'équations différentielles), l'équilibre est défini comme une solution constante de la loi dynamique, et la tendance à l'équilibre est formulée comme la stabilité asymptotique de l'équilibre.

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