THERMODYNAMICS OF IRREVERSIBLE PROCESSES AND THE LYAPUNOV-FUNCTION METHOD

V. L. Bazhanov and I. I. Gol'denblat

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A connection is established between the production of entropy in irreversible processes and the Lyapunov function of the corresponding system of equations. Thermodynamic limitations are formulated on the functions that enter in the kinetic equations. The results are illustrated with relaxation processes in viscoelastic media.

1. Principles of Classical Thermodynamics

Classical thermodynamics is based on the concepts of the element of work performed on the system

$$\delta A = X_1 dy_1 + \ldots + X_n dy_n \tag{1.1}$$

and the element of heat δQ delivered to the system. Here X_k and y_k are generalized thermodynamic forces and coordinates, respectively.

The first law of thermodynamics states that when a system goes from a given state to an infinitesimally close one the increment of the internal energy E is equal to the sum of the heat delivered to the system and the work performed on the system

$$dE = \delta Q + \delta A \tag{1.2}$$

It must be emphasized here that the internal energy of the system is a unique function of its instantaneous state. The increment of the internal energy does not depend on the path traversed by the system from one state to the other. On the contrary, the work performed on the system and the heat delivered to it depend in the general case on the path. Thus, dE is a total differential while δA and δQ are not total differentials.

The second law of thermodynamics states that the amount of heat obtained in any reversible process always has integrating divisors and that among these divisors there is one that depends only on the temperature of the system.

The second law of thermodynamics can be expressed analytically in the form

$$dS = \delta Q / T \tag{1.3}$$

where T is the absolute temperature and S is the entropy of the system.

As is well known, the very concept of the absolute temperature can be introduced only on the basis of the second law. Just like the internal energy, the entropy S is a path-independent function of the state of the system.

Classical thermodynamics asserts also that in the case of nonequilibrium processes there exists the inequality

$$dS > \delta Q / T \tag{1.4}$$

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2. Nonequilibrium States of Thermodynamic Systems

In classical thermodynamics of equilibrium states or processes, all the thermodynamic parameters (including the absolute temperature) and functions have rigorous and exact definitions.

Considerable difficulties arise in the definition of the fundamental thermodynamic parameters when it comes to nonequilibrium states or processes.

The definitions of purely geometric or kinematic parameters, such as particle displacements or velocities, the strain tensor or the strain-rate tensor, etc., encounter no difficulty whatever even in the case of nonequilibrium processes. It is also possible to define uniquely the mass or the density of a medium.

Such concepts, however, as the temperature of a nonequilibrium state of the system or the stress tensor must be suitably defined.

We note that in the case of stationary nonequilibrium processes, the concepts of temperature and stress tensor (as well as of many other thermodynamic parameters) acquire natural phenomenological definitions, since these parameters can be measured by the usual instruments used in the case of equilibrium processes.

As is well known, in papers devoted to the thermodynamics of arbitrary irreversible processes, the widely used main parameters are the thermodynamic parameters for which definitions exist only in the case of equilibrium states. It is assumed in this case, however, that the thermodynamic parameters of the nonequilibrium processes can be assigned a definite meaning by using the methods of statistical physics. This makes it possible to use them also in phenomenological treatments. We note in this connection that "according to testimony left by Planck in his memoirs, even Kirchhoff wanted to restrict the entropy concept to reversible processes. The firm conviction of the generality of the concept, which Planck expressed already in his dissertation, had led him in 1900 to the radiation law and to quantum theory" [3].

3. The Principle of Local Equilibrium and Its Generalization

The thermodynamics of irreversible processes usually begins with the following premises:

1) the second law of thermodynamics of reversible processes remains in force also in the case of irreversible processes, but only locally (this is the so-called principle of local equilibrium state); i.e., it is assumed that relations (1.2) and (1.3) are valid locally.

2) In each local volume, all the thermodynamic functions (internal energy, free energy, entropy, etc.) are functions of the same parameters as in the case of equilibrium; consequently, these functions do not depend explicitly on the coordinates and on the time.

3) The gradients of the velocities, temperatures, stresses, etc. are small enough in the considered system.

4) The total change of the energy and entropy is made up additively of the changes of these functions in the individual elements of the system.

It might seem that the four foregoing premises of the thermodynamics of irreversible processes contradict strongly the principle of classical thermodynamics of reversible processes, particularly the fundamental classical relation that states that the entropy of an adiabatically isolated system increases in any irreversible process. It is easy to verify, however, that there is no contradiction here. Relation (1.3) is assumed valid only locally, so that when the system as a whole is considered the assumption of local equilibrium makes it possible to calculate the entropy change due to the nonequilibrium processes. It is thus possible to demonstrate for an adiabatically isolated system, in full accord with classical thermodynamics, that the entropy as a whole increases for such a system in the case of an irreversible process.

It should be noted, however, that the principle of local equilibrium is valid only for the so-called transport phenomena (thermal conductivity, diffusion, etc.). In the case of viscous resistances, irreversible chemical reactions, etc., relation (1.3) no longer holds even locally. It must be replaced by

$$dS = \delta Q/T + d\sigma \tag{3.1}$$

where $d\sigma$ is the local production of entropy.

Thus, in the case of irreversible processes, both the functional $\int dQ/T$ and the functional of entropy production depend on the path taken by the system from one state to the other. Their sum, however, which is equal to the change of the entropy for the indicated transition, does not depend on the path. This is the most general formulation of the second law of thermodynamics.

The foregoing principles are sufficiently well-known and are used in many papers, although their authors frequently do not formulate precisely the initial assumptions used by them.

We now note the following: it is proved in the general theory of systems that if the parameters of a dynamic system are defined for a continuous time and are sufficiently smooth functions of the time, then, subject to some other conditions which will not be formulated here, the parameters of the dynamic system must satisfy a certain system of differential equations. This theorem, due to R. Kalman, holds also for irreversible processes occurring in thermodynamic systems, since any thermodynamic system satisfies the definition formulated for a dynamic system by R. Kalman, P. Falb, and M. Arbib [4]. We can thus describe irreversible thermodynamic systems with the aid of systems of differential equations.

4. Kinetic Equations of Irreversible Processes, Entropy Production, and the Lyapunov-Function Method

We consider a thermodynamic system whose generalized coordinates (y_k) are made up additively of reversible (y_k°) and irreversible (y_k^*) parts, i.e.,

$$y_k = y_k^\circ + y_k^* \tag{4.1}$$

Assume that the defining equations of the system are expressed for an isothermal process (T = const) as follows:

for the reversible parts of the generalized coordinates

$$y_k^\circ = \sum_i A_{ki} X_i \tag{4.2}$$

for the irreversible parts of the generalized coordinates

$$\frac{dy_k^*}{dt} = f_k(X_1, X_2, \ldots, X_n, T) \tag{4.3}$$

We assume that the coefficients A_{ki} in Eqs. (4.2) and the functions f_k in (4.3) are such that the following conditions are satisfied:

$$\sum_i A_{ki} X_k X_i > 0 \tag{4.4}$$

$$f_k(0, 0, \ldots, 0, T) = 0 \tag{4.5}$$

In addition, we assume that the coefficients in (4.2) are such that $A_{ki} = A_{ik}$.

Differentiating (4.1) and (4.2) with respect to time and taking (4.3) into account, we obtain the following kinetic equations for an isothermal process occurring in the considered system:

$$\frac{dy_k}{dt} = \sum_i A_{ik} \frac{dX_i}{dt} + f_k(X_1, X_2, \ldots, X_n, T) \tag{4.6}$$

According to the definition given above for generalized thermodynamic forces and the generalized coordinates corresponding to them, the rate of entropy production is obviously

$$\sigma = \frac{d_i S}{dt} = \frac{1}{T} \sum_k X_k \frac{dy_k^*}{dt} = \frac{1}{T} \sum_k X_k f_k(X_1, X_2, \ldots, X_n, T) \tag{4.7}$$

The rate of entropy change due to the irreversible processes is designated here, as is customary, by $d_i S/dt$, and should be positive in accord with the principles of thermodynamics.

We emphasize that we do not calculate here the entropy of the system as such. To solve this problem it would be necessary to consider the heat exchange between the system and the ambient. The analysis that follows is based only on the fact that the rate of entropy production due to the irreversible processes in the system should be positive.

Since the temperature is positive, it follows from (4.7) that

$$\sum_k X_k f_k(X_1, X_2, \ldots, X_n, T) > 0 \tag{4.8}$$

Thus, the kinetic equations (4.6) of the considered system are meaningful if the functions f_k are such that this condition is satisfied. This is required by thermodynamics.

We consider now the isothermal process of relaxation of general forces X_k, which occurs at fixed values of the generalized coordinates (y_k = const).

The relaxation equations take the form

$$\sum_i A_{ki}\frac{dX_i}{dt} + f_k(X_1, X_2, \ldots, X_n, T) = 0 \tag{4.9}$$

We shall show that if the thermodynamic condition (4.8) is satisfied, then these equations indeed describe a relaxation process; i.e., they have solutions $X_i \to 0$ as $t \to \infty$. In other words, we must show that the zero-order solution of (4.9) is asymptotically stable as a whole in the Lyapunov sense. We use for this purpose the Lyapunov–Barbashin–Krasovskii theorem, which has the advantage that no limitations whatever are imposed on the values of the generalized forces X_i at the instant of time $t = 0$. We now formulate this theorem [1].

Assume that there exists a function $V(x)$ with real values and with the following properties:

1) $V(x) > 0$ for all $x \neq 0$, $V(0) = 0$

2) $[dV(x)]/dt < 0$ for all $x \neq 0$

3) $V(x) \to \infty$ for $\|x\| \to \infty$

Then the system

$$\frac{dx_i}{dt} = \varphi_i(x_1, x_2, \ldots, x_n, t) \quad (i = 1, 2, \ldots, n)$$

is asymptotically stable as a whole at $\varphi_i(0, 0, \ldots, 0, t) = 0$.

In this formulation of the theorem, x is an n-dimensional vector, i.e., $x = (x_1, x_2, \ldots, x_n)$.

We choose the Lyapunov function for the considered system of relaxation equations (4.9) in the form

$$V = {}^1\!/_2 \sum_{i,k} A_{ki} X_k X_i \tag{4.10}$$

The assumption (4.4) made above concerning the coefficients A_{ki} implies that the presented quadratic form (4.10) is positive definite at $X_i \neq 0$.

The time derivative of the Lyapunov function (4.10) is

$$\frac{dV}{dt} = \sum_{i,k} A_{ki}\frac{dX_i}{dt} X_k$$

Multiplying (4.9) by X_k and summing over i and k, we get

$$\sum_{i,k} A_{ki}\frac{dX_i}{dt} X_k + \sum_k X_k f_k(X_1, X_2, \ldots, X_n, T) = 0$$

Hence

$$\frac{dV}{dt} = \sum_{i,k} A_{ki}\frac{dX_i}{dt} X_k = -\sum_k X_k f_k(X_1, X_2, \ldots, X_n, T) < 0$$

in accord with the thermodynamic condition (4.8).

In addition, it follows from (4.10) that $V(0, 0, \ldots, 0) = 0$ and $V \to \infty$ as $X_i \to \infty$.

Thus, all the conditions of the Lyapunov–Barbashin–Krasovskii theorem are fulfilled. Consequently, if the fundamental thermodynamic requirement (4.8) is satisfied, then Eqs. (4.9) actually describe a relaxation process. It is easy to note that in our system the rate of entropy production as a result of the irreversible relaxation of the thermodynamic forces is equal to

$$\sigma = \frac{1}{T}\sum_k X_k f_k(X_1, X_2, \ldots, X_n, T) = -\frac{1}{T}\frac{dV}{dt} \tag{4.11}$$

It is known that any arbitrary (in a sufficiently broad sense [2]) function of a Lyapunov function is itself a Lyapunov function. One should therefore choose from among these Lyapunov functions those that satisfy the principal thermodynamic relation (4.7) for the considered system. In addition, N. N. Krasovskii [5] has proved the existence of a Lyapunov function for any asymptotically stable system in the sense of Lyapunov. This proves in essence the existence of entropy production by a nonequilibrium process in the considered system.

Equation (4.11) is the starting point for the construction of the Lyapunov function whose properties lead to conclusions concerning the behavior of the investigated system of equations.

We consider now a thermodynamic system whose generalized forces (X_k) are made up additively of reversible ($X_k{}^\circ$) and irreversible ($X_k{}^*$) parts, i.e.,

$$X_k = X_k{}^\circ + X_k{}^* \tag{4.12}$$

Let us assume that the defining equations of the system for an isothermal process (T = const) take the following forms:

for the reversible part of the generalized forces

$$X_k{}^\circ = \sum_i A_{ki} y_i \tag{4.13}$$

for the irreversible part of the generalized forces

$$X_k{}^* = f_k\left(\frac{dy_1}{dt}, \frac{dy_2}{dt}, \ldots, \frac{dy_n}{dt}, T\right) \tag{4.14}$$

We assume that the coefficients A_{ki} and the functions f_k are such that the following conditions are satisfied:

$$\sum_{i,k} A_{ki} y_k y_i > 0 \tag{4.15}$$

$$f_k(0, 0, \ldots, 0, T) = 0 \tag{4.16}$$

Just as before, we assume that the coefficients in (4.13) are such that $A_{ki} = A_{ik}$. The basic kinetic equations of an isothermal process of the considered type can be expressed in the form

$$X_k = \sum_i A_{ki} y_i + f_k\left(\frac{dy_1}{dt}, \frac{dy_2}{dt}, \ldots, \frac{dy_n}{dt}, T\right) \tag{4.17}$$

When the generalized forces are removed, the system under consideration admits of complete relaxation of the generalized coordinates. The relaxation equations are then written as follows:

$$\sum_i A_{ki} y_i + f_k\left(\frac{dy_1}{dt}, \frac{dy_2}{dt}, \ldots, \frac{dy_n}{dt}, T\right) = 0 \tag{4.18}$$

From the point of view of the thermodynamics, it is necessary and sufficient for the relaxation processes in our system that the rate of the entropy growth connected with this process be positive; i.e., it is necessary and sufficient to satisfy the condition

$$\frac{d_iS}{dt} = \frac{1}{T}\sum_k X_k{}^* \frac{dy_k}{dt} = \frac{1}{T}\sum_k \frac{dy_k}{dt} f_k\left(\frac{dy_1}{dt}, \frac{dy_2}{dt}, \ldots, \frac{dy_n}{dt}, T\right) > 0$$

Since, however, the absolute temperature is always positive, it is necessary to have

$$\sum_k \frac{dy_k}{dt} f_k\left(\frac{dy_1}{dt}, \frac{dy_2}{dt}, \dots, \frac{dy_n}{dt}, T\right) > 0 \tag{4.19}$$

We choose a Lyapunov function in the form

$$V = {}^1/_2 \sum_{i,k} A_{ki} y_k y_i$$

Taking the assumptions made above concerning the coefficients A_{ki} and the functions f_k into account, as well as the thermodynamic requirement (4.19), it is easy to show, repeating the reasoning of Sec. 3, that all the requirements of the Lyapunov–Barbashin–Krasovskii theorem are satisfied, and therefore Eqs. (4.18) indeed describe the total relaxation of the generalized coordinates.

Let us consider one more problem. Assume that the generalized forces have reached certain values and then remain constant:

$$X_k = \text{const} \tag{4.20}$$

It can be shown that in accord with (4.17) the generalized coordinates tend in this case to certain finite limits. We assume that the generalized coordinates are made up at an arbitrary instant of time of certain constant quantities $y_k{}^\circ$ and functions of the time $\xi_k(t)$, i.e.,

$$y_i(t) = y_i{}^\circ + \xi_i(t) \tag{4.21}$$

with

$$y_i(0) = y_i{}^\circ + \xi_i(0) = 0, \quad \xi_i(0) = -y_i{}^\circ \neq 0$$

Then, taking (4.20) and (4.21) into account, the basic kinetic equations (4.17) take the form

$$\sum_i A_{ki}\xi_i + f_k\left(\frac{d\xi_1}{dt}, \frac{d\xi_2}{dt}, \dots, \frac{d\xi_n}{dt}, T\right) = 0 \tag{4.22}$$

if it is assumed that

$$X_k = \sum_i A_{ki} y_i{}^\circ \tag{4.23}$$

In accordance with (4.19), the functions f_k satisfy the thermodynamic requirement

$$\sum_k \frac{d\xi_k}{dt} f_k\left(\frac{d\xi_1}{dt}, \frac{d\xi_2}{dt}, \dots, \frac{d\xi_n}{dt}, T\right) > 0 \tag{4.24}$$

We assume also that the coefficients A_{ki} are symmetrical, i.e., $A_{ki} = A_{ik}$, and are such as to satisfy the inequality

$$\sum_{i,k} A_{ki}\xi_k\xi_i > 0 \tag{4.25}$$

If the functions f_k are such that the condition (4.16) is satisfied, then, in perfect analogy with the procedure in the preceding section, we can show that the system (4.22) admits of total relaxation of the generalized parameters ξ_k, i.e., $\xi_k \to 0$ as $t \to \infty$.

Consequently, the solution of Eqs. (4.17) at constant X_k and at initial values of $y_k = 0$ tends to the solutions $y_k \to y_k{}^\circ$ as $t \to \infty$.

In fact, at $t = 0$ we have $y_k = y_k{}^\circ + \xi_k(0) = 0$. But, as shown above, $\xi_k \to 0$ as $t \to \infty$. This proves the statement made above.

5. Relaxation Processes in Viscoelastic Media

The analysis presented in Sec. 4 of the solutions of the kinetic equations of irreversible processes can be used to investigate relaxation processes that occur in various types of viscoelastic media. To this end it is necessary to take the generalized forces to be the stresses σ_{ik} and the generalized coordinates to be the strain-tensor components ε_{ik}.

We consider media with a separable strain tensor

$$\varepsilon_{ik}(t) = \varepsilon_{ik}{}^{\circ} + \varepsilon_{ik}{}^{*}(t)$$

where $\varepsilon_{ik}{}^{\circ}$ is the instantaneous elastic strain and $\varepsilon_{ik}{}^{*}(t)$ is the creep strain that develops in time.

If we assume that the elastic strain obeys Hooke's law, and we use for the creep strains relations of the Bailey type, then the equations that determine the isothermal deformation of the medium of the type considered are written as follows:

$$\frac{d\varepsilon_{ik}}{dt} = \sum_{m,\,n} A_{iknm}\frac{d\sigma_{nm}}{dt} + f_{ik}(\sigma_{11}, \sigma_{22}, \ldots, \sigma_{33}, T) \tag{5.1}$$

We assume that the irreversibility is due to creep strain. Then the thermodynamic requirement

$$d_iS/dt > 0$$

reduces to the requirement that the stress work on the creep strain be positive, i.e.,

$$\sum_{i,\,k} \sigma_{ik}\delta\varepsilon^{*}{}_{ik} > 0 \tag{5.2}$$

or

$$\sum_{i,\,k} \sigma_{ik} f_{ik}(\sigma_{11}, \sigma_{22}, \ldots, \sigma_{33}, T_0) > 0$$

If we stipulate that the functions f_{ik} must satisfy the inequality (5.2) and that conditions analogous to (4.4) and (4.5) be fulfilled, then, in accordance with the analysis given in Sec. 4 for the system (4.9), we can state that Eqs. (5.1) at constant strains (ε_{ik} = const) do indeed describe the stress-relaxation process.

Let us dwell briefly on media of another type, characterized by the fact that the stress tensor can be represented in the form of a sum of two tensors, elastic (reversible) and viscous (irreversible), i.e.,

$$\sigma_{ik} = \sigma_{ik}{}^{\circ} + \sigma^{*}{}_{ik}$$

The defining equations of the isothermal deformation of media of this type can be expressed in the form

$$\sigma_{ik} = \sum_{m,\,n} A_{iknm}\varepsilon_{nm} + f_{ik}\left(\frac{d\varepsilon_{11}}{dt}, \frac{d\varepsilon_{22}}{dt}, \ldots, \frac{d\varepsilon_{33}}{dt}, T_0\right) \tag{5.3}$$

We present a thermodynamic analysis of these equations. We assume that at some instant of time, when the creep strains have reached definite values, the stresses are suddenly removed. The subsequent course of the deformation can be of the relaxation type; i.e., all the strains can asymptotically approach zero. It can be proved that this is indeed the case if the functions f_{ik} are such that the basic thermodynamic requirement

$$\sum_{i,\,k}\frac{d\varepsilon_{ik}}{dt} f_{ik}\left(\frac{d\varepsilon_{11}}{dt}, \frac{d\varepsilon_{22}}{dt}, \ldots, \frac{d\varepsilon_{33}}{dt}, T_0\right) > 0$$

is satisfied, and the coefficients A_{iknm} are such that the following conditions hold:

$$\sum_{i,\,k,\,n,\,m} A_{iknm}\varepsilon_{ik}\varepsilon_{nm} > 0, \quad A_{iknm} = A_{nmik}$$

This proof follows directly from the analysis given in Sec. 4 for the thermodynamic system (4.18).

In complete analogy with the foregoing, we can show that Eqs. (5.3) at constant stresses describe the isothermal process of limited creep if the elastic moduli and the functions f_{ik} satisfy a number of basic thermodynamic requirements and some additional requirements, of the type of (4.24) and (4.25).

The thermodynamic approach to the analysis of solutions of the relaxation equations of the simplest viscoelastic media, which was outlined above in general form, can be used also for more complicated media, particularly for media in which both the stress tensor and the strain tensor are simultaneously separable.

We have demonstrated the close connection that exists between entropy production in irreversible processes and the Lyapunov function.

Satisfaction of the thermodynamic requirements (positive rate of growth of the entropy connected with irreversible processes) makes it possible to impose significant limitations on the character of the kinetic equations describing various irreversible processes. These limitations are important not only from the theoretical but also from the practical point of view, since they can decrease the volume of the experimental work required to establish the concrete form of the kinetic equations of irreversible processes for various systems.

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