ON VARIATIONAL PRINCIPLES OF NONEQUILIBRIUM THERMODYNAMICS

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Analysis of the variational principles for nonstationary nonequilibrium processes [1-5] from the mechanical analogy viewpoint permits it to be established that by starting from the variational condition (6) it is possible to go over to other known extremal modes. The nature of these transformations is similar to the Gauss method for going from the D'Alembert principle to the principle of least constraint in mechanics.

In connection with the diversity of the variational forms existing in the literature [1-5], the question arises as to whether they are alternatives or analytical relationships between them exist.

We show below that the variational condition [5] obtained by detailed analogies between thermodynamic motion and the mechanics of dissipative systems is sufficiently general, and admits of analytical transformations reducing it to other variational formulations. The nature of these transformations is analogous to the classical method of going from the D'Alembert principle to the Gauss principle of least constraint in mechanics [7].

First, let us recall that in the linear modification the thermodynamic and dissipative forces are, respectively

$$X_k = \frac{\partial \Delta S}{\partial x_k}, \quad k = 1, 2, \ldots n, \tag{1}$$

$$Q_k = \frac{\partial D}{\partial \dot{x}_k}, \quad k = 1, 2, \ldots n. \tag{2}$$

The deviation of the entropy from its equilibrium value is expanded in a series with second order accuracy:

$$\Delta S = -\frac{1}{2} \sum_{i,k} g_{ik} x_i x_k, \tag{3}$$

and the dissipation function D is a bilinear from in $\dot{x}_k$

$$D(\dot{x}\dot{x}) = \frac{1}{2} \sum_{i,k} L_{ik}^{-1} \dot{x}_i \dot{x}_k, \tag{4}$$

with reciprocity relations for the phenomenological coefficients

$$L_{ik} = L_{ki}, \quad i, k = 1, 2, \ldots, n. \tag{5}$$

Let us start from the variational condition [5], which is in differential form

$$-\delta(\Delta S) + \sum_i^n Q_i \delta x_i = 0. \tag{6}$$

On the basis of (6) it has been shown in [5] that the kinetic equations

$$\frac{\partial D}{\partial \dot{x}_i} = X_i, \quad i = 1, 2, \ldots, n, \tag{7}$$

have Lagrangean structure taking account of the dissipative forces, hence there is no thermodynamic analog of the kinetic energy in connection with the total noninertia of the irreversible phenomena.

Taking into account that

$$\delta\left(\Delta S\right) = \sum_i X_i \delta x_i,$$ (8)

(6) can be reduced to the following:

$$\sum_i \left(\frac{\partial D}{\partial \dot{x}_i} - X_i\right) \delta x_i = 0.$$ (9)

The Biot variational principle [2] is

$$\left(\frac{\partial D}{\partial \dot{x}_i} - \lambda X_i\right) \delta x_i = 0, \quad i = 1, 2, \ldots, n,$$ (10)

which Biot calls the principle of minimum rate of entropy generation: the true velocities $\dot{x}_i$ minimize entropy production under the condition that the thermodynamic forces and the intensity of their supply $\Sigma X_i \dot{x}_i$ are given. Therefore, the quantity $2D(\dot{x}\dot{x})$ is variated while the quantity $\Sigma X_i x_i$ remains constant, but

$$2D = \sum_i^n X_i \dot{x}_i,$$ (11)

in which connection the Biot principle is represented quite formally [8]. As regards the application of (10) to specific problems, then as has been remarked in [9], such difficulties arise for the case n > 1 that the Biot principle loses its attractiveness. This has not been observed when using the variational condition (9), which has been applied with the same success for any n in examining scalar and vector processes [5].

The variational condition (9) has the nature of the D'Alembert principle and, therefore, is not associated with the extremality concept. It is known that Gauss proposed a remarkable interpretation of the D'Alembert principle by introducing the minimality concept in the latter (the principle of least constraint). Using this idea, let us transform (9).

At some time t let the system state $x_1, x_2, \ldots, x_n$ be given. The system state at the time $t + \tau$ can be determined by the Taylor series

$$x_i(t + \tau) = x_i(t) + \dot{x}_i \tau + \ldots$$ (12)

Since the x_i are given at the initial instant t, then the variation of the first member in (12) vanishes and

$$\delta x_i(t + \tau) \cong \delta \dot{x}_i \tau.$$ (13)

Any virtual changes in the parameter, compatible with the relations including (13) referred to the time $t + \tau$, can be taken as δx_i in (9).

Let us write (9) in application to the time $t + \tau$, let us hence take account of (2) and let us divide both sides of the equality by τ:

$$\sum_i (Q_i - X_i) \delta \dot{x}_i = 0.$$ (14)

Although the transformations going from the D'Alembert to the Gauss principle have not been completed, let us examine (14) in greater detail. It is easy to see that (14) is none other than the Onsager variational principle [1]. Indeed, taking into account that

$$Q_i = \sum_k L_{ik}^{-1} \dot{x}_k,$$ (15)

$$\sum_i X_i \delta \dot{x}_i = \delta \sigma_X (X \dot{x}),$$ (16)

$$\sum_k L_{ik}^{-1} \dot{x}_k \delta \dot{x}_k = \delta D (\dot{x}\dot{x}),$$ (17)

we obtain at once

$$\delta [\sigma(\dot{x}X) - D(\dot{x}\dot{x})]_X = 0.$$ (18)

The forces are not variated in the Onsager variational condition (18). The linear equations of thermodynamics together with the reciprocity relationships are equivalent to the extremal principle (18), which Onsager

called the principle of least energy dissipation. As has been remarked in [8], the name of the principle does not correspond to its actual content.

By transforming (14) it is possible to proceed further and to obtain the variational condition (9) in a form analogous to the Gauss principle of least constraints. Since the thermodynamic forces X_i are considered given and cannot be varied, $\delta \dot{x}_i$ can be represented as

$$\delta \dot{x}_i = \delta \left[\sum_k L_{ik} (Q_k - X_k) \right] \tag{19}$$

and (14) can be rewritten as follows:

$$\sum_i (Q_i - X_i) \, \delta \sum_k L_{ik} (Q_k - X_k) = 0, \tag{20}$$

from which

$$\delta \sum_{i,k} \frac{1}{2} L_{ik} (Q_i - X_i)(Q_k - X_k). \tag{21}$$

Going over to the normal coordinates θ_j by a linear nonsingular transformation

$$x_j = \sum_j^n m_{ij}\theta_j, \tag{22}$$

we find

$$D = \frac{1}{2} \sum_j^n \dot{\theta}_j^2, \tag{23}$$

$$\Delta S = -\frac{1}{2} \sum_j v_j \theta_j^2, \tag{24}$$

and therefore, (21) reduces to the expression

$$\delta \sum_j \frac{1}{2} (Q_j^* - X_j^*)^2 = 0. \tag{25}$$

Here the dissipative Q_j^* and the thermodynamic X_j^* forces are expressed in terms of (23) and (24), respectively. Following Gauss, the quantity

$$Z = \frac{1}{2} \sum_j (Q_j^* - X_j^*)^2 \tag{26}$$

can be called the "measure of constraint" and (25) can be formulated as a principle of least constraint. Otherwise, the thermodynamic motion actually being realized will be such that the quantity Z will take on the least possible value of all the values compatible with the given relations.

If all the x_i are independent, the Z reaches it absolute minimum, zero. In this case we obtain at once

$$Q_j^* = X_j^*, \quad j = 1, 2, \ldots n, \tag{27}$$

which reduces to the linear thermodynamics relationships

$$\dot{\theta}_j = - v_j \theta_j. \tag{28}$$

Exactly as the Biot principle, the variational condition (9) admits of the possibility of inversion. Let us show this below.

Let us express the dissipative function as a bilinear form of thermodynamic forces

$$D(XX) = \frac{1}{2} \sum_{i,k} L_{ik} X_i X_k. \tag{29}$$

The dissipative forces are now expressed thus:

$$Q_i' = \frac{\partial D}{\partial X_i} = \sum_k L_{ik} X_k, \tag{30}$$

and the work of the dissipative forces is

$$\delta A = \sum_i Q_i \delta x_i = \sum_{i,k} L_{ik}^{-1} \frac{\partial D}{\partial X_i} \delta x_i. \tag{31}$$

Substituting this into (6) and taking account of (8), we obtain

$$\sum_{i,k} L_{ik}^{-1} \left(\frac{\partial D}{\partial X_i} - \dot{x}_i \right) \delta x_i = 0, \tag{32}$$

which has the structure of the D'Alembert principles. Now, let us go from (32) over to the Gauss form. Let us carry out the reasoning which led us to (13). However, it is now necessary to transform this latter in conformity with the initial inversion of the formulas. Since the $\dot{x}_i$ satisfy the linear equations

$$I_i \equiv \dot{x}_i = \sum_k L_{ik} X_k, \tag{33}$$

then the inverted form of (13) is

$$\delta \dot{x}_i (t + \tau) = \delta \dot{x}_i \tau = \sum_k L_{ik} \delta X_k \tau. \tag{34}$$

Later the forces X_k and not the fluxes I_j will be varied everywhere. Writing (32) in application to the time $t + \tau$ and dividing both sides of the equality by τ, we obtain

$$\sum_i (Q_i' - I_i) \delta X_i = 0. \tag{35}$$

It is easy to note that

$$\sum_i Q_i' \delta X_i = \delta D (XX), \tag{36}$$

$$\sum_i I_i \delta X_i = \delta_I \sigma (IX), \tag{37}$$

and therefore, (35) is none other than the differential form of the Dyarmaty principle [4]

$$\delta [\sigma (IX) - D (XX)]_I = 0. \tag{38}$$

The Dyarmaty variational condition turns out to have better prospects than the Onsager principle to describe vector processes [4]. Furthermore, since the fluxes are not varied, (35) at once reduces to the Gauss form

$$\delta \sum_{i,k} \frac{1}{2} L_{ik}^{-1} (Q_i - I_i)^2 = 0. \tag{39}$$

The quantity

$$Z' = \frac{1}{2} \sum_{i,k} L_{ik}^{-1} (Q_i - I_i)^2 \tag{40}$$

emerges as the "measure of constraint" Z'. It should be noted that despite the outward similarity, the resistance coefficients L_{ik}^{-1} do not play the part of masses in nonequilibrium thermodynamics. The thermodynamic analog of the mass is not generally detected in this latter [6]. This is related to the complete noninertia of the phenomena under consideration.

Now, let us turn to the Biot principle (10). Summing with respect to i on both sides of the equality, we obtain

$$\sum_i \left(-\frac{\partial D}{\partial \dot{x}_i} - \lambda X_i \right) \delta x_i = 0. \tag{41}$$

798

Performing the transformations which reduced (9) to the Onsager principle (18), we find

$$\delta \left[\lambda \sigma (\dot{x} X) - D (\dot{x}\dot{x}) \right]_X = 0. \tag{42}$$

It is easy to see that (42) is equivalent to the Ziegler principle of the maximum rate of dissipation work [3]. This latter is formulated as: given the thermodynamic forces, the rates are sought, which under the side condition

$$F (\dot{x}) = 2D (\dot{x}\dot{x}) - \sigma (\dot{x} X) = 0 \tag{43}$$

yield the maximum entropy production $\sigma(\dot{x}X)$. The solution is obtained from the relationship

$$\delta \left[\sigma (\dot{x} X) - \mu F (\dot{x}) \right]_X = 0. \tag{44}$$

This latter reduces to (42) with

$$\lambda = \frac{\mu + 1}{2\mu}. \tag{45}$$

Despite the equivalence, in principle, of the variational conditions (10), (18) and (44), which has also been remarked in [8], the Ziegler principle is distinguished by its physical clarity. Moreover it is easily applicable to nonlinear processes, as has clearly been illustrated in [8] in an example of many problems of the mechanics of continuous media. However, the possibilities of the Ziegler principle in the case of non-linearities outside the domain of the mechanics of continuous media have not been investigated adequately.

It follows from all the above that all the variational formulations considered [1-5] are equivalent in principle. Their basis is the D'Alembert structure (9) obtained by the analogy between nonequilibrium processes and the dynamics of dissipative systems. Meanwhile, the form of the representation of the variational principle of thermodynamics turns out to be extremely essential for the solution of specific problems.

NOTATION

S	is the entropy,
Q_k	are the dissipative forces;
D	is the dissipation function;
x_k	are the stream parameters;
L_{ik}	are the phenomenological coefficients;
X_k	are the thermodynamic forces;
I_k	are the fluxes;
λ, μ	are the undetermined Lagrange multipliers;
σ	is the entropy production;
θ_j	are the normal coordinates;
t, τ	is the time.

LITERATURE CITED

1. L. Onsager, Phys. Rev., 37, 405 (1931); 38, 2265 (1931).
2. M. A. Biot, Phys. Rev., 97, 1463 (1955).
3. H. Ziegler, Ing.-Arch., 30, 410 (1961).
4. I. Dyarmaty, Zh. Fiz. Khim., 39, 1489 (1965).
5. I. F. Bakhareva, Zh. Fiz. Khim., 42, 2394 (1968).
6. I. F. Bakhareva, Zh. Fiz. Khim., 41, 1717 (1967).
7. C. Lanczos, Variational Principles of Mechanics [Russian translation], Mir, Moscow (1965).
8. H. Ziegler, Extremal Principles of the Thermodynamics of Irreversible Processes and the Mechanics of Continuous Media [Russian translation], Mir, Moscow (1966).
9. B. A. Finlayson and L. E. Scriyen, Chem. Eng. Sci., 20, 395 (1965).