VARIATIONAL METHOD OF DESCRIBING NONLINEAR EQUILIBRIUM PROCESSES

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A nonlinearity, which is the nonconstancy of the matrix of phenomenological coefficients, is considered. The variational principle obtained on the basis of mechanical analogies in thermodynamics is generalized for this case. The heat conduction phenomenon is examined as an illustration.

A nonlinearity typical for transfer phenomena, which is that the matrix of the phenomenological coefficients L_{ik}

$$L_{ik} = L_{ik}(\Psi_1, \ldots, \Psi_n) \ (i,\ k = 1, \ldots, n) \tag{1}$$

is not constant, is examined herein. Similar processes have been investigated thermodynamically most completely in the case of stationary states by the local potential method [1, 2], which is an expression of the general Prigogine and Glansdorf evolution criterion [1].

Besides being of heuristic interest, a variational method to describe nonequilibrium processes turns out to be useful for the selection of approximate methods of solving nonlinear equations; even more so if the interesting domain of variation of the variable is bounded by the neighborhood of the stationary state, say.

In the linear case (L = const), the parabolic equations describing transfer phenomena can be obtained as a result of either the Dyarmaty variational principle [3], or the variational condition [4] formulated on the basis of the analogy between the nonequilibrium vector process and the mechanics of a continuous medium.

The possibility of this variational principle

$$\int \Big(\delta L - \sum_{i}^{u} Q_i \delta \Psi_i\Big) dv = 0 \tag{2}$$

is investigated below in the case of nonlinear vector processes of the kind mentioned. The density of the Lagrange function

$$L = \frac{1}{2} \rho \sum_{k}^{n} g_k (\nabla \Psi_k)^2 \tag{3}$$

is here related to the entropy by means of the relationship

$$\Delta S = -\frac{1}{2} \int \rho \sum_{k}^{n} g_k (\nabla \Psi_k)^2 dv. \tag{4}$$

In the linear case

$$g_k = \text{const.} \tag{5}$$

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In conformity with the investigated character of the nonlinearity, it can be considered that

$$g_k = g_k(\Psi_1, \ldots, \Psi_n). \tag{6}$$

Now, let us admit that the form of the function ΔS and also condition (3) are hence conserved. The dissipation function R should satisfy the general demand that entropy production should equation the intensity of the dissipative forces

$$2R = \frac{d\Delta S}{dt} = \int \sum_{i}^{n} Q_i \dot{\Psi}_i dv. \tag{7}$$

It is easy to see that in conformity with (7), (4), and (6) the dissipative function is

$$R = \int D dv = \int \left\{ \frac{1}{2} \sum_{i,k}^{n} (l_{ik})^{-1} f \alpha_i \alpha_k \dot{\Psi}_i \dot{\Psi}_k + \frac{1}{2} \sum_{i,k}^{n} + \frac{\partial g_k}{d\Psi_i} (\nabla \Psi_k)^2 \dot{\Psi}_i \right\} dv. \tag{8}$$

In the linear case ($g_k = \mathrm{const}$), (8) goes over into the expression known from [4].

If the dissipation function has been defined truly and (3) is valid for the condition (6), then the nonlinear relationships between the fluxes and forces or their corresponding parabolic equations should be expressed by the Euler–Lagrange equations

$$\frac{\partial (L)}{\partial \Psi_i} - \sum_{p=1}^{3} \frac{\partial}{\partial y_p} \cdot \frac{\partial (L)}{\partial \Psi_{ip}} = 0. \tag{9}$$

Let us now make the above specific by the illustration of heat conduction in a solid. Let us select the absolute temperature T as the parameter Ψ. The density of the Lagrange function and the dissipative function are expressed as follows:

$$L = \frac{1}{2} \rho f \frac{c_v}{T^2} (\nabla T)^2, \tag{10}$$

$$R = \int \left\{ \frac{1}{2} \rho^2 c_v^2 f l^{-1} \left(\frac{\partial T}{\partial t} \right)^2 + \frac{1}{2} \rho f \frac{\partial}{\partial t} \left(\frac{c_v}{T^2} \right) (\nabla T)^2 \frac{\partial T}{\partial t} \right\} dv, \tag{11}$$

$$Q = \partial D / \partial T. \tag{12}$$

The Euler–Lagrange equation becomes

$$\frac{l}{T^2} \Delta T + \frac{l}{c_v} \cdot \frac{\partial}{\partial T} \left(\frac{c_v}{T^2} \right) (\nabla T)^2 = \rho c_v \frac{\partial T}{\partial t}. \tag{13}$$

Assuming l to be proportional to the specific heat

$$l(T) = \alpha c_v(T), \tag{14}$$

we obtain the known nonstationary heat conduction equation

$$\lambda \Delta T + \frac{\partial \lambda}{\partial T} (\nabla T)^2 = \rho c_v \frac{\partial T}{\partial t}. \tag{15}$$

Here the coefficient λ is related to l by the dependence

$$\lambda(T) = -\frac{l(T)}{T^2}. \tag{16}$$

Now, let us examine the stationary state and its neighborhood. Exactly, as in the local potential method, λ(T) can be replaced by $\lambda(T_0)$ for small deviations from the stationary state, where T_0 is the stationary temperature distribution. In this approximation

$$L = \frac{1}{2} \rho f \frac{c_v(T_0)}{T_0^2} (\nabla T)^2, \tag{17}$$

$$R = \int \frac{1}{2} \rho^2 c_v^2 f l^{-1} (T_0) \frac{\partial T}{\partial t} dv. \tag{18}$$

The application of the variational condition (2) results in the following form of the Euler–Lagrange equation

$$\frac{l(T_0)}{T_0^2}\Delta T + \frac{l(T_0)}{c_v(T_0)} \cdot \frac{\partial T}{\partial t}\left(\frac{c_v(T_0)}{T_0^2}\right)\nabla T_0 \nabla T = \rho c_v \frac{\partial T}{\partial t}, \tag{19}$$

which is an approximate equation and goes over into the exact equation only in application to the stationary state.

Comparing the exact equation (15) with (19), the latter should be estimated as sufficiently rigorous to describe the process in the neighborhood of the stationary state. Here (19), in contrast to (15), admits the possibility, in principle, of using the Fourier method to construct an analytical solution since, as is easy to see, the equation characterizing the dependence of the temperature on the coordinates is linear after separation of variables.

The formalism proposed permits description of the stationary state in terms of a variational condition exactly as this is accomplished in the local potential method.

In fact, the exact equation describing the stationary state and being the most rigorous result of the general evolution criterion can be obtained from the extremum (maximum) condition of the functional

$$\Phi(T, T_0) = -\int \frac{1}{2}\rho f \frac{c_v(T_0)}{T_0^2}(\nabla T)^2 \, dv.$$

NOTATION

L	is the density of the Lagrange function;
Ψ	is the generalized thermodynamic parameter;
S	is the system entropy;
R	is the dissipative function;
t	is the time;
T	is the absolute temperature;
D	is the density of the dissipation function;
v	is the volume;
λ	is the coefficient of heat conduction;
Q	is the dissipative force.

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