Variational Principles in Irreversible Thermodynamics with Application to Viscoelasticity

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General differential equations are derived for the time history of a thermodynamic system undergoing irreversible transformations. This is done by using Onsager's principle, and introducing generalized concepts of free energy and thermodynamic potentials. From these equations it is shown that the instantaneous evolution of the system satisfies a principle of minimum rate of entropy production. It is also shown how Prigogine's theorem for the stationary state fits into the present theory. Another variational principle is established for the case where certain variables are ignored in analogy with the methods of virtual work in mechanics. This principle which applies to complex physical-chemical systems is developed more specifically for viscoelastic phenomena, and as an example the differential equations for the deflection of a viscoelastic plate is derived.

1. INTRODUCTION

IT has long been known that a physical system undergoing transformation has a tendency to move in a direction of increasing entropy. This is usually expressed from a statistical viewpoint by stating that the evolution is toward a more probable state or more disorder. This principle is formulated mathematically in classical thermodynamics by the property that the Helmholtz thermodynamic potential is a minimum at equilibrium. This field of thermodynamics which deals with equilibrium problems could more justifiably be called thermostatics.

There has recently been growing a new body of knowledge which deals essentially with nonequilibrium or irreversible phenomena and which more properly deserves the appellation of thermodynamics. Great impetus was given to this development from a unified standpoint by Onsager's theorem which is essentially a reciprocity law of coupled irreversible phenomena. The question of the existence and formulation of variational principles dealing with such irreversible phenomena is the object of the present paper. It will be shown, for instance, that it is quite a general property that a system tends toward the most disordered state but that this occurs with a minimum rate of production of this disorder or entropy.

A first step in this direction was made by Prigogine[1] who formulated a theorem of minimum production of entropy for a thermodynamic system which is in a stationary state, i.e., in a steady state of flow. Such a system for instance is one which is traversed by a steady flow of heat. We are concerned here with principles which are of a more general nature and which do not require steady flow.

Section 2 develops the basic differential equations for irreversible phenomena by the application of Onsager's principle. A quite general formulation is obtained for a perturbed system by the artifice of adjoining to the system considered a large heat reservoir at constant

temperature. The entropy of the total system gives a generalization of the concept of thermodynamic potential for the case of nonuniform temperatures. Several solutions of the basic equations are presented in Sec. 3 based on results obtained by the writer in a previous publication.[2] Equations for a perturbed system were also derived by statistical methods by Onsager and Machlup.[3]

A principle of minimum production of entropy is established in Sec. 4. It deals with the instantaneous direction of evolution of the systems under any nonequilibrium conditions. Section 5 deals with relaxation modes and leads to a new viewpoint in formulating the variational principles for stationary flow.

The case of a system for which certain coordinates are hidden is taken up in Sec. 6. The variational principle developed in this connection constitutes a powerful tool for the calculation of a wide variety of phenomena, involving, e.g., chemical reactions and heat transfer in complicated systems. It is also of particular usefulness in viscoelasticity. How this is done in general is shown by introducing the operational tensor for the stress-strain relations.[2] As an example in Sec. 7 it is applied to the derivation of the integro-differential equations for the deflection of a viscoelastic plate.

2. BASIC THERMODYNAMIC RELATIONS

We consider a system I defined by n thermodynamic state variables. These state variables are taken here to be of quite general nature and may represent such varied physical quantities as a strain tensor, electric charges, local temperatures, concentrations, etc. The entropy of such a system is defined by subdividing it into cells and summing the entropy for each of these cells. This assumes, of course, that each cell is in a state of quasi equilibrium so that its entropy may be defined as if it were in equilibrium. The legitimacy of this definition was investigated by Prigogine.[1] It could also be computed directly, of course, by means of Boltzmann's relation expressing the entropy directly in terms of

* Consultant.
[1] See S. R. De Groot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1952).

[2] M. A. Biot, J. Appl. Phys. **25**, 1385 (1954).
[3] L. Onsager and S. Machlup, Phys. Rev. **91**, 1505 (1953).

certain statistical or disorder parameters as done in problems of second-order transitions.

The system is characterized by n variables q_i which are defined as the departure from a certain reference state taken as origin and for which $q_i=0$. Only small departures from the reference state are considered and it is assumed that in this range of variation the system remains linear. This will generally be true if the system is in the vicinity of an equilibrium state.

In order to apply the principles of irreversible thermodynamics we must consider an isolated system. We therefore adjoin to system I a system II which is a large reservoir at constant temperature T. The total system I+II is now assumed to be isolated and its entropy is expressed as the sum of the entropies of each system:

$$S=S_{\mathrm{I}}+S_{\mathrm{II}}. \qquad (2.1)$$

Let us now find an expression for the entropy S. We consider the heat dh absorbed by System I from the reservoir II. Conservation of energy requires:

$$dh=dU_{\mathrm{I}}-\sum_i Q_i dq_i, \qquad (2.2)$$

where U_{I} is the internal energy of System I and Q_i is a generalized "external force" conjugate to the state variable q_i. This equation may be considered to define the external force as a perturbation acting upon the system in a very general sense. It can be for instance a stress or an electromotive force or can be proportional to a chemical affinity as defined by De Donder. The external forces may be considered part of the isolated system by adding corresponding large energy reservoirs. The increment of entropy acquired by the reservoir II is therefore:

$$dS_{\mathrm{II}}=-\frac{dh}{T}=-\frac{dU_{\mathrm{I}}}{T}+\sum_i \frac{Q_i}{T}dq_i, \qquad (2.3)$$

and the increment of entropy of the total system will be

$$dS=dS_{\mathrm{I}}+dS_{\mathrm{II}},$$
$$dS=dS_{\mathrm{I}}-\frac{dU_{\mathrm{I}}}{T}+\sum_i \frac{Q_i}{T}dq_i. \qquad (2.4)$$

We now define the reference state or zero state for which all coordinates $q_i=0$ as that for which all external forces Q_i are zero and in which the system is in equilibrium at uniform temperature T. The entropy S' of the system I+II when $Q_i=0$, derived from (2.4), is given by

$$TS'=TS_{\mathrm{I}}-U_{\mathrm{I}}=-\tfrac{1}{2}\sum_{ij} a_{ij}q_iq_j. \qquad (2.5)$$

Since we are dealing with an equilibrium state, the entropy S' is a maximum and the quadratic form

$$V=\tfrac{1}{2}\sum_{ij} a_{ij}q_iq_j \qquad (2.6)$$

is positive-definite.

From (2.4) we also derive that under the forces Q_i, the entropy S of the system I+II is given by

$$TS=-V+\sum_i Q_iq_i. \qquad (2.7)$$

The factor T, which is the constant temperature of the reservoir II, is introduced as a factor for convenience.

If the system is displaced from the zero level by applying the external forces very slowly and reversibly, the system follows a succession of equilibrium states given by the condition that the entropy is a maximum, i.e., by the n equations:

$$\partial S/\partial q_i=-\partial V/\partial q_i+Q_i=0. \qquad (2.8)$$

We now consider irreversible processes for which the partial derivatives of the entropy do not vanish. Onsager's principle[1] may be applied to this case. It may be stated in the following form, which is formally different from the usual one but may be seen to be equivalent:

$$T\partial S/\partial q_i=\sum_j b_{ij}\dot{q}_j; \qquad (2.9)$$

namely, the derivatives of the entropy are linear functions of the time rates of change $\dot{q}_j$ of the state variables and the matrix of coefficients is symmetric,

$$b_{ij}=b_{ji}. \qquad (2.10)$$

It should be noted in applying Onsager's relations (2.10) to arbitrary perturbations that because of linearity the principle of superposition is valid and that the system responds as a succession of relaxations under successive applications of constant force increments.

We introduce the quadratic form

$$D=\tfrac{1}{2}\sum_{ij} b_{ij}\dot{q}_i\dot{q}_j. \qquad (2.11)$$

From (2.9) we derive

$$D=\frac{1}{2}T\sum_i \dot{q}_i\frac{\partial S}{\partial q_i}=\frac{1}{2}T\frac{\partial S}{\partial t}. \qquad (2.12)$$

The quadratic form D is positive-definite since it is proportional to the time rate of production of entropy.

From Eqs. (2.7) and (2.9), we derive the basic relations of irreversible processes:

$$\sum_j a_{ij}q_j+\sum_j b_{ij}\dot{q}_j=Q_i. \qquad (2.13)$$

By using the quadratic expressions V and D, they may be written in the Lagrangian form:

$$\partial V/\partial q_i+\partial D/\partial \dot{q}_i=Q_i. \qquad (2.14)$$

The invariant V plays the role of a potential energy and D that of a dissipation function.

It is interesting to note the thermodynamic significance of V and S. From (2.4), we have

$$TdS=TdS_{\mathrm{I}}-dU_{\mathrm{I}}+\sum_i Q_idq_i. \qquad (2.15)$$

Now, suppose that the only external force acting on the system is a constant pressure P. The conjugate variable

is the volume $-v$, and we may write

$$\sum_i Q_i dq_i = -Pdv. \qquad (2.16)$$

Integrating (2.15),

$$-TS = U_I - TS_I + Pv. \qquad (2.17)$$

If the temperature is uniform throughout system I, this expression represents its Gibbs thermodynamic potential so that $-TS$ may be considered as the extension of the concept of thermodynamic potential for the case of nonuniform temperature and any kind of external force Q_i. Similarly, the expression

$$U_I - TS_I = V \qquad (2.18)$$

may be considered an extension of Helmholtz's free energy concept.

Equations (2.13) and (2.14) for a system in the vicinity of equilibrium apply to a large class of phenomena. They may involve, e.g., mechanical dissipation and elastic forces, heat transfer, chemical reactions, electric currents and charges, as well as the coupling between these phenomena. It may be shown that an excess temperature applied to a boundary is an external force with the entropy flow as the conjugate coordinate. In problems which are open to treatment by either classical or quantum statistics, the expression for V may be obtained directly from the partition function. Equations (2.13) and (2.14) may also be represented by a network of springs and dashpots or an RC network. Such a network constitutes therefore an analog computer for the large class of phenomena included in the present theory.[4]

3. SOLUTION OF THE BASIC EQUATIONS AS RELAXATION MODES OR STATIONARY FLOW

Consider a system to which constant forces Q_i are suddenly applied. The system will obviously tend toward some sort of new equilibrium state. This equilibrium state will either be one of static equilibrium where all coordinates are constant, or one in which there is steady flow, i.e., in which all coordinates vary proportionally with time. Proof of this follows from expression (4.10) in reference 2 which gives the general solution of Eqs. (2.1) in the operational form:

$$q_i = \sum_{j=1}^{n} \left[\sum_s \frac{C_{ij}{}^s}{p + \lambda_s} + C_{ij} \right] Q_j, \qquad (3.1)$$

where $p = d/dt$ and $-\lambda_s$ are distinct roots of the determinant:

$$\det |a_{ij} + pb_{ij}| = 0 \qquad (3.2)$$

with p as unknown. We have shown[2] that the values of λ_s are never negative and that the solution is completely

general and is not restricted by any singularity of the matrices or multiplicity of the roots.

If the forces Q_i are constant and are suddenly applied at the instant $t = 0$, they may be represented in terms of the unit step function $1(t)$ as

$$Q_i = Q_i^* 1(t), \qquad (3.3)$$

with constants Q_i^*. Substituting in (3.1), we make use of the operational relation

$$\frac{1}{p + \lambda_s} 1(t) = \frac{1}{\lambda_s} (1 - e^{-\lambda_s t}). \qquad (3.4)$$

We first assume that none of the roots λ_s are zero. Hence (3.1) may be written

$$q_i = \sum_{j=1}^{n} \left[\sum_s \frac{C_{ij}{}^{(s)}}{\lambda_s} + C_{ij} \right] Q_j^* - \sum_{j=1}^{n} \sum_s \frac{C_{ij}{}^s Q_j^*}{\lambda_s} e^{-\lambda_s t}. \quad (3.5)$$

We omit the factor $1(t)$ in (3.4) and (3.5). If none of the roots are zero, we see that the system toward a set of constant equilibrium values for the coordinates q_i. The variable part of the motion may be resolved into a sum of columns, each of which is characterized by a certain exponential decay and which we may call modes of relaxation. However, if some of the roots λ_s are zero, then there is a term of the type $C_{ij}{}^{(s)}/p$ in expression (3.1) corresponding to the operational relation

$$\frac{1}{p} 1(t) = t, \qquad (3.6)$$

which yields in expression (3.5) an additional term of the type

$$q_i = t \sum_{j=1}^{n} C_{ij}{}^s Q_j^*. \qquad (3.7)$$

This corresponds to a stationary flow. We have thus established that the system tends toward a fixed deviation or a steady flow. With

$$q_i^* = \sum_{j=1}^{n} C_{ij}{}^0 Q_j^*, \qquad (3.8)$$

we may also write

$$q_i = q_i^* t \qquad (3.9)$$

and q_i^* represents the stationary state velocities.

4. A GENERAL PRINCIPLE OF MINIMUM RATE ON ENTROPY PRODUCTION

In the previous section we have formulated the general solutions of the system in its evolution toward equilibrium. A somewhat related question is the following. In the configuration space of the state variables q_i, the thermodynamic state of a system is represented by a point of coordinates q_i. When not in equilibrium the system is subject to forces, both internal and external, which are expressed by $Q_i - \partial V / \partial q_i$ and which

[4] The possibility of extending the electric analog to phenomena involving coupling between heat transfer and mechanical energy was pointed out by C. F. Kayan, "Electrical analogger application to the heat pump process," Heating Piping and Air Conditioning, July, 1953.

we shall call "dis-equilibrium forces." These forces may be considered as proportional to the derivatives of the generalized thermodynamic potential. The instantaneous direction of evolution of the system in the configuration space is represented by the velocity vector $\dot{q}_i$. The velocity components $\dot{q}_i$ are also denoted by J_i in the literature and are called fluxes. The question arises whether the direction of this vector can be determined by a variational principle.

Let us first write the fundamental equation (2.14) in a somewhat different form. We denote the dis-equilibrium forces by

$$X_i = Q_i - \partial V/\partial q_i. \tag{4.1}$$

The Lagrangian equations (2.14) are then written

$$\partial D/\partial \dot{q}_i = X_i. \tag{4.2}$$

Consider now the quadratic form D as a function of the n velocity components, and the condition that D be an extremum when we consider all possible values of the vector q_i under the constraint that the vector q_i satisfy the relation

$$\sum_i X_i \dot{q}_i = \text{const}, \tag{4.3}$$

with given values of the forces. This leads to the absolute variational condition,

$$(\partial D/\partial \dot{q}_i - kX_i)\delta q_i = 0, \tag{4.4}$$

with an undetermined Lagrangian multiplier k. Except for this factor, the variational condition (4.4) is equivalent to the equation of motion (4.2). The variational principle therefore determines the direction of the velocity vector $\dot{q}_i$. The undetermined magnitude of the vector may be fixed by the condition

$$2D = \sum_i X_i \dot{q}_i, \tag{4.5}$$

which expresses that the rate of energy dissipation is equal to the power input.

Since D is a position-definite quadratic form, the extremum corresponds to a minimum. Moreover, D is proportional to the rate of entropy production associated with the velocities $\dot{q}_i$ of the system. Hence, we state the following theorem:

Considering a system which is not in equilibrium, its instantaneous velocity direction is such that the rate of entropy production is a minimum for all possible velocity vectors satisfying the condition that the power input of the dis-equilibrium forces is constant.

A dual form of Eqs. (4.2) are obtained if we express D in terms of the forces X_i instead of $\dot{q}_i$. From Euler's theorem on homogeneous functions, we have

$$2D = \sum_i \frac{\partial D}{\partial \dot{q}_i}\dot{q}_i = \sum_i \dot{q}_i X_i. \tag{4.6}$$

Hence,

$$2dD = \sum_i \dot{q}_i dX_i + \sum_i X_i dq_i. \tag{4.7}$$

Since

$$dD = \sum_i \frac{\partial D}{\partial \dot{q}_i}d\dot{q}_i = \sum_i X_i dq_i, \tag{4.8}$$

we derive

$$dD = \sum_i \dot{q}_i dX_i. \tag{4.9}$$

We therefore have the dual form of Eqs. (4.2):

$$\partial D/\partial X_i = \dot{q}_i. \tag{4.10}$$

We may state a *dual minimum entropy production theorem* identical with the above except that the variables X_i and q_i are interchanged. The minimizing vector X_i for D is then in the configuration space of the forces.

It should be noted that the minimum theorems expressed here may be formulated in other mathematically equivalent forms. For instance, we may state that Eqs. (4.2) are equivalent to the statement that the quantity

$$P = D - \sum_i X_i \dot{q}_i \tag{4.11}$$

is a minimum. Another equivalent statement is that under the restraint that the energy dissipated is a constant the power input is a maximum. Certain known minimum theorems on energy dissipation in electrodynamics and fluid mechanics are particular cases of the above.[4]

5. MINIMUM PRINCIPLE FOR STATIONARY STATES AND RELAXATION MODES

We have seen in Sec. 3 that if there are characteristic roots λ_s of the system which vanish, the system will tend toward a stationary state which is defined by (3.9) and for which all velocities are constant. This stationary state is such that for all coordinates q_i in the direction of motion the "restoring force" vanishes, i.e.,

$$\partial V/\partial q_i = 0. \tag{5.1}$$

In that direction the system remains under constant dis-equilibrium forces:

$$X_i = Q_i. \tag{5.2}$$

The minimum theorem of the previous section applies to this case, but the condition of constant power input is now

$$\sum_i Q_i \dot{q}_i = \text{const}. \tag{5.3}$$

A corresponding statement is of course valid for the dual form of the theorem.

The minimum principle considered until now determines the instantaneous velocity of the system. There are, however, as we shall now proceed to show, different variational properties which refer to the long-range time history of the system.

Let us evaluate the rate of entropy production during the evolution of the system toward equilibrium or a stationary state. We have seen in reference 2 that the general equations (2.14) may be written by using

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[4] See, e.g., J. H. Jeans, *The Mathematical Theory of Electricity and Magnetism* (Cambridge University Press, London, 1933), p. 321.

normal coordinates ξ_s. The transformation is

$$q_i = \sum_s \phi_i{}^s \xi_s, \qquad (5.4)$$

where $\phi_i{}^s$ is the modal column corresponding to the relaxation mode s. The corresponding normal forces are

$$\Xi_s = \sum_j \phi_j{}^s Q_j. \qquad (5.5)$$

The modal columns have the property of being orthogonal, namely,

$$\sum_{ij} a_{ij} \phi_j{}^s \phi_i{}^r = \sum_{ij} b_{ij} \phi_j{}^s \phi_i{}^r = 0, \quad s \neq r. \qquad (5.6)$$

Normalization is in such a way that if $\lambda_s \neq \infty$,

$$\sum_{ij} b_{ij} \phi_i{}^s \phi_j{}^s = 1; \qquad (5.7)$$

and if $\lambda_s = \infty$,

$$\sum_{ij} a_{ij} \phi_i{}^s \phi_j{}^s = 1. \qquad (5.8)$$

With these coordinates, the functions V and D become

$$V = \tfrac{1}{2} \sum_s \lambda_s \xi_s{}^2 + \tfrac{1}{2} \sum_k \xi_k{}^2, \quad D = \tfrac{1}{2} \sum \dot{\xi}^2, \qquad (5.9)$$

where the $\xi_k{}^2$ terms correspond to cases of infinite roots. Equations (2.14) become ($p \equiv d/dt$):

$$(p + \lambda_s) \xi_s = \Xi_s, \quad \xi_k = \Xi_k. \qquad (5.10)$$

Solutions of the first equations are

$$\xi_s = \frac{\Xi_s}{p + \lambda_s} = \frac{1}{\lambda_s} (1 - e^{-\lambda_s t}) \Xi_s. \qquad (5.11)$$

If some of the roots λ_s are zero, we denote them by λ_m and write

$$\xi_m = t \Xi_m.$$

The rate of production of entropy is

$$\frac{dS}{dt} = \frac{2D}{T} = \frac{1}{T} \left[\sum_s e^{-2\lambda_s t} \Xi_s{}^2 + \sum_m \Xi_m{}^2 \right]. \qquad (5.12)$$

We may state the following property: *The rate of production of entropy is a monotonically decreasing function which tends toward a constant. All higher time derivatives of the entropy also decrease monotonically and tend to zero.*

We note that $\dot{\xi}_s$, $\dot{\xi}_m$ are proportional to the disequilibrium forces X_s, X_m applied to each normal coordinate:

$$\dot{\xi}_s = \Xi_s - \lambda_s \xi_s = X_s, \quad \dot{\xi}_m = \Xi_m = X_m. \qquad (5.13)$$

We may write the rate of entropy production as

$$dS/dt = \tfrac{1}{2} \sum_s X_s{}^2 + \tfrac{1}{2} \sum_m X_m{}^2. \qquad (5.14)$$

The stationary state corresponds to $X_s = 0$. Therefore, in the stationary state the entropy production considered as a function of the dis-equilibrium forces is a minimum under the constraint that the forces X_m cor-

responding to the stationary velocities are kept constant. This latter property of the stationary state corresponds to a theorem already formulated by Prigogine[1] but derived in a different way.

Another variational property refers to the modes of relaxation themselves. The modal column $\phi_i{}^s$ satisfy the equations:

$$\sum_j a_{ij} \phi_i{}^s - \lambda_s \sum_j b_{ij} \phi_i{}^s = 0, \qquad (5.15)$$

which result from the variational condition that

$$D = \tfrac{1}{2} b_{ij} \phi_i \phi_j \qquad (5.16)$$

be an extremum under the constraint

$$V = \tfrac{1}{2} a_{ij} \phi_i \phi_j = \text{const.} \qquad (5.17)$$

As a familiar example of a system tending toward a steady state, we might visualize the one-dimensional flow of heat across a wall, one side of which is suddenly brought to a constant higher temperature. The system tends to a steady state when the distribution of temperature is linear and the rate of entropy production is constant. The only remaining time varying coordinate is the total entropy input which is proportional to the time. The unsteady part of the temperature distribution is a superposition of sinusoidal modes, each with its own exponential decay.

6. VARIATIONAL PRINCIPLE FOR THE CASE OF HIDDEN COORDINATES

Up to now we have involved all the degrees of freedom in the variational equations. However, it is possible to introduce a variational principle which involves only a partial number of the total degrees of freedom. We have shown[2] that for a system with n degrees of freedom, if k variables are observed, the forces applied to these degrees of freedom are expressed in terms of the coordinates as

$$Q_i = \sum_{j=1}^{k} T_{ij} q_j, \qquad (6.1)$$

with

$$T_{ij} = \sum_s \frac{p}{p + r_s} D_{ij}{}^s + D_{ij} + D_{ij}' p, \qquad (6.2)$$

where the D's are constants, the r's are decay constants, and p is the time operator. The symmetry of the coefficients

$$T_{ij} = T_{ji},$$

leads to a quadratic invariant:

$$I = \tfrac{1}{2} \sum_{ij} T_{ij} q_i q_j, \qquad (6.3)$$

and Eq. (6.1) may be expressed by the relation

$$Q_i \delta q_i = \delta I = \left[\sum_j T_{ij} q_j \right] \delta q_i, \qquad (6.4)$$

to be satisfied identically for all virtual displacements δq_i.

This variational principle, as formulated here, applies to all phenomena expressible by the basic thermodynamic equations on which the present paper is based and is therefore quite general. As an example of the fecundity of this principle, it is of interest to formulate it more specifically for the case of a viscoelastic continuum. In terms of the stress tensor $\sigma_{\mu\nu}$ and the strain tensor $e_{\mu\nu}$, it was shown[2] that for an anisotropic material the relations are

$$\sigma_{\mu\nu}=\sum_{ij} P_{\mu\nu}{}^{ij}e_{ij}, \qquad (6.5)$$

with

$$P_{\mu\nu}{}^{ij}=\sum_{s} \frac{p}{p+r_s}D_{\mu\nu}{}^{ijs}+D_{\mu\nu}{}^{ij}+pD'_{\mu\nu}{}^{ij}. \qquad (6.6)$$

The corresponding operational invariant is, without the summation signs,

$$I=\tfrac{1}{2}P_{\mu\nu}{}^{ij}e_{ij}e^{\mu\nu}, \qquad (6.7)$$

and the variational principle may be expressed as

$$\sigma_{\mu\nu}\delta e^{\mu\nu}=\delta I. \qquad (6.8)$$

The usefulness of this formulation lies in the fact that since the internal stress field is in equilibrium, the total virtual work is equal to that of the forces applied to the boundary of the continuum. Denoting by F_μ this boundary force and by x^μ the boundary coordinates, we have

$$\iiint_V \sigma_{\mu\nu}\delta e^{\mu\nu}dV=\iint_S F_\mu\delta x^\mu dS, \qquad (6.9)$$

where the volume integral is taken in the volume V bounded by S. Hence the variational principle in the form

$$\iint_S F_\mu\delta x^\mu dS=\iiint_V \delta I dV. \qquad (6.10)$$

The procedure exemplified here for a viscoelastic continuum is not restricted to the case of a stress field and may be used to analyze the time history of complex physical chemical systems, by means of a suitable choice of generalized coordinates in a way quite analogous to the example treated hereafter. The disappearance of the virtual work of the internal forces is then replaced by the more general condition of conservation of mass and energy fluxes between the interacting cells.

In the above derivation dynamic effects have been neglected. It can be easily verified that the acceleration of the observed coordinates may be included by introducing the virtual work of the inertia forces as done in the expression of d'Alembert's principle.

7. APPLICATION TO THE BENDING OF A VISCOELASTIC PLATE

As an example of the variational method, we shall treat the problem of two-dimensional bending of a viscoelastic plate of isotropic homogeneous material.

The stress-strain law of such a material is expressed operationally as[2]

$$\sigma_{\mu\nu}=2Qe_{\mu\nu}+\delta_{\mu\nu}Re,$$

$$\delta_{\mu\nu}=\begin{cases} 1, & \mu=\nu \\ 0, & \mu\neq\nu, \end{cases} \qquad (7.1)$$

$$e=\sum_{\mu\nu}\delta_{\mu\nu}e_{\mu\nu},$$

with the operators Q and R given by

$$Q=\sum_s \frac{pQ^s}{p+r_s}+Q+Q_p', \quad R=\sum_s \frac{pR^s}{p+r_s}+R+R_p'. \qquad (7.2)$$

With Cartesian components of displacement u, v, w, the strain tensor is defined as

$$e_{xx}=\frac{\partial u}{\partial x}, \text{ etc.;} \quad e_{xy}=\frac{1}{2}\left(\frac{\partial v}{\partial x}+\frac{\partial u}{\partial y}\right), \text{ etc.} \qquad (7.3)$$

We consider a plate of thickness $2h$. The xy-plane is parallel with the faces located at $z=\pm h/2$. We choose as a representative deformation:

$$u=zq_2(x), \quad v=0, \quad w=q_1(x). \qquad (7.4)$$

This constitutes a two-dimensional bending and shearing deformation parallel with the xz-plane. The functions q_1, q_2 of x are to be determined. Components of the strain tensor are

$$e_{xx}=\partial u/\partial x=zdq_2/dx,$$

$$e_{yy}=e_{zz}=e_{xy}=e_{yz}=0, \qquad (7.5)$$

$$e_{zx}=\tfrac{1}{2}q_2+\tfrac{1}{2}dq_1/dx.$$

The invariant I is

$$I=\tfrac{1}{2}\sigma_{\mu\nu}e^{\mu\nu}=\tfrac{1}{2}\sigma_{xx}e_{xx}+\sigma_{zx}e_{zx}. \qquad (7.6)$$

In order to apply the variational principle (6.10) we must integrate I over the volume. We first integrate along the thickness of the plate and obtain

$$\int_{-h/2}^{h/2} I dz=\frac{B}{2}\left(\frac{dq_2}{dx}\right)^2+\frac{Qh}{2}\left(\frac{dq_1}{dx}+q_2\right)^2, \qquad (7.7)$$

with $B=(h^3/12)(2Q+R)$. We then integrate with respect to x

$$J=\int_0^l dx\int_{-h/2}^{h/2} I dz=\frac{B}{2}\int_0^l\left(\frac{dq_2}{dx}\right)^2 dx$$

$$+\frac{Qh}{2}\int_0^l\left(\frac{dq_1}{dx}+q_2\right)^2 dx. \qquad (7.8)$$

If we assume that δq_1 and δq_2 are zero at the end points

$x=0$ and $x=l$, the variation of J is

$$\delta J = -B \int_0^l \frac{d^2 q_2}{dx^2} \delta q_2 dx + Qh \int_0^l \left[\left(\frac{dq_1}{dx} + q_2 \right) \delta q_2 \right.$$
$$\left. - \left(\frac{d^2 q_1}{dx^2} + \frac{dq_2}{dx} \right) \delta q_1 \right] dx. \quad (7.9)$$

If a force f is applied to the surface of the plate per unit area in the z-direction, the virtual work of this force is

$$\int_0^l f \delta w dx = \int_0^l f \delta q_1 dx. \quad (7.10)$$

Applying Eq. (6.10) of the previous section, the variations (7.9) and (7.10) must be equal. The expressions multiplying δq_1 in (7.9) and (7.10) must be equal and that multiplying δq_2 in (7.9) must vanish. We derive the differential equations:

$$B \frac{d^2 q_2}{dx^2} = Qh \left(\frac{dq_1}{dx} + q_2 \right), \quad Qh \left(\frac{d^2 q_1}{dx^2} + \frac{dq_2}{dx} \right) = -f. \quad (7.11)$$

Eliminating q_2, we find

$$\frac{d^4 q_1}{dx^4} = \frac{f}{B} - \frac{1}{Qh} \frac{d^2 f}{dx^2}. \quad (7.12)$$

The first term on the right-hand side corresponds to a bending deflection while the second term corresponds to a shearing deformation. We must remember that the differential equation (7.12) is also an operational equation in the time variable since B and Q are time operators. It is therefore also an integro-differential equation.